The Structures of a Tetracarba-*nido*-octaborane(8) and a Novel Spiro Derivative of a 2,3,5-Tricarba-*nido*-hexaborane(7)

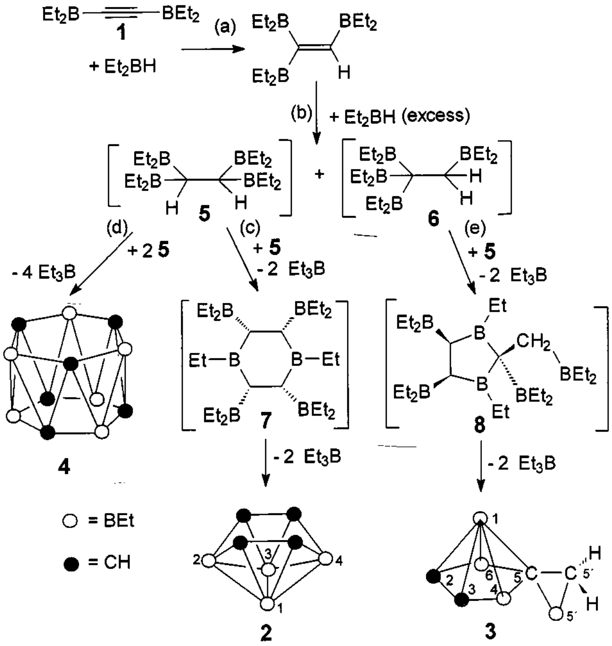
Bernd Wrackmeyer,*[a] Hans-Jörg Schanz,[a] Matthias Hofmann,[b] Paul von R. Schleyer,[b] and Roland Boese[c]

Keywords: Ab initio calculations / Carboranes / NMR / X-ray analysis

Hydroboration of bis(diethylboryl)ethyne (**1**) with tetraethyldiborane(6) leads to a *B*-ethyl-substituted tetracarba-*nido*-octaborane **2**, a spiro-carborane **3**, which belongs to the 2,3,5-tricarba-*nido*-carborane family, and a hexacarba-*arachno*-dodecaborane(12) **4**, along with polymeric material. The X-ray structure analysis of carborane **2**, determined here, is fully consistent with the structure deduced earlier from NMR data. The structure of **3** in solution was established by theoretical analysis of its NMR data. Ab initio calculations of the structures of **2b** and **3b** (**b** denotes the *B*-metyhl-substituted derivatives) and the comparison of calculated with experimental NMR data support the suggested structures of **2** and **3** in solution. The calculated structure of the carborane cage of **2a** also agrees with the experimental geometry of **2**.

Introduction

Tetracarba-*nido*-octaboranes(8) are reported to result from transition metal complex promoted reactions[1,2] or from the reduction of organo-substituted 1,2,5-thiadiborolenes with potassium.[3] However, the evidence for structural assignments is not firm, and the chemistry of these carboranes has not been explored. We prepared the *B*-ethyl-substituted tetracarba-*nido*-octaborane(8) **2** by hydroboration of bis(diethylboryl)ethyne (**1**); the structure was inferred from NMR data in solution along with an X-ray structural analysis of the hexacarbonyldiiron complex of **2**.[4] The hydroboration of **1** (Scheme 1) also leads to other products, e.g. the hexacarba-*arachno*-dodecaborane(12) derivative **4**,[5] and **3**, a spiro-carborane isomer of **2**.[5] We now report the first X-ray-structural analysis of the *nido*-C_4B_4 cage, and our finding of an isomer of **2** with a carborane cage different from that of **2**. We employ the ab initio/GIAO-IGLO/NMR method[6] to elucidate the structures.



