

Tri-*tert*-butylazadiboriridine: a molecule with a basic boron–boron bond¹

M. Müller, P. Paetzold*

Institut für Anorganische Chemie, Technische Hochschule Aachen, D-52056 Aachen, Germany

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¹ Dedicated to Heinrich Nöth on the occasion of his 70th birthday.

* Corresponding author. Tel.: +49 241 804644; fax: +49 241 8888288; e-mail: peter.paetzold@ac.rwth-aachen.de

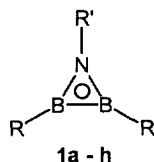
Abstract

The azadiboriridine [$\cdots \text{NR} \cdots \text{BR} \cdots \text{BR} \cdots$] ($\text{R} = t\text{Bu}$), a three-membered ring of Hückel aromaticity, preferentially reacts at the B–B bond. Boranes BX_3 are added as Lewis acids to the B–B bond as the corresponding Lewis base to give a BBB-(3c2e) bond. Brønsted acids may be added in a similar way, but a B–B bond opening may also occur. This opening is the standard reaction, when carbenes and related species are incorporated to give four-membered rings or when unsaturated species $\text{a}=\text{b}$ yield the corresponding five-membered rings. All these findings make the mechanism of a fusion reaction plausible, that transforms azadiboriridines [$\cdots \text{NR} \cdots \text{BR} \cdots \text{BR}' \cdots$] with a group R' , less bulky than $t\text{Bu}$, into *nido*-clusters $\text{N}_2\text{B}_4\text{R}_4\text{R}'_2$ in a stereospecific way. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Azadiboriridines; Basic bonds; Ring expansion

1. Introduction

Azadiboriridines are three-membered rings NB_2R_3 of type **1**. The NB_2 ring skeleton is isoelectronic with the C_3 ring skeleton of cyclopropenyl cations C_3R_3^+ . Azadiboriridines belong to Hückel's class of 2π -electron aromatic rings [1–7].



	R	R'	Lit.
1a	H	H	[1, 2]
b	NH_2	H	[1]
c	$t\text{Bu}$	$t\text{Bu}$	[3]
d	$t\text{Bu}$	Mes	[4]
e	$t\text{Bu}$, Mes	$t\text{Bu}$	[5]
f	$\text{N}i\text{Pr}_2$	$t\text{Bu}$	[6]
g	Tmp	$t\text{Bu}$	[7]
h	$\text{N}i\text{Pr}_2$, Tmp	$t\text{Bu}$	[7]

The parent molecule **1a** and its 2,3-diamino derivative **1b** had been investigated by ab initio calculations. The triorgano and the 2,3-diamino-1-organo derivatives **1c–h** are experimentally well characterized molecules (Tmp = 2,2,6,6-tetramethylpiperidino). The structures of **1d–g** are known from X-ray analyses.

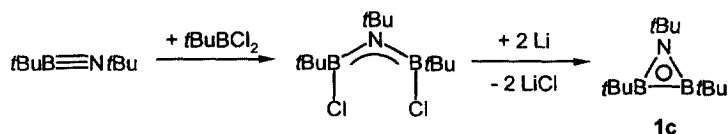
The bonding situation of **1a** was discussed in different ways. On the one hand, the considerably short B–B bond, 162 pm as compared to the calculated value of 171 pm in the planar diborane(4) $\text{H}_2\text{B}-\text{BH}_2$ [1], was considered to be mainly due to the contraction typical for small rings, though a small B–B π -overlap population and hence a certain B–B double bond character was also stated [1]. On the other hand, the shortness of the B–B bond was interpreted in terms of so-called σ -bridged π -bonding [2], which is a modified σ -donation π -back-donation model,

so successfully applied to the three-membered cyclic adducts of C–C double bonds and fragments of transition metal complexes. A contraction of the B–B single bond would then be accompanied by an increase of the angle H–B–B, which actually was calculated to be 168° in **1a**, as compared to 150° in the hypothetical three-membered ring B_3H_3 .

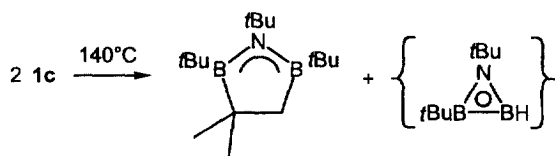
This bonding picture is supported by experimental evidence. The B–B bond lengths of **1d–g** in the crystal vary in the range from 156 (**1d**) to 161 pm (**1g**) and the angles R–B–B in the range from 176° (**1e**) to 160° (**1g**). Taking the standard B–B double bond length to be 151 pm from theoretical work on diborane(2), $HB=BH$ [8], the experimental values indicate considerable double bond character of the B–B bond in type **1** rings.

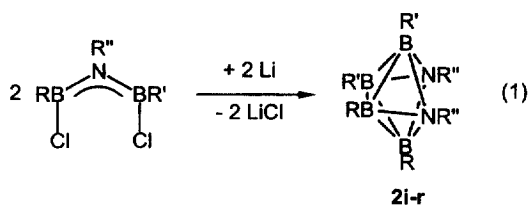
Triorganoazadiboriridines can be stored at ambient temperature, when sterically demanding organic ligands are present, as in **1c–e**. Otherwise, a characteristic fusion reaction takes place (Section 2). We studied the reactivity of the storable tri-*tert*-butyl species **1c** in detail and detected a number of unexpected reactions, which we describe in the Section 3–7. These reactions provide a key for understanding the mechanism of the fusion reaction (Section 8).

The title compound can be rather easily synthesized from the known iminoborane $tBuB\equiv NtBu$ in a two-step reaction: chloroboration of the iminoborane and subsequent dechlorination by the aid of alkali metal [3]; lithium gives the best yield [5].



Compound **1c** melts at -7°C and shows a characteristic ^{11}B NMR shift of 51.9 ppm (CDCl_3 , $\text{BF}_3 \cdot \text{OEt}_2$). X-ray diffraction data could not be sufficiently refined because of disorder in the crystal. Thermally stable up to 100°C , **1c** decomposes at approx. 140°C to give a five-membered ring, apparently by the addition of isobutene to **1c** (see Section 6). The isobutene is presumably formed from one half of the starting material by dehydroboration. The corresponding dehydroboration product, an azadiboriridine NB_2HtBu_2 , or subsequent products had not been identified; a pure five-membered ring had been isolated from the reaction mixture in a 89% yield [9].





