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Small boranes, carboranes, and heterocarboranes*

W. Siebert‡, C.-J. Maier, A. Maier, P. Greiwe, M. J. Bayer, M. Hofmann, and H. Pritzkow

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Abstract: Dehalogenation of 1,2-dichloro-diborane(4) derivatives with Na/K alloy does not lead to planar *cyclo*-tetraboranes but to the blue puckered diisopropylamino compound and to the yellow 2,2,6,6-tetramethylpiperidino-tetraboratetrahedrane derivative, respectively. With smaller dialkylamino substituents, the formation of orange-red *cyclo*-hexaborane $(BNMe_2)_6$ and the green *closo*-hexaborane $(BNEt_2)_6$ is observed. When a 1:1 mixture of Me_2NBCl_2 and $[Me_2N(Cl)B]_2$ is dehalogenated, a small amount of colorless crystals of the planar diamond-shaped tetrabora-*bicyclo*-butane $[(Me_2N)_2BB{-}BNMe_2]_2$ is obtained. Its MO analysis reveals that eight framework electrons are used to form two 3c,2e σ bonds, one 4c,2e π bond, and one 4c,2e σ bond along the edges.

A new approach to reactive *closo*-dicarbapentaboranes involves the hydroboration of dichloroboryl-*t*butylacetylene with $HBCl_2$ leading to $Me_3CCH_2C(BCl_2)_3$. On heating, it is transformed into the *closo*-dicarbapentaborane $(Me_3CCH_2C)_2(BCl)_3$, in which the chlorine atoms may be substituted to give new derivatives.

By reacting B_2Cl_4 with C_5Me_5-$SiMe_3$ the *nido*-1-borane-2,3,4,5,6-pentacarbahexaborane(6) is stabilized by the Lewis acid BCl_3 to give $(MeC)_5B{-}BCl_3$.

Hydroboration of 3,4-bis(isopropylidene)-1,3-diborolanes leads to the formation of *nido*-2,3,5-tricarbahexaboranes(7), which may be deprotonated to give the corresponding anions isolobal with $C_5H_5^-$. Heterotricarbahexaboranes are obtained when a 3,4-bis(dichloroboryl)-2,5-hexadiene derivative is reacted with heptamethyldisilazane and hexamethyl-disilthiane to give the corresponding 1,2,5-azadiborolane and thiadiborolane. Their hydroboration leads to the aza- and thia-*nido*-dicarbahexaboranes, respectively.

INTRODUCTION

A study of the chemistry of small boranes has illustrated a unique structural interplay between *cyclo*- and polydeltahedral boron compounds. The planar *cyclo*-tetraborane(4) **1**, which has not been unambiguously characterized to date [1,2], stabilizes itself by folding along a diagonal to give **2**, and an extension of this folding could finally lead to tetraboratetrahedranes **3** (R = Cl [3], CMe_3 [4]). The extend of folding is controlled by electronic and/or steric properties of R. Substituents with different donor/acceptor capabilities (R, R′) may cause the formation of a planar *bicyclo*-tetraborane **4** [R = NMe_2, R′ = $B(NMe_2)_2$] [5,6] having the familiar diamond shape of two adjacent deltahedral faces found in polyhedral boranes and carboranes. One can regard **4** as the smallest polydeltahedron, the dihedron. Alternatively, it may be described as a flat butterfly.

