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Chemistry of Diborane(4) Derivatives: Mixed Tetraaminodiboranes(4) and Additions of Diborane(4) Derivatives to an Amino-imino-borane

Dirk Loderer, Heinrich Nöth*, Hans Pommerening, Wilfried Rattay, and Hannes Schick

Institut für Anorganische Chemie der Universität München,
Meiserstraße 1, D-80333 München, Germany

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Several transamination reactions of $B_2(NMe_2)_4$ (**1a**) with secondary amines have led to mixed tetraaminodiborane(4) compounds $B_2(NMe_2)_{4-n}(NR_2)_n$ (**2**–**4**), and $B_2(NC_5H_{10})_4$ (**1d**) has been characterized by an X-ray structure analysis which reveals the presence of a rather long B–B bond (1.75 Å). However, tetraaminodiboranes(4) of type $R_2N(Me_2N)B-B(NMe_2)NR_2$ are more readily accessible from $LiNR_2$ and $B_2(NMe_2)_2Cl_2$. Similarly, amination of $B_2(NMe_2)_2Cl_2$ with *N,N'*-dimethylethylenediamine (**7**) yields *B*-[bis(dimethylamino)boryl]-*N,N'*-dimethyl-1,3,2-diazaborolidine (**8**), while reactions with $Li(Me)N-CH_2-CH_2-N(Me)Li$ (**9**) lead also to 2,3-bis(dimethylamino)-1,4-dimethyl-1,4,2,3-diazadiborinane (**10**) as the kinetically controlled product. This is further substantiated by the reaction of the $B_2(NMe_2)_2Br_2$ with **9** which gives exclusively the corresponding 1,4,2,3-diazadiborinane **11**. Diborane(4) dihalides $B_2(NMe_2)_2X_2$ (X = Cl, Br) react only in a 1:1 ratio with tmp-B≡N–CMe_3 (**13**) leading to **14a, b**. However, both a 1:1 and a 1:2 methoxyboration of **13** has been observed with $B_2(OMe)_4$ with formation of **15** and **16**.

Amongst the increasing number of diborane(4) derivatives $B_2(NMe_2)_4$ is still the most easily accessible[2]. It can be used for the preparation of a large number of other diborane(4) compounds such as $B_2(NMe_2)_2Hal_2$[3], $B_2(NMe_2)_2R_2$[4], $B_2R_2X_2$, and ultimately also B_2R_4[5]. In spite of several efforts all attempts to develop $B_2(NMe_2)_4$ into a synthon for diborane(4) tetrahalides have so far met with little success[6,7]. Moreover, the structural chemistry of diborane(4) derivatives is not well explored, and conformational problems are not yet really understood[8].

In the course of exploiting the chemistry of electron-precise triborane(5) and tetraborane(6) derivatives[9] we investigated several reactions of diborane(4) compounds as models on which we report in this paper.

Results

Tetraaminodiboranes(4) by Dehalogenation

The established method of preparing $B_2(NR_2)_4$ compounds is the dehalogenation of bis(amino)boron halides. Previous work has shown that the bromides $(R_2N)_2BBr$ provide better yields than the chlorides[2a]. Also, the yield of the $B_2(NR_2)_4$ compounds decreases as the size of the groups R increases from Me to Et[2]. In a study aimed at the optimization of the synthesis of $B_n(NR_2)_{n+2}$ compounds[9] we have reinvestigated the dehalogenation of some $(R_2N)_2BCl$ compounds to have at hand authentic species for comparison with products obtained from transamination reactions.

Reactions according to eq. (1) have been performed under comparable conditions by using liquid $NaK_{1.8}$ alloy in pentane for dehalogenation. Matching previous results[2], we have obtained **1a** in >80% yield, which decreased to 10–25% for **1b**[10]. Dipiperidinoboron chloride does not react at all with NaK alloy in spite of the fact that its amino group requires less space than an Et_2N group. Even ultrasonic activation fails to start dehalogenation. However, dipyrrolidinoboron chloride is reduced to **1c** in 46% yield. In each case, when low yields result, non-volatile brown oils to pasty "solids" are obtained, which contain higher aminopolyboranes.

$$2\,(R_2N)_2BCl \xrightarrow[-MCl]{NaK_{1.8}} \underset{\mathbf{1}}{(R_2N)_2B\text{-}B(NR_2)_2} \quad (1)$$

R_2N	Me_2N	Et_2N	N	N
	1a	**1b**	**1c**	**1d**
yield %	>80	10–25	46	-

Transaminations

Transaminations have widely been used in BN chemistry as a versatile preparative route, and factors governing the relative rates have been evaluated[11]. Steric effects predominate over electronic effects in controlling these reactions.

Compared with $B(NMe_2)_3$ the boron atoms in **1a** are sterically better shielded. Consequently, transamination of **1a** requires rigorous conditions. While no reaction has been observed between **1a** and Et_2NH at reflux temperature, part of the Me_2N groups can be replaced by passing Et_2NH into

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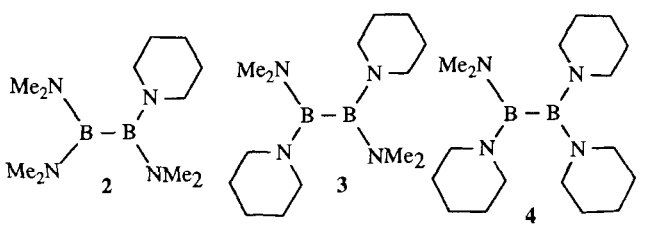
$B_2(NMe_2)_4$ (**1a**) at ≈ 200°C. Most of the starting material **1a** has been recovered unchanged (94%) besides a mixture of **1a** and a compound that is presumably $B_2(NMe_2)_3NEt_2$. Piperidine (pipH) reacts more readily with **1a**, but quantitative conversion of **1a** into **1d** requires at least 100°C. However, in boiling toluene only partial replacement of the Me_2N groups occurs, and mixtures of compounds **2**–**4** have been isolated. Addition of small amounts of $[Et_3NH]Br$ or $[C_5H_{10}NH_2]Br$ fails to catalyze these transaminations. In order to allow an unambiguous assignment of the NMR signals of **2**–**4**, compound **3** has been synthesized from $B_2(NMe_2)_2Cl_2$ and Li(pip). In contrast, transamination of **1a** with pyrrolidine (pyrH) proceeds more smoothly than with piperidine. An almost quantitative yield of **1c** has been achieved with a slight excess of the amine under reflux conditions.



Using nBu_2NH to transaminate $B_2(NMe_2)_4$, we have not achieved a quantitative conversion of **1a** into $B_2(NBu_2)_4$. A mixture of $B_2(NMe_2)(NBu_2)_3$ and $B_2(NBu_2)_4$ results, from which only pure $B(NMe_2)(NBu_2)_3$ has been isolated.