	2i	2j	2k	2l	2m	2n	2o	2p	2q	2r
R	Me	Et	Et	<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu
R'	Me	<i>i</i> Pr	<i>s</i> Bu	<i>i</i> Pr	<i>t</i> Bu	<i>i</i> Pr	Me	Et	<i>i</i> Pr	<i>i</i> Pr
R''	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>i</i> Pr	<i>i</i> Pr	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	SiMe ₃

2. Fusion

By starting from diborylamines Cl—BR'''—NR'''—BR'—Cl with a set of ligands R, R' and R'', one, two, or all of which are smaller than *t*Bu, the dechlorination with alkali metal gives the dimers **2** instead of **1** [Eq. (1)] [3,10,11].

NMR data as well as the X-ray structural analysis of **2i** reveal an N₂B₄ cluster skeleton of the *nido*-type, which is derived from the corresponding *closo*-type pentagonal bipyramid by taking off an equatorial vertex. In most cases, e.g. in the carbaborane C₂B₄H₈ and its derivatives, the *nido*-six-vertex cluster is found to be a pentagonal pyramid, derived from the bipyramid by removing an axial vertex. This structure is not favourable for N₂B₄H₆ and its derivatives, as can be made plausible in terms of the (3c2e)/(2c2e) localized orbital scheme (Fig. 1). In the pyramidal pentadeltahedral structure, at least one N vertex necessarily takes part in a (3c2e) bond, which is avoided in the real hexadeltahedral structure. One (3c2e) bond and three (2c2e) bonds at nitrogen would increase the formal charge from +1 [ammonium type N atom with four (2c2e) bonds] to +4/3, and since the real charge at the electronegative N atom remains negative, the BN bonds in the pentadeltahedral structure would be highly polarized and weak.

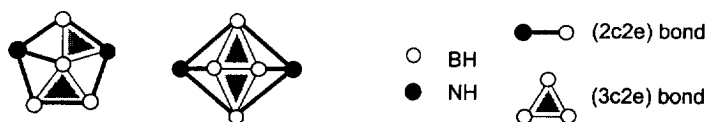
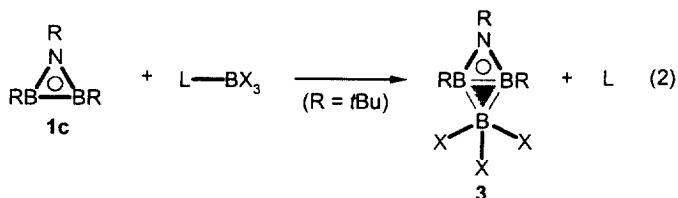


Fig. 1. Planarized structural formulae for N₂B₄H₆ in the hypothetical pentadeltahedral and the real hexadeltahedral structure.

The cluster products with different ligands R and R' offer three types of ligand distribution in axial or equatorial positions with respect to the bipyramidal fragment: ax,ax/eq,eq (C_{2v}), eq,eq/ax,ax (C_{2v}) and ax,eq/ax,eq (C_1) for R,R/R',R'. Mixtures of these three isomers are isolated, when the ligands are not too big. In the case of two bulky *t*Bu groups (**2o–q**), however, the C_1 -isomer is formed in a stereo-specific way, that must be due to the multi-step mechanism of reaction (1). The first step is clear, at least in the case of **2q**, because the corresponding azadiboriridine **1q** can be isolated and characterized at -78°C , before it undergoes dimerization on warming the solution up to room temperature [12]. We assume that three-membered rings of type **1** are intermediates generally. The mechanism of the fusion reaction **1** \rightarrow **2** and its stereospecificity in the case of bulky ligands can be made plausible, when the basic character of the B–B bond of **1** is considered.

3. Addition of boranes

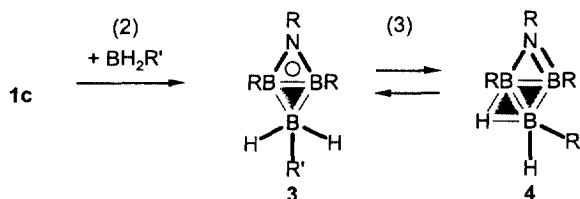
The chemist's first intuition on adding a borane BX_3 to the azadiboriridine **1c** would be that the π -electrons would be localized at the ring-N atom and that this lone pair would give a coordinative bond to BX_3 . However, the ring-B atoms would then loose their electronic saturation, and boranes BX_3 actually add across the B–B bond of **1c** under formation of a BBB-(3c2e) bond, whatever stabilization step might follow. (Note that we symbolize a closed (3c2e) σ -bond by a greyish triangle; the closed (3c2e) π -bond of **3** is symbolized by a circle in the triangle.)



3.1. Addition of alkylhydroboranes

Alkyldihydroboranes were added to **1c** either as the corresponding diboranes $\text{B}_2\text{H}_4\text{R}'_2$ or as adducts $\text{L-BH}_2\text{R}'$ ($\text{L} = \text{NMe}_3$, thf, etc.) [12,13]. An equilibrium mixture of the isomers **3** and **4** was isolated in general ($\text{R}' = \text{Me}$, *s*Bu, *t*Bu, CMe_2iPr , Ph).

In the case of BH_3 , 100% of **3a** ($\text{R}' = \text{H}$) is formed [12]. The triangles BNB and BBB enclose an angle of 142.6° in the crystalline product of the *nido*-cluster type. B–N and B–B bonds of comparable lengths (141.2, 142.1 and 175.2–178.5 pm,



respectively) make plausible that NMR data reveal **3a** to be a molecule of C_s symmetry in solution. The dialkylhydroboranes BHR'_2 ($\text{R}'_2 = \text{Et}_2$, cyclooctane-1,5-diyl), on the other hand, yield products of the type **4** only [13].

The equilibrium (3) had been studied in some detail in the case of $\text{R}' = t\text{Bu}$: **3b** \rightleftharpoons **4b**. The ratio of isomers was found to be 1:3 at room temperature in thf. The equilibrium constant was determined in a temperature range from -60 to $+40^\circ\text{C}$; the equilibrium (3) turned out to be slightly exothermic ($\Delta H = -3.0 \text{ kJ mol}^{-1}$) and exotropic ($\Delta S = -1.0 \text{ J mol}^{-1} \text{ K}^{-1}$). The isomer **4b** can be crystallized at low temperature, and the crystals are stable at room temperature, but immediately undergo equilibration, when dissolved in thf again. The equilibration is slow enough to allow the observation of the NMR shifts of both isomers. The structural data of crystalline **4b** clearly indicate a B–N single bond (147.3 pm) and a B=N double bond (139.4 pm). A folding angle of 139.8° at the RB–BR axis and a rather symmetric BHB bridge (B–H distances: 123 and 124 pm) are in accord with a *nido*-cluster structure.

