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IMINOBORANES

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I. Introduction

Iminoboranes may be identified as a class of molecules with an imino group NR and a varying group X (e.g., F, RO, R_2N, R_3C) bonded to boron. Iminoboranes (XBNR) belong to the family of neutral two-coordinated boron species which may be arranged systematically in the following way:

$XBCR_2$	XBNR	XBO
$XBSiR_2$	XBPR	XBS
⋮	⋮	⋮

Experimental data for alkylidenoboranes ($XBCR_2$) (*1*), oxoboranes (XBO) (*2*), and thioboranes (XBS) (*3–7*) are described in the literature. All these molecules exhibit novel multiple bonds between boron and its neighboring atoms. For some years, doubly or triply bonded main group elements, involving not only boron, but also silicon, phosphorus, sulfur, and others, have modified the traditional qualitative concepts of bonding. As a counterpart, chemists have also become aware of multiple bonds, including quadruple bonds, between transition metals.

In particular, iminoboranes (XBNR) are isoelectronic with alkynes (XCCR). Well-known comparable pairs of isoelectronic species are aminoboranes (X_2BNR_2) and alkenes (X_2CCR_2), amine–boranes (X_3BNR_3) and alkanes (X_3CCR_3), borazines [$(XBNR)_3$] and benzenes [$(XCCR)_3$], etc. The structure of aminoboranes, amine–boranes, and borazines is well known from many examples. It has turned out that these BN species are not only isoelectronic, but also have structures comparable with the corresponding CC species. In the case of borazines, the aromatic character was widely discussed on the basis of theoretical and experimental arguments. The structural and physical properties of

BN species parallel those of CC. This parallelism does not hold so nicely for reactivity. The polarity and relative weakness of B—N bonds make BN species much more reactive than comparable CC species, at least with respect to polar additions or substitutions, and the reaction paths as well as the products may differ greatly. The chemistry of BN compounds with three- or four-coordinated B and N atoms is summarized in advanced textbooks, and the details can be found in Gmelin's handbook.

This article describes what is known about the formation, structure, and reactivity of iminoboranes. The chemistry of iminoboranes is in its beginnings, and so we cannot paint a complete picture. A comparison between iminoboranes and the corresponding alkynes will serve as a background throughout this novel field of boron chemistry.

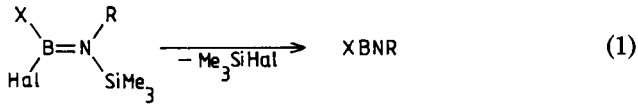
II. Formation of Iminoboranes

A. Metastable Iminoboranes

Since iminoboranes are thermodynamically unstable with respect to their oligomerization (Section IV,A), they can be isolated under laboratory conditions by making the oligomerization kinetically unfavorable. Low temperature, high dilution, bulky groups R and X, or a combination of these is necessary.

The parent compound HBNH was the first iminoborane to be identified unequivocally (*8*). It was formed by photolysis of solid H_3BNH_3 and trapped, together with further products, in a rare gas matrix which provided low temperature and high dilution for this extremely unshielded molecule. Evidence for the iminoborane in the mixture came from a vibrational analysis, all four atoms in turn being isotopically labeled.

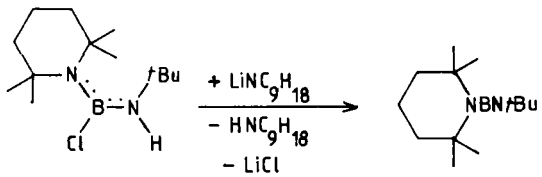
The first iminoborane that could be handled at $-30°C$ in a liquid 1:1 mixture with Me_3SiCl was $(F_5C_6)BNtBu$ (*9*). It was synthesized by the general elimination reaction in Eq. (1) (Hal = halide) from the corresponding aminoborane. A "hot tube procedure" must be employed for



(1)

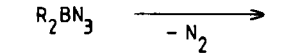
this type of elimination with temperatures near 500°C and pressures near 10^{-3} Torr. The products are trapped at liquid nitrogen temper-

ature. The halosilane can be separated by low-temperature evaporation, provided that the iminoborane formed is relatively stable (*10–14*). The extreme shielding effect of X = $(Me_3Si)_3C$ and X = $(Me_3Si)_3Si$ makes the corresponding iminoboranes (R = $SiMe_3$) storable at room temperature (*15*); it may be that these particular iminoboranes are stable toward oligomerization even in a thermodynamic sense. The compound $(Me_3Si)_3CBNSiMe_3$ could be prepared in the liquid phase at 60°C, according to Eq. (1). The 2,2,6,6-tetramethylpiperidino group, $C_9H_{18}N$, also exhibits a strong shielding effect, so that the aminoiminoborane $C_9H_{18}NBNtBu$ may be synthesized at room temperature by base-induced HCl elimination after Eq. (2), without considerable product loss by dimerization (*16*).



(2)

Thermal decomposition of azidoboranes [Eq. (3)], and of [trimethylsilyl(trimethylsilyloxy)amino]boranes [Eq. (4)], permits a simple synthesis of "symmetric" iminoboranes RBNR (*17–19*). A hot tube procedure at about 300°C and 10^{-3} Torr turned out to be useful. The iminoborane *i*PrBN*i*Pr, for example, was prepared at a rate of 10 g/hour by the azidoborane method. No separation problems are met with this method. Handling the liquid reactants of Eqs. (3) and (4) is hazardous.



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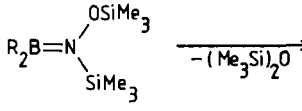


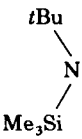
(4)

The violence of uncontrolled decompositions decreases markedly with the bulk of R, and explosions are more violent in the case of azidoboranes. Hot tube experiments at 400°C, aiming at the preparation of aminoiminoboranes XBNR [X = $Me_3Si(tBu)N$, R = *i*Pr, Bu] from the corresponding azidoboranes $XRBN_3$, have been unsuccessful insofar as the cyclodimers of XBNR were the only isolable products (*14*).

At present, 17 iminoboranes are known as sufficiently well-characterized liquids (Table I). Spectroscopically, there are two typical

TABLE I

ISOLATED IMINOBORANES XBNR

X	R	Preparation equation number	Spectroscopic evidence	Reference
Me	Me	(3), (4)	NMR (^{1}H, ^{11}B, ^{13}C), IR, PE	*19*
Me	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR	*13*
Et	Et	(4)	NMR (^{1}H, ^{11}B), IR	*19*
Et	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR	*10*
Pr	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR	*10*
*i*Pr	*i*Pr	(3), (4)	NMR (^{1}H, ^{11}B), IR	*17, 19*
*i*Pr	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR	*12*
Bu	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR	*10*
*i*Bu	*i*Bu	(3)	NMR (^{1}H, ^{11}B), IR	*17*
*s*Bu	*s*Bu	(3)	NMR (^{1}H, ^{11}B), IR	*17*
*s*Bu	*t*Bu	(1)	NMR (^{11}B), IR	*19*
*t*Bu	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N), IR, Raman, PE	*11*
F_5C_6	*t*Bu	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F), IR	*9*
$(Me_3Si)_3C$	$SiMe_3$	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N, ^{29}Si), IR	*15*
$(Me_3Si)_3Si$	$SiMe_3$	(1)	NMR (^{1}H, ^{11}B, ^{13}C, ^{14}N, ^{29}Si), IR	*15*
	*t*Bu	(2)	NMR (^{1}H, ^{11}B, ^{13}C), IR	*16*
	*t*Bu	(1)	NMR (^{1}H, ^{11}B), IR	*14*

features, easily accessible at low temperature: (1) ^{11}B-NMR chemical shifts are found in a range from 2.3 to 6.3 ppm ($Et_2O \cdot BF_3$ as the external standard), depending on the ligands X and R and on the solvent. These shifts are far from the ^{11}B shifts of the corresponding oligomers. Outside of that range, an ^{11}B signal appears at -2.7 ppm with $(F_5C_6)BNtBu$, apparently due to the extraordinary electronic effect of the pentafluorophenyl group. ^{11}B-NMR shifts at 21.0 and 21.9 ppm for the iminoboranes with R = $SiMe_3$ are far away from the typical range, perhaps due to the N-bonded $SiMe_3$ group. (2) A broad intense absorption peak in the range 2008–2038 cm^{-1} is observed in the infrared spectrum of alkyl(alkylimino)boranes R'BNR, together with a less intense band in the range 2063–2090 cm^{-1}. These bands can be assigned to the ^{11}BN and ^{10}BN vibrations, respectively (Section III,C). Aminoiminoboranes cause absorptions at lower frequencies: 1990 cm^{-1} for the N^{11}BN and 2020–2025 cm^{-1} for the N^{10}BN asymmetric stretch-

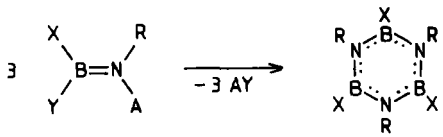
ing vibration. The $^{11}BN/^{10}BN$ band couple for $[(Me_3Si)_3E]BNSiMe_3$ falls out of the typical range: 1885, 1940 cm^{-1} (E = C) and 1985, 1925 cm^{-1} (E = Si). A monomeric structure including a linear CBNC skeleton was proven for *t*BuBN*t*Bu in the solid state at −85°C (Section III,B). Since the typical spectroscopic data for this particular molecule are in accord with the data of all iminoboranes R'BNR, one can ascribe the same structural features to all of them.

Iminoboranes exhibit marked differences in their kinetic stability. The methyl derivative is the most unstable, as expected; cocondensation of equal amounts of MeBNMe, $(Me_3Si)_2O$ [Eq. (4)], and pentane gives a mixture that is liquid at −90°C and needs to be worked up quickly for spectra or further reactions; after 2 days at −90°C, MeBNMe is no longer detectable, and the stabilization product, $(MeBNMe)_3$, is a by-product from the beginning. The stability of EtBNEt is not much greater, whereas pure liquid *i*BuBN*i*Bu with β-branched alkyl groups may be handled, but not stored, at −80°C. α-Branched alkyl groups markedly stabilize iminoboranes; *i*PrBN*i*Pr and *s*BuBN*s*Bu can be stored as pure liquids at −80°C for some time, but trimerize rapidly at room temperature, liberating a detectable amount of heat. Finally, 1 g of *t*BuBN*t*Bu with the doubly α-branched *t*Bu groups dimerizes with a half-life of 3 days at +50°C; this iminoborane may be handled as a normal, air-sensitive organoborane at 0°C. The two aminoiminoboranes (Table I) seem to be even more stable.

Production of iminoboranes by a hot tube procedure is obviously restricted to those reactants that can be transported into the gas phase without decomposition. Owing to this restriction the reactions according to Eqs. (3) and (4) cannot be applied to reactants with alkyl groups larger than C_4H_9 or with aryl groups.

B. Iminoboranes as Intermediates

Equation (5) represents a general formation of borazines, performed in solution or in the melt from the starting aminoborane, carried out either thermally or with the aid of bases. Apparently, Eq. (5) is a more or

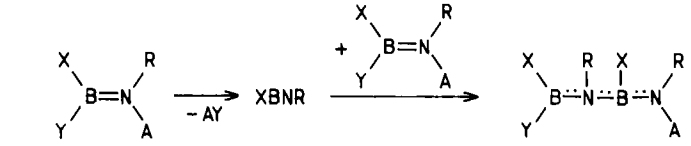


(5)

A = H, R'_2B, Me_3Si, etc.

Y = H, F, Cl, Br, R'O, R'_2N, etc.

less complicated multistep process. If we consider the first step only, there will be at least two plausible mechanistic alternatives: (1) formation of iminoborane by elimination of AY, [Eq. (6)], and (2) a bimolecular association equilibrium [Eq. (7)]. We do not know of a proposed mechanism via iminoboranes that is supported by substantial evidence.



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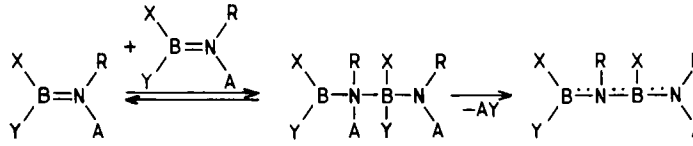


(7)

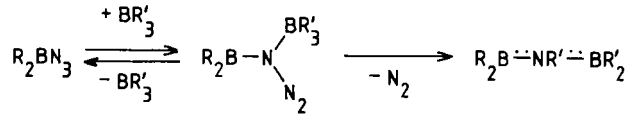
Equation (8) represents the decomposition of liquid azidoboranes at a temperature lower than 100°C (*17*). At higher temperatures, additional decomposition transforms the products into the corresponding borazines $(XBNR)_3$, according to Eq. (5).

$$2\ R_2BN_3 \xrightarrow[-N_2]{} R_2B{=}NR{=}BR{=}N_3 \qquad (8)$$

R = Pr, *i*Pr, Bu, *i*Bu, *s*Bu, *n*-C_6H_{11}

Iminoboranes were suggested as intermediates, which were azidoborated by an excess of reactants. It was argued that the same products are formed when isolated iminoboranes, RBNR, produced according to Eqs. (1), (3), and (4), are azidoborated with R_2BN_3 (Section V,C). Further support for iminoboranes as intermediates came from the observation that the trapping function of the azidoborane in Eq. (8) can be overcome by an excess of independent trapping agents (e.g., trialkylboranes BR'_3, the reagents that are known to give the same products in reactions with isolated iminoboranes) (*10–14, 17, 18*). Transposing the mechanistic alternatives of Eqs. (6) and (7) to the decomposition of R_2BN_3 in the presence of BR'_3, we should consider the two final products of Eqs. (9) and (10), which are easily distinguishable by NMR.