NMR Spectra

The new tetraaminodiborane(4) compounds have been identified by their ^1H-, ^{11}B- and ^{13}C-NMR spectra.

As expected, the shielding of the boron nuclei depends only insignificantly on the nature of the R_2N substituent, and no two ^{11}B-NMR signals were observed for the asymmetrically substituted tetraaminodiborane(4) compounds due to the relatively large line width and the expected small shift differences for the non-equivalent boron atoms. At ambient temperature there is no hindered rotation about the respective BN bonds as demonstrated by only two ^1H- and ^{13}C-NMR signals for **1c**. $B_2(pyr)_3(NMe_2)$ exhibited only one set of signals for the pyrrolidino groups although at least two should be observable. The signals are rather broad, indicating insufficient resolution or exchange.

A similar situation is observed in the series $B_2(NMe_2)_{4-n}(pip)_n$. The presence of the piperidino group is indicated by only three signals in the ^{13}C-NMR spectra while five should be observed if hindered rotation was operative in **1d** or **2**. However, the three ^1H-NMR signals of equal intensities for the CH_3 groups in **2** suggest three different chemical environments for these groups, and this excludes free rotation about the B–B bond as well as a perpendicular orientation of the two BN_2 moieties. In **4** two sets of data in a 1:2 ratio are observed for the two kinds of piperidino units, and for **3** two different ^{13}C-NMR signals are recorded for atoms C1 and C2 but only a single signal for C3. In addition, two ^{13}C-NMR signals appear for the Me_2N groups, indicating hindered rotation.

Nevertheless, the preferred conformation cannot be deduced for **3** from these data unambiguously. Most likely, the two halves of the molecule are oriented more or less perpendicularly to one another. This would be in accord with two different CH_3 groups and five signals for a static $C_5H_{10}N$ group.

X-Ray Structure of 1d

In order to obtain some additional information on the perferred conformation of the tetraaminodiboranes(4) in the solid state the structure of **1d** has been determined by X-ray methods. Figure 1 shows the molecular structure. As expected, all B and N atoms are surrounded by next neighbor atoms in a plane-approaching local trigonal-planar symmetry. B–N bond lengths range from 1.420 to 1.439(6) Å (average 1.426 Å), the B–B bond length is 1.750(8) Å. The dihedral angle N1–B1–B2–N4 of 73.5° demonstrates that the two BN_2 planes in **1d** approach orthogonality. Moreover, the respective C_2N planes of the piperidino units, which exhibit a chair conformation, are tilted against the BN_2 plane by 20.4–23.4°. The structure of **1d**, therefore, is noticeably different from that of compound **5**[12] and close to the structure of **1a** whose bonding parameters have been determined by electron diffraction[13].

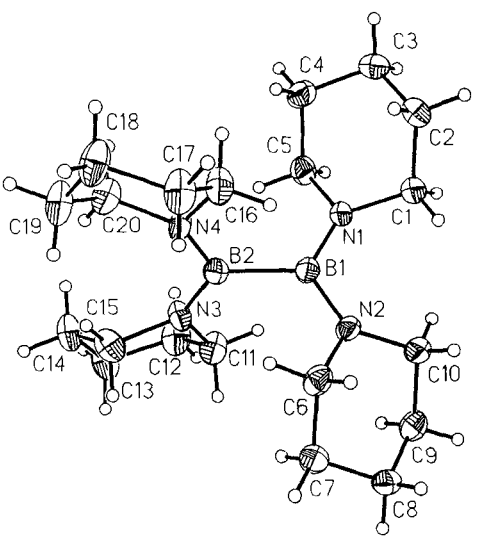


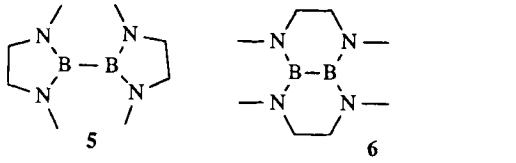
Figure 1. Molecular structure of $B_2(pip)_4$ (**1d**) in the solid state. Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å]: B1–B2 1.750(8), B1–N1 1.422(5), B1–N2 1.439(6), B2–N3 1.420(6), B2–N4 1.422(8). Selected bond angles [°]: N1–B1–B2 119.7(4), N2–B1–B2 118.3(3), N2–B1–N1 122.0(4), N3–B2–B1 119.0(5), N4–B2–B1 118.3(4), N4–B2–N3 122.6(4), C1–N1–B1 126.3(4), C5–N1–B1 122.1(3), C5–N1–C1 111.3(3), C6–N2–B1 122.2(4), C10–N2–B1 125.7(4), C15–N3–B2 121.9(4), C20–N4–B2 121.9(4), C16–N4–B2 127.1(4)

Compound **5** exhibits a significantly shorter B–B bond [1.693(9) Å] than **1d** which seems to be slightly shorter than the B–B bond length in **1a** [1.726(11) Å], but the difference in the B–B bond lengths of the latter two compounds is within the limits of significance. Also, the B–N bond lengths in **5** [1.417(8) and 1.414(7) Å][12] as well as in **1a** [1.408(3) Å] are shorter than in **1d**. The twist angle N–B–B–N is 59.2° in **5**, 73.5° in **1d**, and 90° in **1a**[13].

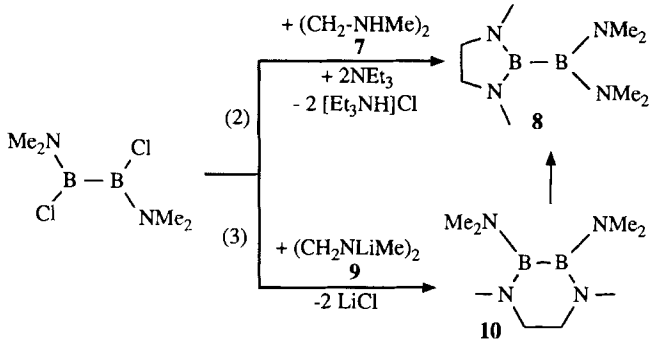
This is surprising since one would expect less steric interaction between the amino groups in **1d** than in **5** due to the presence of exocyclic methyl groups in **5**. However, this effect is obviously counterbalanced by a wider N–B–N bond angle in **1d** (average 122.3°) as compared with **5** (106.6°). The varying conformation of tetraaminodiboranes(4) is determined by a balance between the BN bond lengths and the steric requirements of the amino groups.

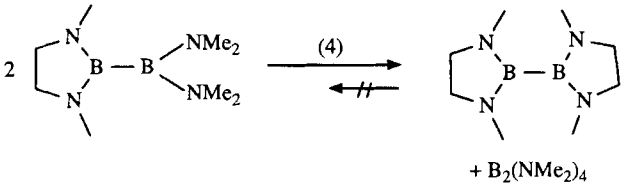
Reaction of $B_2(NMe_2)_2Cl_2$ with N,N'-Dimethylethylenediamine

As has been shown previously transamination of **1a** with *N,N'*-dimethylethylenediamine gives exclusively **5** but not the bicyclic isomer **6**[14]. It is not yet understood why the formation of **5** is perferred over **6**. In order to gain some insight into factors governing the formation of these two compounds the reactions (2) and (3) have been investigated.