Scheme 1. Hydroboration of bis(diethylboryl)ethyne (**1**) using an excess of Et_2BH: formation of polymers and of the carboranes **2**, **3** and **4**

Results and Discussion

The routes to the carboranes **2**−**4** are shown in Scheme 1. The mechanism is speculative. The suggested intermediates **5**−**8** were not detected, but are inferred [as associated diborane(6) species due to the excess of tetraethyldiborane(6)] from the products. The formation of polymeric material is suggested if the diethylboryl groups in **7** or **8** are not in the correct positions for BH-catalyzed intramolecular elimination of Et_3B (these isomers of **7** or **8** are not shown in Scheme 1). In the case of **8** intramolecular elimination of Et_3B from the $Et_2BCH{-}CHBEt_2$ moiety leads to the apical BEt group and therefore, it can be predicted that a second intramolecular elimination of Et_3B, forming the spiro compound, should give the three-membered ring with an endocyclic C5−B5′ bond as in **3**. The proposed structure of **3** is unique in carborane chemistry and therefore, extensive NMR studies and ab initio MO calculations were per-

---

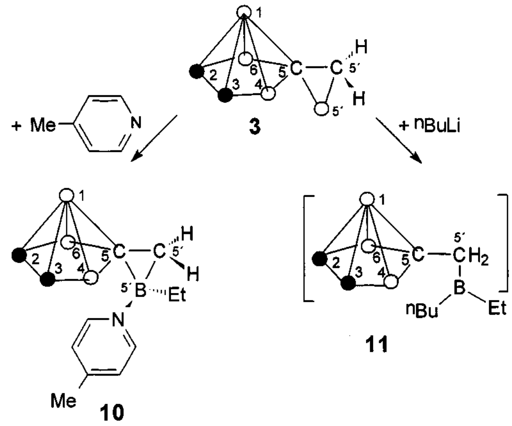
[a] Laboratorium für Anorganische Chemie, Universität Bayreuth,
D-95440 Bayreuth, Germany
Fax: (internat.) + 49(0)921/552157
E-mail: b.wrack@uni-bayreuth.de
[b] Center for Computational Quantum Chemistry,
University of Georgia,
1004 Cedar Street, Athens, GA 30602-2525, USA
Fax: (internat.) + 1-706/542-0406
E-mail: schleyer@paul.chem.uga.edu
[c] Institut für Anorganische Chemie, FB 8, Universität-GH Essen,
Universitätsstraße 5−7, D-45117 Essen
Fax: (internat.) + 49(0)201/1832535
E-mail: boese@structchem.uni-essen.de

1434−1948/99/0303−0533 $ 17.50+.50/0

formed to prove its existence, in particular in the absence of direct structural evidence.

In contrast to **2** and **4**, the carborane **3** is extremely sensitive towards oxygen. It is therefore not observed when the usual work-up procedures are used. However, if the reaction mixtures are not oxidized or hydrolyzed, **3** can be obtained in a mixture with **2** by fractional distillation, and a complete set of NMR data of **3** can be recorded. The ^{11}B-NMR signal at $\delta = -28.9$ with relative intensity 1 indicates the presence of a boron atom (B1) in apical position, and the signal at $\delta = +23.3$ with relative intensity 2 is typical of boron atoms B4,6 in basal positions. A third ^{11}B-NMR signal at rather low field ($\delta = +64.0$), much more typical of triorganoboranes than of carboranes is assigned to the boron atom in the three-membered ring. The connectivity between the ^{11}B4,6 and ^{13}C2,3 nuclei is evident from the sharpening of relevant ^{13}C-NMR signals as the result of selective ^{11}B decoupling experiments (see Figure 1). Irradiation of the ^{11}B resonance at $\delta = +64.0$ sharpens two ^{13}C(CH$_2$) signals, one due to the BEt group and the other to the unique CH$_2$ moiety in the three-membered ring. The carborane **3** is the first 2,3,5-tricarba-*nido*-hexaborane derivative[7,8] without an *endo*-C5−H bond. For the parent carborane a hyperconjugative interaction of the *endo*-C5−H bond with B4 (or B6) was found computationally.[9] This participation in the cluster bonding satisfies the electron counting rules.[10] In comparison with the δ^{11}B data of hexaethyl-2,3,5-tricarba-*nido*-hexaborane(7) **9** (Table 1) the apical ^{11}B nucleus in **3** is deshielded by 8 ppm. This can be the result of the different substituents linked to C5 (vide infra), and it can also be caused (however, less likely) by the missing ethyl groups at C2,3 in **3**.

