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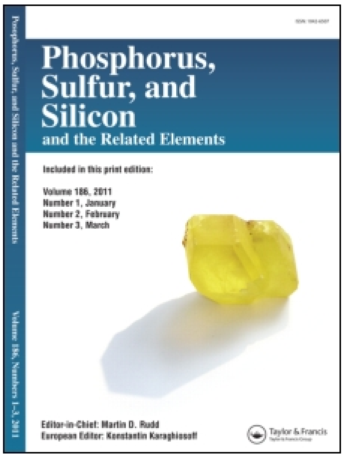

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BORON-NITROGEN ANALOGUES OF CYCLOBUTADIENE, BENZENE AND CYCLOOCTATETRAENE: INTERCONVERSIONS

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Abstract Iminoboranes RB≡NR', isoelectronic with alkynes, cyclooligomerize to give B-N rings $(RBNR')_n$ that are either analogues of cyclobutadienes (n = 2) or benzenes or Dewar benzenes (n = 3) or cyclooctatetraenes (n = 4), depending on the ligand set R/R' and on conducting the oligomerization either thermally or catalytically. Cyclodimers and cyclotetramers may either undergo reversible interconversions or cyclotetramers are formed irreversibly from cyclodimers. The (4+2) cycloaddition of cyclodimers and iminoboranes yields cyclotrimers. Cyclotrimers may thermally be converted into cyclodimers, and poly(iminoboranes), isoelectronic with polyalkynes, can thermally be depolymerized into cyclotrimers. nido-Cluster derivatives of $N_2B_4H_6$, arachno-cluster derivatives of $N_2B_3H_7$, four-membered rings $N_2B_2R_3R'$, or five-membered rings $N_2B_3R_4R'$ are isolated, when three-membered rings NB_2R_3, isoelectronic with cyclopropenyl cations, either dimerize or add aminoboranes $H_2B{=}NR'_2$ or insert nitrenes R'N (from $R'N_3$) or insert iminoboranes R'B≡NR into the B-B bond, respectively.

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INTRODUCTION

It goes back to the twenties that chemists became aware of the isoelectronic analogy of a carbon-carbon and a boron-nitrogen couple. An early explored example in the world of rings is the analogy between benzene and borazine. Six planarly arranged ring bonds of equal lengths in both of these rings, settled in a range between single and double bond lengths, demonstrate the structural similarity, which corresponds to a striking analogy in some physical properties; the chemical reactivity, however, turned out to be distinctly different. This difference, like differences in the chemistry of C-C and B-N analogues generally, can be explained mainly by the difference in the bond strengths of the C-C and the B-N bond, as far as the cleavage of these bonds is concerned. For comparison, the standard enthalpy for the dissociation of the diatomic molecules C_2 and BN into atoms amounts to 607 and 389 kJ/mol, respectively. - Figure 1 presents selected boron-nitrogen rings of type **1** - **6**. The selection in Figure 1 presents those boron-nitrogen rings for which interconversions have become known, recently. Owing to their greater reactivity, more such interconversions are known for boron-nitrogen than for the corresponding carbon rings.

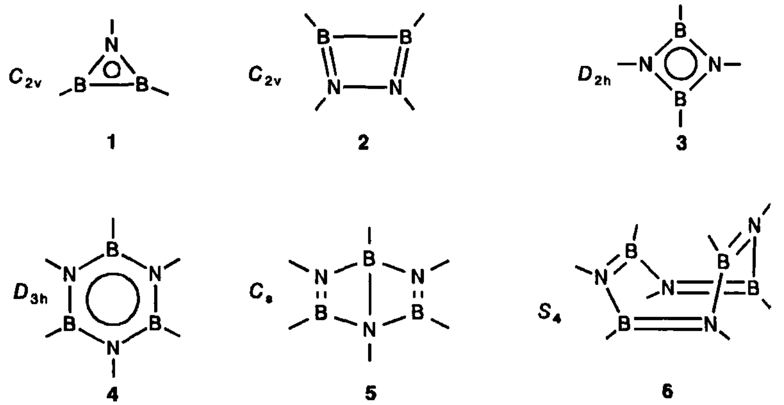

FIGURE 1 Selected BN rings.