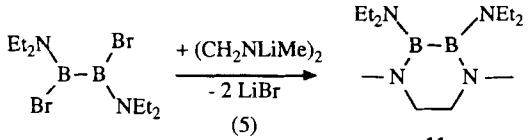
5 **6**





In the case of reaction (2) only **8** is obtained besides a fair quantity of **1a** and **5**. This indicates that a ligand exchange occurs according to eq. (4). This exchange seems to be irreversible because compound **8** is not formed when **1a** is allowed to react with **5**.

When the lithium amide **9** is used instead of the amine **7** a mixture of products is formed again. However, new signals are observed in the NMR spectra which can be assigned to an isomer of **8**, the diazadiborinane **10**. However, only **10** is present besides **1a** and **5** generated in a reaction analogous to eq. (3) in which the bromide $B_2(NMe_2)_2Br_2$ is used instead of $B_2(NMe_2)_2Cl_2$. Heating of **10** to 100°C or prolonged standing of this compound leads to the formation of **8**. Thus, **10** is characterized as the kinetically controlled and **8** as the thermodynamically more stable product. This result is further ascertained by the reaction of 1,2-bis(diethylamino)diboron dibromide with **9** as depicted in eq. (5) which results in a mixture of **11** and **12**.



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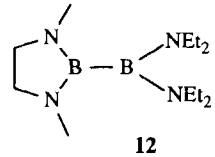

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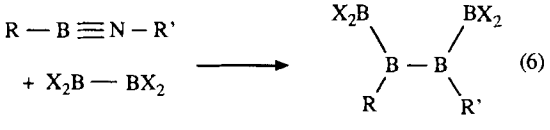
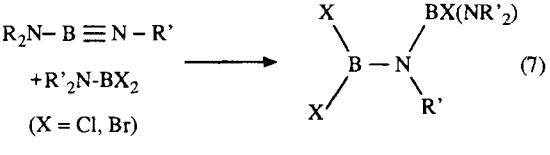
However, when $B_2(NEt_2)_2Cl_2$ is allowed to react with **9** only the isomer **11** is formed. Obviously, the larger Et_2N groups prevent a rapid rearrangement to its 2-[bis(diethylamino)boryl]-1,3,2-diazaborolidine isomer **12**. In the light of exchange processes between boron-containing heterocycles studied with ^{10}B-labelled compounds[15] it is reasonable to assume that the rearrangement of **10** to **8** proceeds intermolecularly, and the fact that **10** can be detected as an intermediate in reaction (3) but not in (2) is most likely due to the higher nucleophilicity of **9** as compared to **7** making reaction (3) faster than reaction (2).

Reactions of Diborane(4) Derivatives with an Amino-imino-borane

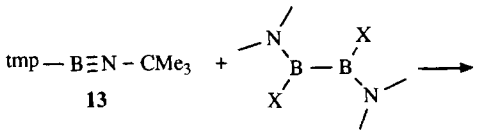
It is well-known that iminoboranes add a large variety of borane(3) derivatives[16]. In the case of diborane(4) derivatives boroboration of the iminoborane RB≡NR' according eq. (6) may be expected, in analogy to the reaction of B_2X_4 or $B_2R_2X_2$ with acetylenes[17]. A reaction following eq. (6) would provide an easy access to tetraborane(6) derivatives. However, there may be a competition between the insertion of the B–X bond of B_2X_4 and the B–B bond.





When BX_3 compounds are allowed to react with the amino-imino-borane **13**[18] only a single product is expected and formed by haloboration of the BN triple bond to give R_2N-B(X)-NR'-BX_2 with X = F, Cl, Br. However, when boranes of type X_2BY are used the reaction may occur at the B–Y or B–X bond. In the case of aminoboron halides R_2NBHal_2 and $(R_2N)_2BHal$ it has been demonstrated that the amino-imino-borane **13** is specifically haloborated as

depicted in eq. (7)[18,19]. The expectation that 1,2-bis(dimethylamino)diboron dihalides would react analogously has been experimentally verified. However, irrespective of the ratio of the reagents employed only the 1:1 stoichiometry according to eq. (8) has been observed.



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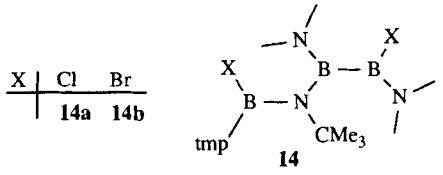
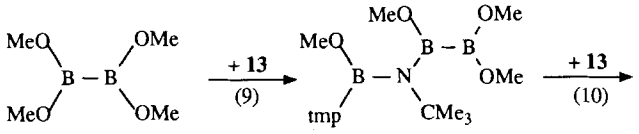
tmp = 2,2,6,6,-tetramethylpiperidino group (8)



14a **14b**

14



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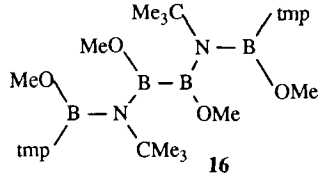

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The second boron-halogen bond of $B_2(NMe_2)_2Hal_2$ does not insert into the BN triple bond of a second molecule of **13** even at 100°C. Both the chemospecificity and the 1:1 stoichiometry is most likely due to the steric shielding of the boron atoms and the higher reactivity of the B–Hal bond as compared to the B–N bond. Thus, the 2:1 reaction of **13** with $X(Me_2N)B-B(NMe_2)X$ stops at the 1:1 ratio at ambient temperature. After the 1:1 addition to **14** has occurred the unreacted **13** starts dimerizing to the corresponding 1,3,2,4-diazadiboretedine[20]. That steric factors play a dominating role in these insertion reactions is demonstrated by the fact that tBu$(Me_2N)B-B(NMe_2)Cl$ does not react at all with **13**.

In contrast, methoxyboration of **13** with $B_2(OMe)_4$ is observed both in a 1:1 and 2:1 ratio giving access to the diborane(4) derivatives **15** and **16** as shown in eqs. (9) and (10).