Whereas the equilibrations **3b** \rightarrow **4b** and **4b** \rightarrow **3b** are rapid, the equilibration **3c** \rightarrow **4c** ($\text{R}' = \text{Me}$) takes 20 days at ambient temperature, and **3c** is the only detectable product from the instantaneous reaction of **1c** and $\text{Me}_3\text{N}-\text{BH}_2\text{Me}$ during the first hours. It might be that **3a** ($\text{R}' = \text{H}$) is stable with respect to the corresponding **4a** only for kinetic reason, though the steric demand of R' decreases in the series **3b** $>$ **3c** $>$ **3a**.

During the rearrangement of **3** into **4**, a $\text{BH}-(2c2e)$ σ -bond and a $\text{BNB}-(3c2e)$ bond of predominantly π -character are transformed into a $\text{BHB}-(3c2e)$ bond and a $\text{BN}-(2c2e)$ π -bond. Rearrangements of this type occur frequently in the chemistry of electron-deficient molecules and are called *[3c,2c] translocations* [14].

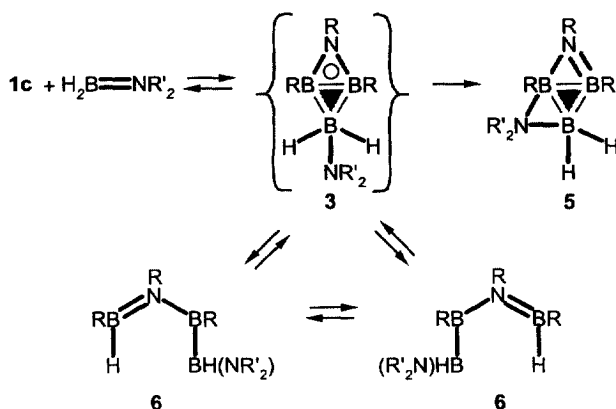
The general result is that the B–B bond of **1c** acts as a Lewis base with alkylhydroboranes as the corresponding Lewis acids. The addition of BH_3 to the parent molecule **1a** was calculated to be more exothermic ($-191.2 \text{ kJ mol}^{-1}$) than to ammonia ($-119.2 \text{ kJ mol}^{-1}$) [12]. This means that **1a** is a stronger base than the classical base NH_3 . If the borane is introduced as a Lewis acid–base adduct $\text{L}-\text{BX}_3$, as in reaction (2), an $\text{LB}-(2c2e)$ bond and a $\text{BB}-(2c2e)$ bond will be transformed into a lone pair at the base L and a $\text{BBB}-(3c2e)$ bond. Such reactions are called *[2c,2c] dislocations*; they are called *[3c,1c] collocations* in the reverse direction [14].

Trialkylboranes BR'_3 ($\text{R}' = \text{Me}, \text{Et}$) do not react with **1c** at room temperature,

but do react in boiling thf. A *nido*-cluster $N_2B_4R_4R'_2$ of type **2** in stereochemical purity (C_1 symmetry) is the product, apparently after a transformation of NB_2R_3 (**1c**) into NB_2R_2R' [13].

3.2. Addition of amino- and (alkylthio)boranes

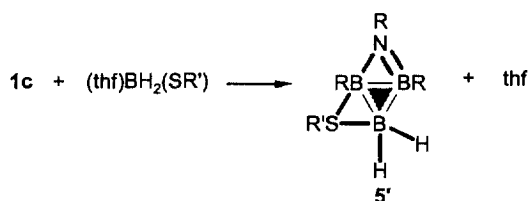
Aminoboranes $H_2B=NR'_2$ are added to **1c** to give two different products: In the case of relatively small steric demand of NR'_2 ($NHPr$, $NHtBu$, NMe_2 , NEt_2), products of type **5** are observed. With large steric demand of NR'_2 (e.g. $NiPr_2$), the open-chain product **6** is formed in a reversible reaction. The ratio of product **6** and the starting components is 93:7 at $-40^\circ C$, but is 52:48 at $65^\circ C$. At this temperature, **6** undergoes a degenerate rearrangement, according to NMR observations [13]. Presumably, the cluster **3** is an intermediate during the formation of **5** and **6** and also during the rearrangement of **6**.



The crystal structure analysis of **5** ($R' = Et$) reveals two B–N single bonds with four-coordinate nitrogen (159.2, 159.3 pm), a B–N single bond with three-coordinate nitrogen (149.9 pm) and a B=N double bond (138.2 pm). Note that the formation of **5** from **3** is a [3c,1c]-collocation. The three triangles of **5** enclose interplanar angles of 141.1 and 142.5° , thus inviting to identify **5** to be an *arachno*-cluster molecule, derived from a pentagonal bipyramid as the corresponding *closo*-structure. Actually, the unknown parent molecule of the family **5**, $N_2B_3H_7$, is isoelectronic and structurally comparable with *arachno*-pentaborane, B_5H_{11} .

In crystalline **6**, the chain $B=N-B-B=N$ defines the two nearly orthogonal plains $B=N-B$ and $B-B=N$ (82.6°). The sequence of bond distances 139.5, 149.0, 171.3, and 139.1 is in clear accord with the adopted single and double bond character of these bonds.

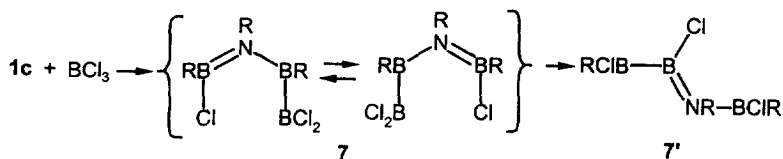
(Organylthio)boranes H_2B-SR' ($R' = Pr, Ph$) behave similar to aminoboranes.



The products of type 5' also constitute *arachno*-clusters, and the parent molecule SNB_3H_6 is also isoelectronic with B_5H_{11} . A B=N double bond (137.3 pm) can be clearly distinguished from a B–N single bond (147.3 pm) in crystalline 5' with $\text{R}' = \text{Ph}$ [15].

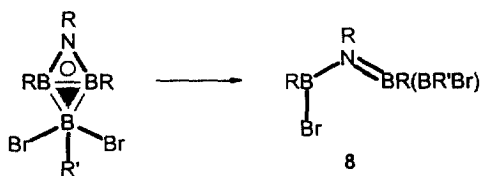
3.3. Addition of boron halides

Trichloroborane opens the B–B bond of 1c in a similar way as the aminoborane $\text{H}_2\text{B}=\text{NiPr}_2$, presumably via an adduct of type 3. According to NMR observations, the product 7 undergoes a degenerate, 1,3-dyotropic rearrangement at room temperature, similar to 6, which can be frozen out at -60°C . The borane 7 rearranges slowly and irreversibly at room temperature to give 7', presumably via a 1,2-dyotropic exchange of Cl and $\text{NR}(\text{BRCI})$ across the B–B bond of 7 [9].