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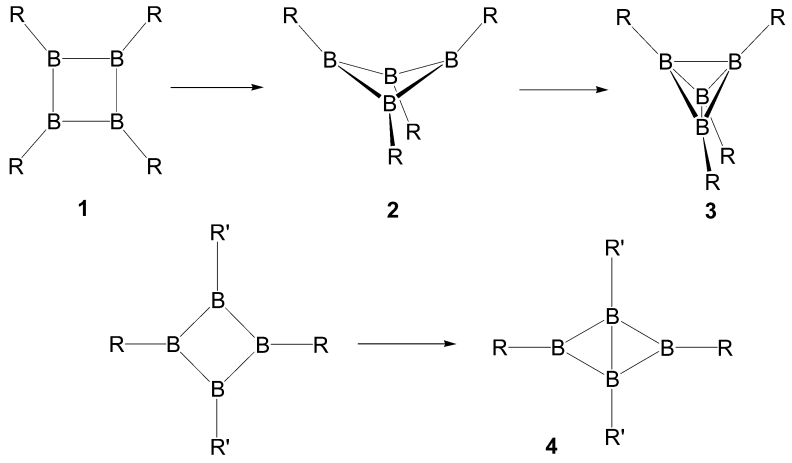
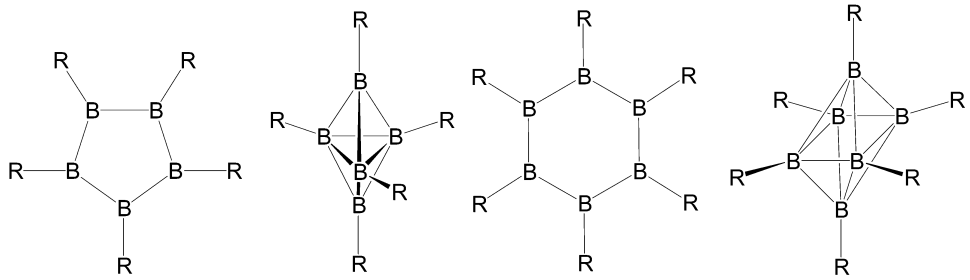
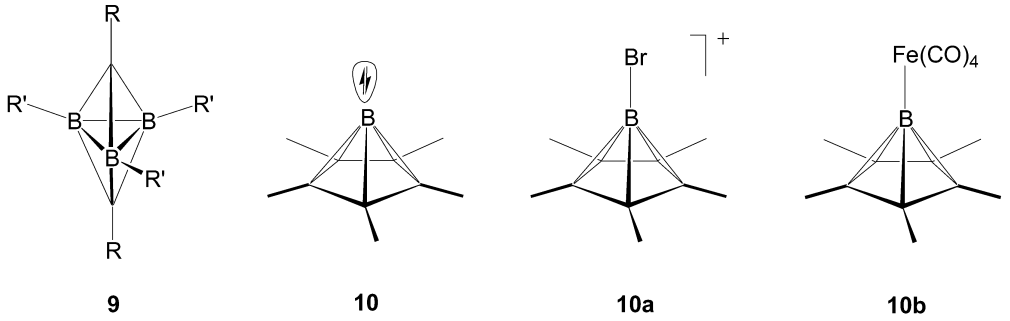
‡Corresponding author: Fax: (internat.) +49-(0)6221-54-5609; E-mail: walter.siebert@urz.uni-heidelberg.de



Cyclo-pentaborane(5) **5** and its *closo*-deltahedral isomer **6** are unknown, whereas orange-red *cyclo*-hexaboranes **7** (R = NMe_2 [7], NEt_2 [8]) and the green octahedral cluster **8** (R = NEt_2) [8] have been reported. The best access [9] to **7** and **8** is by dehalogenation of diborane(4) derivatives R(Cl)B–B(Cl)R.



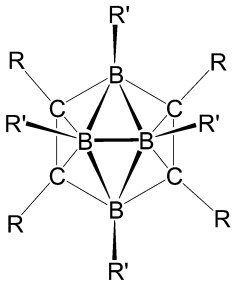
The *closo*-$(RC)_2(BR')_3$ carboranes (**9**) are of particular interest because their structures and bonding may be described as midway between classical and nonclassical. The small *closo*-carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ were obtained from B_5H_9/C_2H_2 mixtures by electric glow discharges in low yields (<2 %), which could be increased when thermal reactions at 490 °C in a H_2 stream were carried out [10]. The synthesis of pentaalkyl-1,5-dicarba-*closo*-pentaboranes(5) [11] was achieved by hydroboration of dialkyl(1-alkynyl)boranes with tetraalkyldiboranes. Later, a better approach was developed by using a large excess of $(Et_2BH)_2$ as a "hydride bath" [12]. To synthesize the reactive



$(RC)_2(BCl)_3$ carboranes, we hydroborate dichloroboryl-alkynes with $HBCl_2$ prepared in situ followed by thermal condensation [13].

The unknown *nido*-carborane species $(Me_5C_5)B$: has been stabilized by Lewis acids. Formal addition of the bromonium ion Br^+ leads to **10a** which was first obtained through cleavage of the Me_5C_5–$GeMe_3$ bond by an excess of BBr_3 to give the **10a**$^+$ cation and BBr_4^- as the anion [14]. The analogous reaction of $[(Me_5C_5)Al]_4$ with BBr_3 afforded **10a**$^+$ $AlBr_4^-$, which was confirmed by an X-ray diffraction study [15]. The preparation of the iron complex **10b** has been reported [16] together with a theoretical study on free and complexed **10**. We found a new approach [17] to stabilize **10** with BCl_3 and Cl_2B–$SiCl_3$.

Carbon-rich *nido*-carboranes $(RC)_4(BR')_4$ **11** have been reported by several groups [18–21], and the X-ray diffraction study of $(CH)_4(BEt)_4$ [22] has confirmed the proposed *nido*-C_4B_4 framework. The synthesis and reactivity of $(EtC)_4(BCl)_4$ (**11a**) is reported. The chemistry of *nido*-tricarbahexaboranes **12** has been developed [23], and we describe some aspects of the chemistry of the heterocarboranes **13** (X = NMe) and **14** (X = S).