Compounds **14** contain three chemically non-equivalent boron atoms, but only two signals in a 1:2 ratio are observed in their ^{11}B-NMR spectra. The high-field signals (δ = 30.3, 28.0) result from the BN_2X moiety, the other ones from the diborane(4) part of the molecule (δ = 38.5 and 39.2) in spite of the fact that they are present in B_2NB and B_2N_2 structural units[21]. In addition, three ^{13}C-NMR signals and two rather broad ^{1}H-NMR signals appear for the Me_2N groups. Therefore, rotation about the B–N bonds is obviously hindered for only one Me_2N group (most likely at the $BBrNMe_2$ unit). Similary, only two ^{11}B-NMR signals are observed for **15**. Their 2:1 intensities suggest that the signal at δ = 27.9 has to be assigned to the N_2BOCH_3 moiety while the signal at δ = 35.3 stems from the $BB(OMe)_2$ and B_2ON moiety. In **16** the signal ratio has turned to 1:1. It is, however, somewhat unexpected that the ^{11}B resonance of the diborane(4) unit has moved downfield as compared to $B_2(OMe)_4$ ($\delta^{11}B$ = 31)[21]. This indicates a lower π electron density at its boron atoms, but little if any support is provided by the ^{1}H- and ^{13}C-NMR data of the OMe groups. Its number (see Experimental) indicates free rotation around the boron-boron bond.

Discussion

Although dehalogenation of bis(dialkylamino)boron halides by alkali metals provide access to tetraaminodiborane(4) compounds[2] this reaction seems to be sterically hindred, and this finding cannot be readily rationalized. For the series of chlorides the reactivity of the $(R_2N)_2BCl$ compounds and the yield of diborane(4) derivative decrease in the order $Me_2N > NC_4H_8 > NEt_2 > NC_5H_{10}$.

No diborate(4) species $B_2X_4^{2-}$ has yet been detected in the residues of the dehalogenation products as formed from B_2mes_4 or $B_2R_2(NMe_2)_2$ and alkali metals[22]. This is most likely due to the comparatively high electron density at the boron atoms of aminodiborane(4) compounds provided by BN-π-back bonding, thus making its BB π orbital not available for electron uptake.

Factors governing the transamination of aminoboranes $R_{3-n}B(NMe_2)_n$[11] also hold for the transamination of $B_2(NMe_2)_4$. Not unexpectedly, transaminations proceed stepwise with subsequent replacement of Me_2N groups and, consequently, the series of compounds $B_2(NMe_2)_{4-n}(NR_2)_n$ can either be isolated or detected spectroscopically. However, the best way to arrive at the symmetrically substituted tetraaminodiborane(4) compounds $R_2N(Me_2N)B-B(NMe_2)NR_2$ in a preparative manner is the amination of $B_2(NMe_2)_2Cl_2$ with $LiNR_2$.

Although only a selection of diborane(4) compounds has been studied the addition of these to the amino-imino-borane **13** usually stops at a 1:1 ratio of the reactants because the steric shielding of the boron atoms is significantly in the addition product. However, if Me_2N groups are replaced by the sterically less demanding methoxy groups one methoxy group per $B(OMe)_2$ unit reacts with **13**. No boroboration of **13** with diborane(4) compounds has yet been observed, a reaction usually proceeding by treatment of B_2Cl_4 with acetylenes[17] which are isoelectronic with iminoboranes[16]. We will therefore continue studies with more reactive diborane(4) derivatives in order to evaluate this aspect.

We thank *Fonds der Chemischen Industrie* and *BASF Aktiengesellschaft* for continuous support of our research and the *technical staff at the Institute of Inorganic Chemistry* for recording NMR, IR, and mass spectra, and for performing elemental analysis. Dr. *G. Linti* collected the X-ray data of B_2pip_4.

Experimental

All experiments were performed under strictly anhydrous conditions by using Schlenk techniques in oxygen-free, dry dinitrogen

or in vacuo. Commercial chemicals were purified before use if necessary. Literature procedures were applied for the preparation of the compounds $B_2(NMe_2)_4$ (**1a**)[2], $B_2(OMe)_4$[2], tmp-B≡NCMe$_3$[18], $B_2(NMe_2)_2Cl_2$[3], $B(NC_5H_{10})_3$[23]. – All reactions were monitored either by ^{1}H- or ^{11}B-NMR spectroscopy using Bruker AP 200, Jeol 270, or Varian M 60 spectrometers. NMR data were recorded in C_6D_6 solutions. – IR: Perkin Elmer 325. – MS: Varian CH7 (70 eV). – X-Ray: Nicolet R3, SHELXTL PLUS PC programmes.

Chlorodipyrrolidinoborane: A solution of 12.3 g (55.6 mmol) of $B(NC_5H_{10})_3$ in 60 ml of pentane and 15 ml of benzene was cooled with an ice bath, and 2.41 ml (27.8 mmol) of BCl_3 was condensed into the stirred solution. A yellow solution resulted after warming to ambient temp. The solvents were removed after 3 h by evaporation in vacuo. Distillation of the residue yielded 13.82 g of $ClB(NC_4H_8)_2$ (96%), b.p. 90–95°C/10^{-3} Torr. – NMR (δ, C_6D_6): ^{1}H: 1.46 m (NCH_2CH_2), 3.22 m (NCH_2CH_2); ^{11}B: 25.0, ^{13}C: 26.7 (NCH_2CH_2), 49.2 (NCH_2). – $C_{18}H_{16}BClN_2$ (172.5): calcd. C 55.70, H 9.35, N 8.12; found C 54.92, H 9.21, N 8.10.

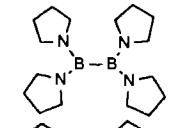
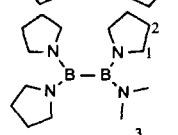
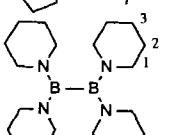
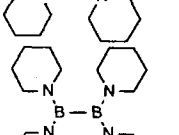
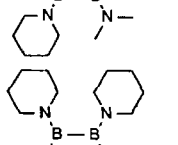
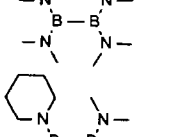
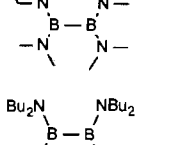
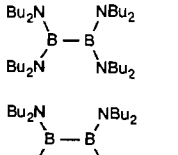
Tetrapiperidinodiborane(4) (**1d**): 5.0 ml (21.6 mmol) of $B_2(NMe_2)_4$ was heated to 100°C, and 9.9 ml (100 mmol) of piperidine was added by means of a syringe. The mixture was then heated to gentle reflux while a slow stream of nitrogen removed the liberated Me_2NH. It was aborbed in HCl. After 1.5 h no more Me_2NH evolved. On cooling colorless crystals separated which were recrystallized from 50 ml of pentane. Yield: 6.3 g of **1d** (82%), m.p. 142–143°C. – NMR: Table 1. – $C_{20}H_{40}B_2N_4$ (358.2): calcd. C 67.07, H 12.26, N 15.64; found C 65.10, H 10.99, N 15.38.