Two reactions of **3** (Scheme 2) provide further evidence for its unique structure. If γ-picoline is added to the mixture of **2** and **3**, the ^{11}B-NMR signal at $\delta = +64.0$ disappears, and a new broad signal at $\delta = +13.5$ is observed. The spiro cage structure of **3** appears to be retained, since the effect on all other ^{11}B and ^{13}C(cage) signals is small. The carborane **2** does not react. Treatment of the mixture of **2** and **3** with BuLi also does not affect **2**, but **3** reacts by ring opening to give the 2,3,5-tricarba-*nido*-hexaborate(1−) derivative **11**. The reaction can be controlled by using slightly less then one equivalent of BuLi. The ^{11}B-NMR spectrum shows signals with correct integral intensities for B(1) and B(4,6) at $\delta = -38.5$ and $+21.7$, respectively, and a signal at $\delta = +86.7$ for the Et(Bu)B group in the typical range of non-cyclic trialkylboranes.[11] The δ^{11}B(1,4,6) values are close to those determined for corresponding 2,3,5-tricarba-*nido*-hexaborates(1−) [e.g. *nido*-Et$_6$-2,3,5-C$_3$B$_3$-hexaborate(1−): δ^{11}B1 = −44.2 and δ^{11}B(4,6) = +17.2.[8]]



Scheme 2. Reactivity of the spiro-carborane **3** towards γ-picoline and BuLi

The NMR data of **2** in solution discussed previously,[4] are fully consistent with the molecular structure of **2** in the solid state.[12] The X-ray data of **2** confirm the proposed[4,13] hexagonal open face formed by the four carbon atoms, linked in pairs, and two boron atoms (Figure 2). In

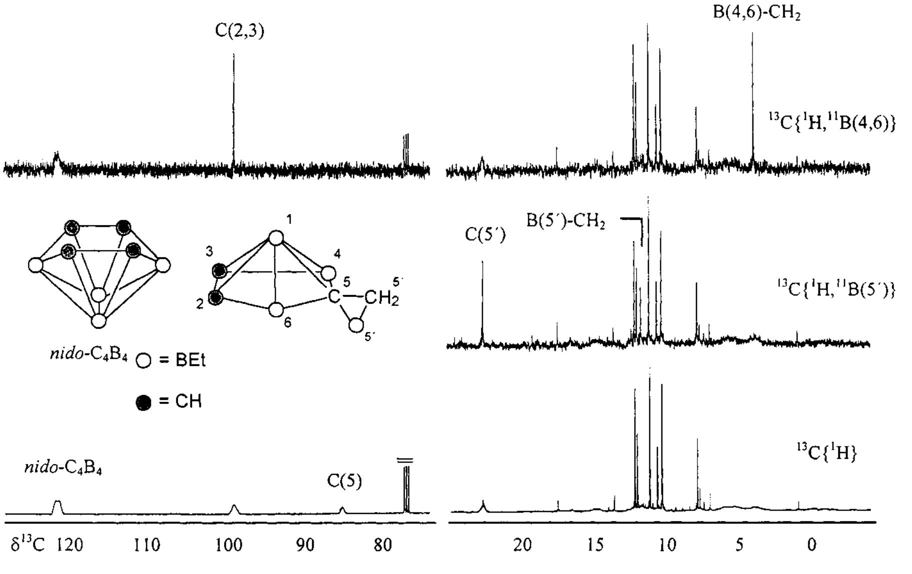


Figure 1. 125.8-MHz ^{13}C-NMR spectra of a mixture of **2** and **3** (ca. 10 mg in 0.5 mL of CDCl$_3$); **A**: normal ^{13}C{^{1}H}-NMR spectrum spectrum; **B**: the selective heteronuclear ^{13}C{^{1}H,^{11}B(4,6)} triple-resonance experiment shows sharpening of the B(4,6)-^{13}CH$_2$, and ^{13}C(2,3) signals; **C**: the selective heteronuclear ^{13}C{^{1}H,^{11}B(1)} triple-resonance experiment only gives rise to sharpening of the ^{13}CH$_2$-B(1) signal