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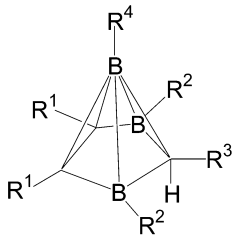

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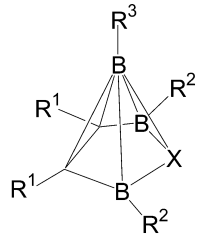


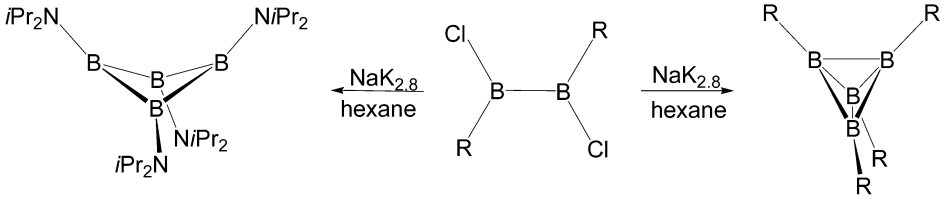
13 X = NR, **14** X = S

RESULTS AND DISCUSSION

cyclo-Boranes and *polyhedral*-boranes

Our attempts to obtain planar derivatives of **1** (R = NMe_2 [2], NEt_2 [8]) by dehalogenation of diborane(4) derivatives **14** were not successful. Molecular orbital (MO) studies [2] have indicated that planar B_4 rings are unstable. By reacting the more sterically hindered diisopropylamino derivative of **14** with Na/K alloy, we were surprised by isolating blue crystals of **2a** (18 %, λ_{max} = 620 nm, ε = 40, $\delta^{11}B$ = 65) and the colorless tetraborane(6) $(i Pr_2N)_4B_4H_2$ (2 %), both confirmed by X-ray diffraction studies [9]. In addition, some colorless diborene $(iPr_2N)_2B_2$ was detected as a part of a mixture that included other unidentified products. In the folded B_4 ring of **2a** [angle between planes B1B2B2′ and B2B1′B2′ 59.3(1)°], the B–B distances are almost identical [1.710(3), 1.711(3) Å], the exocyclic B–N bonds are short [1.396(3) Å] which indicates significant π interactions.

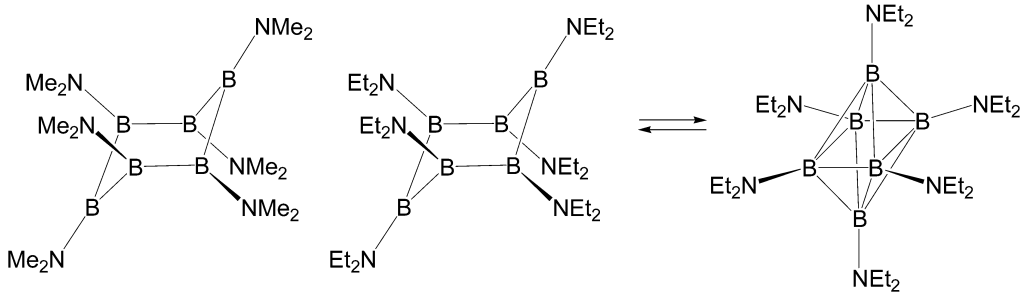
When **14** with the less flexible substituent R = 2,2,6,6-tetramethylpiperidino (tmp) is dehalogenated, yellow crystals (37 %, λ_{max} = 312 nm, ε = 15300) were formed. The spectroscopic data of the product indicated the presence of the tetraboratetrahedrane **3a**, which was confirmed by an X-ray structural analysis. Two opposite edges are short [B1–B1′ 1.695, B2–B2′ 1.701(7) Å], the others are longer



2a **14** **3a** R = tmp

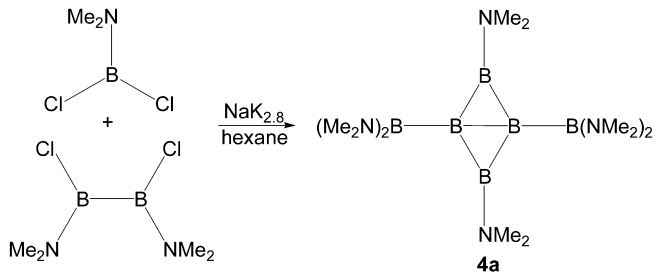
[B1–B2′ 1.752, B1–B2 1.765(5) Å]. The B–N bonds are longer as in **2a**, indicating no or only weak π interactions. We assume that the "corset" effect of the bulky tmp substituents causes the complete folding to yield the tetrahedrane structure. Theoretical studies [2] on $B_4(NH_2)_4$ (D_{2d}) and tetrahedrane structure (calculated B–B distances 1.672–1.733 Å) were carried out. The calculations suggested that the energy difference between HOMO and LUMO of $B_4(NH_2)_4$ for the tetrahedrane is 10.8 eV and for the D_{2d} structure 9.8 eV, which is in qualitative agreement with the observed color difference between **2a** and **3a**. These data indicate that the tmp-substituted yellow tetraboratetrahedrane **3a** is more stable than the blue, folded *cyclo*-tetraborane **2a**.