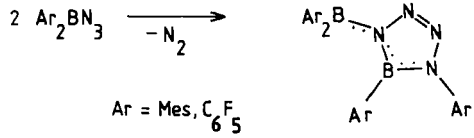
$$R_2BN_3 \xrightarrow[-N_2]{} RBNR \xrightarrow{+\,BR'_3} RR'B{=}NR{=}BR'_2 \qquad (9)$$



(10)

With the ligands R of Eq. (8) and with BEt_3 as the trapping agent, the diborylamines of Eq. (9) were formed, but no product of Eq. (10) was detected (*17*), thus strongly supporting the idea of iminoborane intermediates.

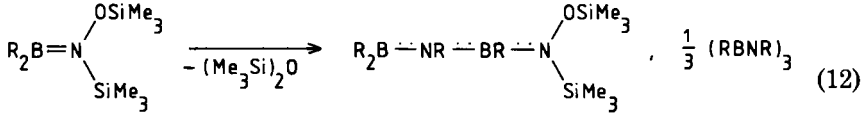
The situation is different when diarylazidoboranes, Ar_2BN_3, decompose. First, the overall reaction differs from Eq. (8). Simple aryl groups like phenyl or *o*-tolyl cause the formation of iminoborane cyclooligomers, without primary trapping products being isolable. The pentafluorophenyl or the mesityl group makes products available that might have been formed again by trapping iminoboranes by the starting compounds; but instead of azidoboration products [Eq. (8)], [2 + 3]-cycloaddition products are isolated [Eq. (11)] (*20*). With BEt_3



(11)

as the trapping agent, products in accord with Eq. (9) were found, pointing to iminoboranes ArBNAr as intermediates for all four aryl groups under investigation. But in the case of phenyl and pentafluorophenyl, a second product in accord with Eq. (10) is formed as the major product, indicating two different mechanisms. The second one seems to involve greater steric requirements in the primary step and is inhibited, therefore, for Ar_2BN_3 with the bulky groups *o*-tolyl and mesityl. A difficulty for this interpretation comes from the observation that a bulky agent like $BsBu_3$ does trap iminoboranes ArBNAr, but predominantly (Ar = Ph) or even exclusively (Ar = C_6F_5) in accord with Eq. (9).

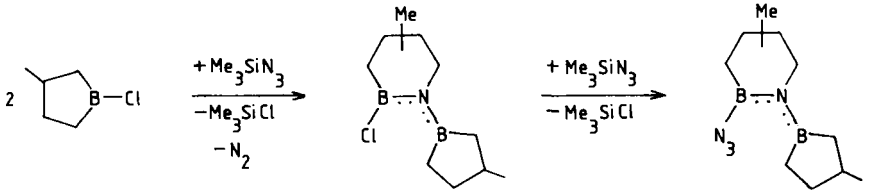
[Silyl(silyloxy)amino]boranes decompose in the liquid phase to a mixture of products [Eq. (12)] (*18, 19*). Again, the formation of the



(12)

product with the BNBN chain was explained by the presence of intermediate iminoboranes, which had been trapped by the starting borane. Again, the same product was found by aminoboration of the isolated iminoboranes with the reactants of Eq. (12) (Section V,C). Once more, BEt_3 proved to be a trapping agent. For the role of PhN_3 and Me_3SiN_3 as reagents for trapping iminoboranes, we refer to the above-cited literature (see also Sections V,C and VI,B).

There is some evidence for cyclic iminoboranes as intermediates. When cyclic chloroboranes react with Me_3SiN_3 at room temperature (i.e., the normal route for attaching an N_3 group to boron), evolution of N_2 is observed and one of the products of Eqs. (13) and (14) is isolated,



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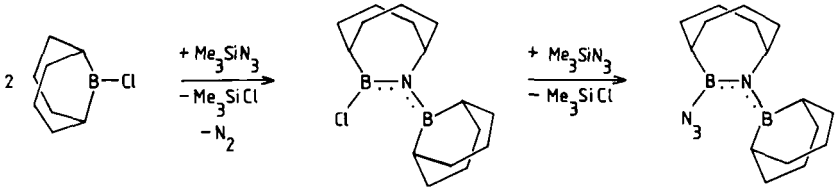
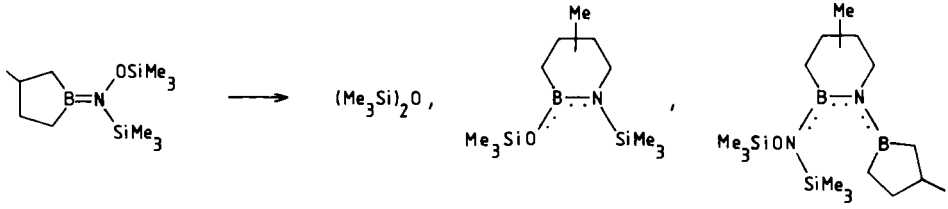


(14)

depending on the amount of Me_3SiN_3 (*19*). The most plausible mechanistic interpretation involves as an initial step the formation of the corresponding cyclic azidoboranes, which are unstable at room temperature. Elimination of N_2 is accompanied by ring expansion, yielding the cyclic iminoboranes **I** and **II**, respectively. By analogy with cycloalkynes having less than eight ring members, **I** and **II** are expected to be extremely reactive and to be chloroborated immediately by the starting borane.

I II

The chloroborane reactants of Eqs. (13) and (14) can be aminated to isolable [silyl(silyloxy)amino]boranes, which decompose at 120 and 70°C, respectively, to give a mixture of products, three of which were identified in both cases [Eqs. (15) and (16)] (*19*). Again, the iminoboranes



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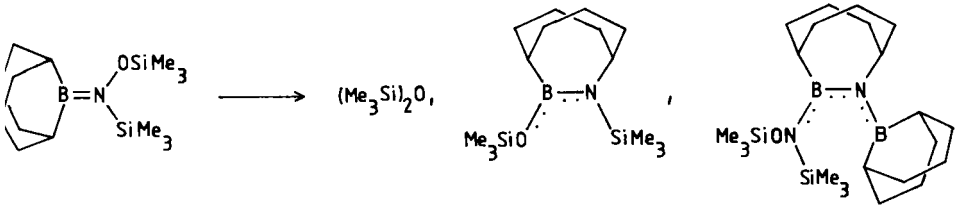
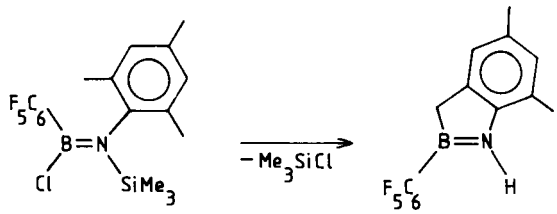


(16)

I and **II** are postulated as reactive intermediates, adding, rather unspecifically, both the primary elimination product $(Me_3Si)_2O$ ("oxysilation") and the reactant ("aminoboration"). Performing the decomposition in an excess of siloxane $(Me_3Si)_2O$ gives only the oxysilation product.

Finally, three examples are reported in which iminoboranes as intermediates do not react with trapping agents but stabilize themselves intramolecularly in the gas phase during a hot tube procedure [Eqs. (17)–(19)]. A prerequisite is the steric availability of side groups with respect to the BN bonds (*9, 21*). The products are well established either by solvolytic degradation (*9*) or by *X*-ray analysis (*21*). Note that



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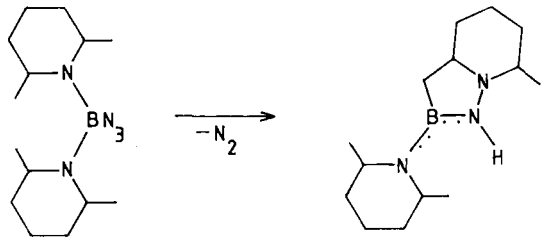

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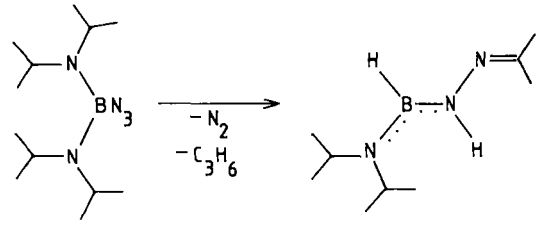
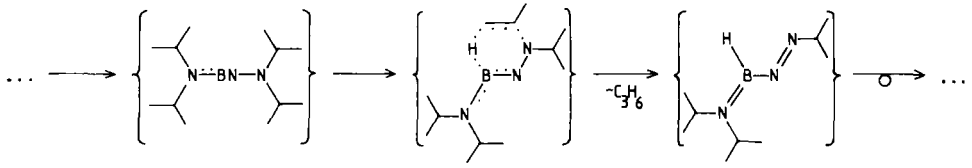


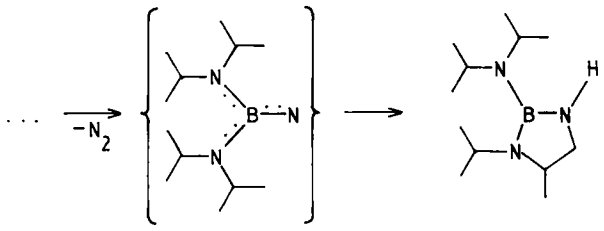
(19)

the elimination of N_2 in Eqs. (18) and (19) is accompanied by the migration of an amino group, replacing a strong B—N by a weak N—N bond! Iminoboranes are the plausible intermediates in all three cases. The stabilization involves addition of a C—H bond to the iminoborane B—N bond ("alkylohydration"), provided that sterically fixed methyl groups are available [Eqs. (17), (18)]. In the course of Eq. (19), the iminoborane is presumed to eliminate propene via a six-membered transition state, leaving an azo compound that readily rearranges to the finally isolated hydrazone [Eq. (19a)].



(19a)

When thermolyzing azido compounds, the question arises as to whether an observed rearrangement is achieved in one step, concerted to the elimination of N_2, or whether there are two steps, elimination and rearrangement, with nitrenes as intermediates. Generally, thermolysis of azidoboranes is more probably a concerted process (*22*). The decomposition of $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{BN}_3$, however, carried out at 450°C, gives a product, besides the main product of Eq. (19), that has to be interpreted in terms of a nitrene stabilized by an intramolecular CH insertion [Eq. (19b)].



(19b)

III. The Structure of Iminoboranes

A. Theoretical Evidence

There are several nonempirical theoretical approaches to HBNH, starting from different bases (*23, 24*). The optimum arrangement of the atoms turns out to be a linear chain, point group $C_{\infty v}$, with BN bond lengths of 127 (*23*) and 123 pm (*24*), respectively. The highest occupied molecular orbitals (HOMOs) are the degenerate BN π-orbitals [orbital energies: -12.7 eV (*23*), -11.0 eV (*24*)], followed by the BN σ-orbital [-16.6 eV (*23*), -15.6 eV (*24*)]. The lowest unoccupied molecular orbitals (LUMOs) are the degenerate π^*-orbitals.

The BN bonding energy was found to be 88 kcal/mol. When compared with 94 kcal/mol for the isoelectronic ethyne, the B—N bond in HBNH seems to be somewhat weaker than a C≡C triple bond. (Both values were calculated without taking electron correlation into account and would be lower, therefore, than values from experiments; this does not limit a qualitative comparison.) The total BN overlap population was found to be 0.765, while the corresponding values for a B—N bond in the cyclooligomers $(HBNH)_2$ and $(HBNH)_3$ are 0.392 and 0.425, respectively.

Apparently there is a substantial contribution to the B—N bond of HBNH from one σ- and two orthogonal π-bonds. Expressed in simple terms, there is a B≡N triple bond in iminoboranes. Concerning a structural formula for HBNH, the real situation is represented best by H—B≡N—H.

The compound HBNH is expected to be thermodynamically unstable toward oligomerization. The cyclodimer, $(HBNH)_2$, isoelectronic with cyclobutadiene, is found to be more stable by 63.3 kcal/mol, and the cyclotrimer, $(HBNH)_3$, by 193.8 kcal/mol than 2 or 3 mol of HBNH, respectively (*23*). The oligomerization energy is due to an increase in the number of σ-bonds at the expense of the relatively weak π-bonds. Note that the situation is the same for acetylene. Oligomers like cyclobutadiene, benzene, benzvalene, and cyclooctatetraene are

thermodynamically more stable than acetylene, and the formation of polyacetylene is also an exothermic reaction. Certainly, benzene is the most stable product of the stabilization of acetylene. In the corresponding BN case, the calculated oligomerization energies prove the cyclotrimer also to be more stable than the cyclodimer. Ring strain effects are responsible for that, and, at least in carbon ring systems, the cyclic delocalization of π-electrons plays an important role, according to Hückel's rule.

From gross electronic populations, the excess atomic charges can be derived as follows:

H———B≡≡≡≡N———H				
0.03	0.26	−0.62	0.32	(*23*)
−0.03	0.21	−0.43	0.25	(*24*)

Apart from differences in the calculated values, the B—N bond in HBNH is a polar bond with a $\delta+$ charge on boron and a $\delta-$ charge on nitrogen. All three bonds exhibit some ionic character. Thus each of the π-bonds was found to be 39% ionic. This polarity does not imply that the π-bonds are substantially weakened; the ionic character reduces the π-bond strength from 100 to 89%. Applying the concept of formal charges to HBNH, a formula results that does not only overemphasize the amount of polarity, but also gives the wrong sign: $H—\bar{B}\equiv\overset{+}{N}—H$. Such a formalism has no physical meaning and cannot be recommended, as the only advantage seems to be increased clarity in electron counting. The dipole moment of HBNH was estimated to be 0.86 D (*24*).