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IMINOBORANES: BASIC UNITS OF BORON-NITROGEN RINGS

Rings of type **3** - **6** (Figure 1) can be formed from imino(organo)boranes R-B≡NR' as the basic units[1]. We do not consider amino(imino)boranes R_2N-B≡NR' in this context[2], because imino(organo)boranes are much more versatile in forming boron-nitrogen rings. The thermal stability of iminoboranes towards cyclooligomerization is comparable to that of polar alkynes, e.g. FC≡CtBu[3], i.e. iminoboranes are metastable and storable at more or less low temperature, but cyclooligomerize at ambient temperature, provided there are no huge ligands that prevent oligomerization. The half-life time of tBu-B≡N-tBu, which is one of the best investigated iminoboranes, is about 3 d at 50°C. The structure of this particular iminoborane is compared to that of tBu-C≡C-tBu in Table 1. Apparently, the CC triple bond is shorter and stronger than the BN triple bond. This difference as well as the polarity of the iminoborane, which, though small, is not negligible, contribute to the distinctly higher reactivity of the iminoborane.

TABLE 1 Structural properties of the CC and ^{11}BN triple bond[4].

	bond length	wave number	force constant	dipole moment
tBuC≡CtBu	117.9 pm	2244 cm^{-1}	15.9 N/cm	0.00 D
tBuB≡NtBu	125.8 pm	2018 cm^{-1}	13.3 N/cm	0.20 D

Though different in velocity, the reactions of iminoboranes and alkynes are comparable: cyclooligomerizations, that may be catalytically governed, polymerization, addition of

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polar and unpolar molecules to the triple bond, cycloadditions from the (2+1) to the (2+4) type, and reactions in the coordination sphere of transition metals[1]. A difference in the area of cycloadditions is that (2+2) cycloadditions are rare with alkynes, but are quite common with iminoboranes; in contrast to unpolar alkynes, the two-step mechanism for a (2+2) cycloaddition is reasonable for the slightly polar iminoboranes, whereas the suprafacial one-step mechanism violates the principle of conservation of orbital symmetry in both cases.

STRUCTURE AND STABILITY OF BORON-NITROGEN RINGS

The parent molecule NB_2H_3 (**1a**) in the azadiboriridine series (**1**; Figure 1) is the analogue of cyclopropenyl cation. It may be discussed in terms of a Hückel 2π-electron system with a large resonance energy, but only a modest B-B π-bond contribution[5]. Another description starts from a diborane(2) HB=BH, which donates π-electrons to a nitrene NH via a σ-bond and accepts nitrene p-electrons into antibonding π-orbitals, thus exhibiting a modified Dewar-Chatt-Duncanson model of the coordination of alkenes or alkynes to later transition metals[6]. The calculated B-B bond length and the angle H-B-B of **1a** (Table 2) approach those of diborane(2) HB=BH (151 pm, 180°)[7] as compared to diborane(4) H_2B-BH_2 (171 pm)[7] or cyclotriborane B_3H_3 (173.2 pm, 150.0°)[6]. The observed data for crystalline [-(tBu)B-B(tBu)-N(Mes)-] (**1b**)[8] underline this bonding model (Table 2). - Type **1** three-membered rings $R'NB_2R_2$ are unstable with respect to the formation of clusters $R'_2N_2B_2R_4$, unless bulky groups R prevent such a dimerization, e.g. R/R' = tBu/Mes (**1b**), tBu/tBu (**1c**).