As outlined above, our attempts to obtain the planar *cyclo*-tetraborane **1a** (R = NMe_2) by dehalogenation of $Me_2N(Cl)B$-$B(Cl)NMe_2$ was not successful. Instead, we observed the formation of the orange-red *cyclo*-hexaborane **7a** in 1 % yield. **7a** was first reported in 1980 [7]. Ten years later, the corresponding diethylamino derivative **7b** was described, and it was found that on standing in solution the orange-red color of **7b** changed to green [8]. This new isomer **8b** has a *closo*-structure, however, because of disorder of the crystal the exact bond lengths could not be determined. On heating, **8b** is transformed into **7b**. The dehalogenation of $Et_2N(Cl)B$–$B(Cl)NEt_2$ with Na/K alloy leads to the green isomer **8b** in 40 % yield. Our attempts to elucidate the precise structure of **7b** and **8b** did not lead to better results than those reported previously [8].

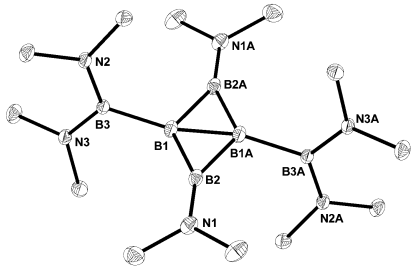


7a **7b** **8b**

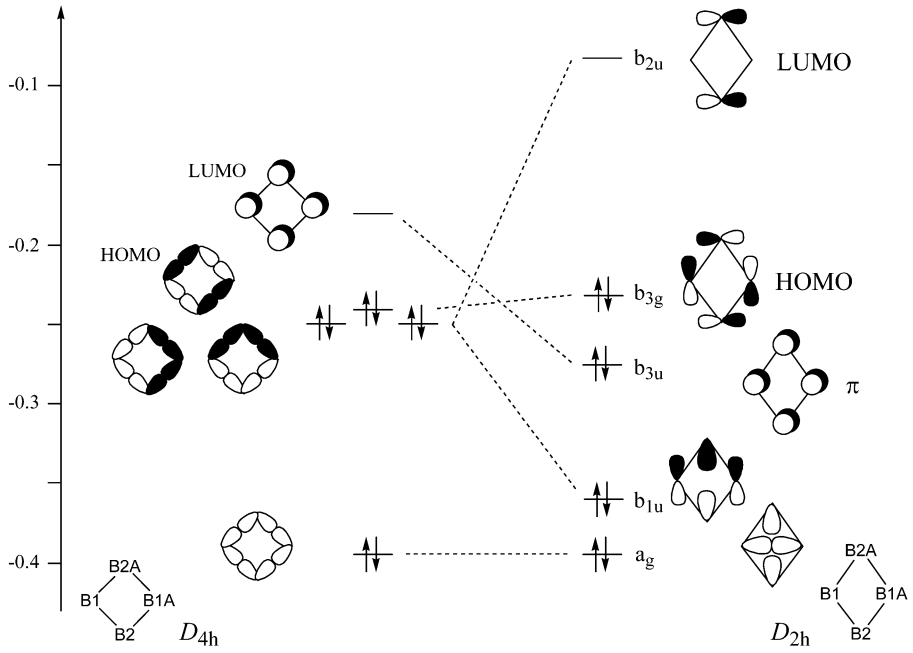
In an attempt to dehalogenate a 1:1 mixture of Me_2NBCl_2 and $Me_2N(Cl)B$–$B(Cl)NMe_2$ to obtain the corresponding *cyclo*-triborane(3) and *cyclo*-pentaborane(5), we isolated colorless crystals of the composition $(BNMe_2)_6$, which exhibited three ^{11}B NMR signals (δ = 5.4, 37.1, 63.4). These data correlate well with the calculated chemical shifts (7.4, 38.2, 63.1). The crystal-structure analysis of **4a** shows the presence of a planar, diamond-shaped [5] B_4 ring with a short diagonal [1.633(2) Å], indicating a bond between B1 and B1A. In the diamond-shaped tetraborane(6) **15a**, the transannular B–B bond [1.524(3)] and that of its pyridin adduct [1.511(3) Å] are even shorter [6].