A striking difference between alkynes and iminoboranes appears to be their kinetic stability. As was pointed out in Section II, iminoboranes are metastable, in general, at temperatures far below room temperature. Alkynes are also metastable, but their stabilization requires either high temperature or effective catalysts. We assume the polarity of the B—N bond to be a chief reason for these differences. This idea is supported by the observation that strongly polar alkynes (e.g., FC≡CH, FC≡C*t*Bu) do oligomerize or polymerize at room temperature quite rapidly (*25*). Polar additions will generally be the predominant reaction for iminoboranes (Sections V,VI).

Considering derivatives of the "parent compound," HBNH, a MNDO/1 calculation was done on the dimethyl derivative, MeBNMe (*11*). Again, a linear CBNC chain turned out to represent the optimal geometry, point group C_{3v}, with a B—N bond distance of 119 pm. The HOMOs, once more, are two degenerate BN π-orbitals (−11.3 eV), followed by degenerate CH_3 σ-orbitals (−14.2 eV) and by the BN σ-orbital (−14.3 eV). A small dipole moment, 0.14 D, was proposed.

B. X-Ray Structural Evidence

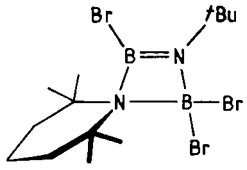
The crystal and molecular structure of a single crystal of *t*BuBN*t*Bu was investigated by X-ray methods at −85°C (*11*). The substance crystallizes in the space group *Pnma*, isostructural with the isoelectronic alkyne *t*BuCC*t*Bu (*26*). Boron and nitrogen atoms are disordered. The linear CBNC skeleton is framed by six methyl groups in an eclipsed conformational arrangement, leading to the point group C_{3v} for the iminoborane and D_{3h} for the alkyne. The central bond lengths were found to be 125.8 pm (BN) and 118.0 pm (CC).

In a recent summary on C≡C bond lengths, widespread values for 23 different bonds were cited with an average value of 118.5 pm, referring to X-ray determinations at room temperature; bond lengths from electron diffraction data or from microwave analysis were found to be distinctly longer (*27*). For a mostly qualitative general discussion we take 118 pm as typical for a C≡C bond. Apart from exotic examples, bond lengths for C—C single and C=C double bonds in crystals are found in a quite narrow range; values of 154 pm and 133 pm, respectively, can generally be accepted.

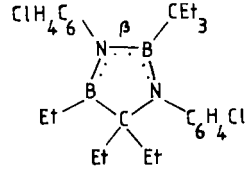
In noncyclic crystalline amine–boranes with noncyclic components BX_3 and NR_3, the upper limit of known B—N bond lengths is 160.2 pm in Br_3BNMe_3 (*28*), and the smallest value is 157.5 in Cl_3BNMe_3 (*29*); an average B—N bond length of 158.7 pm results, including seven further amine–boranes and including BX_3 components like BH_3, BF_3, $BH_2(NCS)$, and $[BHBrPic]^+$ (Pic = 4-picoline). We have to mention that in cyclic amine–boranes as well as in amine–boranes with cyclic components, larger BN distances are reported (e.g., 166.2 pm in the adduct from borane, BH_3, and urotropine (*30*)]. Boron–nitrogen bonds in gaseous amine–boranes seem to be larger, too; the two values 158.5 and 163.6 pm are found for the same substance, $F_3B—NMe_3$, in its crystalline and in its gaseous state, respectively (*31, 32*). For purposes of a gross comparison we take 159 pm as typical for the B—N single bond.

In order to obtain a typical bond length for the B=N double bond, we take into account aminoboranes X_2BNR_2 with planar tricoordinated boron and nitrogen atoms. With this restriction, diaminoboron cations with a dicoordinated boron atom [e.g., $[Me_2N=B=NC_9H_{18}]^+$ (*33*)] or (alkylidenamino)boranes with a dicoordinated nitrogen atom [e.g. $Mes_2B=N=CPh_2$ (Mes = mesityl) (*34*)], are not considered; these molecules may have particularly short B—N distances, the extreme value being 130 pm (*33*). Molecules where boron and nitrogen are in an exceptional steric situation are also not considered [e.g., the trapezoidal molecule **III**, whose B=N bond length is only 134 pm (*16*)]. On the other hand, extremely long B—N distances may be found when

such groups are bonded to nitrogen that compete with the boron atom for the nitrogen π-electrons [e.g. $F_2B{=}N(SiH_3)_2$, $d(B{=}N) = 149.6$ pm (from electron diffraction) (*35*)]. Finally, an extra-long B—N bond might be found for the central bond in molecules with BNBN chains, which are isoelectronic with 1,3-dienes [e.g. **IV**, $d(BN)_\beta = 148.8$ pm (*36*)].



III



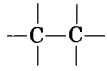
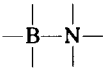
IV

The B—N distances for five noncyclic aminoboranes were reported with an average distance of 141.4 pm, the extreme values being 137.9 pm in $Cl_2B{=}NPh_2$ (*37*) and 143.9 pm in $B(NMe_2)_3$ (*38*). The relatively large B—N bond length for the triaminoborane can be well understood, because three nitrogen lone pairs have to share one vacant boron *p*-orbital. The crystal and molecular structures of 30 cyclic aminoboranes are reported to have B—N bond lengths similar to those for noncyclic aminoboranes, the average value being 141.8 pm. Borazines $(XBNR)_3$, which were included in the averaging procedure, tend to have longer B—N bonds ($\sim$143 pm) than the average value. The difference from the average value would be rather small if the C—C bond lengths in the isoelectronic species alkene and benzene, 133 and 140 pm, respectively, were considered. One might have in mind, however, that too detailed conclusions from bond lengths could become meaningless for methodical reasons, because of crystal effects in the case of X-ray analysis, because of the lack of simple correlations between bond lengths and electronic properties, etc. The highest values in averaging the B—N bond lengths of cyclic aminoboranes were contributed by three diazadiboretidines $(XBNR)_2$, the cyclodimers of iminoboranes (Section IV,B), with bond lengths close to 145 pm.

Though adoption of a "typical" B=N bond length may be questionable, we suggest 141 pm as a possible value, referring to noncyclic aminoboranes. The most questionable course is to generalize the one experimentally established B≡N triple bond distance of 126 pm. On the other hand, the steric situation at least will not be too different, if the substituents R and X in XB≡NR, distant from each other, are altered. Thus we take 126 pm as a typical B≡N triple bond distance. The preceding discussion is summarized in Table II.

TABLE II

COMPARISON OF CC AND BN BOND LENGTHS

CC species	d (pm)	Δd (pm)	BN species	d (pm)	Δd (pm)
	154			158	
		21			17
	133			141	
		15			15
—C≡C—	118		—B≡N—	126	

The difference between a single and a double bond distance is nearly 20 pm but it is only 15 pm between a double and a triple bond. Boron–nitrogen bonds are longer than the corresponding C—C bonds, the difference being nearly 5 pm for the single bonds and nearly 8 pm for the double and triple bonds.

C. Spectroscopic Evidence

Much is known empirically on ^{11}B-NMR data (*39*). Restricting boron compounds to noncyclic molecules with no or one nitrogen atom and two, three, or four carbon atoms bonded to boron and omitting sterically overcrowded alkyl groups R and R′, we find four classes with the following typical chemical shift ranges ($Et_2O \cdot BF_3$ as the external standard):

$[R'_4B]^-$	$R'_3B{-}NR_3$	$R'_2B{=}NR_2$	R'_3B	
−22 to −16	−9 to +5	+42 to +49	+83 to +88	ppm

Trialkylboranes represent the smallest electronic shielding of the ^{11}B nucleus; only three σ-bonds are available for a sextet boron atom. One additional π-bond in aminoboranes increases the shielding effect. Four σ-bonds in amine–boranes exhibit still stronger shielding, and an additional negative charge in tetraalkyl borates brings a maximum shielding in this series. Iminoboranes R′B≡NR have two σ- and two π-bonds. The typical ^{11}B-NMR shifts in the range 2.3–6.3 ppm (Section II,A) apparently cannot be explained in the above oversimplified σ/π

bond picture. The orthogonal π-electron distribution may cause an unusual effect of diamagnetic anisotropy. A theoretical elucidation would be desirable.

A vibrational analysis is reported for HBNH (*8*) and *t*BuBN*t*Bu (*40*). Infrared data for the parent compound in an argon matrix were obtained with 10 isotopically labeled species, including the isotopes ^{1}H, D, ^{10}B, ^{11}B, ^{14}N, and ^{15}N. With restriction to the species $H^{11}B^{14}NH$, most common from natural material, two Σ^+ stretching modes were found at 3700 and 1785 cm^{-1}, which were readily assigned to the asymmetric hydrogen stretch ν_1 (with more NH character) and to the BN stretching vibration ν_3. The third Σ^+ mode (i.e., the symmetric hydrogen stretch ν_2, with more BH character), could not be detected. All three Σ^+ vibrations were calculated from a set of three force constants; of the resulting wave numbers, 3700, 2800, and 1785 cm^{-1}, two are in ideal accord with the observed values. The relatively weak intensity of ν_3 and the vanishing intensity of ν_2 lead to a very small dipole moment for HBNH, so that the vibrations ν_2 and ν_3 become comparable to the IR-inactive Σ_g^+ vibrations of the isoelectronic molecule HCCH. One of the two expected Π bending frequencies was detected at 460 cm^{-1}, representing more BNH than HBN bending character. The best force constant k(BN) turned out to be 13.14 N/m.

The IR and Raman spectra of liquid *t*BuBN*t*Bu with fairly pure ^{10}B and in natural isotopic abundance were recorded, together with the corresponding spectra of the isoelectronic alkyne *t*BuCC*t*Bu. In accord with a normal coordinate analysis, the fundamental frequencies were assigned in terms of a linear central skeleton and a staggered arrangement of the methyl groups. The resulting D_{3d} symmetry of the alkyne was found to agree with the exclusion principle for IR and Raman intensities in the presence of a center of symmetry. Though there is no such center in the iminoborane with C_{3v} symmetry, the same exclusion principle is at least indicated by corresponding strong or weak intensities and vice versa in both spectra, representing evidence, once more, for a small dipole moment of the iminoborane and a distinct structural similarity of the two isoelectronic species. The more unfavorable eclipsed conformation of both molecules in the solid state seems to be evoked by crystal lattice forces. The ^{11}B—N stretching frequency was found at 2009 cm^{-1}; the C≡C Raman band of the corresponding alkyne appears at 2226 cm^{-1}. The large difference of 224 cm^{-1} in the ^{11}BN frequencies of HBNH and *t*BuBN*t*Bu is due to the strong coupling between the symmetric stretching vibrations ν_2 and ν_3 of HBNH and does not imply a difference in the bond strengths. A force constant k(BN) = 12.79 N/m was the best fitting value for *t*BuBN*t*Bu.

The BN force constants of HBNH and *t*BuBN*t*Bu (13.14 and 12.79 N/m, respectively) are similar in magnitude. The corresponding CC force constants of HCCH and *t*BuCC*t*Bu [15.59 (*41*) and 15.58 N/m, respectively] indicate the C≡C triple bond to be stronger than the B≡N triple bond. From average values [k(B≡N) = 12.9 and k(C≡C) = 15.6 N/m] we find k(B≡N) = 0.83k(C≡C). The same trend was deduced from MO calculations and from bond lengths (Sections III,A,B). The relationship between alkynes and iminoboranes can be compared to the relationship between the isoelectronic molecules N_2 and CO: The N≡N bond (109.76 pm) is shorter than the C≡O bond (112.82 pm) (*42*), and the force constant of N_2 (22.98 N/cm) is larger than that of CO (18.47 N/cm) (*43*), according to k(CO) = 0.80k(N_2). This trend does not hold for the dissociation energy, which is larger for CO than for N_2.

The photoelectron spectrum of *t*BuBN*t*Bu shows the first ionization energy to be 9.35 eV (*11*), compared to 9.05 eV for the corresponding alkyne *t*BuCC*t*Bu (*44*). The photoelectron is expected to be one of the four π-electrons.

D. Dipole Moments

A value of 0.20 D was found for the dipole moment of *t*BuBN*t*Bu in cyclohexane (*11*). Theoretically estimated values are 0.86 D for HBNH and 0.14 D for MeBNMe with $\delta+$ on boron and $\delta-$ on nitrogen (Section III,A). The vibrational analysis of *t*BuBN*t*Bu indicates a small dipole moment (Section III,C). If conclusions from reaction paths to ground states are permitted, the dipole direction in all known iminoboranes will be the one predicted by theory, since addition of polar agents AY to the BN bond principally directs the positively charged fragment A to nitrogen and the negatively charged fragment Y to boron (Sections IV–VI).

More generally, "symmetric" iminoboranes RBNR, with identical ligands at both triply bonded atoms, seem to have a small dipole moment in common with carbon monoxide, CO, whose dipole moment is 0.112 D. In spite of being small, the polarity of the BN bond as well as that of the CO bond is large enough to make iminoboranes as well as carbon monoxide more reactive toward polar addition than the isoelectronic alkynes and dinitrogen, respectively. A difference between RBNR and CO is the direction of the dipole; in CO, the more electronegative oxygen bears the small positive charge (*45*), which happens to be in accord with the sign of the formal charges in the structural formula $[\overset{-}{C}\equiv\overset{+}{O}]$. Although not theoretically sound, an experimentally verifiable

conclusion would be that the carbon atom in CO works as the Lewis base center, which is well established for BH_3 or certain transition metal compounds as the corresponding Lewis acids.

E. Conclusions Concerning Structural Formulas

It can be concluded from the discussions in Sections IIIA–D that B=N double bonds in aminoboranes and B≡N triple bonds in iminoboranes represent a realistic picture. It is here recommended, therefore, to indicate these bonds in structural formulas as usual, but to omit erroneous formal charges, e.g., amine–borane: $X_3B—NR_3$; aminoborane: $X_2B=NR_2$; iminoborane: XB≡NR. [Note that $R_3N \cdot BX_3$ is recommended as the correct molecular formula for amine–boranes (*46*), but one is not bound to rules in constructing structural formulas, e.g., $X_3B—NR_3$.]