Crystal Structure Determination of **1d**: Colorless plates from hexane, size: 0.6 × 0.2 × 0.6 mm, mounted in an argon atmosphere in a glass capillary. – *Crystallographic Data:* $C_{20}H_{40}B_2N_4$, M = 358.17, triclinic, a = 10.051(2), b = 10.511(2), c = 11.914(2) Å, α = 107.76(3), β = 90.01(3), γ = 112.45(3)°, V = 1098.1(6) Å^3, $F(000)$ = 396, Z = 2, space group: $P\bar{1}$(No. 2), μ = 0.06 mm^{-1}. – *Data Collection:* 2-Θ range = 2–48° in h, ±k, ±l, scan speed = 4–29.3°/min, scan width = 0.9°, 2 standards after every 48 intensity measurements; reflections: 5474 measured, 3062 unique, 1941 observed [$I > 4\sigma(I)$], Lorentz and polarization corrections. – *Structure Solution and Refinement:* Direct methods, non-hydrogen atoms refined with anisotropic displacement parameters, all hydrogen atoms found and refined, 22 hydrogen atoms in fixed positions, fixed U_i during final refinement. GOOF 0.75, parameters refined 235, R = 0.0673, R_w = 0.0645 with $w^{-1} = \sigma^2(F) + 0.000357(F)^2$. Largest residual electron density = 0.40 e/Å^3. Further details on the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, by quoting the depository number CSD-58159, the names of the authors, and the literature citation.

1,2-Bis(dimethylamino)-1,2-dipiperidinodiborane(4) (**3**): A suspension of 1.53 g (16.8 mmol) of $LiNC_5H_{10}$ in 10 ml of *n*-hexane was dropped into a solution of 1.52 g (8.40 mmol) of $B_2(NMe_2)_2Cl_2$ in 30 ml of hexane at −78°C. The stirred suspension was allowed to attain ambient temp. within ≈1 h. Stirring was continued overnight, the insoluble material removed by filtration (0.85 g), and the solvent evaporated in vacuo. The remaining semisolid residue provided crystals from pentane at −78°C. Yield: 1.84 g of **3** (79%), m.p. 98–100°C. – $C_{14}H_{32}B_2N_4$ (278.1): calcd. C 60.47, H 11.60, N 20.15; found C 61.63, H 11.55, N 18.15.

Tetrakis(diethylamno)diborane(4) (**1b**): 10 ml of $(Et_2N)_2BCl$ (46.8 mmol) was added to a quickly stirred suspension of 30 ml of a liquid $K_{2.8}Na$ alloy in 200 ml of *n*-pentane. Should the reaction not start within 20 min, then an additional 10 ml of $(Et_2N)_2BCl$ was added and the mixture heated to reflux. Often, the reaction proceeded only slowly even under these condition. In this case the pentane was replaced by hexane with continuous removal of the pentane by distillation. Finally, the black-blue suspension was kept at reflux for 5 h. Then all insoluble material was removed and the solution distilled. Fractions obtained were $(Et_2N)_2BCl$ (60%), 0.86 g of **1**, b.p. 88–92°C/1 Torr (10%), and a glassy brownish residue with strongly reducing properties. NMR data of $B_2(NEt_2)_4$ were in accord with published data[2].

Table 1. ^{1}H-, ^{11}B- and ^{13}C-NMR data of tetraaminodiboranes (recorded in C_6D_6 solutions)

	δ^{11}B	δ^{13}C	δ^{1}H
	34.1	49.9 C1 26.9 C2	3.39 m H1 1.63 m H2
	34.1	49.9 C1 41.5 Me 26.9 C2	3.30 m H1 2.82 s Me 1.61 m H2
	38.2	50.4 C1 28.6 C2 26.2 C3	2.95 t H1 1.46 m H2, H3
	38.1	50.0, 49.9, 48.2 C1 41.5 Me 28.4, 28.3, 27.8 C2 25.9 C3	3.03 m H1 (12H) 2.68 s Me (3H) 2.63 s Me (3H) 1.48 m H2,3 (18H)
	36.0	50.5, 50.4 C1 41.9, 41.6 Me 28.7, 28.6 C2 26.2 C3	3.17 m H1 (4H) 2.75 s Me (3H) 2.73 s Me (3H) 1.52 m H2, 3 (6H)
	36.6	49.9 C1 41.4, 41.3 Me 41.1 Me 28.3 C2 25.8 C3	3.04 m H1 (4H) 2.67, 2.66, 2.63 s (6Me) 1.50 m H2, 3 (6H)
	35.2	49.9 C1 28.5 C2 20.2 C3 13.3 C4	2.79 m H1 (2H) 1.83 m H2 (2H) 1.36 m H3 (2H) 0.95 m H4 (3H)
	35.5	51.1 C1 41.4 Me 33.0 C2 20.7 C3 14.2 C4	3.99 m H1 (12H) 2.79 m H2 (12H) 2.72 s Me (6H) 1.38 m H3 (12H) 0.92 m H4 (18H)

Tetrapyrrolidinodiborane(4) (**1c**): 9.07 g of $(C_4H_8N)_2BCl$ (52.1 mmol) was slowly added to a rapidly stirred suspension of 4.40 ml of $NaK_{2.8}$ alloy in 80 ml of *n*-hexane. Usually, the reaction started within 10–15 min. After the exothermic reaction had almost ceased stirring was continued overnight followed by heating to reflux for 1.5 h. The solid material was then removed, the volume of the yellow filtrate reduced by 2/3, and the solution cooled to −78°C. Yield 3.28 g of **1c** (46%), m.p. 80–81°C. – NMR: Table 1. – $C_{16}H_{32}B_2N_4$ (302.1): calcd. C 63.62, H 10.68, N 18.55; found C 61.92, H 10.56, N 17.44. – Mol. mass (MS, 70 eV, ^{11}B): 302.

Attempted Preparation of $B_2(NEt_2)_4$ (**1b**) *by Transamination:* 10.0 ml of $B_2(NMe_2)_4$ (**1a**) was heated to 200°C and Et_2NH (one

bubble at approximately every 2 s) passed through **1a** for 24 h. Fractional distillation at 10 Torr gave 8.03 g of **1a**, b.p. 85–87°C, and 0.29 g of a product, b.p. 91°C, which by analysis of its N contents (26.81%) indicated the presence of a mixture of **1b** (calcd. N 28.29%) and $B_2(NMe_2)_3NEt_2$ (calcd. 24.78%).

(Dimethylamino)piperidinodiboranes(4) **2–4**: A solution of 11.6 ml of **1a** (50 mmol) in 20 ml of toluene and 24.8 ml of piperidine (250 mmol) was heated to reflux. After 2 d the Me_2NH evolution had almost ceased. Fractional distillation yielded 3 fractions analyzed by ^{1}H-NMR spectroscopy: 1) b.p. up to 57°C/10^{-3} Torr, a mixture of $B_2(NMe_2)_3$pip and $B_2(NMe_2)_2pip_2$ (**3**); 2) b.p. 62–68°C/10^{-3} Torr, a mixture of **3** and $B_2(NMe_2)pip_3$ (**4**); 3) 98–110°C/10^{-3} Torr, a mixture of **4** and B_2pip_4, (**1c**). The same result was obtained by adding ≈0.2 g of $[Et_3NH]Br$ or [tmp H_2]Br as possible catalysts.