the cage, the short distances d_{CC} [138.0(3), 138.5(3) pm] and rather short distances d_{B4C} and d_{B2C} [157.7(4), 159.0(4), 158.4(4), 158.6(4) pm] characterize the bonding situation in the open face. In particular, d_{B4B1} = 189.5(4) and d_{B2B3} = 190.5(4) pm are long when compared with the short d_{B1B3} = 171.0(4) pm separation. The other d_{BC} distances in the cage are similar to the known deltahedral B−C bond lengths. Variations of bond lengths in the hexacarbonyldiiron complex of **2** are less significant. The B−C−C angles in the BEt groups are 116.0(3)° (mean value), in the same range as in pentaethyl-1,5-dicarba-*closo*-pentaborane,[14] in which the B−C−C angles were interpreted in terms of hyperconjugational effects.[15]

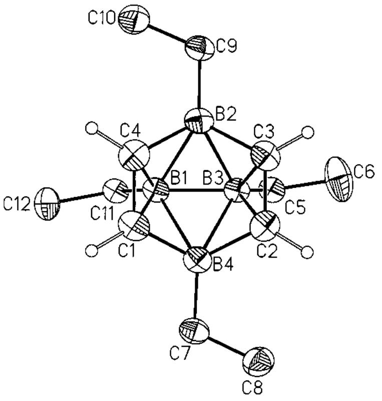


Figure 2. Presentation of the molecular structure of **2** with 50% thermal ellipsoids (ethyl hydrogen atoms are omitted for clarity); selected bond lengths [pm] and angles [°]: B1−C1 172.5(3), B1−C4 172.6(3), B1−B3 171.0(4), B1−B4 189.5(4), B1−C11 157.6(3), B2−C3 158.4(4), B2−C4 158.6(4), B2−C9 159.6(4), B2−B3 190.5(4), C1−C4 138.0(3), C2−C3 138.5(3); C1−B4−C2 109.9(2), C3−B2−C4 110.2(2), C10−C9−B2 115.4(2), C12−C11−B1 116.5(2)

Geometries were optimized at the MP2(fc)/6-31G* level of theory using the Gaussian 94 program.[16] Chemical shifts were evaluated from GIAO-SCF/6-31G* computations of chemical shieldings employing B_2H_6 (σ = 107.0) as a primary reference. Reported values are converted to the experimental standard, $BF_3 \cdot OEt_2$ using $\delta(B_2H_6)$ = 16.6.[17]

The parent $C_4H_8B_4$ spiro-carborane, optimized assuming a classical C_2B three-membered ring attached to a C_2B_3 cluster by two C−B connections, gave a C_s-symmetric geometry **12**. This was characterized as a transition structure at RHF/6-31G*. (Optimization without symmetry constraints converged to a spirocyclic structure with a six- and a three-membered ring.) Computed ^{11}B-NMR-chemical shifts for **12** of +32.5 (B1), +3.2 (B4,5) and +84.6 ppm are in gross disagreement with experimental data (−28.9, +23.3, +64.0 ppm). An alternative starting geometry whose larger B4−B5 separation allows the spiro carbon atom to become part of the cluster optimized to structure **3a**, 63.9 kcal mol^{-1} lower in energy than **12**. Chemical shifts computed for **3a** (B1: −34.0, B4,6: 8.7, B5′: 40.2; C2,3: 108.6, C5: 93.6, C5′: 10.4) are in acceptable agreement with measured values (see Table 1) when substituent effects are