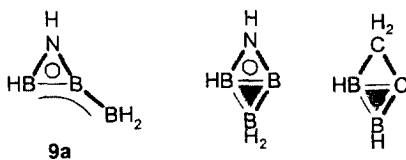


Chlorodihydroborane was added to 1c by its sulphane adduct $(\text{Me}_2\text{S})\text{BH}_2\text{Cl}$, that contains approx. 10% of $(\text{Me}_2\text{S})\text{BH}_3$ and 10% of $(\text{Me}_2\text{S})\text{BHCl}_2$. The adduct $\text{NB}_2\text{R}_3(\text{BH}_2\text{Cl})$ of type 3, unstable at room temperature, was quantitatively formed at low temperature and identified by NMR methods, besides the adduct $\text{NB}_2\text{R}_3(\text{BH}_3)$ (3a) and a third product of unknown structure. The same adduct $\text{NB}_2\text{R}_2(\text{BH}_2\text{Cl})$ and the product 7' were both identified, when $(\text{Me}_2\text{S})\text{BHCl}_2$ was reacted with 1c; this reaction apparently involves the dismutation of BHCl_2 into BH_2Cl and BCl_3 [9].

The type 3 adduct of 1c and $\text{R}'\text{BBr}_2$ ($\text{R}' = \text{Me}, \text{Bu}, i\text{Bu}, \text{PhCH}_2$, etc.) can be identified by NMR spectroscopy at -78°C . A B–B opening process gives the open-chain products 8 at higher temperature. Two non-degenerate isomers in a ratio, that depends on R' , are observed, which are presumably *E* / *Z*-isomers with respect to the B=N double bond [9,14].

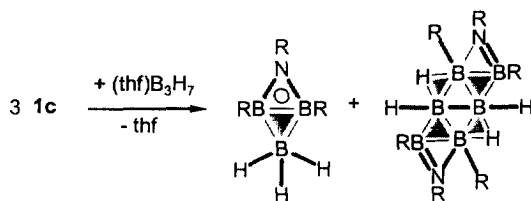


The debromination of the products **8** gives boranes $\text{NB}_3\text{R}_3\text{R}'$ (**9**); the one with $\text{R}' = i\text{Bu}$ is the only one that can be obtained in analytical purity. In order to elucidate the structure of **9**, the geometry of the parent molecule NB_3H_4 (**9a**) was calculated on the RMP2(fc)/6-31G* level [5]. Six minima were found on the energy hypersurface. The isomer of lowest energy turned out to be a linear molecule of type $\text{H}_2\text{B}-\text{B}-\text{N}-\text{BH}_2$ with a central $\text{B}\equiv\text{N}$ triple bond ($\approx 0 \text{ kJ mol}^{-1}$). The highest energy must be attributed to a tetrahedrane-type structure of C_{3v} symmetry with a triplet ground-state (288 kJ mol^{-1}). Two structures, an N-boryl derivative of **1a** (C_{2v} ; 8 kJ mol^{-1}) and a non-planar four-membered ring (C_s ; 53 kJ mol^{-1}), are not compatible with the C_1 structure of the products **9**, concluded from the NMR spectra. From two structures, that can be distinguished in the localized-orbital description by a closed or an open ($3c2e$) bond, that of higher energy (87 kJ mol^{-1}), a B-boryl derivative of **1a**, must be related to **9**, as its IGLO-calculated ^{11}B NMR shifts fit well to those observed for **9**. This is not so for a structure of lower energy (54 kJ mol^{-1}) with a closed instead of an open BBB -($3c2e$) bond; this molecule would correspond to the minimum-energy structure of the isoelectronic molecule $\text{C}_2\text{B}_2\text{H}_4$ [16] and its experimental counterpart $\text{C}_2\text{B}_2\text{R}'_2\text{R}''_2$ [17]. Anyhow, the debromination of **8** is accompanied by a migration of R from one to the other B atom.



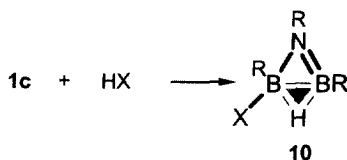
3.4. Addition of diborane(4)

The triborane LB_3H_7 , stabilized by the base L, is a potential source of the unstable molecules BH_3 and B_2H_4 by dismutation. Accordingly, the reaction of **1c** and $(\text{thf})\text{B}_3\text{H}_7$ yields **3a** and the adduct of a molecule **1c** to each of the BH_2 halves of the hypothetical B_2H_4 . Reliable distances cannot be concluded from the crystal structure analysis of this *arachno*-cluster $\text{N}_2\text{B}_6\text{H}_4\text{R}_6$ because of disorder [18].



4. Addition of Brønsted acids

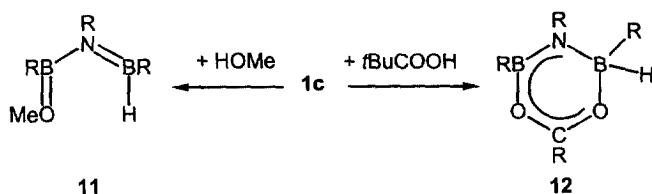
The B–B bond of **1c** exhibits basic character towards boranes as Lewis acids. How do protons behave? When acids HX are reacted with **1c**, the proton actually adds to the B–B bond under the formation of a BHB(3c2e) bond. An electron-deficient cation $[\text{NB}_2\text{R}_3\text{H}]^+$ would not be stable, and therefore the anion X^- also adds to one of the B atoms. The product **10** is stable provided the anion X^- cannot contribute a second lone pair for BX π -bonding [19].



A suitable acid is triflic acid $\text{H-OS}(\text{CF}_3)_2$ (product **10a**), because the lone pairs of the basic O atom are deactivated for π -donation by the electron withdrawing ability of the sulphonyl group $\text{S}(\text{CF}_3)_2$. Azaborane clusters $\text{H-NB}_a\text{H}_b$ are also suitable acids, which do not contain lone pairs because of electron deficiency, e.g. $\text{H-NB}_{10}\text{H}_{13}(\text{N}_3)$ (**10b**), $\text{H-NB}_{10}\text{H}_{12}$ (**10c**), etc. [19,20]. X-ray analytical data of **10a–c** show that there is a short double bond B1–N and a B–N single bond B2–N and that the BHB bridge is asymmetric with a shorter distance B1–H; the distances B1–B2 are clearly within the range of a B–B bond (Table 1). The BHB bridge is also identified by the corresponding cross peaks in the 2D- $^{11}\text{B}/^1\text{H}$ NMR spectra.