Arrows instead of dashes for the representation of so-called coordinative covalent bonds call for mention. The history of bond formation may not be represented in a formula. Furthermore, in formulas like $[R_3N \rightarrow BH_2—NR_3]^+$ or XB≡NR, for example, two symmetrically equivalent bonds are represented by a plotting procedure different for each of the two, a rather illogical way, particularly, since it is uncertain which of the two bonds, if either, had been the coordinative one during the formation.

There is no general objection to writing down mesomeric structures, e.g.,

$$\{X_2B—\bar{N}R_2 \longleftrightarrow X_2B=NR_2\}$$

but the less complicated method of omitting the structure of obviously little weight seems to be preferable. When a π-electron pair is delocalized over more than two atoms, it is preferable to draw one formula with dotted lines along the area of delocalization. For example, in the case of diaminoboranes $XB(NR_2)_2$:

$$R_2N \overset{\cdot\cdot}{=} B(X) \overset{\cdot\cdot}{=} NR_2,$$

is preferred over a pair of mesomeric structures:

$$\{R_2N=B(X)—NR_2 \longleftrightarrow R_2N—R(X)=NR_2\}$$

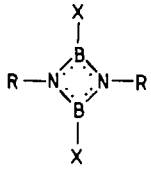
The cyclic delocalization of π-electrons in diazadiboretidines $(XBNR)_2$, or borazines, $(XBNR)_3$, etc., will be indicated by dotted lines over bonds, again favored over mesomeric structures.

IV. Oligomerization of Iminoboranes

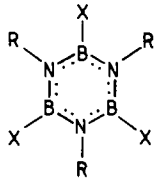
A. Survey

The activation barrier for the oligomerization of alkynes may be overcome thermally or catalytically. Because the classical thermal transformation of ethyne into benzene in a hot tube is rather ineffective (*47*), more emphasis has been placed on working out catalytic routes for the synthesis of linear oligomers, cyclooligomers, and polymers. Transition metal compounds have proved to act as effective catalysts in homogeneous as well as in heterogeneous processes (*48*).

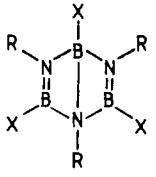
The stabilization of iminoboranes can yield five different types of products: cyclodimers (1,3,2,4-diazadiboretidines, **Di**), cyclotrimers (borazines, **Tr**), bicyclotrimers (Dewar borazines, **Tr'**), cyclotetramers (octahydro-1,3,5,7-tetraza-2,4,6,8-tetraborocines, **Te**), and polymers (polyiminoboranes, **Po**); these substances are isoelectronic with cyclobutadienes, benzenes, Dewar benzenes, cyclooctatetraenes, and polyalkynes, respectively, which are all known to be products of the thermodynamic stabilization of alkynes.



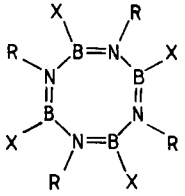
Di



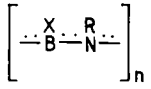
Tr



Tr'



Te

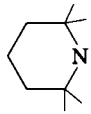
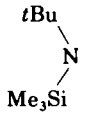


Po

A correlation between the iminoboranes and their thermal stabilization products is given in Table III. *Thermal,* in this context, means "at room temperature." Mixtures of two products can be separated either by extraction of the soluble component (**Tr**/**Po**) or by distillation

TABLE III

PRODUCTS FROM THE STABILIZATION OF IMINOBORANES XBNR

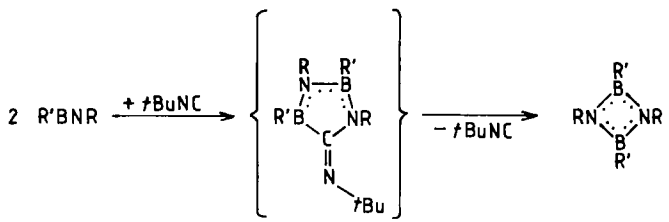
X	R	Product of stabilization: Thermal	Product of stabilization: Catalytic	Reference
Me	Me	**Tr**	**Tr**	*19*
Me	*t*Bu	**Tr**	**Di ⇄ Te**	*13*
Et	Et	**Tr, Po**		*18, 19*
Et	*t*Bu	**Tr**	**Di**	*10, 13*
Pr	*t*Bu	**Tr**	**Di**	*10, 13*
*i*Pr	*i*Pr	**Tr**	**Di ⇄ Te**	*17, 19*
*i*Pr	*t*Bu	**Tr'**	**Di**	*12*
Bu	*t*Bu	**Tr**	**Di**	*10, 49*
*i*Bu	*i*Bu	**Tr, Po**		*17*
*s*Bu	*s*Bu	**Di, Tr**	**Di**	*17, 19*
*s*Bu	*t*Bu	**Di, Tr'**		*19*
*t*Bu	*t*Bu	**Di**		*11*
F_5C_6	*t*Bu	**Di**		*9*
	*t*Bu	**Di**		*16*
	*t*Bu	**Di**		*14*

(**Di/Tr, Di/Tr'**). A general result is that sterically normal ligands X and R cause the trimerization of iminoboranes to borazines, whereas steric strain by X and R can make the cyclodimers more favorable. Obviously, the space available for the ligands of planar rings decreases with the number of ring members. A borderline situation arises with two of the doubly α-branched *sec*-butyl groups as ligands; in this case a mixture of the cyclodimer and -trimer is formed.

One doubly α-branched and one triply α-branched ligand mark the very special situation where Dewar borazines become stable (*i*Pr/*t*Bu, *s*Bu/*t*Bu); these ligands are small enough to permit more than a cyclodimerization but are too big to make borazines favorable. Going one step further to two triply α-branched ligands (*t*Bu), the cyclodimer becomes the only possible stabilization product. Polymers $(RBNR)_n$ together with borazines are the products of heating metastable iminoboranes with two α-unbranched groups R. A corresponding mixture was recovered from the hot tube thermolysis of R_2BN_3 (*17*) and

of $R_2BN(SiMe_3)OSiMe_3$ (*18*) (R = Pr, Bu), without isolating and characterizing the monomers. Little is known about the polymers. They are colorless, waxlike materials, which are insoluble in all kinds of organic solvents and can be stored in the open air for some time. The mass spectrometric fragmentation gives cations $(RBNR)_m^+$ with a maximum value of $m = 5$; nothing is known, however, about the true size of what are called *polymers*. Their insolubility and lack of swelling capability (*19*) make a truly polymeric structure not unlikely. Polymers could not be detected during the stabilization of MeBNMe (*19*).

Catalysts, working below 0°C, have been found that induce the formation of cyclodimers from those iminoboranes which give borazines at room temperature. Cymantrene, $CpMn(CO)_3$, and similar coordination compounds of transition metals, exhibit catalytic activity (*19*), but the most effective catalyst turned out to be *tert*-butylisonitrile, *t*BuNC (*12, 13, 49*). Four cyclodimers, which were available only by such a catalytic procedure (Table III), proved to be thermally stable toward transformation into the corresponding borazine, which obviously will be thermodynamically more stable. In two cases an equilibrium mixture of the cyclodimer and the cyclotetramer was obtained (Table III); neither the cyclodimer nor the cyclotetramer could be transformed into the corresponding borazine. Low-temperature NMR data indicate a possible mechanism for the catalytic activity of *t*BuNC according to Eq. (20) (*19*).

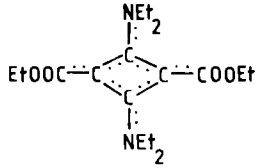


(20)

B. The Cyclodimers

Diazadiboretidines are isoelectronic with cyclobutadienes. A rectangular D_{2h} structure with localized π-bonds is indicated for cyclobutadiene by theory and is strongly supported by experimental evidence (*50*). Being a highly reactive diene as well as a strong dienophile, cyclobutadiene will readily undergo a Diels–Alder cycloaddition with itself and is, therefore, unstable. The same is true for its derivatives, unless the ring ligands exhibit particular steric or electronic effects.

For example, the sterically overcrowded tetra-*tert*-butylcyclobutadiene, whose photochemical transformation into the corresponding tetrahedrane is of principal interest (*51*), is a rather stable substance with a nonplanar ring skeleton (*52*). Four ring ligands with clockwise opposed electronic effects define so called push–pull cyclobutadienes (e.g., **V**), which are storable at room temperature (*53*). The ring skeleton of **V** is rhombic, instead of rectangular, with an acute angle of 87.2° at the carbon atoms that bear the EtOOC groups (*54*). The π-electrons are delocalized over the ring and the four adjacent external bonds.



V

In the homologous boron–nitrogen four-membered ring systems the ring atoms themselves, not the ligands, push and pull the electrons. The structures of four examples were analyzed in the crystalline state. Like its carbon homologue, the tetra-*tert*-butyl derivative shows slight deviations from a planar structure (*11*), but diazadiboretidines with sterically less outstanding ligands have a planar, rhombic ring skeleton with the acute angle at the nitrogen atoms, comparable to the push–pull cyclobutadiene (Table IV).

Ab initio calculations were reported for the parent compound, $(HBNH)_2$ (*23, 56*). A rhombic C_{2v} structure with a B—N bond length of 147 pm and a B—N—B angle of 87° was predicted. The π-bonding

TABLE IV

STRUCTURE OF IMINOBORANE CYCLODIMERS $(XBNR)_2$

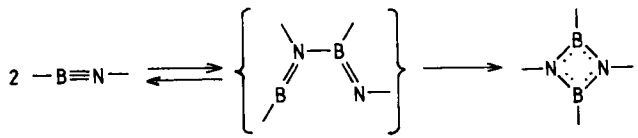
X	R	Mean ring bond lengths (pm)	Mean ring angles (degree) BNB	NBN	Reference
Bu	*t*Bu	145.8	85.3	94.7	*14*
*t*Bu	*t*Bu	148.6	86.6	90.6	*11*
F_5C_6	*t*Bu	143.1	84.3	95.7	*9*
$(Me_3Si)_2N$	$SiMe_3$	145.4	82.2	97.8	*55*

energy is greater by 11 kcal/mol than for two isolated BN π-bonds, in contrast to $(HCCH)_2$, for which the delocalization energy is predicted to be negative (*56*). The ionization potential was calculated to be 10.8 (*23*) and 8.1 eV (*56*). A rhombic D_{2h} structure with a B—N bond length of 146 pm, a B—N—B angle of 88°, and an ionization potential of 9.13 eV was calculated for $(MeBNMe)_2$ (*11*). In all calculations, the HOMO is predicted to be the π-orbital of b_g symmetry, whose electron density is localized at the two nitrogen atoms. The photoelectron spectrum of $(t\text{BuBN}t\text{Bu})_2$ shows the ionization energy to be 7.35 eV (*11*), not very different from the 6.35 eV reported for the corresponding $(t\text{BuCC}t\text{Bu})_2$ (*57*). The small value, compared to the one calculated for $(MeBNMe)_2$, was ascribed to the inductive effect of the *tert*-butyl groups.

One could expect diazadiboretidines to be converted into Hückel aromatic systems either by adding or by subtracting one pair of π-electrons. The addition of two electrons to diazadiboretidines of the type $(RBNtBu)_2$ can be achieved by the action of alkali metals. The dianions $[(RBNtBu)_2]^{2-}$ are stable in solution and can be reconverted into the diazadiboretidines by oxidants. Because they contain six π-electrons, "aromatic character" may be attributed to the dianions (*19*). Cyclodimers of the type $(R'BNR)_2$ are also readily oxidized, but the adoption of an "aromatic" dication $[(R'BNR)_2]^{2+}$ as a product would be mere speculation at present.

Whereas push–pull cyclobutadienes are not formed by thermal cyclodimerization of the corresponding alkynes, there are six iminoboranes mentioned in Table III that undergo thermal cyclodimerization, and four further iminoboranes are likely to be formed as gas-phase intermediates before dimerizing to the well-characterized compounds $[MesBN(SiMe_3)]_2$ (*9*), $[(F_5C_6)BN(SiMe_3)]_2$ (*9*), $[Me_3Si(t\text{Bu})NBNi\text{Pr}]_2$ (*14*), and $[Me_3Si(t\text{Bu})NBNBu]_2$ (*14*).

For reason of symmetry conservation, a thermal concerted [2 + 2]-cycloaddition is forbidden as far as D_{2h} symmetry can be assumed for the activated complex. This is not necessarily the case for the concerted dimerization of iminoboranes, in which the symmetry requirements seem to be essentially lowered. Nevertheless, a two-step mechanism according to Eq. (21) must be taken into account. The assumed intermediate in Eq. (21) contains a sextet boron atom with a linear

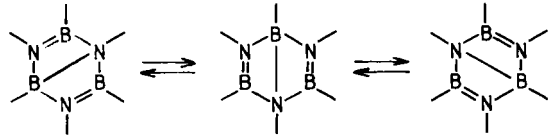


(21)

coordination, which seems to be rather unfavorable; the aminoboron cation $[C_9H_{18}N{=}B{-}Me]^+$, containing a boron atom of that type, is reported, however, to be metastable at low temperatures (*33*).