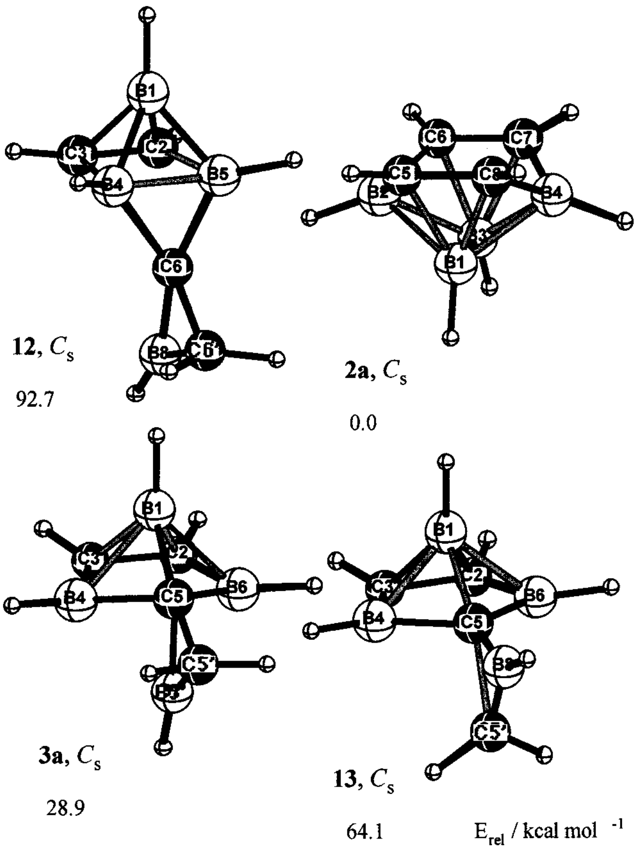


Figure 3. Structures and relative energies [MP2(fc)/6-31G* + 0.89 ZPE(HF/6-31G*] of some $C_4B_4H_8$ isomers

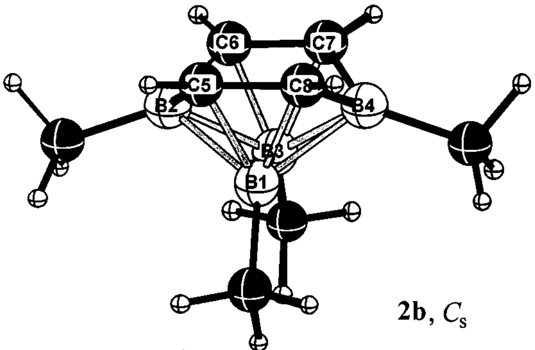
Table 1. Experimental chemical shifts[a] of the cage nuclei of **2**, **3**, **9**, **10** and **11** in comparison to values computed for model compounds **2b** and **3b**[b] (compare Figure 4) at GIAO-SCF/6-31G*//MP2(fc)/6-31G*

	2	**3**	**9**[c]	**10**	**11**	**2b**	**3b**
$\delta^{11}B(1,3)$	0.6					−3.0	
$\delta^{11}B(1)$		−28.9	−36.9	−30.2	−38.5		−30.0
$\delta^{11}B(2,4)$	−4.5					−7.9	
$\delta^{11}B(4,6)$		+23.3	+22.1	+25.0	+21.7		+17.6
$\delta^{13}C$	120.8					128.9	
$\delta^{13}C(2,3)$		98.9	105.9	94.0	n.m.		98.5
$\delta^{13}C(5)$		85.1	55.2	83.6	n.m.		82.5
$\delta^{13}C(5')$		22.5	16.5	23.0	n.m.		7.2
$\delta^{11}B(5')$		+64.0		+13.5	+86.7		+49.8

[a] Solution of a mixture of **2** and **3** in $CDCl_3$ (25°C); solutions of mixtures of **2** and **9** and **2** and **10** in C_6D_6 (25°C); n.m.: not measured. − [b] **2b** and **3b** are the *B*-methyl-substituted analogs of **2** and **3**. − [c] Hexaethyl-2,3,5-tricarba-*nido*-hexaborane(7).[8]