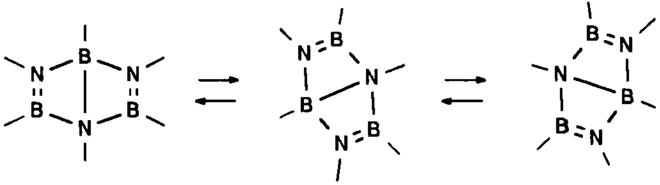
TABLE 2 Calculated and observed structural data of type **1** rings

	B-B	BN	H-B-B/C-B-B
1a (calc.)	162.1 pm	142.1 pm	168.3°
1b (obsd.)	155.8 pm	137.3/135.6 pm	176.0/172.3°

The analogues of cyclobutadienes with a rectangular diene structure are the 1,2,3,4-diazadiboretidines (**2**; Figure 1), which may have a trapezoid diene structure. They are not formed by head-head cyclodimerization of RB≡NR'. Because of their polarity, iminoboranes undergo head-tail cyclodimerization exclusively. No structural data are available for the rings **2**, which have a short life-time in solution at 0°C, but can be trapped by insertion of oxygen (from Me_3NO) or nitrene (from azides) into the B-B bond[9]. The notorious tendency of rectangular cyclobutadienes to undergo (4+2) cycloadditions with themselves seems to be also true for rings of type **2** (see below).

Much more is known of the rhombic 1,3,2,4-diazadiboretidines **3** (Figure 1). They are analogues of those rhombic cyclobutadienes, which are stabilized by clockwise opposed electronic effects of the ring ligands. Such electronic "push-pull effect" is performed by the ring atoms themselves in the case of the B-N rings **3** . The planar, rhombic ring skeleton with acute angles at the nitrogen is structurally well documented[1]. The BN bond lengths are found in the range of 143 - 146 pm, i.e. between BN double bonds (138 - 141 pm) and single bonds (148 - 151 pm), which are formed by three-coordinated B and N atoms with coplanar or orthogonal coordination planes, respectively. - Rather large ligands are necessary to make the four-membered rings **3** isolable and storable. tert-Butyl groups at both ring N atoms are sufficient, but four primary alkyl groups as ligands would not allow to isolate such rings.

The structural analogy between borazines **4** and the benzene family is discussed in textbooks. - Dewar borazines **5** (Figure 1), on the other hand, have been known for only ten years[10]. In the bicyclic skeleton of **5** two BNBN trapezoids have a single-bond edge in common, whereas the opposite edges represent short double bonds[10, 11]. In the case of benzenes, the Dewar isomer may be kinetically stable, but thermodynamically instable, e.g. C_6Me_6. Steric strain, however, can make the Dewar benzene thermodynamically more favorable, e.g. with four tBu and two MeOOC substituents. The prerequisite for making Dewar borazines **5** more stable than borazines **4** is steric strain again, exhibited, e.g., by three iPr and three tBu groups. In contrast to the CC analogues, Dewar borazines which are less stable than borazines cannot be isolated as metastable species. Apparently, the activation barrier for the rearrangement **5** → **4** is very small. This is in accord with a degenerate rearrangement in solution between three Dewar borazine isomers [Eq. (1)], that is rapid at room temperature with respect to the NMR time scale. The transition state of this rearrangement may have a structure closely related to the corresponding borazine. Such a fluctuation is unknown for Dewar benzenes.


(1)

Cyclooctatetraenes and tetraazatetraborocanes **6** (Figure 1) have a tub-like ring structure in common[12-14]. The tub-structure of **6** is stable with respect to ring inversion. This can be deduced from the NMR spectroscopic non-equivalence of methylene protons (in substituents Et, Pr, iBu, CH_2Ph) and of methyl groups (in substituents iPr,

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iBu)[14]. As in cyclooctatetraenes, there is a system of alternating BN single and double bonds in the rings of type **6**. Once formed, the products **6** are stable and storable.

BORON-NITROGEN RINGS FROM IMINOBORANES

The thermal oligomerization of alkynes does not play an important role in chemistry, though Berthelot detected the formation of benzene on passing acetylene through a hot tube as early as in 1866[15]. The catalytic oligomerization of alkynes, however, to give benzenes, Dewar benzenes, cyclooctatetraenes etc. is a broadly explored area in chemistry. It is reasonable to distinguish between the thermal and the catalytic oligomerization also with iminoboranes RB≡NR'. "Thermal" means a temperature more or less beneath room temperature, depending on the steric demand of the ligands R/R'. The thermal stabilization of RB≡NR' may give rings of type **3** - **6** (Figure 1) or poly(iminoborane) $(RBNR')_x$ (**7**). The catalytic oligomerization of iminoboranes has not yet been intensively explored. Anyhow, catalysts may govern the oligomerization to yield four-membered rings **3**, whereas the corresponding borazines **4** or Dewar borazines **5** are formed thermally.