(Dimethylamino)tripyrroldinodiborane(4) and Tetrapyrrolidinodiborane(4) (**1c**): A mixture of 5.0 ml of **1a** (21.6 mmol) and 7.58 ml of pyrrolidine (94.9 mmol) was slowly heated and kept for 2 h at reflux and then subjected to fractional distillation. At b.p. 90–100°C/10^{-3} Torr 3.9 g of $B_2pyr_3(NMe_2)$ (65%) was collected. The residue was dissolved in a minimum amount of hexane and the solution cooled to −78°C to yield 1.95 g of **1c** (30%), m.p. 80–81°C. – $B_2pyr_3(NMe_2)$: NMR: Table 1. – $C_{14}H_{30}B_2N_4$ (276.0): calcd. C 60.92, H 10.95, N 20.30; found C 60.38, H 11.20, N 19.68. – **1c**: δ^1H = 1.62 (m, 2H), 3.39 (m, 2H); δ^{11}B = 34; δ^{13}C = 49.9 (NCH_2), 26.9 (CCH_2).

(Dibutylamino)(dimethylamino)diboranes(4): 5.0 ml of **1a** (21.6 mmol) was heated to 100°C, and 16 ml of Bu_2NH was added dropwise. Liberated Me_2NH was removed by a slow stream of nitrogen. The temperature was raised to 200°C within 4 h. Fractional distillation yielded 3 fractions, analyzed by NMR spectroscopy: 1) b.p. 25°C/10^{-3} Torr, 0.9 g of Bu_2NH (7%); 2) b.p. 150°C/10^{-3} Torr, 3.79 g of $B_2(NMe_2)(NBu_2)_3$, (42%); 3) b.p. 150–160°C/10^{-3} Torr, 3.4 g of a mixture of $B_2(NMe_2)(NBu_2)_3$ and $B_2(NBu_2)_4$. – $B_2(NMe_2)(NBu_2)_3$, $C_{26}H_{60}B_2N_4$ (439.6): calcd. C 71.04, H 13.76, N 12.74; found C 70.02, H 13.59, N 12.33. – Mol. mass (MS, ^{11}B): 440.

1,2-Bis(dimethylamino)-1,2-dipiperidinodiborane(4) (**3**): A suspension of 1.53 g of $LiNC_5H_{10}$ (16.8 mmol) in 10 ml of *n*-hexane was added with stirring to a solution of 1.52 g of $B_2Cl_2(NMe_2)_2$ (8.4 mmol) in 25 ml of hexane. Stirring was continued and the insoluble material (0.85 g) removed. From the clear solution all volatile material was evaporated in a vacuo (1 Torr). The partly crystalline residue was recrystallized from pentane. Yield: 1.84 g of **3** (79%), m.p. 98–100°C. – NMR: Table 1. – $C_{14}H_{32}B_2N_4$ (278.1): calcd. C 60.47, H 11.60, N 20.15; found C 61.63, H 11.55, N 19.15. – Mol. mass (MS, ^{11}B): 278.

2,3-Bis(dimethylamino)-1,4-dimethyl-1,4,2,3-diazadiborinane (**10**) *and 2-[Bis(dimethylamino)boryl]-1,3-dimethyl-1,3,2-diazaborolidine* (**8**)

a) A solution of 3.08 g of *N,N'*-dimethylethylenediamine (35 mmol) and 7.78 g of NEt_3 (77 mmol) in 60 ml of *n*-hexane was added at −30°C to a stirred solution of 6.33 g of $B_2(NMe_2)_2Cl_2$ (35 mmol) in 30 ml of hexane. A suspension formed, and a small part was freed from the solid, the hexane removed by evaporation in vacuo, the residue dissolved in C_6D_6 and analyzed by NMR spectroscopy (see Figure 2). The suspension was heated for 17 h to reflux, then freed from the solid by centrifugation, the hexane evaporated from the solution and the remaining material subjected to fractional distillation (15-cm Vigreux column). Two fractions were obtained: 1) b.p. 70–71°C/3 Torr, 3.07 g of a mixture containing 40% of **1a**, ca. 40% of **8**, and ca. 20% of **5**; 2) b.p. 71–75°C/1 Torr, 0.57 g of a mixture containing ca. 55% of **5**, ca. 30% of **9** and ca. 15% of **1a**. – NMR data of **8**: δ^1H = 2.66 (NMe_2, 12H), 2.71 (NMe, 6H), 3.14 m (CH_3, 4H); δ^{11}B = 34.7; δ^{13}C = 35.3 (NMe), 41.2 (NMe_2), 52.8 (Ch_2).

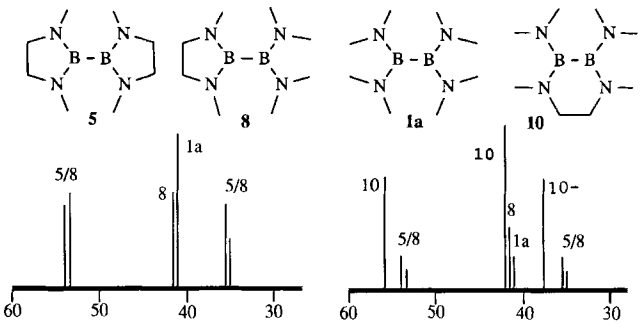


Figure 2. ^{13}C-NMR spectra (δ scale) of the reaction products obtained a) from $B_2(NMe_2)_2Cl_2$ and $MeNHCH_2CH_2NHMe_2$, b) from $B_2(NMe_2)_2Cl_2$ and $Me(Li)NCH_2CH_2N(Li)Me$

b) 1.72 g of *N,N'*-dimethylethylenediamine (18.5 mmol) was dissolved in 30 ml of hexane and metalated with 24.7 ml of a 1.56 M *n*-hexane solution of LiBu. The resulting suspension was heated to reflux for 2 h, and after cooling to −60°C a solution of 5.25 g of $B_2(NMe_2)_2Br_2$ (19.5 mmol) in 10 ml of *n*-hexane was added with vigorous stirring. The suspension was then allowed to attain ambient temp., all insoluble material was removed and a small part analyzed by NMR spectroscopy. Hexane was evaporated from the main part of the solution and the residue subjected to fractional distillation. 1) b.p. 58–62°C/2 Torr, 0.3 g of a mixture of ≈65% of **1a** and ≈35% of **8**; 2) b.p. 62–64°C/2 Torr, 1.1 g of a mixture of ca. 70% of **8**, ca. 20% of **5**, and ca. 10% of **1a**; 3) b.p. 64–65°C/2 Torr, 1.6 g of a mixture of ca. 75% of **8**, ca. 15% of **10**, and ca. 10% of **5**. Fraction 3 was kept for 5 months at 0°C and consisted then of 85% of **8**, <5% of **10**, and ca. 10% of **5**.