Table 1
Bond lengths (pm) of **10a–c**

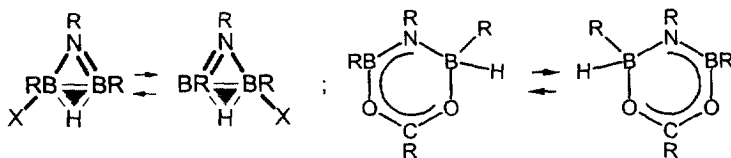
	B1–N	B2–N	B1–B2	B1–H	B2–H	B1–X
10a	134.7(12)	150.1(9)	188.8(14)	133(9)	140(7)	153.5(8)
10b	135.2(3)	151.0(3)	189.6(4)	128(3)	136(3)	158.0(3)
10c	130.4(2)	157.4(2)	180.1(2)	98	135	161.0(2)



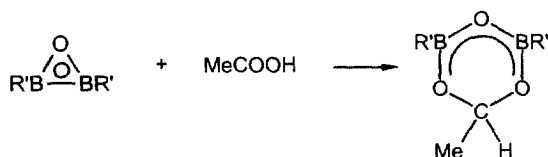
When X^- , on the other hand, can give double bonds, the B–B-bond will be opened completely to yield products of type **11** ($X = \text{OMe}$) [19] or **12** ($X = \text{OOC}t\text{Bu}$) [21].

The B–N single and the B=N and B=O double bonds of **11** can be correlated to typical distances, measured from crystalline material: 149.2, 140.3, and 135.8 pm, respectively.

The products **10** and **12** undergo a 1,3-sigmatropic migration of the triflate anion and a 1,5-sigmatropic migration of H, respectively, in solution, which is fast at room temperature with respect to the NMR time scale.



Oxadiboriridines $\text{OB}_2\text{R}'_2$ are isoelectronic with azadiboriridines $\text{NB}_2\text{R}'_3$. One of the rare reactions that had been observed for the only hitherto known oxadiboriridine ($\text{R}' = \text{C}(\text{SiMe}_3)_3$) [22] is the opening of the B–B bond by acids like MeCOOH . Though the product is comparable to **12**, neither does **12** give a 1,3-sigmatropic migration of H from the B to the C atom nor is the reverse migration possible for the product from $\text{OB}_2\text{R}'_2$ and MeCOOH .



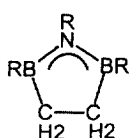
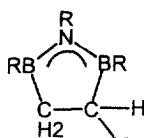
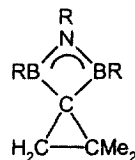
5. Addition of carbenes and related species

Carbenes and related species Y open the B–B bond of **1c** to give four-membered rings, which may undergo subsequent reactions.



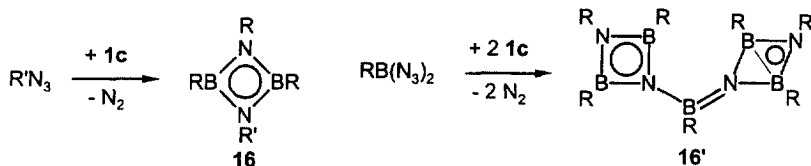
5.1. Addition of carbenes

Bromolithiomethane $\text{Li}(\text{Br})\text{CH}_2$, 2-bromo-2-lithiopropene $\text{Li}(\text{Br})\text{CMe}_2$, and 1-bromo-1-lithio-2,2-dimethylcyclopropane $[-\text{Li}(\text{Br})\text{C}-\text{CH}_2-\text{CMe}_2-]$ eliminate LiBr when reacted with **1c**. Two CH_2 units are incorporated into **1c** to give **13**, irrespective of the ratio of starting materials. The carbene CMe_2 may be incorporated into **1c**, but the product rearranges by a dyotropic proton/boryl exchange at the C–C bond to yield **14**. The product **15** is formed by the standard incorporation of dimethylcyclopropylidene into **1c** [23].

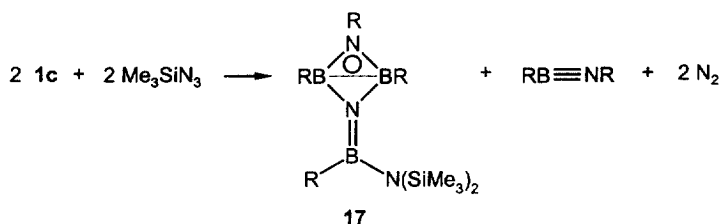
**13****14****15**

5.2. Addition of nitrenes

A nitrene unit is incorporated into the ring skeleton of **1c** by the reaction with azides $\text{R}'\text{N}_3$ ($\text{R}' = \text{Bu}, \text{Ph}, \text{PhCH}_2$). Both azido groups of $t\text{BuB}(\text{N}_3)_2$ are attacked in the same way by **1c** [23,24]. The four-membered diazadiboretidines **16** and **16'**, well known isoelectronic analogues of cyclobutadiene [25], are the products.

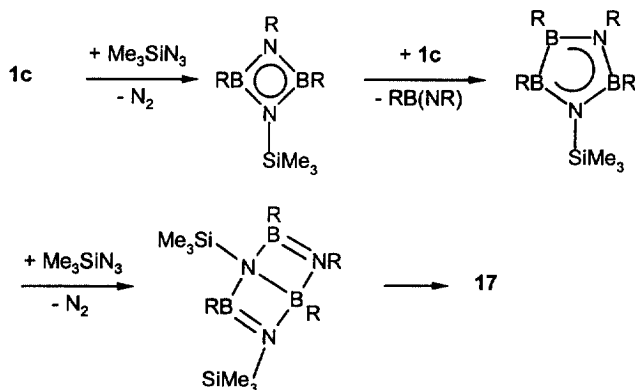


The azidosilane Me_3SiN_3 reacts in a different way to yield **17** besides the known iminoborane $\text{RB}(\text{NR})$ [26].