C. The Cyclotrimers

Borazines, the normal products of the thermal stabilization of iminoboranes, constitute a well-characterized class of molecules (*58*). The parent compound, $(HBNH)_3$, has been known for 60 years (*59*). Some of the physical properties of borazine and benzene are so similar that borazine was called *inorganic benzene* (*60*). Many of the theoretical contributions concerned the degree of aromaticity of borazines. On the other hand, the first Dewar borazine, formed by trimerization of the iminoborane *i*PrBN*t*Bu, was reported in 1984 (*12*). In the crystalline state, the bicyclic skeleton is built from two trapezoids, joining the longer edge and including an angle of 115.2°. The common central edge forms an extra-long B—N single bond of 175.2 pm, whereas the two opposite short edges of the trapezoids indicate rather short B=N double bonds with a BN distance of 136.4 and 138.4 pm, respectively. A fluxional rearrangement of $(i\text{PrBN}t\text{Bu})_3$ in a solution of $CDCl_3$ was suggested [Eq. (22)], which was fast at 20°C on the NMR time scale. Though solutions of this rather insoluble Dewar borazine at low temperature were not available, the NMR spectra at 20°C differed from the expected spectra of the corresponding borazine, not by the number of signals, but by the chemical shifts, which were in accord with the shifts expected by averaging plausible Dewar borazine shifts.



(22)

A closely related Dewar borazine, $(t\text{BuBN}i\text{Pr})_3$, was prepared from the corresponding fluoroborazine $(\text{FBN}i\text{Pr})_3$ by substitution of all three fluorine atoms. This Dewar borazine is soluble at −50°C in a mixture of $CDCl_3$ and CH_2Cl_2. The NMR spectra at that temperature correspond to the expected Dewar borazine structure, the signals coalescing at higher temperature (*61*). The activation energy for the valence isomerization [Eq. (22)] seems to be small. The transition state will have a structure not very different from a borazine structure. If only one methyl group in each *tert*-butyl group is replaced by a hydrogen atom,

the Dewar borazine structure will become unfavorable, since the borazine (iPrBNiPr)$_3$ is a well-established stable substance, formed for instance by the thermal stabilization of monomeric iPrBNiPr (Table III). The compound (sBuBNtBu)$_3$ was also found to be a Dewar borazine from spectroscopic data, which were similar to those of (iPrBNtBu)$_3$ (*19*).

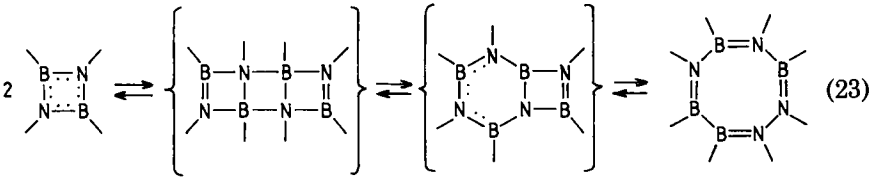
Dewar benzene derivatives have been known since 1962 (*62*), the parent compound, C_6H_6, since 1963 (*63*). The rearrangement of a normal Dewar benzene to the corresponding benzene is an exothermic reaction, but derivatives like hexamethyl Dewar benzene are metastable at room temperature (*64*), and the parent compound can be stored in a pyridine solution below 0°C. Strong steric strain can make the Dewar benzene more favorable than the benzene even thermodynamically; four *tert*-butyl groups together with two methoxycarbonyl groups can exhibit such a strain (*65*). Apparently, a similar situation is met with the Dewar borazines. A fluxional behavior, however, is not reported for the strained Dewar benzenes, a conversion by simple thermal opening of the central C–C bond being forbidden by reason of orbital symmetries. The structures of Dewar benzene and Dewar borazine are comparable. An electron diffraction study of hexamethyl Dewar benzene showed that the two equal trapezoid moieties include an angle of 124°; the lengths of the central CC bond and of the opposite C=C double bonds are 163 and 135 pm, respectively (*66*). With respect to iminoboranes, it is remarkable that the Dewar benzene C_6F_3tBu$_3$ is one of the products of the spontaneous oligomerization of the polar alkyne FC≡CtBu (*25*). A yield of 60–70% is reported for the synthesis of hexamethyl Dewar benzene from MeC≡CMe in the presence of $AlCl_3$ (*64*).

D. The Cyclotetramers

Cyclooctatetraene, C_8H_8, has a D_{2d} tublike structure with four rather isolated double bonds. Cyclooctatetraenes can be the products of the catalytic cyclotetramerization of alkynes, and cyclobutadienes may be the intermediates. The BN homologues of cyclooctatetraenes have been known since 1962 (*67*). Like cyclooctatetraene, molecules of [(SCN)BNtBu]$_4$ were shown to have a tublike ring structure of S_4 symmetry with alternating bond lengths of 140 and 146 pm, the shorter ones perpendicular to the direction of the S_4 axis (*68*).

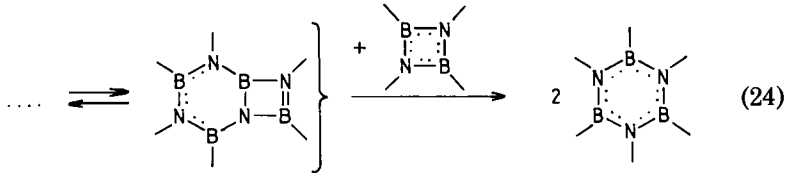
The equilibrium **2Di** ⇄ **Te** was observed after a catalytic iminoborane stabilization in the case of two particular combinations of the ligands X and R: Me/tBu (*13*) and iPr/iPr (*19*) (Table III). The equilibrium

strongly depends on temperature: At 20°C, only the cyclotetramers are detectable by NMR; at 70°C (Me/*t*Bu) and 100°C (*i*Pr/*i*Pr), respectively, the cyclotetramers are completely transformed into the cyclodimers, and mixtures are found at intermediate temperatures. The fragmentation **Te** → 2**Di** can be achieved within a few minutes (Me/*t*Bu) or more slowly (*i*Pr/*i*Pr), but the reverse reaction 2**Di** → **Te** at 20°C takes hours and needs to be completed by UV irradiation in the case of X/R = *i*Pr/*i*Pr. We develop a mechanistic proposal in Eq. (23): a Diels–Alder homologous cycloaddition, followed by rapid opening of two bonds between tetra-coordinated boron and nitrogen atoms.



(23)

Going from the ligand combination X/R = Me/*t*Bu to the slightly larger set of ligands Et/*t*Bu, the cyclodimer remains thermally stable; no cyclotetramer is observable. The transformation **Di** ⇄ **Te** seems to be very sensitive to the steric situation in the ligand sphere of the cyclodimers. On the other hand, diazadiboretidines with a set of smaller ligands (e.g., Me/Me, Et/Et) have never been isolated. They may exist as intermediates, but there will be a favorable route to the formation of borazines, possibly through the intermediates of Eq. (23), as indicated in Eq. (24).



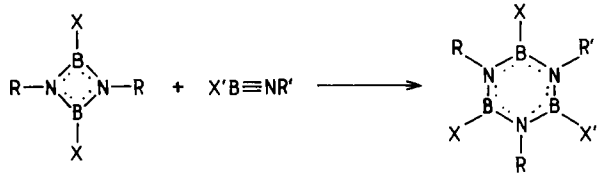
(24)

E. Interconversions between Cyclooligomers

Interconversion of cyclodimers and cyclotetramers was dealt with in Section IV,D. A very special conversion, the photochemical isomerization of tetra-*tert*-butyldiazadiboretidine to the corresponding tetrahedrane, might be expected by analogy with the behavior of tetra-*tert*-butylcyclobutadiene (*51*); all attempts in this field, however, have

failed (*19*). Conversion of the cyclodimer into the cyclotrimer may be possible in the case of unstable cyclodimers, as was pointed out in the preceding section, but once formed as storable products, such a conversion was not observed. The opposite is not true. The Dewar borazine (tBuBNiPr)$_3$ (Section IV,C) can be converted into the corresponding cyclodimer (tBuBNiPr)$_2$ by a thermal process at 200°C (*61*). The mechanism of such a process, $2\mathbf{Tr}' \rightarrow 3\mathbf{Di}$, is unknown. Thermodynamically, the bicyclotrimer seems to be only slightly better in energy, so that an entropy term may provide the driving force at 200°C.

Apart from a real interconversion, cyclodimers can be transformed into borazines, however, by addition of iminoboranes [Eq. (25)]. In order to carry out such a reaction, a solution of the iminoborane in a dropping funnel, kept at −80°C, is slowly dropped into a solution of the cyclodimer at 50°C. The yield of borazines is quantitative. The procedure can be applied to components with the same set of ligands, but different sets may also be applied, permitting the synthesis of borazines with an unsymmetric arrangement of more than two different ligands (*13, 19*).



(25)

X:	Et	Pr	Bu	*s*Bu	Et	Pr	*i*Pr	Bu	*i*Bu	*s*Bu
R:	*t*Bu	*t*Bu	*t*Bu	*s*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
X′:	Et	Pr	Bu	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr
R′:	*t*Bu	*t*Bu	*t*Bu	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr	*i*Pr

By analogy with Eq. (25), the cyclodimer (iPrBNtBu)$_2$ will give the corresponding Dewar borazine, if reacted with iPrBNtBu (*12*). If the iminoborane iPrBNiPr, instead of iPrBNtBu, is added to the same cyclodimer, however, only the normal borazine is formed (*19*). Whether the normal or the Dewar borazine will be more stable depends on the difference of one single methyl group. The cyclodimer (sBuBNtBu)$_2$ behaves in the same way as (iPrBNtBu)$_2$: Only the normal borazine is formed by addition of iPrBNiPr. Equation (25) can be interpreted as a [4 + 2]-cycloaddition giving the corresponding Dewar borazine as an intermediate, which will be readily transformed into the borazine if ligands with normal steric requirements are present.

Equation (25) may shed light on the general path of the iminoborane oligomerization. I propose the formation of cyclodimers to be the first stage of such oligomerizations. If a cyclodimer is stable to an excess of iminoborane, it will be isolated (Table III). Otherwise the cyclodimer is attacked by the excess iminoborane according to Eq. (25), and the borazine is formed via the Dewar borazine. In special cases, the Dewar borazine will be the final product. The first step determines the rate of such a sequence of reactions. If the cyclodimerization step becomes relatively fast, so that the first and the second step are comparable in rate, both the cyclodimer and the cyclotrimer will be found; this is true for the thermal stabilization of *s*BuBN*s*Bu. Catalysts for the cyclodimerization make the first step more rapid than the second one.

A plausible alternative mechanism involves as a first step the formation of a linear dimer, XB=NR—BX=NR, according to the left part of Eq. (21). This linear dimer will be more stable in entropy but less stable in energy than the corresponding cyclodimer. The second step would be addition of iminoborane to the open-chain dimer giving the borazine in either a concerted or a two-step mechanism. The intramolecular cyclization of the open-chain dimer, according to the right-hand side of Eq. (21), would compete addition of an iminoborane. We cannot definitely exclude a mechanism via open-chain dimers.

Polymers are formed, together with borazines, from iminoboranes RBNR with α-unbranched alkyl groups. By absolute control of the temperature, the stabilization would presumably be directed toward the borazine. Loss of thermal control will cause a loss of kinetic control, so that hot iminoborane molecules will trimerize or polymerize rather unspecifically.

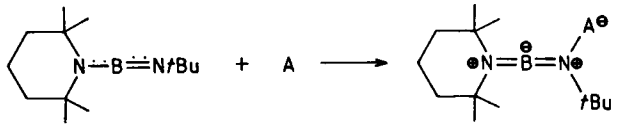
There is one further remarkable interconversion. The four polymers $(RBNR)_n$ (mentioned in Section IV,A) are thermally stable, except for $(EtBNEt)_n$, which can be transformed into the borazine $(EtBNEt)_3$ at 150°C (*18*). Such a depolymerization will proceed without considerable change of energy but with a substantial gain in entropy. For kinetic reasons, it cannot proceed with alkyl groups larger than ethyl.

V. Polar Additions to Iminoboranes

A. Addition of Lewis Acids and Bases

Neutral Lewis acids can be bonded to the nitrogen atom of the aminoiminoborane $C_9H_{18}NBNtBu$ (*69*) [Eq. (26)]. The product is related to the well-known diaminoboron cations of the type $[C_9H_{18}N{=}B{=}$

$NR_2]^+$ (*33*); the positive charge is compensated intramolecularly, however, and not by a separate anion.

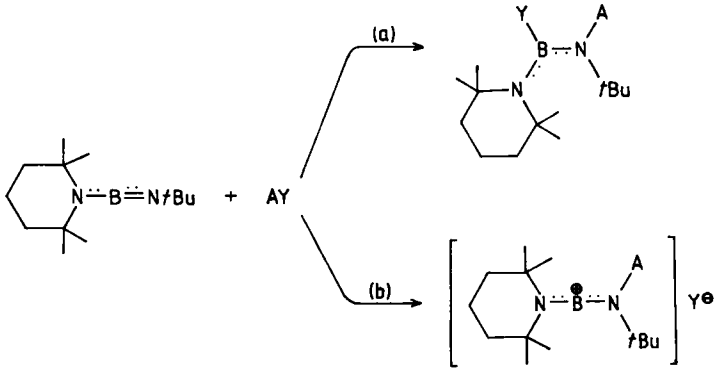


(26)

A = $AlCl_3$, $AlBr_3$, $GaCl_3$

Efforts to add Lewis acids to dialkyliminoboranes R'BNR were not so successful, as would be expected, since betaine structures of the type $R'B=\overset{+}{N}R—\bar{A}$ with an unfavorable linear sextet boron atom would be formed (*19, 33*). Equation (26) is restricted to iminoboranes XBNR with a π-electron donating group X.

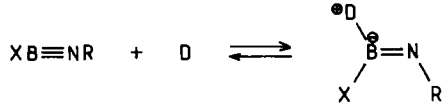
Polar reagents AY (Section V,B-D) generally attack both triply bonded atoms of iminoboranes to yield aminoboranes [Eq. (27a)]. In special cases, the cationic fragment A^+ of AY is added to the nitrogen atom and Y^- remains a separate anion [Eq. (27b)]; such a reaction path seems to be governed by steric factors, but seems also to be restricted to aminoiminoboranes (*70*).