The thermal oligomerization of iminoboranes gives a mixture of borazines **4** and polymers **7** in the case of primary alkyl ligands R/R'; the ligand set Me/Me, however, yields the borazine only. Because of the general insolubility of the polymers, the borazines can easily be extracted from the mixture. - An alkyl ligand combination R/R' of the type primary/primary or secondary/secondary makes borazines available, mostly as the only products. In contrast to the combination R/R' = Me/tBu, the reversed combination tBu/Me presents the only known example of a direct formation of an eight-membered ring **6** from an iminoborane. - Dewar borazines are formed from iminoboranes with a ligand set R/R', which is too large to make borazines stable, but not large enough for forcing the oligomerization to stop at the four-membered rings **3**. - These rings of type **3** are the products from the thermal stabilization of iminoboranes in the case of very large ligands R/R'. We do not understand, however, why the ligand sets R/R' = iPr/tBu, Ph/tBu on the one hand and the reversed sets R/R' = tBu/iPr, tBu/Ph on the other hand govern the oligomerization to yield Dewar borazines or diazadiboretidines, respectively. The oligomerization situation is summarized in Table 3. - The oligomerization may be completely blocked by extremely bulky ligands, e.g. R/R' = $(Me_3Si)_3C$/tBu[16], $iPrCMe_2/2,6\text{-}iPr_2C_6H_3$[17].

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TABLE 3 Products of the thermal stabilization of RB≡NR'[1].

R/R':	Me/Me	Me/tBu	Et/Et	Et/tBu	Pr/Pr	Pr/tBu	iPr/iPr	iPr/tBu
Product:	4	4	4,7	4	4, 7[18]	4	4	5
R/R'	Bu/Bu	Bu/tBu	iBu/iBu	sBu/sBu	sBu/tBu	tBu/Me	tBu/iPr	
Product:	4/7[18]	4	4,7	3,4	5[19]	6[19]	3[20]	
R/R':	tBu/tBu	tBu/Ph	tBu/Mes	tBu/SiMe$_3$	CH$_2$tBu/CH$_2$tBu			
Product:	3	3[20]	3[19]	3[19]	3[20]			
R/R':	CH$_2$SiMe$_3$/CH$_2$SiMe$_3$	Ph/tBu	C$_6$F$_5$/tBu					
Product:	4[20]	5[11]	3					

We explain the formation of the products 3, 4, 5, and 7 by assuming the formation of short-lived adducts from two iminoborane molecules as the first step, according to Figure 2. A linear borane of the type R-B=Y with an electron sextet, which would be a fragment of that adduct, would not be too unusual, since the borane Me-B=C(SiMe$_3$)$_2$, e.g , had been isolated[22]. Those adducts could either be closed to rings of type 3 or could add another molecule of iminoborane to give open-chain trimers. Ring closure or chain prolongation could be the subsequent reactions, allowing to isolate borazines 4 or polymers 7, respectively, as the final products. A (4+2) cycloaddition involving a cyclodimer 3 and iminoborane needs also be taken into account, yielding Dewar borazine 5 and, subsequently, borazine 4; such cycloadditions can be performed independently (see section below). The final formation of one of the products 3 - 5 (Table 3) seems to follow thermodynamic control, influenced by sometimes subtle steric differences between the ligand sets R/R'. The singular formation of the eight-membered ring (tBuBNMe)$_4$ from tBuB≡NMe is not understood.