4a



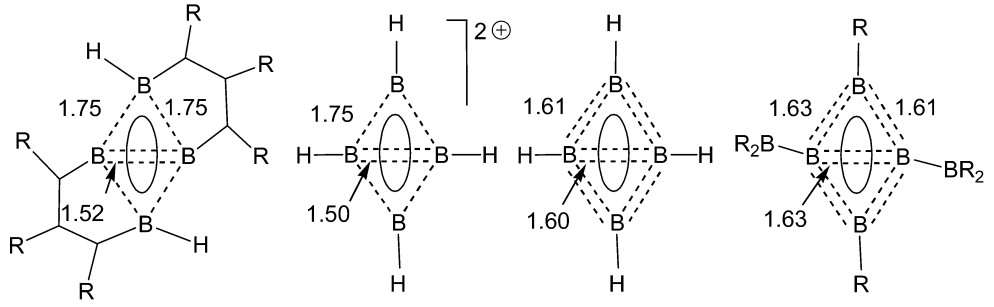
In **4a**, the opposite edges have the same bond lengths [1.605(2) and 1.632(2) Å]. It is interesting that the boron atoms of the exocyclic $(Me_2N)_2B$ substituents are 0.4 Å above and below the B_4 plane. The planes (N2,B3,N3 and N2A,B3A,N3A) of the exocyclic substituents are almost perpendicular to that of the B_4 diamond. Since the B–N bonds at B2 and B2A are short [1.381(2) Å], a π bond is present, whereas the B–N bonds of B3 and B3A are long. The structure of **4a** confirms the presence of a



tetrabora-*bicyclo*-butane structure. However, the four boron atoms of the B_4 frame supply only eight electrons, therefore, the bonding requires the presence of nonclassical bonds.

To explain the electronic structure of **4a**, a density functional calculation was carried out. For the B_4H_4 compound, a D_{4h} symmetric ring does not represent the minimum on the potential energy hyperface. A more stable bonding results in the D_{2h} structure: The π MO resulting from the four p_z atomic orbitals is occupied with an electron pair of one of the four σ MOs of the B_4 ring. Jahn-Teller distortion leads to a D_{2d} structure, whereby one of the originally degenerate MOs (e_u) is raised and remains unoccupied (b_{2u}). As a result of a favorable 1,3-interaction between B1 and B1A, the b_{1u} MO is strongly stabilized. The third σ MO (b_{3g}, HOMO) is slightly higher in energy than in the D_{4h}-symmetric structure.

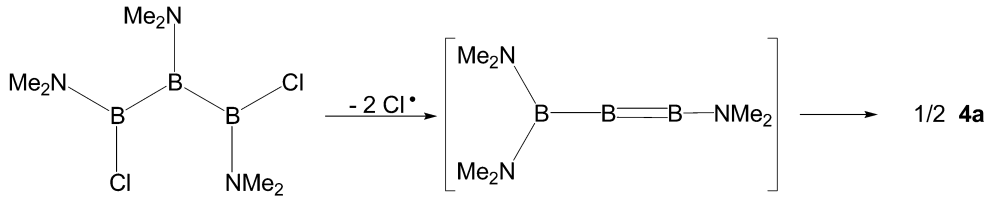
In **4a**, there are eight framework electrons (6σ + 2π FEs), but only six in the tetraborane(6) **15a** [6] (4σ + 2π FEs), because 2σ electrons are needed to bind the two additional H atoms. These form two 3c,2e σ bonds (shown as triangular dashed lines) and one 4c,2e π bond (ellipsoid). In **4a**, there is an additional 4c,2e bond (dashed diamond), which shows bonding character along the edges, but antibonding character with regard to the shorter diagonals (1.63 Å in **4a** compared to 1.52 Å in **15a**).



15a R = $SiMe_3$ **4u**$^{2+}$ (4 σ FE) **4u** (6 σ FE) **4a** R = NMe_2

The bonding situation and the relationship between **4a** and **15a** is supported by calculations: The results for **4u** (edge length 1.61, diagonal length 1.60 Å) fit the experimental values of **4a**. In the dication $\mathbf{4u}^{2+}$ the edges (1.75 Å) and the short diagonal (1.50 Å) correspond to those of **15a**.