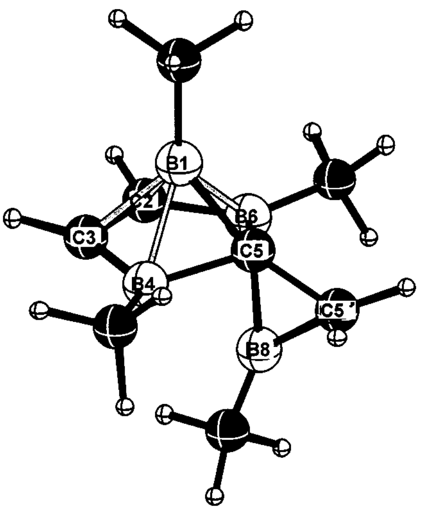
taken into account. A model better than **3a**, the tetrakis(*B*-methylated) structure **3b**, gives satisfactory overall agreement although the B5′ chemical shift is 14.2 ppm too low. We compute a B4,6−B5′ separation of 206.2 pm for the parent **3a**. But this distance is increased to 211.6 pm for the better per(*B*-methylated) model (and probably is even larger with ethyl substitution). The $C_4B_4H_8$ tetracarba-*nido*-octaborane structure **2a** is 28.9 kcal mol^{-1} more stable than **3a**. The difference between the tetrakis(*B*-methyl) derivatives **2b** and **3b** is 26.2 kcal mol^{-1} (//MP2(fc)/6-31G*).

Compound **3a** is a derivative of 2,3,5-tricarbahexaborane(7), for which the *endo*-C5−H bond was shown to be asymmetrically bent towards one neighboring boron atom (partially bridging).[9] For **3a**, no evidence for a similar bending of the *endo*-C5−B5 bond was found; the C_s structure is a minimum and the C5−B5 distance is not significantly elongated (150.9 pm). However, the *endo*-B atom does interact with the cage: Hyperconjugative donation from the cage results in a 0.34-electron population of the formally empty p(B5′) orbital according to an NBO analysis (0.31 for **3b**).[18] As a consequence, the NLMO/NPA[18] bond order between the *exo*-B5′ atom and the basal B4,6 atoms is 0.23 (0.31 for **3b**). This compares with 0.73 and 0.87 (0.62 and 0.70 for **3b**) between B5′ and C5 and the methylene C5′ atom, respectively. This hyperconjugation confers considerable stabilization. Thus, **13**, where B5′ is in *exo* position, is 35.3 kcal mol^{-1} less stable than **2a**. The B4,6−B5′ bond order in **3** is only 0.06 and the p(B5′) orbital has a population of only 0.06 electrons. (The *exo*-B5′ isomer related to **12** is only 4.9 kcal mol^{-1} higher in energy than **12**.)



2b, C_s

E_{rel} / kcal mol $^{-1}$ 0.0



3b, C_s

E_{rel} / kcal mol $^{-1}$ 26.2

Figure 4. Geometries (bond lengths in pm) of model compounds **2b** (B1−C2 172.8, B1−B4 184.9, B1−C5 161.0, C2−C3 144.5, C2−B6 152.0, B4−C5 161.4, C5−C5′ 150.8, C5−B5 151.1, C5′−B5 158.3) and **3b** (B1−B2 186.5, B1−B3 172.9, B1−C5 170.7, B2−C4 158.5, C5−B8 139.3), optimized at MP2(fc)/6-31G*

Experimental Section

General: The preparation and the handling of samples was carried out under N_2 or Ar, observing all necessary precautions to exclude traces of oxygen or moisture. Commercial starting materials were employed (γ-picoline, BuLi in hexane (1.6 M)] or were prepared as described [Et_2BH,[19] $Et_2B{-}C{\equiv}C{-}BEt_2$[4]]. − NMR spectra: Bruker ARX 250 and DRX 500 spectrometers; the latter was equipped with a triple-resonance probehead for $^{13}C\{^1H,^{11}B\}$ experiments; chemical shifts are given with respect to Me_4Si [δ^1H ($CHCl_3/CDCl_3$) = 7.24; δ^1H ($C_6C_5CD_2H$) = 2.03; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{13}C$ ($C_6D_5CD_3$) = 20.4] and $Et_2O \cdot BF_3$ [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 Mhz].