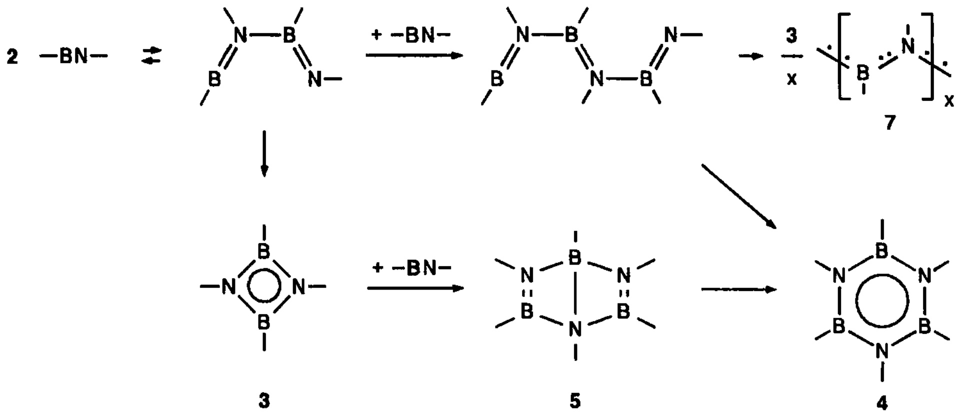

FIGURE 2 Hypothetic mechanism of the thermal stabilization of RB≡NR'.

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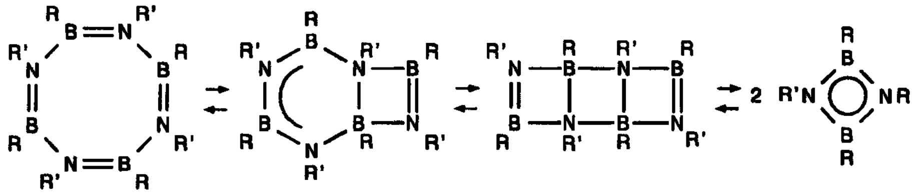
The iminoboranes RB≡NtBu (R = Et, Pr, iPr, Bu) yield the cyclodimers **3** upon stabilization in presence of catalytic amounts of the isonitrile C≡NtBu[1]. Without this catalyst, cyclotrimers of type **4** or **5**, respectively, are the stabilization products (Table 3). The same catalyst governs the iminoborane MeB≡NtBu to give the corresponding eight-membered ring **6**; certainly, a catalyzed cyclodimerization is the first step, which is followed by the known dimerization of the cyclodimer of type **3** to give **6** at room temperature (see next section). - The iminoborane iPrB≡NiPr, stabilized by cyclotrimerization thermally, undergoes a cyclodimerization in the presence of a catalytic amount of η^5-(C_5H_4Me)Mn$(CO)_2$(THF); and the resulting cyclodimer $(iPrBNiPr)_2$ is slowly transformed into the corresponding eight-membered ring $(iPrBNiPr)_4$ at room temperature[21]. - Nothing is known of the activated complex. Once formed catalytically, however, the four- and the eight-membered rings are stable with respect to a conversion into six-membered rings, which are presumable the thermodynamically more stable isomers.

INTERCONVERSIONS BETWEEN FOUR- AND EIGHT-MEMBERED RINGS

A reversible equilibrium between rings of type **3** and **6** was found for two particular ligand sets, R/R' = Me/tBu[1] and iPr/iPr[21]. The equilibrium can easily be followed kinetically and thermodynamically by NMR methods[13]. The eight-membered ring predominates at room temperature, the four-membered one at 70 or 100°C, respectively. Apparently, the rings of type **6** are more favorable in energy, presumably because of a lower ring tension, but are obviously worse in entropy than rings of type **3**. We assume the BN analogue of bicyclo[4.2.0]octa-2,4,7-triene and the Diels-Alder adduct of two molecules of **3** to be intermediates in the equilibration process **6** → **3**, according to Eq. (2). Cyclooctatetraene, C_8H_8, is known to be in equilibrium with a small amount of bicyclo-[4,2,0]octatriene; cyclobutadiene, C_4H_4, gives irreversibly the Diels-Alder dimer on thawing it in an Ar matrix. A complete reversibility as in Eq. (2) is unknown for CC analogues.