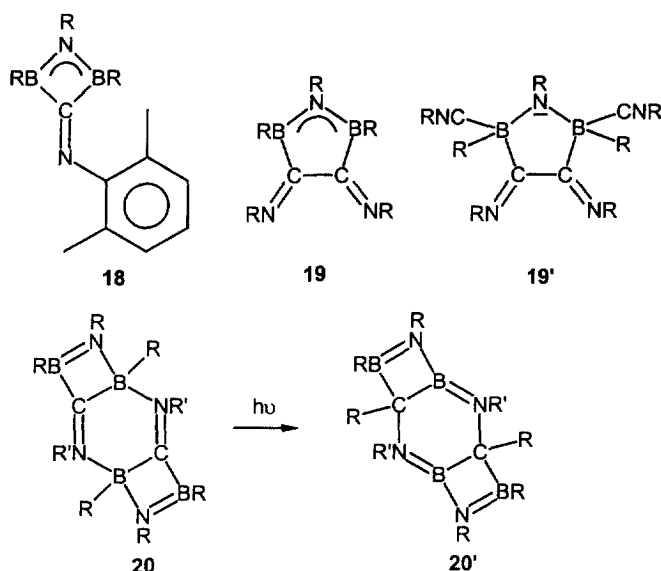
The X-ray structural analysis of **17** reveals a non-planar four-membered ring bent at the B–B axis by 150° . The transannular B–B distance of 187.6 pm may be correlated to a bonding interaction, say by a closed BNB-(3c2e) π -bond. Whereas the two bonds RB–NR are found in the range expected for boron–nitrogen rings with π -bond contributions (143.4 and 144.0 pm), the other two ring B–N bonds must be attributed to single bonds (150.7 and 148.7 pm). This is in accord with an exocyclic B=N double bond (141.6 pm) and single bond (150.1 pm). The geometrical situation is similar to that of one of the four-membered rings in crystalline **16'**. The other one is a planar ring of expected geometry, whose ring plane is almost orthogonal to the bond plane of the central B atom of **16'**, comparable to the orthogonal bond planes of the exocyclic B and N atom in **17** [23].

A plausible mechanism of the formation of **17** starts by the expected formation of a four-membered ring of type **16**, from which the iminoborane RB(NR) is eliminated by the attack of a second molecule **1c**. By the subsequent attack of a second molecule of Me_3SiN_3 at the B–B bond, a Dewar borazine of known type [25] is formed, which by a 1,3-sigmatropic silyl migration is transformed into **17**.



5.3. Addition of isonitriles

The products from the reaction of isonitriles $R'NC$ and **1c** depend on the steric demand of the ligand R' [23]. The bulky ligand 2,6-dimethylphenyl makes the product **18** available by the standard opening of the B–B bond of **1c**. The ligand *tert*-butyl permits the incorporation of two isonitrile species to give **19**, in some analogy to the formation of **13** in the case of the carbene CH_2 . The 4:1 adduct **19'** from CNR ($R = tBu$) and **1c** is formed, when an excess of CNR is applied. If the ligands exhibit a small steric demand ($R' = Me, Et$), the unsaturated (imino-methyl)borane fragment of the type $R'N=C(X')-BX_2$, present in the standard product **18**, will not be stable and undergoes a [3 + 3] cyclodimerisation to give **20**. Such dimerisations are well known from the primary products $R'N=CR''-BR''_2$ of the alkylboration of $R'NC$ by BR''_3 [27,28].



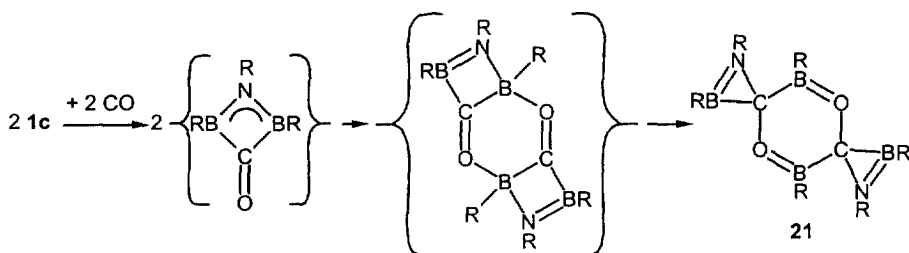
The crystal structure of the centrosymmetric molecule **20** ($R' = Me$) reveals two B–N single bond lengths (inner ring 159.9 pm, outer ring 160.2 pm), a B=N double bond length (141.5 pm), and a C=N double bond length (129.9 pm) [23]. The tricyclic products **20** are transformed into the isomers **20'** on photolysis by a sigmatropic shift of two groups R from the B to the C atoms of the six-membered ring. One can observe one B–N single, two B=N double, and a C–N (ring) single bond in crystalline, centrosymmetric **20'** ($R' = Me$) (146.1, 140.8, 144.0, and 148.7 pm, respectively) [21].

A rearrangement of the type $20 \rightarrow 20'$ is known for the monocyclic six-membered rings $[-BR''_2-CR''=NR'-]_2$, formed from $R'NC$ and BR''_3 , as mentioned

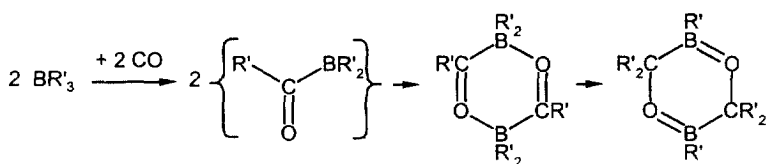
above. A sigmatropic shift of two alkyl groups R'' is observed as thermal process at approx. 200°C to give $[=BR''-CR''_2-NR'_2]_2$ [28].

5.4. Addition of carbonoxide

Our title compound **1c** is one of the rare substances, that react quantitatively with CO at a temperature as low as -78°C . The tricyclic product **21** is formed, the structure being comparable to product **20'** [24]. The observations made with isonitriles make a three-step mechanism strongly probable that starts with the standard B–B bond opening, followed by a [3 + 3] cyclisation and subsequent sigmatropic migration of two boron-bound groups to carbon; these groups are amino groups in this case and not alkyl groups as in the transformation **20** \rightarrow **20'**, thus contracting four-membered to three-membered rings.

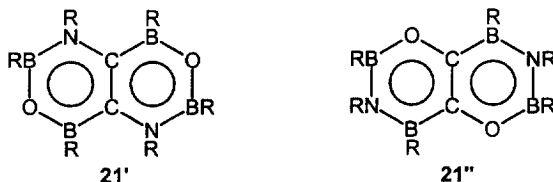


This mechanism is reminiscent of the well known reaction of BR'_3 with CO; both of the six-membered rings are isolable and the final rearrangement is a thermal process at elevated temperature [29].