c) 0.88 g of *N,N'*-dimethylethylenediamine (10 mmol) was metalated as described in b) and the dilithio derivative allowed to react with a solution of 1.18 g of $B_2(NMe_2)_2Cl_2$ (10 mmol) in 10 ml of *n*-hexane at ambient temp. After 30 min the insoluble material was removed and the solution worked up by distillation, b.p. 42–52°C/0.1 Torr, ca. 25% of **1a**, ca. 25% of **5**, ca. 30% of **8**, ca. 20% of **10**. After standing at ≈20°C for 3 month **10** could no longer be detected by NMR spectroscopy. – NMR data of **10**: δ^1H = 2.76 (NMe_2, 12H), 2.79 (NMe, 6H), 2.85 (CH_2, 4H); δ^{11}B = 34.9; δ^{13}C = 38.7 [$^1J(^{13}C^1H)$ = 133 Hz, NMe], 41.4 [$^1J(^{13}C^1H)$ = 132 Hz, NMe_2], 54.9 (m, CH_2).

Attempted Ligand Exchange: In an NMR tube 0.11 g of **1a** and 0.11 g of **5** were dissolved in 2 ml of CH_2Cl_2, the tube was sealed and heated to 50°C for 2 d. There was no change in the number and signal intensities even in the presence of a drop of pyridine or a small amount of $[Me_2NH_2]Cl$.

2,3-Bis(diethylamino)-1,4-dimethyl-1,4,2,3-diazadiborinane (**11**) *and Rearrangement to* **12**: 1.42 g of $MeHNCH_2CH_2NHMe$ (16.1 mmol) was metalated with a 1.56 M LiBu solution in a 1:2 ratio. The resulting suspension was then cooled to −60°C, and a solution of 5.24 g of $B_2(NEt_2)_2Br_2$ (16.1 mmol) in 20 ml of *n*-hexane was added with stirring. After this addition the suspension was allowed to warm up to room temp. and then kept for 30 min at reflux. Solid material was separated and the clear solution distilled. Yield: 3.55 g of **11** (86%), b.p. 69–72°C/10^{-3} Torr. – δ^1H = 1.04 [t, $^3J(^1H,^1H)$ = 7 Hz, CH_2CH_3, 6H], 2.78 (NMe), 3.10 [$^3J(^1H^1H$ = 7 Hz) CH_2CH_3], 2.87 (m, $MeNCH_2$); δ^{11}B = 35.1; δ^{13}C = 15.9 (CH_3CH_2), 38.7 (NCH_3), −42.4 (NCH_2CH_3), 55.2 ($MeNCH_2$). –

$C_{12}H_{30}B_2N_4$ (252.0): calcd. C 57.19, H 12.00, N 22.23; found C 57.99, H 12.09, N 21.38. – Mol. mass (MS, ^{11}B): 252.

A solution of 730 mg of **11** in 2 ml of CH_2Cl_2 was filled into an NMR tube which was sealed. After heating to 50°C for 2 d the signals of **11** had vanished and only those of **12** were present. – **12**: δ^1H = 1.02 (CH_2CH_3), 2.68 (NCH_3), 2.98 (NCH_2Me), 3.13 ($MeNCH_2$); $\delta^{11}B$ = 34.8; $\delta^{13}C$ = 16.7 [$^1J(^{13}C^1H)$ = 124.8, CH_2CH_3], 35.7 (^1J = 132 Hz, NCH_3); 44.3 (t, ^1J = 132 Hz, NCH_2CH_3), 52.0 ("t", ^1J = 135.8 Hz, $MeNCH_2$).

1-{tert-Butyl[chloro(2,2,6,6-tetramethylpiperidino)boryl]amino}-2-chloro-1,2-bis(dimethylamino)diborane(4) (**14a**): A solution of 0.8 ml of $B_2(NMe_2)_2Cl_2$ (5.0 mmol) in 10 ml of *n*-hexane was added to 8.5 ml of a 0.59 M solution of tmp-B≡$NCMe_3$ (5.0 mmol, **13**) in hexane. After 30 min the solvent was evaporated in vacuo. Distillation of the residue afforded only one fraction, b.p. 50–60°C/10^{-2} Torr, as a very viscous liquid. Yield: 0.8 g of **14a** (40%). – δ^1H = 1.70 (H2,3,4), 1.46 (H6,7), 1.36 (CMe_3), 2.72, 2.54 (NMe_2); $\delta^{11}B$ = 38.5, 30.3; $\delta^{13}C$ = 55.3 (CMe_3), 52.4, 52.3 (C1,5), 38.0 (C-2,4), 32.8 (CMe_3), 31.5 (C6,7), 18.9 (C3), 42.4, 41.1, 38.9 (NMe_2). – $C_{17}H_{39}B_3Cl_2N_3$ (402.9): calcd. C 50.68, H 9.76, N 13.91; found C 50.94, H 9.49, N 13.80.

1-Bromo-2-{[bromo(2,2,6,6-tetramethylpiperidino)boryl]-tert-butylamino}-1,2-bis(dimethylamino)diborane(4) (**14b**): Prepared as described for **14a** from 20.9 mmol of **13** and 20.9 mmol of $B_2(NMe_2)_2Br_2$ (5.0 ml) in 40 ml of *n*-hexane. Compound **14b** crystallized from the solution at <–10°C. Yield: 8.4 g (82%), m.p. 105–107°C. – δ^1H = 1.65 (H2,3,4), 1.45 (H6,7), 1.36 (CMe_3); 2.81, 2.51 (NMe_2); $\delta^{11}B$ = 39.2, 28.0; $\delta^{13}C$ = 56.5 (CMe_3), 53.0, 52.8 (C1,5), 37.3 (C-2,4), 32.8 (CMe_3); 31.5 M (C6,7); 18.8 (C3), 41.9, 41.1, 39.5 (NMe_2). – $C_{17}H_{39}B_3Br_2N_3$ (491.8): calcd. C 41.52, H 7.99, N 11.39; found C 41.67, H 8.09, N 11.35. – Mol. mass (MS, ^{11}B, ^{79}Br): 492.

If **13** was employed in excess [**13**: $B_2(NMe_2)_2Br_2 \approx 2:1$] and the solution freed from **14b** after 1 h the filtrate contained unreacted **13** ($\delta^{11}B$ = –4.4) which on storage was converted to the diazadiboretidine derivative ($\delta^{11}B$ = 32)[9c].