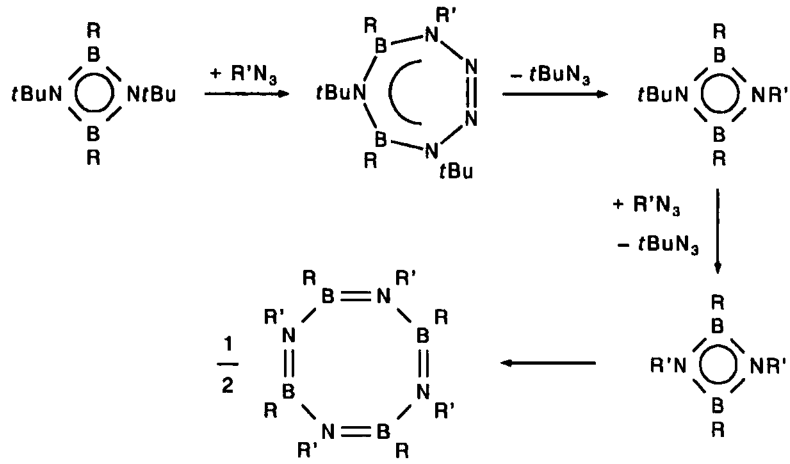


(2)

6 **3**

On the other hand, the long-known eight-membered rings $(XBNR')_4$ (X = Cl, Br, NCO, NCS, NCSe; R' = tertiary alkyl group)[23] do not undergo equilibria of type (2). They are thermally stable, mostly beyond their melting points. The thermal decomposition at a more or less high temperature is not a neat reaction, but may yield some borazine $(XBNR')_3$. These eight-membered rings exhibit, by the way, an unexpected solvolytic stability, even when containing Cl or Br atoms, which are so easily substituted in normal haloboranes; Cl in $(ClBNtBu)_4$, e.g., cannot be exchanged by Me upon applying LiMe, though the requested product is easily formed from MeB≡NtBu (see preceding section).

A remarkable formation of eight-membered rings $(RBNR')_4$ is observed, when azides $R'N_3$ act on four-membered rings $(RBNtBu)_2$ [Eq. (3)]. This reaction involves the exchange of both NtBu fragments in the type **3** rings by NR' fragments and the dimerization of the intermediates $(RBNR')_2$ to give the products, which cannot be converted into rings of other size[14]. A mechanism was proposed , according to which $R'N_3$ acts as a 1,3 dipolar agent in the introductory cycloaddition step. Loss of the well characterized $tBuN_3$ completes the exchange of the first ring fragment NtBu. A reaction sequence of the same type and subsequent dimerization of $(RBNR')_2$ yield the final product. Support for this mechanstic picture comes from the reaction of a nitrone with four-membered rings **3**, which can be rationalized by assuming an introductory cycloaddition of the same type as in Eq. (3)[14].



(3)

R	Et	*i*Pr	*i*Pr	*i*Pr	*i*Bu	*i*Bu	*i*Bu	*i*Bu
R'	Ph	Pr	*i*Bu	CH_2Ph	Pr	*i*Bu	Ph	CH_2Ph

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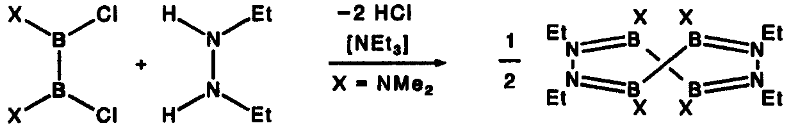
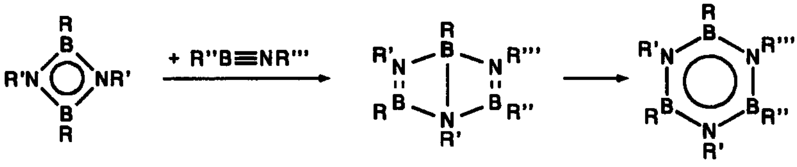
Efforts to gain a four-membered ring of type 2 by condensation of a diborane(4) with diethylhydrazine give an eight-membered ring, presumably via the corresponding four-membered ring (type 2) [Eq. (4)]. The product exhibits an unprecedented twist-type structure of D_2 symmetry in the crystal, but, according to NMR data, not in solution[9].