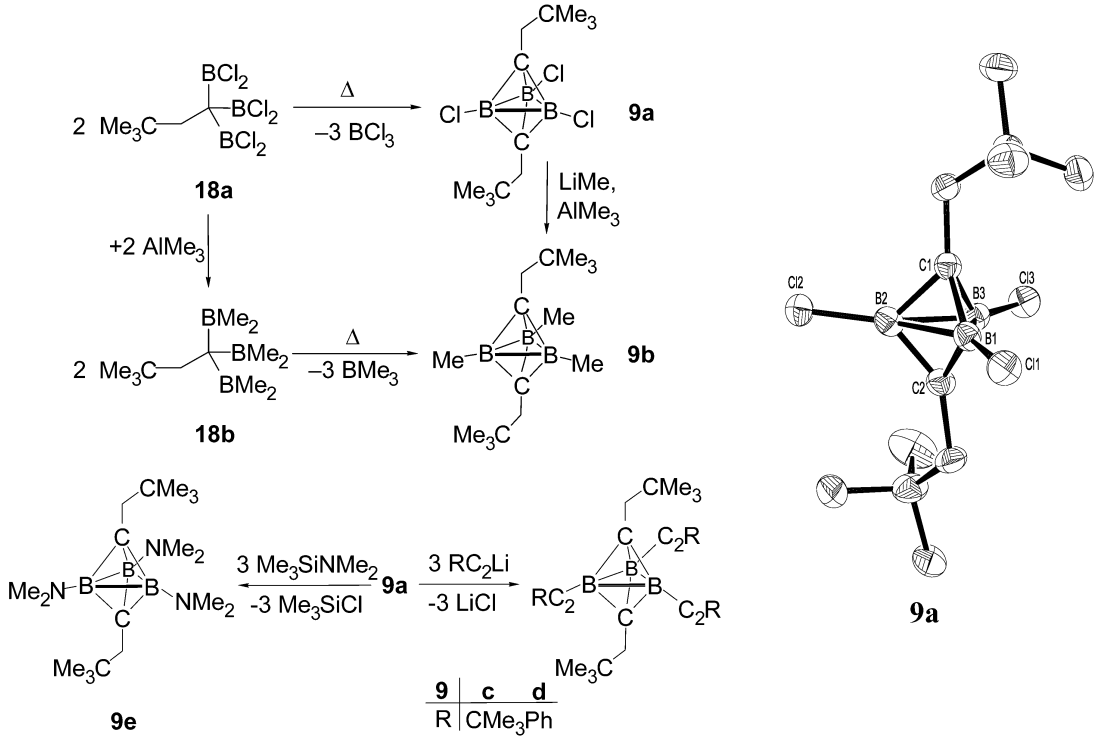
The formation of **4a** in low yield by dehalogenation of a mixture of $(Me_2N–BCl)_2$ and $Me_2N–BCl_2$ in hexane occurs via the dichlorotriborane **16a**, which most likely is dehalogenated to give after migration of one Me_2N group the triborene(3) intermediate **17a**, followed by dimerization to yield **4a**. The mechanism is proposed by Berndt et al. [6], who showed that the dehalogenation of **16a** with lithium naphthalenide in THF leads to **4a** in 40–50 % yield.



16a **17a**

closo- and *nido*-Carboranes

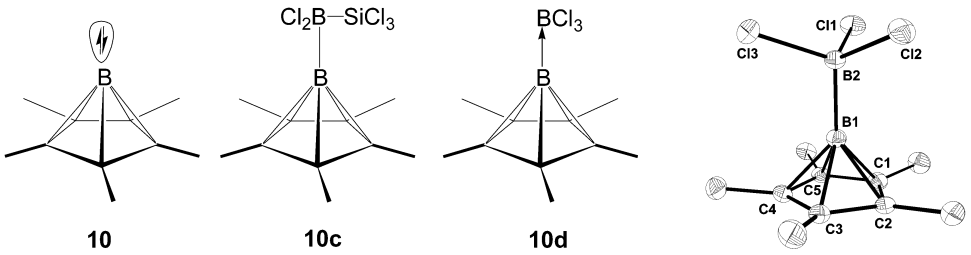
For the synthesis of **9a**, the tris(dichloroboryl)neopentylmethane (**18a**) is needed [13]. It is obtained via lithiation of 3,3-dimethyl-1-butyne, followed by boron/lithium exchange to give the intermediate $Me_3C–C{\equiv}C–BCl_2$, which then is hydroborated with $HBCl_2$ prepared in situ. The resulting **18a** may be transformed into *closo*-dicarbapentaborane by heating for 2 h, causing the elimination of BCl_3 with formation of the *closo*-cluster **9a** in 25 % yield. The ^{11}B NMR signal at $\delta = 22.1$ is indicative for a *closo*-structure, which was confirmed by an X-ray structural analysis (see below).



The trimethyl derivative **9b** is formed by methylation of **9a** with LiMe or $AlMe_3$. The second entry to **9b** proceeds via methylation of **18a** to yield **18b**. On heating, it gives **9b** and BMe_3. The ^{11}B NMR signal of **9b** is shifted to $\delta = 17.3$. Further replacements of the chloro substituents of **9a** were possible with Me_3CC_2Li, PhC_2Li, and Me_3SiNMe_2 to give the tris(acetylenic) derivatives **9c** and **9d**, as well as the trisamino compound **9e** [13].

In the C_2B_3 framework, the B–B [1.842(3)–1.855(3) Å] and B–C bonds [1.541(3)–1.586(3) Å] are similar to those of the parent *closo*-$C_3B_2H_5$. The B–B bonds are shorter than in two amino derivatives [24], classified as *bicyclo*-organoboranes. The C_2B_3 polyhedron may be described as a trigonal bipyramid having 2c,2e B–C bonds without electron density in the B_3 plane. Electron density distribution [22] of the *closo*-cluster $C_2B_3Et_5$ indicated no electron density between the boron atoms, but it was found above each triangular CB_2 face, the equivalent of a closed 3c,2e bond. Spectroscopic data (δ ^{11}B = 22.1; 17.3) clearly indicate that **9a** and **9b** are carboranes and not *bicyclo*-organoboranes.