1-{tert-Butyl[methoxy(2,2,6,6-tetramethylpiperidino)boryl]-amino}-1,2,2-trimethoxydiborane(4) (**15**): A solution of 1.0 ml of $B_2(OMe)_4$ (6.6 mmol) in 10 ml of pentane was added dropwise to a stirred solution of tmp-B≡$NCMe_3$ (**13**) (15.3 ml of a 0.43 M solution, 6.6 mmol) in hexane. After stirring overnight a colorless oil remained after removal of the solvent in vacuo. This oil solidified slowly on standing and yielded 1.8 g of **15** (73%) by crystallization from pentane, m.p. 65–67°C. – δ^1H = 1.49 m (H2,3,4); 1.59 (H6,7), 1.56 (CMe_3), 3.56, 3.45, 3.42 (OCH_3); $\delta^{11}B$ = 28.0, 28.8; $\delta^{13}C$ = 16.6 (C3), 32.1, 33.4 (C6,7), 33.3 (CMe_3), 39.8 (C2,4), 54.2 (C-1,5), 54.3 (CMe_3), 50.0, 51.2, 51.4 (OCH_3). – Mol. mass (^{11}B): 368; correct isotope pattern. – $C_{17}H_{39}B_3N_2O_4$ (367.9): calcd. C 55.49, H 10.68, N 7.61; found C 54.01, H 10.68, N 7.61.

1,2-Bis{tert-butyl[methoxy(2,2,6,6-tetramethylpiperidino)boryl]-amino}-1,2-dimethoxydiborane(4) (**16**): 0.8 ml of $B_2(OMe)_4$ (5.0 mmol) was added through a syringe to 10 ml of a 1.0 M solution of tmp-B≡$NCMe_3$ (**13**) (10 mmol). The mixture was stirred for 6 d. The precipitate formed was collected by filtration and proved to be pure **16** by NMR spectroscopy. Yield: 1.78 g (69%), m.p. 135–137°C. – NMR (C_6D_6): δ^1H (CH_2 signals not well resolved) = 1.48 (CMe_3), 1.56 (H6,7), 3.51, 3.56 (OMe); $\delta^{11}B$ = 36.2, 28.3; $\delta^{13}C$ = 17.1 (C3), 31.2, 31.3, 34.5, 34.9 (C6,7); 33.7 (CMe_3), 40.8 (C2,4), 54.1 (C1,5), 54.3 (CMe_3). – Mol. mass (^{11}B): 590; correct isotope pattern. – $C_{30}H_{66}B_4N_4O_4$ (590.1): calcd. C 61.06, H 11.27, N 9.49; found C 61.27, H 11.57, N 9.50.

[1] Contribution 221: H. Nöth, H. Stolpmann, M. Thomann, *Chem. Ber.* **1994**, *127*, 81–86.

[2] [2a] R. J. Brotherton, A. L. McCloskey, L. L. Petterson, H. Steinberg, *J. Am. Chem. Soc.* **1960**, *82*, 6242–6245. – [2b] H. Nöth, W. Meister, *Chem. Ber.* **1961**, *94*, 509–514.

[3] [3a] H. Nöth, W. Meister, *Z. Naturforsch., Part B*, **1962**, *17*, 714–718. – [3b] M. P. Brown, H. B. Silver, *Chem. Ind.* **1963**, 85–86.

[4] [4a] R. J. Brotherton, H. M. Manasevit, A. L. McCloskey, *Inorg. Chem.* **1962**, *1*, 749–754. – [4b] H. Nöth, P. Fritz, *Z. Anorg. Allg. Chem.* **1963**, *324*, 129–145.

[5] [5a] W. Biffar, H. Nöth, H. Pommerening, *Angew. Chem.* **1980**, *92*, 63–64; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 56. – [5b] K. Schlüter, A. Berndt, *Angew. Chem.* **1980**, *92*, 64–65; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 57. – c) H. Nöth, H. Pommerening, *Chem. Ber.* **1981**, *114*, 3044–3055.

[6] H. Nöth, H. Schick, W. Meister, *J. Organomet. Chem.* **1964**, *1*, 401–410; H. Nöth, P. Fritz, W. Meister, *Angew. Chem.* **1961**, *73*, 76.

[7] H. Schick, Ph. D. Thesis, University of Munich, **1966**.

[8] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Chem. Soc., Dalton Trans.* **1992**, 2429–2434.

[9] [9a] K. H. Herrmansdörfer, T. Matejčikova, H. Nöth, *Chem. Ber.* **1970**, *107*, 516–527. – [9b] W. Rattay, Ph. D. Thesis, University of Munich, **1987**. – [9c] D. Loderer, Ph. D. Thesis, University of Munich, **1989**.

[10] Higher yields are obtained with solvents whose b.p. are > 80°C, e.g. in benzene a 48% yield was achieved[2b].

[11] D. W. Aubrey, M. F. Lappert, M. K. Majumdar, *J. Chem. Soc.* **1962**, 4088–4094; H. Nöth, *Z. Naturforsch. Part B*, **1961**, *16*, 470–471.

[12] H. Fußstetter, J. C. Huffman, H. Nöth, R. Schaeffer, *Z. Naturforsch., Part B*, **1976**, *31*, 1441–1445.

[13] P. T. Brain, A. J. Downs, P. Mac Cullum, D. W. H. Rankin, H. E. Robertson, G. A. Forsyth, *J. Chem. Soc., Dalton Trans.* **1991**, 1995–1200.

[14] M. P. Brown, A. E. Dann, D. W. Hunt, H. B. Silver, *J. Chem. Soc.* **1962**, 4648–4652.

[15] H. Nöth, R. Staudigl, *Chem. Ber.* **1982**, *115*, 1555–1567; **1982**, *115*, 3011–3024.

[16] P. Paetzold, *Adv. Inorg. Radiochem.* **1987**, *31*, 123–170.

[17] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, H. I. Schlesinger, *J. Am. Chem. Soc.* **1959**, *81*, 6368–6372; M. Zeldin, A. R. Gatti, T. Wartik, *ibid.* **1967**, *89*, 4217–4218; R. W. Rudolph, *ibid.* **1967**, *89*, 4216–4217.

[18] H. Nöth, *Angew. Chem.* **1988**, *100*, 1663–1684; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1603–1622.

[19] M. Schwartz, Ph. D. Thesis, University of Munich, **1987**.

[20] H. Nöth, M. Schwartz, S. Weber, *Chem. Ber.* **1985**, *118*, 4716–4724.

[21] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Vol. 14 of Basic Principles and Progress (Eds.: P. Diehl, E. Fluck, E. Kosfeld), Springer Publishers, Heidelberg, New York, **1978**.

[22] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715–2717; A. Moezzi, R. A. Bartlett, P. P. Power, *Angew. Chem.* **1992**, *104*, 1075–1076; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1082.

[23] W. D. English, A. L. McClosky, H. Steinberg, *J. Am. Chem. Soc.* **1961**, *83*, 2122–2124.

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