(4)

INTERCONVERSIONS INCLUDING SIX-MEMBERED RINGS

As mentioned above, four-membered rings are formed catalytically from iminoboranes RB≡NtBu (R = Et, Pr, iPr, Bu), which yield six-membered rings by a thermal procedure. We found out that these particular four-membered rings undergo a (4+2) cycloaddition at about 50°C, when RB≡NtBu is added from a cooled dropping funnel[11]. It can be concluded that the (4+2) cycloaddition is faster than the (2+2) cyclodimerization of the iminoborane. The borazines are formed, apparently, via the Dewar borazines as intermediates. In the case of iPrB≡NtBu, the Dewar borazine is the final product, as expected. The generalization of this cycoaddition might allow the synthesis of borazines with a mixed set of ligands. We restricted this synthesis to the reaction of the four-membered rings (RB≡NtBu)$_2$ (R = Et, Pr, iPr, Bu) with the iminoborane iPrB≡NiPr [Eq. (5)].



(5)

An interconversion of rings 3 into thermodynamically more favorable rings 4 has never been observed in the absence of iminoboranes, apparently because of a high activation barrier. Differences in the delocalization of π-electrons and ring-strain arguments may be discussed as reasons for the lower energy of rings 4, as compared to rings 3. But the four-membered should be better in entropy than the six-membered rings. Is there a temperature, at which rings 4 could be converted into rings 3 for thermodynamic reason, high enough to allow the interconversion kinetically, but low enough to prevent uncontrolled radical reactions of the organic ligands? We first conducted the thermolysis of the borazines (RBNtBu)$_3$ (R = Me, Et, Pr, Bu) in the gas phase and found out a temperature of 650°C to be necessary in order to decompose the borazines completely[11]. Iminoboranes RB≡NtBu were found as the products in a cooled trap at the end of the hot tube. We suppose a (4+2) cycloreversion [reverse of Eq. (5)] to be the first step and the (2+2) cycloreversion of intermediate four-membered ring to be the second step of the over-all fragmentation. Independent experiments with $(RBNtBu)_2$ showed that these rings undergo such (2+2) cycloreversions at 650°C in the gas phase[11]. - The situation is different when the same borazines **4** are decomposed in their melt. Diazadiboretidines **3** are then isolated as the main products at 200-320°C. The same is true for the Dewar borazines $(RBNtBu)_3$ (R = iPr, Ph)[11]. Again we suppose the reverse of Eq. (5) to be the first step of this interconversion, followed by the cyclodimerization of iminoborane.

Poly(iminoboranes) **7**, formed from iminoboranes RB≡NR with primary alkyl groups R, can be thermally converted into the corresponding borazines $(RBNR)_3$ at temperatures that range from ca. 150°C (R = Et) to 250°C (R = iBu). A comparable process is unknown for the conversion of the isoelectronic polyacetylene into benzene, though both processes seem to be thermodynamically favored.

BORON-NITROGEN CLUSTERS FROM THREE-MEMBERED NBB RINGS

Whereas azadiboriridines $R'NB_2R_2$ (**1**) are stable at room temperature if protected by large groups R/R' (e.g. R/R' = tBu/tBu, tBu/Mes), they may otherwise be identified at -78°C by NMR methods, but dimerize at higher temperature or even at -78°C, forming hexaalkyl derivatives of diaza-nido-hexaborane $N_2B_4H_6$, according to Eq. (6). This azaborane is the isoelectronic BN analogue of the carbaborane $C_4B_2H_6$, which, as well as the boranes B_5H_9, $C_2B_4H_8$, and $C_3B_3H_7$, was found to have a pentagonal-pyramidal structure. Both structures, that of $C_4B_2H_6$ and $N_2B_4H_6$ derivatives, are derived from the pentagonal bipyramid as the corresponding closo-structure by removing a higher coordinated apical or - generally less favorable - a lower coordinated equatorial vertex. The structural difference can be qualitatively explained by assuming the cluster skeletons to be built up from localized (2c2e) and (3c2e) bonds and by assuming also that (3c2e) bonds are not favorable for the electronegative N atom. Such bonds can be restricted to the two B_3 triangles in the $N_2B_4H_6$ structure, leaving four (2c2e) bonds for each of the ammonium-type N atoms. In a pentagonal pyramid, on the other hand, one of the N atoms would necessarily take part in an unfavorable (3c2e) bond.