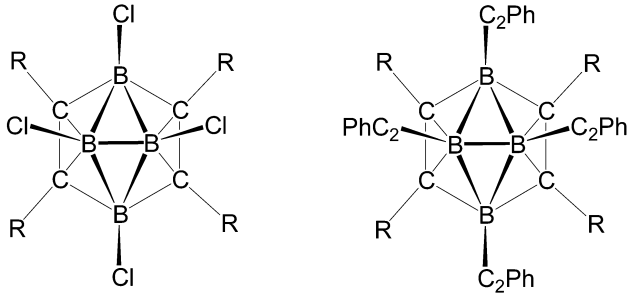
As outlined in the Introduction, the free (unstable) *nido*-1-borane-2,3,4,5,6-pentamethyl-2,3,4,5,6-pentacarbahexaboranes(6) **10** may be stabilized by Lewis acids. We have reported the first examples in which the hypothetical borandiyl cluster coordinates to the chloroboranes BCl_3 and Cl_3Si-BCl_2 to give the *nido*-carboranes **10c** and **10d**. When B_2Cl_4 was condensed with $(\eta^5\text{-}C_5Me_5)_2Si$ in hexane at low temperature, a complex reaction took place, giving first a red, then a yellow solution and a colorless solid. The MS data indicated the presence of the two compounds $(C_5Me_5)B\text{–}BCl_2\text{–}SiCl_2C_5Me_5$ and $(C_5Me_5)B\text{–}BCl_2\text{–}Si(C_5Me)_2Cl$. **10c** was obtained by recrystallization, NMR data supported its formation, which was confirmed by a crystal-structure analysis. Treating B_2Cl_4 with $C_5Me_5\text{–}SiMe_3$ yielded an elegant access to the carborane **10d** (53 % yield). The clusters exhibit high-field ^{11}B NMR signals for the apical boron $\delta = -51.7$ and –53.0 and for the sp^3 boron δ = –6.2 and 2.8. Both structures are very similar, although the structure determination of **10d** is more accurate. Attempts to replace the chloro substituents in **10d**, as well as replacement of the Lewis acid BCl_3, failed to give any isolable products.



10 **10c** **10d**

A recent MO study [25] supports the high stability of **10d** towards substitution and the presence of a very strong donor-acceptor bond $(C_5Me_5)B\rightarrow BCl_3$.

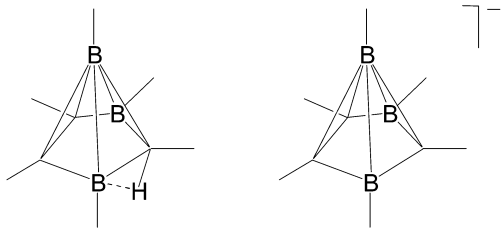
In carboranes of the type **10**, the *apex*-boron atom has a high connectivity (coordination number 6), whereas the carbon atoms are classically (connectivity 4) coordinated. The *nido*-tetracarbaoctaborane **11** represents another example of a compound with the carbon atoms having a classical connectivity of 4, and boron atoms with connectivities 5 and 6. Several synthetic strategies for the formation of the C_4B_4 cluster have been reported [18–20]. Wrackmeyer et al. [21] found a good route to **11a**, when bis(diethylboryl)ethyne is hydroborated with $(Et_2BH)_2$ in $(Et_2BH)_2$ as the solvent. The structure of $(CH)_4(BEt)_4$ (**11a**) followed from spectroscopic data (δ ^{11}B = –15.1 and – 4.6), which was confirmed by an X-ray structural analysis [22]. We have observed the formation of $(EtC)_4(BCl)_4$ when Z-3,4-bis(dichloroboryl)-3-hexene reacted with copper (in a cocondensation reaction [26]) or with $NaK_{2.8}$ in hexane. From the resulting brown oil, crystals of $(EtC)_4(BCl)_4$ (**11b**) and of C_6Et_6 were obtained [27]. The composition of **11b** followed from NMR (δ ^{11}B = –5.4, –1,5), the X-ray diffraction study confirmed the structure of the *nido*-carborane.



11b **11c**

It is of interest that the chloro substituent in **11b** may be replaced with PhC_2Li to give a mixture of $(EtC)_4(BC_2Ph)_4$ (**11c**), $(EtC)_4(BCl)(BC_2Ph)_3$, and $(EtC)_4(BCl)_2(BC_2Ph)_2$, which could not be separated [27].