1,2,3,4-Tetraethyl-5,6,7,8-tetracarba-*nido*-octaborane(8) (2) and Its Spiro Isomer 3: After heating of a solution of 3.57 g (21.7 mmol) of bis(diethylboryl)ethyne in 5.0 mL of Et_2BH (57.1 mmol hydride[20]) at 80°C for a period of 24 h, it was saturated with ethene (reactive B−H are converted into B−Et bonds). Fractional distillation under reduced pressure first gave 0.97 g (21%) of a mixture (65:35) of compounds **2** and **3** (b.p. 75−85°C/10^{-4} Torr). The residue contained polymeric material and **4** which could be isolated as described.[5] Repeated distillation did not lead to further separation of **2** and **3**, and a small amount of this mixture was used to obtain the NMR data of **3** and to carry out the reactions of **3** with γ-picoline and BuLi (by adding the γ-picoline and BuLi to the carborane mixture at −78°C, warming to room temperature and removing all volatile material in vacuo). Treatment of 0.9 g (4.2 mmol) of the carborane mixture with a solution of Na[Et_3BH] in hexane (6 M; 0.5 mL; 3 mmol of hydride) at room temperature gave, after filtration and washing of the insoluble material with hexane (15 mL), a colorless solution containing only Et_3B and the carborane **2** (^{11}B NMR). Compound **2** (0.41 g; 9% relative to **1**; b.p. 82°C/10^{-4} Torr) was obtained as a colorless liquid in high purity (suitable for growing single crystals for X-ray analysis; vide infra) after threfold fractional distillation (see ref.[4] for NMR and MS data of **2**).

3: ^1H NMR (500.1 MHz, 25°C, $CDCl_3$): δ = 5.24 (s, 2 H, C2,3-H), 1.64 (s, 2 H, C5−CH_2), 0.19, 0.56 (q, t, 5 H, B1−Et), 0.83, 0.69, 1.06 (m, m, t, 10 H, B4,6−Et), 1.20, 1.01 (m, t, 5 H, C5−BEt). − ^{11}B NMR (80.3 MHz, 25°C, $CDCl_3$): δ = −28.9 (B1), 23.3 (B4,6), 64.0 (B5′). − ^{13}C NMR (125.8 MHz, 25°C, $CDCl_3$): δ = 98.9 (br., C2,3), 85.1 (br., C5), 22.5 (br., CH_2), −0.4 (br.), 10.6 (B1−Et), 4.0 (br.), 11.2 (B4,6−Et), 11.7 (br.), 12.0 (BEt).

Structure Determination of 2: Compound **2**, $C_{12}H_{24}B_4$, formula weight 211.55, crystallized from the colorless neat liquid by cooling to 168 K and application of a miniature zone-melting procedure using a CO_2 laser beam[21] as a cylindrical crystal (diameter 0.3 mm) which was measured at 120 K with a Nicolet R3 diffractometer with graphite-monochromized Mo-K_α radiation. Cell dimensions of the triclinic system: $a = 8.044(4)$, $b = 9.114(4)$, $c = 10.557(5)$ Å, $\alpha = 71.89(3)$, $\beta = 88.79(4)$, $\gamma = 70.13(3)°$, $V = 688.7(5)$ Å^3, $Z = 2$, space group *P*1bar, $\rho_{calcd.} = 1.020$ gcm^{-3}, $\mu = 0.052$ mm^{-1}, ω-scan data collection of 2567 intensities ($2\Theta_{max} = 50°$), 2422 independent ($R_{merg} = 0.0388$), 1756 observed [$F_o \geq 4\sigma(F)$], structure solution with direct methods and refinement on F^2 with Siemens SHELXTL-Plus program package (version 5.03), $R1$(obsd. data) = 0.0577, $wR2$(all data) = 0.1866, GOF = 1.060, $w^{-1} = \sigma^2(F_o{}^2) + (0.0558 \cdot P)^2 + 0.55 \cdot P)$, where $P = [(\max F_o{}^2) + (2\ F_c{}^2)]/3$, maximum/minimum residual electron density 0.208/−0.196 e Å^{-3}.

Acknowledgments

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

---

[1] [1a] T. P. Fehlner, *J. Am. Chem. Soc.* **1977**, *99*, 8355−8356. − [1b] T. P. Fehlner, *J. Am. Chem. Soc.* **1986**, *102,* 3426−3430.

[2] [2a] M. G. L. Mirabelli, L. G. Sneddon, *Organometallics* **1986**, *5*, 1510−1511. − [2b] R. N. Grimes, personal communication, **1998**.

[3] W. Siebert, M. E. M. El-Esawi, *Chem. Ber.* **1979**, *112*, 1480−1481.