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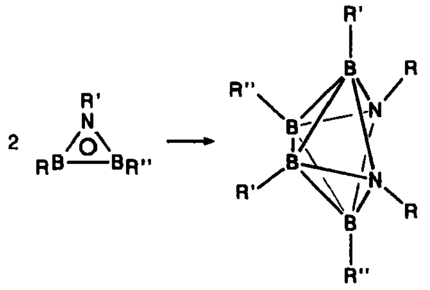
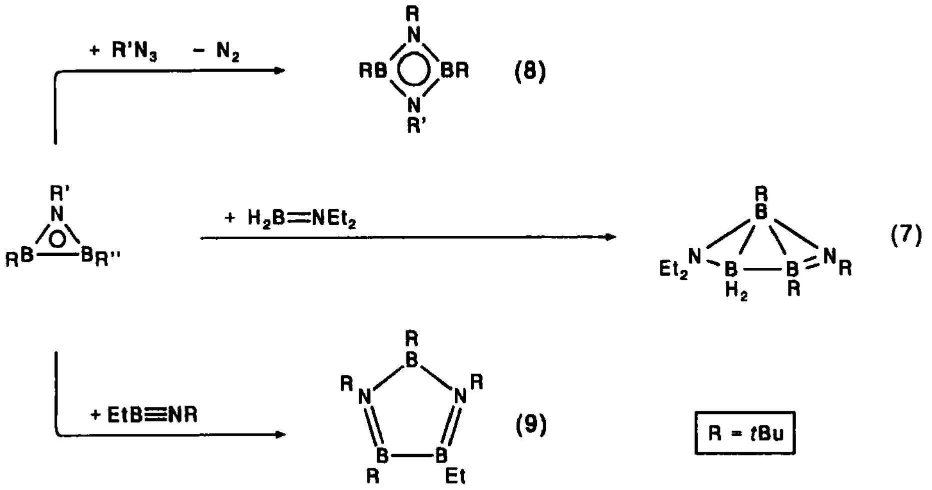


(6)

R'	R	R"	R'	R	R"
*i*Pr	*i*Pr	*i*Pr	*t*Bu	Et	*t*Bu
*i*Pr	*i*Pr	*t*Bu	*t*Bu	*i*Pr	*i*Pr
*t*Bu	Me	Me	*t*Bu	*i*Pr	*t*Bu
*t*Bu	Me	*t*Bu	Me_3Si	*i*Pr	*t*Bu
*t*Bu	Et	*i*Pr			

Upon the addition of the aminoborane $H_2B{=}BEt_2$, the stable azadiboriridine $NB_2\underline{t}Bu_3$ can be transformed into a derivative of diaza-arachno-pentaborane, $N_2B_3H_7$, isoelectronic with arachno-B_5H_{11} [Eq. (7)]^{25}. The one (3c2e) bond, which needs be attributed to $N_2B_3H_7$ in a localized bond description, can be restricted to the one B_3 triangle. A (2c2e) π-bond, that is deduced from that description, corresponds to an observed B-N bond length of 138.2 pm.

The three-membered ring $NB_2\underline{t}Bu_3$ can be expanded by cleaving its B-B bond, either by a nitrene unit from azides $R'N_3$^{26} or by an iminoborane^{24}. Four-membered rings of type **3** [Eq. (8); R' = iPr, Bu, Ph, $PhCH_2$, iPr_2B] or five-membered rings with an N_2B_3 skeleton [Eq. (9)] are formed, respectively. Bond lengths of 140.4 and 140.6 pm in the five-membered ring indicate the presence of two B-N double bonds.



(8)

(7)

(9)

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