(27)

(b): A—Y = Me_3Si—I, Me_3Si—$OS(CF_3)O_2$

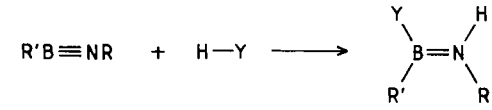
The typical ^{11}B-NMR signals of iminoboranes are essentially unaltered when iminoboranes are dissolved in liquids with Lewis base activity (e.g., tertiary amines, tetrahydrofuran) (*19*). I conclude that equilibria like Eq. (28) are shifted far to the left, even in the presence of an excess of the Lewis base D.



(28)

B. Addition of Protic Agents

Each of six protic agents was added to both of two representative iminoboranes, *i*PrB≡N*i*Pr and BuB≡N*t*Bu; the expected 12 aminoboranes were isolated, chiefly in good yield [Eq. (29)] (*71*). The yield of distilled pure products may be smaller, but primarily the addition of protic agents is a quantitative reaction, fast even far below 0°C. This means a distinct difference to the slow addition of the same protic agents to alkynes which affords catalytic support at temperatures above 0°C.

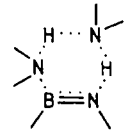


(29)

HY = HCl, *t*BuOH, Et_2NH, iPr_2NH, $tBuNH_2$, $(Me_3Si)_2NH$

Analogous products were recovered from the addition of HCl, *i*PrOH, and $tBuNH_2$ to the aminoiminoborane Me_3Si-(*t*Bu)N⋯B⋯N*t*Bu (*14*) and from the addition of three acids (CH_3COOH, CF_3COOH, CF_3SO_3H), five alcohols ROH (R = Me, *i*Pr, *t*Bu, Ph, 2,4,6-$tBu_3C_6H_2$), four amines RNH_2 (R = H, *i*Pr, *t*Bu, Ph), five secondary amines (Me_2NH, pyrrole, pyrrolidine, pyrazole, imidazole), and two hydrazines (Me_2NNH_2, MeHNNHMe) to the aminoiminoborane $C_9H_{18}N$⋯B⋯N*t*Bu (*70, 72*).

Apparently, Eq. (29) represents a polar nonradical addition. If a two-step mechanism is conceived, intermediates of the type $[XB{=}NRH]^+$ will be reasonable, though such cations proved to be rather unstable as isolated species (unless X represents a π-electron donating group) (*33*). Intermediates of the type HY—B(X)=NR would explain the fast reaction with protic bases of vanishing Brönsted acidity. The results, however, mentioned in Sections V, A, and V, C, favor to some extent the picture of iminoboranes as preferring electrophilic to nucleophilic attack. The high activity of amines can also be rationalized in terms of a concerted process, with a transition state of type **VI**.



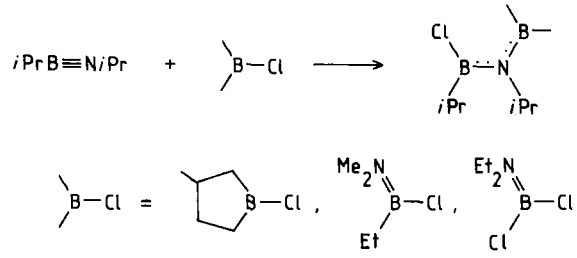
VI

C. Boration and Related Reactions

In analogy to the well-known hydroboration, we call addition of $X_2B—Cl$, $X_2B—N_3$, $X_2B—SR$, $X_2B—NR_2$, and $X_2B—R$ to an unsaturated system a *chloro-*, *azido-*, *thio-*, *amino-*, and *alkyloboration*, respectively.

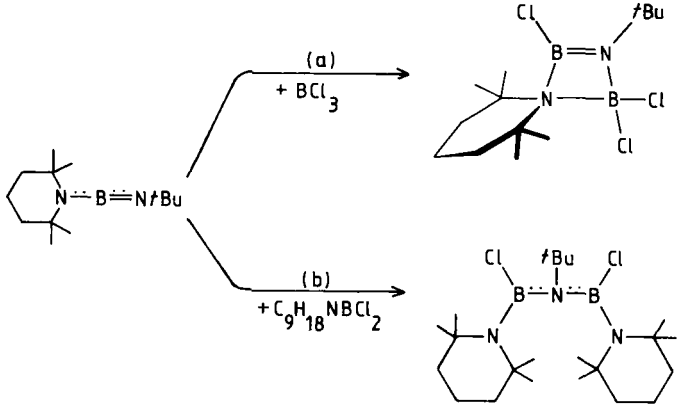
1. Chloroborations

As a typical dialkyliminoborane, the isopropyl derivative, *i*PrBN*i*Pr, was chloroborated by three different chloroboranes. In the fast reaction, no alkylo- or aminoboration, respectively, was observed as a potential side reaction competing with the chloroboration [Eq. (30)]. With BCl_3 as chloroborating agent, a vigorous reaction took place which did not yield well-defined products.



(30)

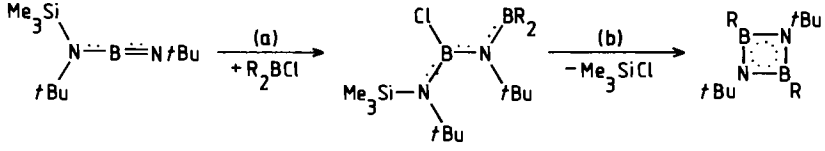
A well-defined product could be isolated from the haloboration of the aminoiminoborane $C_9H_{18}NBNtBu$ with BCl_3 or BBr_3, since the primary product is stabilized by intramolecular BN coordination [Eq. (31a)] (*16*); the corresponding bromoboration yields compound **III**



(31)

(Section III,B). The same aminoiminoborane undergoes a normal chloroboration with $C_9H_{18}NBCl_2$ [Eq. (31b)] (*73*).

The aminoiminoborane $Me_3Si—(tBu)N=B=NtBu$ can be chloroborated with R_2BCl (R = *i*Bu, *s*Bu) in the expected manner [Eq. (32a)]. The chlorosilane Me_3SiCl is eliminated from the chloroboration product at 140°C [Eq. (32b)], providing a novel synthesis for diazadiboretidines. Addition of chloroboranes R_2BCl with smaller R groups (R = Me, Et, Pr, *i*Pr) proceeds directly to the diazadiboretidine, the primary addition product not being isolable.

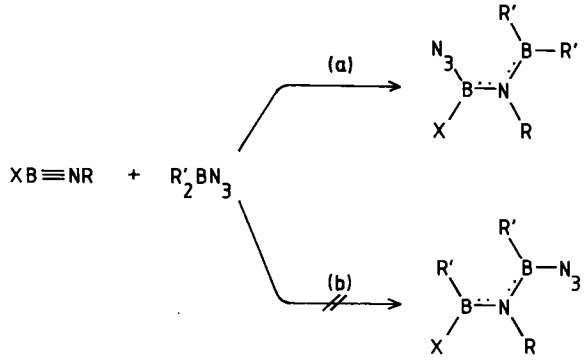


(32)

Generally, chloroborations seem to be vigorous reactions. The haloboration of 1-alkynes with haloorganoboranes is also known to be rapid under mild conditions (*74*).

2. *Azidoborations*

Azidoborations of iminoboranes are smooth and facile reactions [Eq. (33a)] (*14, 19*). For X = alkyl, the azidoboration products cannot easily be distinguished from hypothetical alkyloboration products



(33)

X: Bu *i*Bu $Me_3Si—(tBu)N$

R: *t*Bu *i*Bu *t*Bu

R': Pr Bu Bu

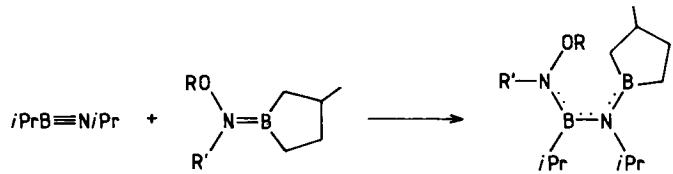
[Eq. (33b)], which must be considered, because alkyloboration of iminoboranes with trialkylboranes is a well-known reaction (Section V,C,5). Following addition of $[^{10}B]Bu_2BN_3$ to *i*BuBN*i*Bu, ^{11}B-NMR proved azidoboration to be the actual reaction path. Alkynes cannot be azidoborated.

3. *Thioborations*

Only one example has been established for thioboration: addition of $B(SPr)_3$ to *i*PrBN*i*Pr giving 30% yield of PrS—(*i*Pr)B⋯N(*i*Pr)⋯$B(SPr)_2$ (*19*).

4. *Aminoborations*

The aminoboranes $Et_2B{=}NEt_2$ and $Et_2B{=}N(SiMe_3)_2$ do not react with BuB≡N*t*Bu (*19*). Hydroxylaminoborane derivatives, however, can be brought to reaction with *i*PrBN*i*Pr [Eq. (34)] (*19*).



(34)

R: Me Me $SiMe_3$

R′: Me $SiMe_3$ $SiMe_3$

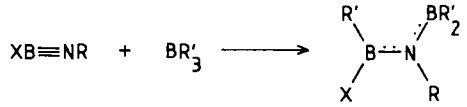
The same type of reaction was achieved with the hydroxylaminoboranes $R_2B{=}N(SiMe_3)OSiMe_3$ and the iminoboranes EtBNEt (R = Pr), *i*PrBN*i*Pr (R = Bu), BuBN*t*Bu (R = Et) (*18, 19*). Following the addition of $[^{10}B]Bu_2B{=}N(SiMe_3){-}OSiMe_3$ to *i*PrBN*i*Pr, ^{11}B-NMR spectra excluded alkyloboration instead of aminoboration (*19*).

Hydroxylamino groups differ from normal amino groups by their smaller π-donating power. Hydroxylaminoboranes, therefore, are stronger Lewis acids than aminoboranes, having a vacant boron *p*-orbital more easily available. The lack of reactivity of aminoboranes indicates that the Lewis acidity of the boranes plays an important role in the boration of iminoboranes. Again, iminoboranes seem to favor electrophilic attack.

5. *Organoborations*

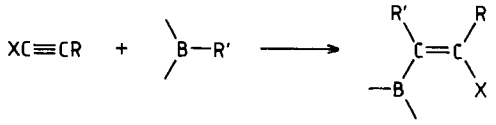
The ethyloboration of dialkyl iminoboranes (*10–13, 17, 18*) and aminoiminoboranes (*14*) with BEt_3 is a smooth reaction, that has been

applied to nearly all well-characterized iminoboranes [Eq. (35)]. There is not a great difference in going from BEt_3 to BBu_3 (*10*). Phenyloboration with BPh_3 is comparable to alkyloboration (*19*). Looking for trialkylboranes with a larger steric requirement, it turned out that MeB≡NMe is alkyloborated by $BiPr_3$, but does not react with $BsBu_3$ (*19*).[1]



(35)

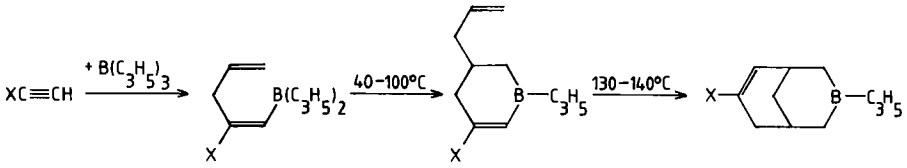
Alkynes XC≡CR cannot be organoborated, when X represents an alkyl group. In the case of X = H (*74*) or X = Me_3Sn (*75*), a particular type of alkyloboration, coupled to the migration of X, is possible [Eq. (36)]. Such a reaction was not observed with iminoboranes.



(36)

6. *Allyloboration*

The smooth allyloboration of alkynes is known to proceed via an allyl rearrangement, probably including a six-membered cyclic transition state. Thermal treatment of the product initiates a second allyloboration step and a vinyloboration thereafter; the whole procedure [Eq. (37)] opens a synthesis of boraadamantanes by further reaction steps (*76*).

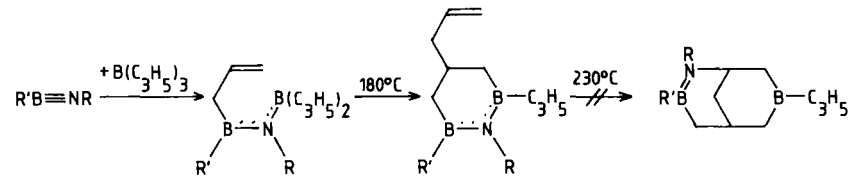


(37)

The allyloboration of the iminoboranes *i*PrBN*i*Pr and BuBN*t*Bu can readily be accomplished [Eq. (38)]. An intramolecular second allyloboration step requires a temperature of 180°C, demonstrating

[1] In this context, *no reaction* means that iminoboranes react faster with themselves than with additional components.

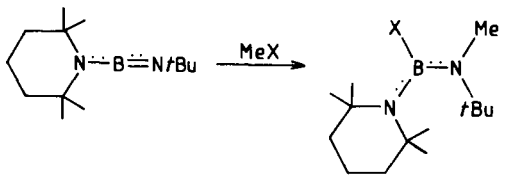
that diallyl(amino)boranes are weaker allyloboration reagents than diallyl(vinyl)boranes, which is a consequence of the stronger electron-donating effect of the amino group compared to the vinyl group. The third step in analogy to Eq. (37) would be an intramolecular aminoboration of an olefinic bond. This cannot be achieved, even at 230°C, as was expected, since aminoborations of this type are generally unknown (*19*).