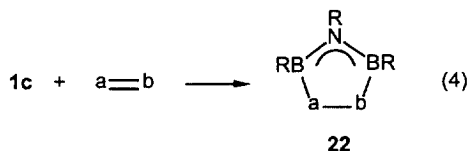
The two three-membered rings and the planar six-membered ring are found in an orthogonal arrangement in the centrosymmetric spirocyclic crystalline product **21**, characterized by a B=N (132.9 pm) and a B=O double bond (136.0 pm) [24]. Crystalline **21** is storable at room temperature, but is transformed into the isomer **21'** upon a 1-week storage in solution. The same product **21'** is formed by the photolysis of a mixture of **1c** and $\text{Fe}(\text{CO})_5$ at -30°C . Nothing is known about the mechanism of the isomerisation **21** \rightarrow **21'** [24]. The situation finally becomes obscure, when the product **21''** from the photolysis of **1c** and $(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_3$, is considered: Both of the isomers **21'** and **21''** are comparable to naphthalene,

though their bicyclic skeleton is non-planar. They are both well characterized by crystal-structure analyses [5,24].



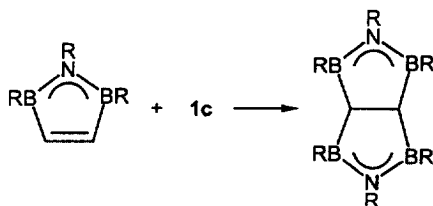
6. Addition of molecules with multiple bonds

Alkenes and alkynes are 1,2-diborated by diborane(4) derivatives of the type X_2B-BX_2 [30,31]. Less reactive diboranes can be activated by catalysts like $BF_3(OEt_2)$ [32], platinum [33], or rhodium complexes [34]. The title substance **1c**, a cyclic diborane(4) with a strained B–B bond, quantitatively diborates multiple bonds in species $a=b$ without a catalyst, according to the general Eq. (4).

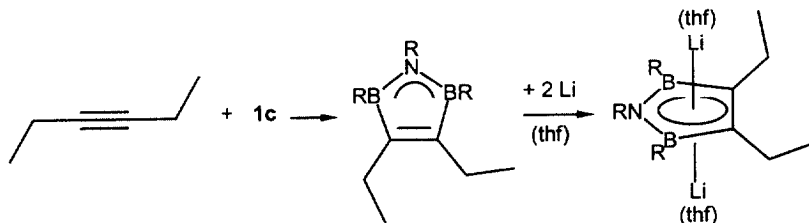


We added **1c** to a series of 1-alkenes and found additions of type (4) below 0°C , e.g. with ethene, propene, isobutene, and trimethylvinylsilane [21]. 2,3-Dimethyl-1-butene afforded 3 days stirring in order to complete the reaction.

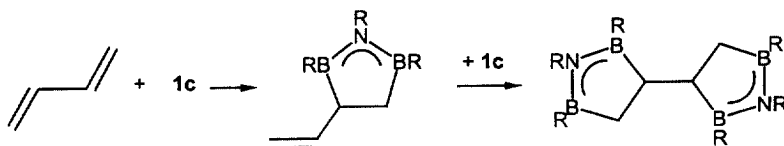
Alkynes and **1c** give five-membered rings of type **22** in quantitative yield, that contain a C=C double bond; ethyne, 2-butyne [35], and 3-hexyne [10] were applied. In the case of ethyne, a second molecule of **1c** reacts, when $BF_3(OEt_2)$ is used as catalyst [35].



The product from **1c** and 3-hexyne can be reduced by Li to give a pentagonal bipyramidal structure with two Li atoms in the apical positions [10].



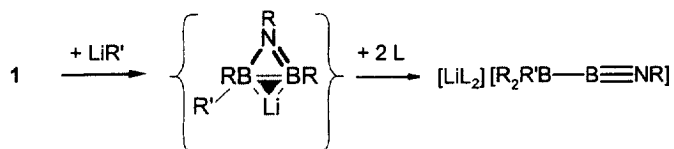
Butadiene is 1,2-diborated by **1c** to give a vinyl derivative of **22**, but a second molecule **1c** can diborate the second double bond. A 9:1 mixture of racemate and *meso*-product is formed. The *meso*-product can be crystallized in its centrosymmetric conformation, as revealed by a crystal structure analysis [21].



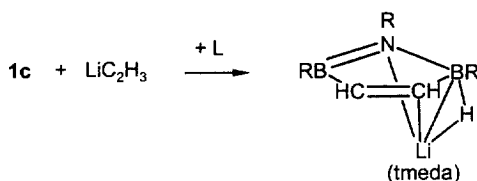
The C=O double bond of a series of aldehydes $R'HCO$ ($R' = \text{Me}, t\text{Bu}, \text{Ph}$), ketones R'_2CO ($R' = \text{Ph}$), formic acid derivatives HCOX ($X = \text{OMe}, \text{NMe}_2$), and acetic acid derivatives MeCOX ($X = \text{Cl}, \text{OEt}$) is also easily added to **1c** to give the corresponding products of type **22** [5]. The same is true for the multiple bonds of PhHC=NPh [21], $t\text{BuC}\equiv\text{P}$ [2], PhN=NPh [35], and $\text{EtB}\equiv\text{N}t\text{Bu}$ [10].

7. Addition of alkyllithium

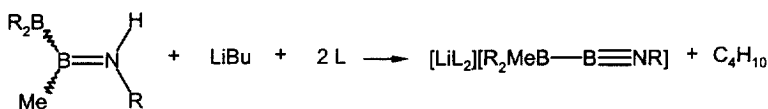
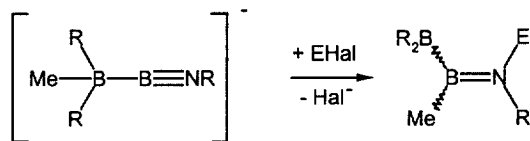
Instead of the B-B bond a B-N bond of **1c** is opened and a *t*Bu group migrates from one to the other B atom, when alkyllithium LiR' ($R' = \text{Me}, \text{Bu}, \text{Me}_3\text{C-CH}_2, \text{Me}_3\text{Si-CH}_2$) attacks **1c** in the presence of tetramethylethylenediamine (tmeda, L) [36,37]. A B-B single bond (172.5 pm) and a B \equiv N triple bond (125.0 pm) are present in the linear (iminoboryl)borate anion in the crystalline product ($R' = \text{Me}$). A species, which is similar to the product **10** from **1c** and acids HX, is presumably formed as an intermediate.