[4] B. Wrackmeyer, H.-J. Schanz, W. Milius, *Angew. Chem.* **1997**, *109*, 1145−1147; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1117−1119.

[5] B. Wrackmeyer, H.-J. Schanz, M. Hofmann, P. v. R. Schleyer, *Angew. Chem.* **1998**, *110*, 1329−1331; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1245−1247.

[6] [6a] M. Bühl, in *Encyclopedia of Computational Chemistry* (Ed.: P. v. R. Schleyer), Wiley, Chichester, in press. − [6b] M. Bühl, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1992**, *114*, 477−491. − [6c] M. Bühl, J. Gauss, M. Hofmann, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 12385−12390. For an extensive list of references to ab initio/IGLO/NMR applications see: [6d] M. Diaz, J. Jaballas, D. Tran, H. Lee, J. Arias, T. Onak, *Inorg. Chem.* **1996**, *35*, 4536.

[7] [7a] A. Feßenbecker, A. Hergel, R. Hettrich, V. Schäfer, W. Siebert, *Chem. Ber.* **1993**, *126*, 2205. − [7b] T. Kuhlmann, H. Pritzkow, U. Zenneck, W. Siebert, *Angew. Chem.* **1984**, *96*, 994−996; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 965−967. − [7c] J. Zwecker, T. Kuhlmann, H. Pritzkow, W. Siebert, U. Zenneck, *Organometallics* **1988**, *7*, 2316. − [7d] W. Siebert, *Pure Appl. Chem.* **1988**, *60*, 1345. − [7e] W. Siebert, in *Current Topics in the Chemistry of Boron* (Ed.: G.W. Kabalka), Royal Society of Chemistry, Cambridge, **1994**, pp. 269−274.

[8] B. Wrackmeyer, H.-J. Schanz, *Main Group Met. Chem.* **1998**, *21*, 29−32.

[9] M. Hofmann, M. A. Fox, R. Greatrex, R. E. Williams, P. v. R. Schleyer, *J. Organomet. Chem.* **1998**, *550*, 331−340.

[10] [10a] K. Wade, *J. Chem. Soc., Chem. Commun.* **1971**, 792−793. − [10b] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−67. − [10c] R. E. Williams, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.

[11] H. Nöth, B. Wrackmeyer, "NMR Spectroscopy of Boron Compounds" in *NMR − Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), vol. 14, Springer, Berlin, **1978**.

[12] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101626. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[13] R.E. Williams, in *Electron Deficient Boron and Carbon Clusters* (Eds.: G.A. Olah, K. Wade, R.E. Williams), Wiley, New York, **1991**, chapter 2.

[14] M. Antipin, R. Boese, D. Bläser, A. H. Maulitz, *J. Am. Chem. Soc.* **1997**, *119*, 326−333.

[15] R. Boese, D. Bläser, N. Niederprüm, M. Nüsse, W. A. Brett, P. von Ragué Schleyer, M. Bühl, N. J. R. van Eikema Hommes, *Angew. Chem.* **1992**, *104*, 356−358; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 314−316.

[16] Geometries have been optimized at the MP2(fc)/6-31G* level of theory using the Gaussian 94 program: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian 94, Revision E.2*, Gaussian, Inc., Pittsburgh PA, **1995**.

[17] T. P. Onak, H. L. Landesman, R. E. Williams, *J. Phys. Chem.* **1959**, *63*, 1533.

[18] A. E. Reed; L. A. Curtis; F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[19] R. Köster, P. Binger, *Inorg. Synth.* **1974**, *15*, 141−149.

[20] B. Wrackmeyer, H.-J. Schanz, W. Schüßler, R. Köster, *Fresenius J. Anal. Chem.*, in the press.

[21] [21a] R. Boese, M. Nussbaumer, in *Correlations, Transformations, and Interactions in Organic Crystal Chemistry*, vol. 7 (Ed.: D. W. Jones, A. Katrusiak), Oxford University Press, Oxford, England, **1994**, p. 20−37. − [21b] V. R. Thalladi, H.-C. Weiss, D. Bläser, R. Boese, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.*, in press.

Received October 13, 1998
[I98352]