(38)

7. *Addition of Alkylation Reagents*

Aminoiminoboranes may be methylated by the esters of strong acids [Eq. (39)]. Benzylation with $PhCH_2Hal$ (Hal = Cl, Br) was not possible (*70*).



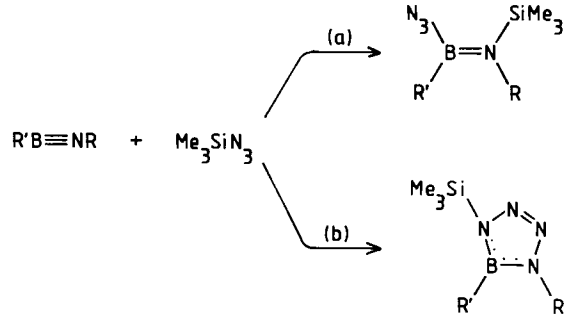
(39)

X = I, $OS(CF_3)O_2$

8. *Addition of Halosilanes and Related Compounds*

Iminoboranes R'BNR do not add the silane Me_3SiCl to the B≡N triple bond; the synthesis of iminoboranes according to Eq. (1) would then be a reversible and unsuccessful reaction. The aminoiminoborane $C_9H_{18}N{\cdot\cdot}B{\cdot\cdot}NtBu$ is reported not to react with Me_3SiCl and Me_3SiBr, but it does react with Me_3SiI and $Me_3Si{-}OS(CF_3)O_2$ [Eq. (27b)] (Section V,A) (*70*). However, addition of Me_3SiN_3 to the B≡N triple bond is a generally applicable reaction, proceeding in analogy to azidoboration [Eq. (33a)]. This "azidosilation" is not a uniform reaction unless the iminoborane is sterically overcrowded [e.g., with *t*BuB≡N*t*Bu (*11*) or $Me_3Si{-}(tBu)N{\cdot\cdot}B{\cdot\cdot}NtBu$ (*14*)]. Usually,

a 9:1 mixture of the azidosilation product [Eq. (40a)] and the [3 + 2]-cycloadduct [Eq. (40b)] will be formed (*10–13, 17*).

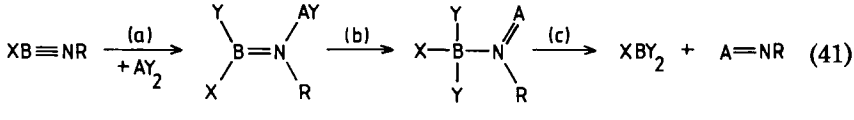


(40)

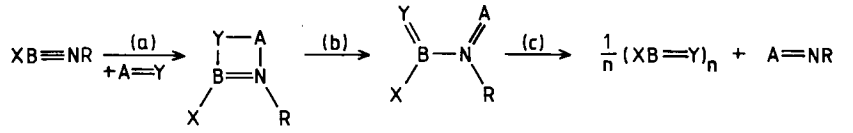
The reaction of BuB≡N*t*Bu with an excess of Me_3SiOEt gives the oxysilation product EtO···(Bu)B···N(*t*Bu)—$SiMe_3$ in good yield. Insofar as cyclic iminoboranes are produced as intermediates, the second of the three products in either of Eqs. (15) or (16) (Section II,B) will apparently have been formed by the addition of Me_3Si—$OSiMe_3$ to the reactive intermediate. At first glance, silanes Me_3Si—Y will be added to iminoboranes, if the group Y is bonded to silicon via an atom of the second period of the periodic table (e.g., Y = N_3, OEt, $OSiMe_3$), whereas addition of Me_3SiCl, etc., is not favorable.

D. Addition to Both π-Bonds of Iminoboranes

In this section, we consider the addition of both A—Y single bonds of AY_2 [Eq. (41)], or of an A=Y double bond [Eq. (42)] to the B≡N triple bond of iminoboranes.

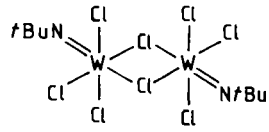


(41)



(42)

There is only one reported example for Eq. (41): addition of WCl_6 to tBuBNtBu gives tBuBCl$_2$ and compound **VII**. Possible intermediates corresponding to hypothetical steps (a) and (b) were not observed (*77*).



VII

Reactions of the type in Eq. (42) have been achieved with aldehydes and ketones [Eq. (43)] (*9, 19*). None of the intermediates according to Eq. (42) was isolated. A [2 + 2]-cycloaddition (step a) probably occurs, since [2 + 2]-cycloadducts can be isolated from the reaction of iminoboranes and oxoalkanes in particular cases (Section VI,A). As far as alkynes are concerned, addition of oxo compounds proceeds in the presence of BF_3 as a catalyst, but without a break of the CC σ-bond [in analogy to step c in Eq. (42)]; rather polar alkynes are needed [Eq. (44)] (*78*).

$$XB{\equiv}NR + O{=}CR'R'' \longrightarrow \tfrac{1}{3}(XBO)_3 + R'R''C{=}NR \qquad (43)$$

X :	*i*Pr	*i*Pr	*t*Bu	*t*Bu	F_5C_6
R :	*i*Pr	*i*Pr	*t*Bu	*t*Bu	*t*Bu
R′ :	H	H	H	H	Ph
R″:	*t*Bu	Ph	*t*Bu	Ph	Ph

$$XC{\equiv}CR + O{=}\overset{\diagup}{\underset{\diagdown}{C}} \longrightarrow O{=}C(X){-}C(R){=}\overset{\diagup}{\underset{\diagdown}{C}} \qquad (44)$$

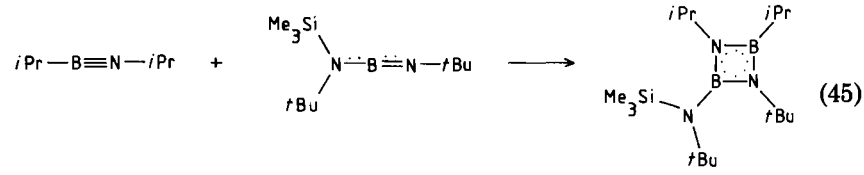
X = R′O, R′S, R′$_2$N, Ph

VI. Iminoboranes as Components in Cycloaddition Reactions

A. [2 + 2]-Cycloadditions

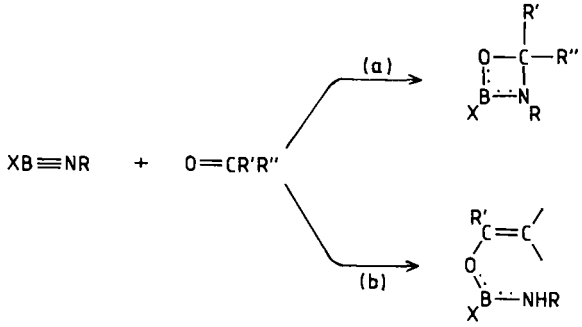
Thermal or catalytic cyclodimerization of iminoboranes is obviously a [2 + 2]-cycloaddition (Section IV). A mixture of two different iminoboranes may be stabilized by formation of three different cyclodimers. If the relative stability of the two iminoboranes, however, differs distinctly, the mixed cyclodimer will be formed preferentially by

dropping the cooled, less stable component to the relatively warm, more stable one [e.g. Eq. (45)] (*14*).



(45)

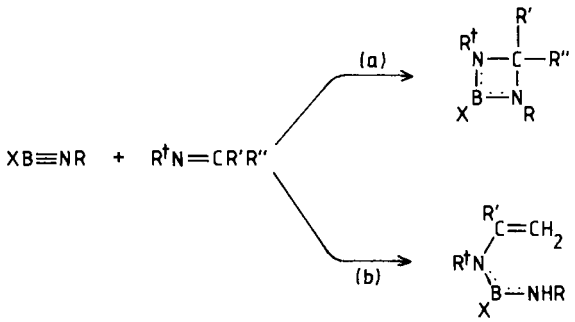
Reaction of aldehydes and ketones with iminoboranes has been widely investigated. Conditions for the [2 + 2]-cycloaddition between XBNR and R′R″CO are relatively good stability of the iminoborane and lack of enolic protons in the oxo compound [Eq. (46)] (*14, 19*). Relatively less stable iminoboranes, but in some cases the stable ones too, may react with oxo compounds by a total opening of the B≡N triple bond [Eq. (43)], presumably via a [2 + 2]-cycloaddition [Eq. (42)] (Section V,D). A relatively stable iminoborane and a ketone containing enolic protons may yield an open-chain product, probably through a six-membered cyclic transition state [Eq. (46b)] (*19*).



(46)

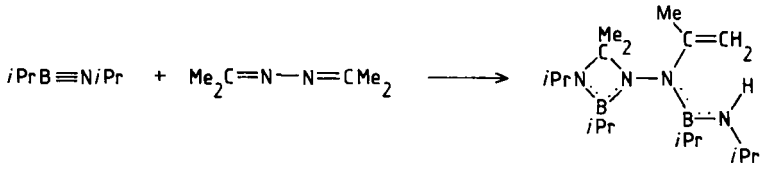
X	:	*t*Bu	$Me_3Si(tBu)N$	$Me_3Si(tBu)N$	$Me_3Si(tBu)N$	*t*Bu	*t*Bu
R	:	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R′	:	CF_3	H	H	H	*t*Bu	Ph
R″	:	CF_3	Ph	—CH=CHMe	$—CMe=CH_2$	Me	Me
Pathway:		a	a	a	a	b	b

Alternative reaction pathways, corresponding to Eq. (46), are also observed in the reaction of iminoboranes with iminoalkanes; the ligand $R^{\dagger}$, bonded to the iminoalkane nitrogen atom, seems to govern the reaction path [Eq. (47)] (*9, 19*). Offering the two C=N double bonds of



(47)

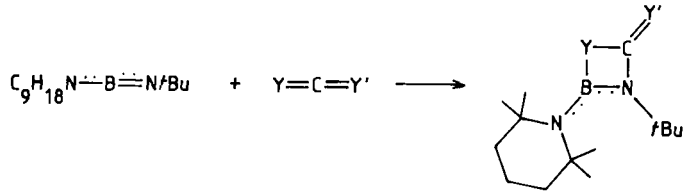
X	:	*i*Pr	F_5C_6	*i*Pr	*i*Pr
R	:	*i*Pr	*t*Bu	*i*Pr	*i*Pr
R'	:	Me	Ph	Me	Ph
R''	:	Ph	Ph	Me	Me
R†	:	Ph	*t*Bu	*i*Pr	*i*Pr
Pathway:		a	a	b	b



(48)

$Me_2C{=}N{-}N{=}CMe_2$ to the attack of *i*PrB≡N*i*Pr, both possible paths are realized [Eq. (48)] (*19*).

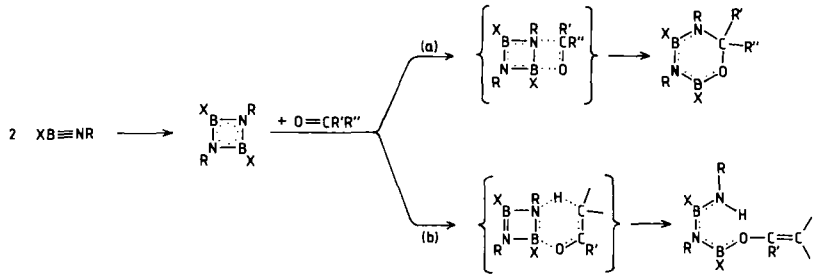
The aminoiminoborane $C_9H_{18}N{\cdots}B{=}N$*t*Bu gives [2 + 2]-cycloadducts with the heteroallenes Y=C=Y' [Eq. (49)]. The cycloadducts can be transformed thermally as well as photolytically into the novel four-membered ring systems $(C_9H_{18}NBY)_2$ (Y = O, S, Se), according to Eq. (42b) and (42c) (*79*).



(49)

Y:	O	S	S	Se	
Y':	O	O	S	Se	

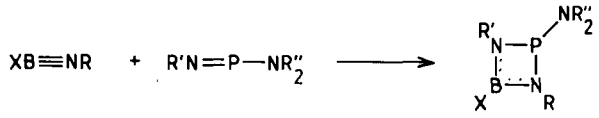
In the combination of moderately reactive oxoalkanes with highly reactive iminoboranes, cyclodimerization of the iminoboranes is preferred to heterodimerization, but neither the diazadiboretidines nor the corresponding borazines are found as final products. According to Eq. (50a), heterocyclic six-membered rings are the products when no enolic protons are available in the oxo component. Otherwise open-chain products can be isolated, according to Eq. (50b). An exception is acetophenone, which reacts in both ways, despite containing enolic protons. Both reactions [Eqs. (50a) and (50b)], can also be achieved by starting with the same well-defined diazadiboretidines, which are assumed to be intermediates in the reaction of iminoboranes with oxo compounds. Both reaction sequences may go through concerted [4 + 2] steps, indicated by their transition states in Eq. (50), but the alternative two-step process via intermediates cannot be ruled out (*9, 19*).



(50)

X	:	*i*Pr	*i*Pr	Bu	F_5C_6	F_5C_6	F_5C_6	F_5C_6
R	:	*i*Pr	*i*Pr	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R′	:	CF_3	Me	CF_3	H	H	Me	$-(CH_2)_5-$
R″	:	CF_3	Ph	CF_3	$-CH=CH_2$	$-CH=CHMe$	Me	
Pathway:		a	a	a	a	a	b	b

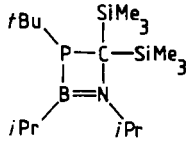
Iminoboranes and iminophosphanes may be coupled in a (2 + 2)-cycloaddition [Eq. (51)] (*19, 80*).