An unexpected product is identified, when vinyl lithium is reacted with **1c** in the presence of tmeda [37]. A lithium atom is trihapto bound to a five-membered ring of type **22** with three distances in a range from 228 to 231 pm. A B=N and C=C double bond (143.0 and 130.8 pm) can clearly be distinguished from three single bonds in the range 156–160 pm in the five-membered ring. A hydrogen atom is found in a BHLi bridging position.

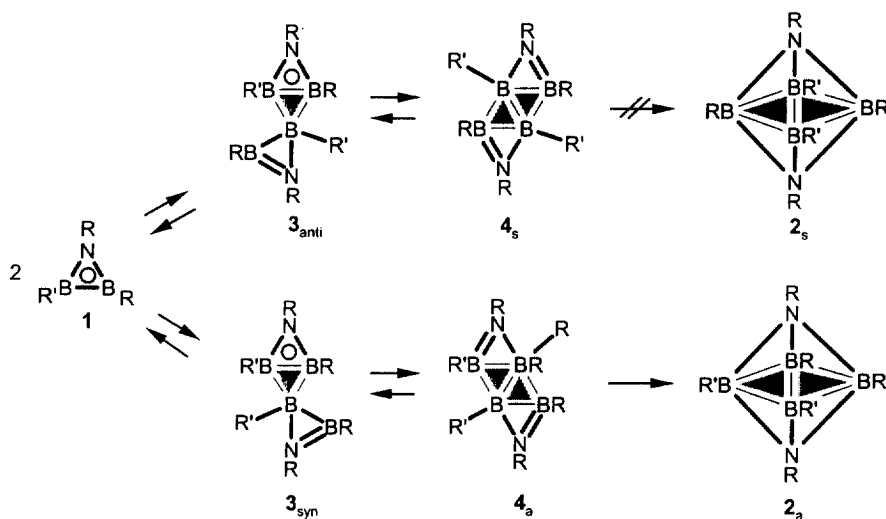


The reaction of (iminoboryl)borates with electrophiles EHal like HCl, MeI, and Me₃SiI had been investigated [37]. The electrophile adds to the N atom and an alkyl group is shifted from one to the other B atom. In the case of E = H, this reaction can be reversed by the addition of LiBu and tmeda (L) [37].



8. Mechanism of the fusion

A three-step mechanism is proposed for the fusion of **1** to give **2**, according to the over-all Eq. (1) [38]. The first step is the addition of the borane **1** as a Lewis acid to the borane **1** as a Lewis base, according to the general equation (2). The ligand R may be *t*Bu, and the ligand R' is assumed to be less bulky than R. The BR' moiety will then react with **1** prior to BR. A *syn*- and an *anti*-orientation of the two ligands R' are possible in the product of type **3**. The second step will be an equilibrium analogous to the [3c,2c]-translocation (3); a BB- instead of a BH-(2c2e) bond gives a BBB- instead of a BHB-(3c2e) bond. The product from **3**_{syn} is asymmetric (*C*₁; **4**_a), the product from **3**_{anti} is symmetric (*C*₂; **4**_s). The third step is an intramolecular irreversible [2 + 2] cycloaddition of the two B=N double bonds. Since in the non-planar tetracyclic systems **4**_a and **4**_s one B=N double bond will be situated in an almost orthogonal position above the other one, the cycloaddition is possible as a thermally allowed antarafacial concerted process. The product **2**_a (*C*₁) is formed from **4**_a as a racemate, corresponding to the observed stereo-specific formation of **2o-q**. The product **2**_s (*C*_{2v}) cannot be expected, though allowed with respect to the conservation of orbital symmetry, because four bulky *t*Bu groups frame the B=N double bonds in **4**_s and make the cycloaddition impossible for steric reason.



Arguments for this mechanistic proposal come not only from the analogy of the first and the second step with the well explored reactions (2) and (3). A product of type **4**_s could be isolated as crystalline material from the dechlorination of Cl—B(R)···N(R)···B(CH₂R)—Cl [38]; note that the neopentyl group CH₂R is

considered to be less bulky than the *tert*-butyl group. Three crystallographically independent molecules were found in the unit cell, all three of them not far away from C_2 symmetry. The four helically arranged triangles are separated by interplanar angles of approx. 144, 127, and 143°. The average values of the B=N double and single bonds are 137 and 151 pm, respectively; three types of B–B bonds are found with average bond lengths of 177 pm (central B–B bond; two (3c2e) bonds are effective), 186 pm (in the BNB triangles) and 192 pm (outside B–B bonds). The crosswise arrangement of the B=N double bonds makes an antarafacial [2 + 2] cycloaddition plausible, which does not occur, however, with this molecule, because the steric demand of the *t*Bu groups block it.

9. Conclusion

Though sterically shielded by three *tert*-butyl groups, the title molecule **1c** exhibits a surprising reactivity at the B–B bond, surprising not only because of the mostly mild conditions, but also because of the dual character of that reactivity, revealing the molecule to act either as an acid or a base. The acidic character could have been expected as far as the diboration of electron-rich alkenes is concerned, since this reaction is also given by B–B bonds in open-chain molecules. However, the quantitative addition of CO to the B–B bond of **1c**, even at -78°C , is unique and deserves further attention in the future. It may be a prejudice to think about CO and similar molecules predominantly as bases. An elementary process may work here, that makes use of the σ -basic and the π -acidic nature of these molecules. Whereas we understand most of the steps of the formation of the product **21** from **1c** and CO, we have no insight into the first step, that elementary process.

The basicity of the B–B bond could also have been expected, since the addition of Lewis acids like protons, boranes BX_3 , or metal complex fragments to B–B bonds in electron-deficient borane clusters has been known for years. The title compound **1c**, however, does not only present a vivid simple model for the reaction of a B–B bond as a base, it also presents a base of unexpected strength, being stronger towards BH_3 than ammonia.

The addition of BH_3 to **1c** seems to be a particularly simple one step reaction. Actually a molecule BH_3 is unlikely to exist as a reacting moiety. With $\text{BH}_3(\text{thf})$ as the starting material, a nucleophilic substitution of thf by **1c** takes place, presumably. In terms of localized orbitals, this elementary process involves the transformation of two (2c2e) bonds, the B–B bond of **1c** and the B–O bond of $\text{BH}_3(\text{thf})$, into a BBB-(3c2e) bond and a (1c2e) lone pair at thf. We call such a process a [2c,2c] dislocation and the reverse process a [3c,1c] collocation. Elementary processes of this type occur rather often and their general designation seems to be useful. The same is true for rearrangements that involve the transformation of a (2c2e) to a (3c2e) bond and synchronously of a (3c2e) to a (2c2e) bond, the equilibrium (3) being an example. We call such reactions [3c,2c] translocations.

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