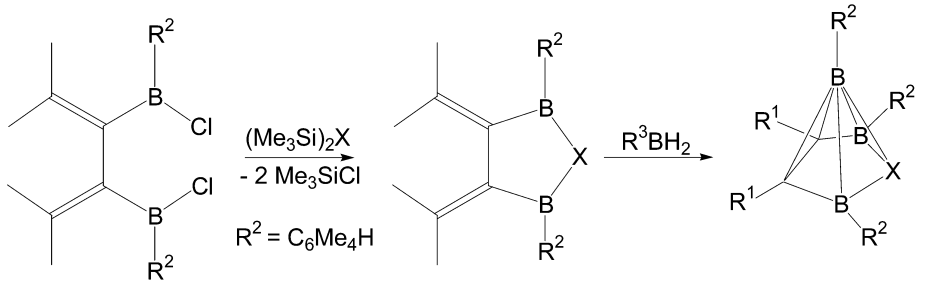
As in **11**, the ratio of boron to carbon vertices is 1:1 in the *nido*-2,3,5-tricarbahexaboranes(7) **12** [23]. Any carborane with three carbon vertices requires the presence of an extra hydrogen atom, which is located on the pentagonal face and bonded to the C5 carbon atom. This has a connectivity of five, its weak C–H bond is involved in an agostic 3c,2e C–H–B interaction. Deprotonation of **12** leads to the tricarbahexaboranyl anion $(\mathbf{12}\text{-H})^-$. As it is isolobal with the $C_5H_5^-$ a number of *closo*-metallacarboranes have been prepared [23]. Several syntheses have been explored for *nido*-tricarbahexaboranes, one occurs by hydroboration of 3,4-bis(isopropylidene)-1,3-diborolanes to give **12** [23].



12 $(\mathbf{12}\text{-H})^-$

Heterotricarbahexaboranes

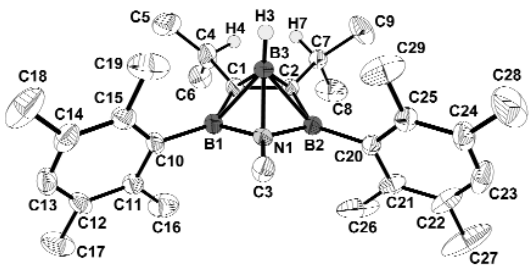
The formation of heterotricarbahexaboranes **13** and **14** is achieved according to the following reaction sequence [28]: The 3,4-diborylhexadiene derivative **19a**, $R^2 = C_6Me_4H$, and heptamethyldisilazane reacted to give the corresponding 1,2,5-azadiborolane **20a** with two isopropylidene groups. Hydroboration with $H_3B{\cdot}thf$ in a 1:1 ratio proceeds to the azacarborane **13a**, $R^1 = CHMe_2$, $R^2 = C_6Me_4H$, $R^3 = H$. When



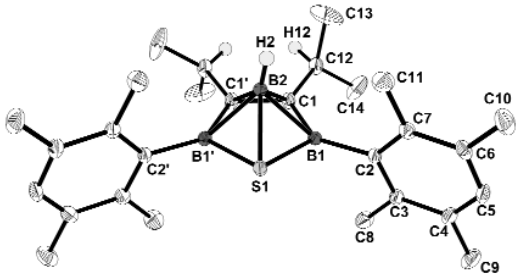
19a **20a** X = NMe
21a X = S
13 X = NMe, **14** X = S

an excess of borane reagent is used, the azadiborolane is hydrogenated at the hexadiene part (formally a 2,5-addition of hydrogen) to give the corresponding azadiborole.

The compounds have been characterized spectroscopically and confirmed for **13a** by an X-ray structural analysis. The reaction of **19a** with $(Me_3Si)_2S$ leads to the thiadiborolane **21a**, and its hydroboration yields the 4,5-dicarba-3,6-diduryl-4,5-diisopropyl-2-thia-*nido*-hexaborane(5) (**14a**). Its composition follows from spectroscopic data and an X-ray structural analysis [29].



13a



14a

CONCLUSION

In this paper, we report recent results in the chemistry of small boranes, carboranes, and heteroboranes. It has been demonstrated that the substituents at the boron atoms influence its steric and/or electronic properties, the ring size, and shape of resulting boranes. Most surprisingly, the folded *cyclo*-tetraborane **2a** is blue, and the *cyclo*-hexaboranes (**7a,b**) are orange-red. In contrast, a structural isomer of $(BNMe_2)_6$ is colorless and has a unique diamond structure **4a** with two exocyclic $B(NMe_2)_2$ groups. The bonding in the planar diamond-shaped B_4 frame may be described by two 3c,2e σ bonds, one 4c,2e π bond, and one 4c,2e σ bond.

New approaches for the synthesis of the reactive *closo*-carborane $C_2B_3R_5$ (**9a**) and to 1-borane-pentacarbahexaboranes (**10c**,**d**) were developed. It was possible to substitute the chlorine atoms in **9a**, as well as in the *nido*-$(EtC)_4(BCl)_4$ carborane (**11a**) with organyl groups.

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