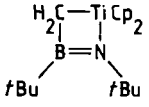
(51)

X :	Bu	Bu	*i*Bu
R :	*t*Bu	*t*Bu	*i*Bu
R′ :	*t*Bu	Me_3Si	Me_3Si
R″ :	*i*Pr	Me_3Si	Me_3Si

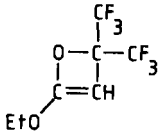
Turning from iminophosphanes to alkylidenophosphanes (phosphaalkenes), the orientation of the [2 + 2]-cycloaddition is inverted, as far as phosphorus is concerned; only one example has been worked out (product **VIII**) (*19*). The phosphaalkyne *t*BuC≡P does not react with the iminoborane BuB≡N*t*Bu, which instead trimerizes (*19*). An exotic [2 + 2]-cycloaddition is observed when the very reactive titanaethene



VIII



IX

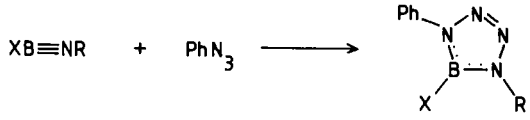


X

$Cp_2Ti{=}CH_2$ (Cp = cyclopentadienyl) is liberated from a titanacyclobutane primer by thermal cleavage in the presence of an iminoborane (product **IX**) (*81*). Alkynes may also undergo [2 + 2]-cyclodimerizations with unsaturated polar molecules. Rather polar alkynes seem to be favorable, e.g., ethoxyethyne, which can react with hexafluoroacetone to give the rather unstable product **X** (*78*).

B. [3 + 2]-Cycloadditions

Alkynes have been well explored as dipolarophiles in the [3 + 2]-cycloaddition with almost all possible 1,3-dipoles (*78*), whereas the reaction of iminoboranes as dipolarophiles has focused on covalent azides as 1,3-dipoles. Most well-characterized iminoboranes were reacted with phenyl azide, according to Eq. (52) (*11–14, 17, 20*).

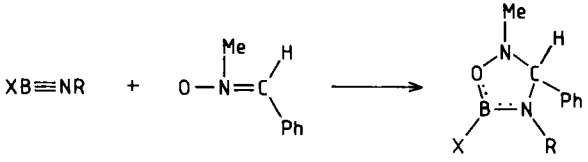


(52)

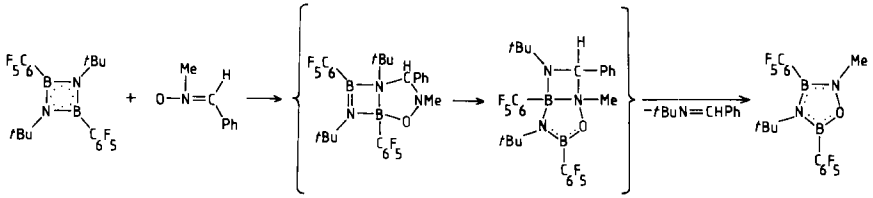
The same type of product was isolated from the reaction of the iminoborane *t*BuB≡N*t*Bu with 10 different alkyl azides $R'N_3$ (R′ = Me, Et, Pr, Bu, *i*Bu, *s*Bu, *n*-C_5H_{11}, cyclo-C_5H_9, cyclo-C_6H_{11}, $PhCH_2$) (*19*). The azidosilane Me_3SiN_3 may also behave as a 1,3-dipole [Eq. (40b)], but addition of the SiN bond to iminoboranes [Eq. (40a)] is usually the preferred reaction (Section V,C,8). This is not so when Me_3SiN_3 is present during the formation of diaryliminoboranes, ArB≡NAr, as intermediates: Both reaction pathways [Eqs. (40a) and (40b)]

are followed to an equal extent for Ar = C_6F_5, *o*-MeC_6H_4; the [3 + 2]-cycloadduct is the only product in the case of Ar = Ph, Mes (*20*). In contrast to dialkyliminoboranes, the diaryliminoboranes MesB≡NMes and $F_5C_6B{\equiv}NC_6F_5$ as intermediates are not azidoborated (Section V,C,2), but rather undergo [3 + 2]-cycloaddition with excess of the generating reactants Mes_2BN_3 and $(F_5C_6)_2BN_3$, respectively, according to Eq. (11) (*20*).

The nitrone PhCH=N(Me)—O was successfully applied as a 1,3-dipole to MesB≡NMes and to Me_3Si-(*t*Bu)N⋯B⋯N*t*Bu [Eq. (53)] (*14, 20*). The rather reactive iminoborane $F_5C_6B{\equiv}NtBu$, however, cyclodimerizes before being attacked by that nitrone, but the nitrone does attack the initially formed cyclodimer [Eq. (54)] (*9*).



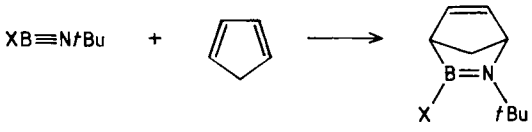
(53)



(54)

C. [4 + 2]-Cycloadditions

Diels–Alder reactions with alkynes as dienophiles have been known for a long time. Iminoboranes, however, will more readily cyclodimerize than react with dienes, and even the cyclodimers are generally superior to dienes in the competition for excess iminoborane. Among many attempts, therefore, only two reactions with iminoboranes as dienophiles have been successful, and in both of them the diene is cyclopentadiene [Eq. (55)] (*9, 14*).



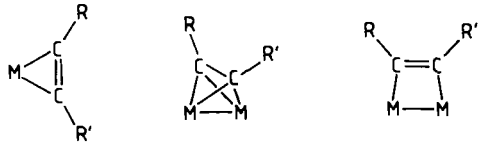
(55)

X = F_5C_6, Me_3Si(*t*Bu)N

The formation of Dewar borazines from iminoboranes and their cyclodimers is also a [4 + 2]-cycloaddition, whether or not the Dewar borazines are the final products or are rearranged to normal borazines (Section IV,E).

VII. Iminoboranes in the Coordination Sphere of Transition Metals

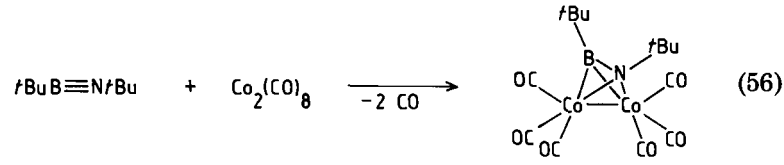
Alkynes RC≡CR′ may be η^2-bonded to transition metals M (**XI**). More often alkynes occupy a bridging position between two metal atoms, either perpendicular (**XIIa**) or parallel (**XIIb**) to the M—M bond (*82*).



XI XIIa XIIb

1:1-Coordination compounds between iminoboranes and transition metals corresponding to **XI** have not yet been detected. Stilbene, $C_{14}H_{12}$, cannot be displaced from $Cp_2Mo(C_{14}H_{12})$, and ethene cannot be displaced from $[(C_2H_4)PtCl_2]_2$, by iminoboranes (*19*), whereas alkynes do replace these alkenes (*83, 84*). Ethene in $(C_2H_4)Pt(PPh_3)_2$ can be substituted by the phosphaalkyne *t*BuC≡P (*85*), but not by the iminoborane *t*BuB≡N*t*Bu (*19*). There is a parallel situation with the isoelectronic molecules N_2 and CO. Both are well known to form end-on coordination compounds of the type M—N≡N and M—C≡O, but a sideways coordination, comparable to **XI**, is possible only for N_2, not for CO (*82*). So the structural similarity between the isoelectronic couples XCCR/XBNR and N_2/CO (Section III) finds a counterpart in reactivity, as far as the π-bonds are concerned.

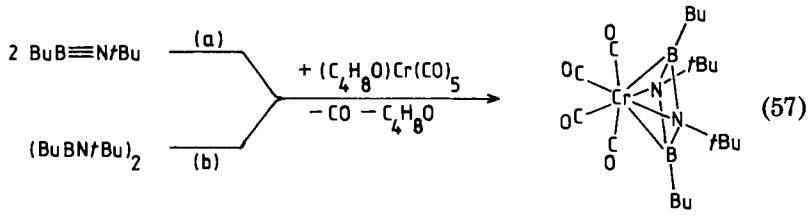
In the infant chemistry of iminoboranes only one example of insertion into a bridge position has been found [Eq. (56)] (*86*). That the structure of the product [Eq. (56)] corresponds to structure **XIIa** has been deduced from the CO absorption bands in the IR spectra, which



*t*BuB≡N*t*Bu + $Co_2(CO)_8$ —2 CO (56)

nearly coincide with those of the well-characterized analogous compound $(OC)_6Co_2(t\text{BuCC}t\text{Bu})$ (*87*).

η^4-Cyclobutadiene metal compounds may be formed by cyclodimerization of alkynes in the ligand sphere of a metal atom [e.g. $(Ph_4C_4)CoCp$ from $PhC{\equiv}CPh$ and $CoCp_2$] (*88*). In contrast to the uncomplexed species, η^4-coordinated cyclobutadienes have a square-planar structure. The compound $BuB{\equiv}Nt\text{Bu}$ was the first iminoborane that cyclodimerized at a transition metal [Eq. (57a)] (*49*).



(57)

The same iminoborane is thermally stabilized by cyclotrimerization, but may be cyclodimerized by the catalytic aid of $t\text{BuN}{\equiv}C$ (Section III). The cyclodimer $(BuBNt\text{Bu})_2$ produces the same product [Eq. (57b)] as for Eq. (57a). Nine further products of the same type, $M[(R'BNR)_2]$, were prepared either from iminoboranes, from their cyclodimers, or from both; the second starting component was either $M(CO)_5(OC_4H_8)$ (M = Cr, Mo, W), or $Fe(CO)_5$ or $CpCo(C_2H_4)_2$, respectively (Table V).

The structures of $(OC)_4Cr[(BuBNt\text{Bu})_2]$ (*49*), $(OC)_4W[(BuBNt\text{Bu})_2]$ (*89*), and $(OC)_3Fe[(PrBNt\text{Bu})_2]$ (*89*) were determined by X-ray methods. The diazadiboretidine ring skeleton is no longer planar; the MB bonds

TABLE V

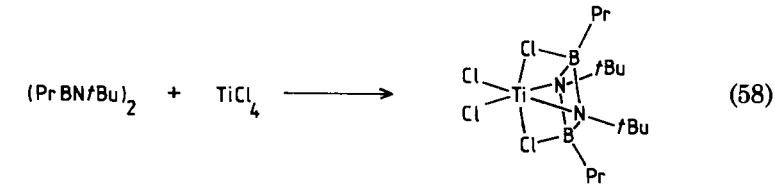
η^4-DIAZADIBORETIDINE METAL COMPOUNDS $M[(R'BNR)_2]$

M	R	R'	Synthesis equation No.	^{11}B-NMR [δ (ppm)]	Reference
$(OC)_4Cr$	*t*Bu	Me	(57a,b)	15.1	*13*
$(OC)_4Cr$	*t*Bu	Et	(57a,b)	16.4	*13*
$(OC)_4Cr$	*t*Bu	Pr	(57a,b)	15.7	*13*
$(OC)_4Cr$	*t*Bu	Bu	(57a,b)	16.7	*49*
$(OC)_4Cr$	*i*Pr	*i*Pr	(57a,b)	17.6	*19*
$(OC)_4Mo$	*t*Bu	Et	(57b)	20.6	*19*
$(OC)_4W$	*t*Bu	Et	(57b)	19.0	*19*
$(OC)_4W$	*t*Bu	Bu	(57b)	19.5	*49*
$(OC)_3Fe$	*t*Bu	Pr	(57b)	11.2	*19*
CpCo	*t*Bu	Pr	(57b)	8.0	*19*

are longer than the MN bonds with a difference of 15 pm (M = Cr), 16 pm (M = W), and 10 pm (M = Fe) (i.e., nearly the difference between the atomic radii of B and N). The coordination figure around Cr and W is a distorted octahedron of four carbon and two nitrogen atoms. The two CO groups above the CCNN plane, hosting the metal, are bent away from the boron atoms, which cap the two NCN octahedral faces closer to the nitrogen atoms. A simple picture of the bonding situation involves six-coordinated bonds from the carbon and nitrogen atoms along the distorted octahedral axes and two back-donating bonds from Cr or W to the boron atoms, fed by metal *d*-electrons in orbitals of adequate symmetry.

This picture is supported by ^{11}B-NMR data. In uncomplexed diazadiboretidines of the type $(R'BNR)_2$, ^{11}B-NMR shifts are found in the range 42–45 ppm ($Et_2O \cdot BF_3$ external standard). Provided all BN, BC, and NC bonds in the complexed cyclodimer remained normal σ-bonds, the complexation would make the π-electrons no longer available for boron and the NMR signals of the deshielded ^{11}B-atoms would shift downfield to values beyond 60 ppm, typical for sextet boron atoms (*39*), if there was no back-donation from the metal. In fact, there is a remarkable highfield shift (Table V), demonstrating the feedback of electrons to boron. Measuring the metal-to-boron back-donation by such an ^{11}B-NMR highfield shift, the back-donation is strengthened by going from chromium via iron to cobalt, in parallel to an increasing number of *d*-electrons. The structural and bonding situation, including ^{11}B-NMR highfield shifts, parallels the situation that is met with the well-known η^6-coordination of borazines to metals of the chromium group [e.g., $(OC)_3Cr[(MeBNMe)_3]$] (*90*).

The picture of the nitrogen atoms in diazadiboretidines acting as Lewis base centers is also supported by the formation of a 1:1 coordination compound with $TiCl_4$ [Eq. (58)] (*91*). The ^{11}B-NMR signal of 22.7 ppm indicates a highfield shift, which cannot be due to *d*-electrons from tetravalent d^0-titanium. X-Ray structural analysis shows that bridging chlorine atoms provide the observed electronic saturation of the boron atoms.



(58)

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