2,3,4-Tricarba-*nido*-hexaboranes(7) with a Bridging B−Ethyl−B Moiety

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

Laboratorium für Anorganische Chemie, Universität Bayreuth[a]
D-95440 Bayreuth (Germany)
Fax: Int. code +49(0)921/552157
E-mail: b.wrack@uni-bayreuth.de

Institut für Organische Chemie, Universität Erlangen-Nürnberg[b]
Henkestr. 42, D-91054 Erlangen (Germany)
Fax: Int. code +49(0)9131/859132
E-mail: pvrs@organik.uni-erlangen.de

Received December 8, 1997

Keywords: Ab initio calculations / Boron / Carboranes / NMR spectroscopy

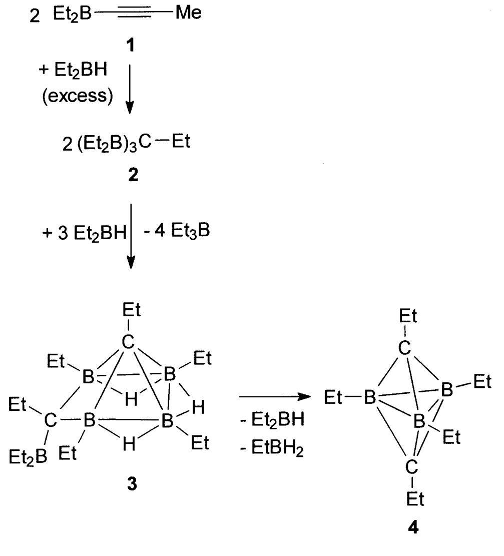
Hydroboration of diethyl(1-propynyl)borane **1** with tetraethyldiborane(6) in the presence of a catalytic amount of trimethyl- or tributyltin chloride gave two new organo-substituted carboranes **6** and **7** with 2,3,5-tricarba-*nido*-hexaborane(7) and 2,3,4-tricarba-*nido*-hexaborane(7) skeletons, respectively, along with polymeric material and the known organo-substituted 1-carba-*arachno*-pentaborane(10) (**3**) and pentaethyl-1,5-dicarba-*closo*-pentaborane(5) (**4**). Selective ^{11}B(5,6) decoupled ^{13}C-NMR spectra indicate an unprecedented B(5)−ethyl−B(6) bridge in **7**. This structure is supported by the agreement between experimental and calculated ^{11}B- and ^{13}C-chemical shifts on a model compound **7d** with methyl groups in the 1,2,3,5,6-positions and an ethyl group bridging B(5) and B(6).

Introduction

Treatment of tetraborane(10) with alkynes gave the first 2,3,4-tricarba-*nido*-hexaboranes(7) with a B(5)−H−B(6) bridge;[1] these early observations have, at least in part, been confirmed recently,[2] and the formation of the parent compound has been reported for the first time.[2b] Köster et al. have tentatively assigned (on the basis of mass spectra) the structure of 1,5,6-triethyl-2,3,4-trimethyl-2,3,4-tricarba-*nido*-hexaborane(7) to one of the minor products in the complex mixture which is obtained by dehalogenation of diethylboron chloride with lithium in THF.[3] An alternative route to small carboranes involves hydroboration of 1-alkynyl(diethyl)boranes in the presence of a large excess of Et_2BH,[5] which gives rise to hydroboration followed by Et_2BH-catalyzed condensations.[5][6][7] This method has afforded [Eq. (1)] the *arachno*-carborane **3**,[7] which is a precursor of the *closo*-carborane **4**. The formation of **3** in high yield requires that the hydroboration of **1** takes place stereoselectively to give **2** as a reactive intermediate prior to the condensation reactions. If this is not the case, products other than **3** will be formed, as reported in this work.

Results and Discussion

Synthesis. Conditions that reduce the stereoselectivity of the hydroboration of **1** will lead to mixtures containing compounds **2** and **5** [Eq. (2)]; hence, condensation reactions may give carboranes other than **3**. Therefore, we have studied the reaction of **1** with Et_2BH under various conditions. As long as a large excess of Et_2BH is used, **3** is the major product, although more side-products are formed if **1** is added to Et_2BH at room temperature or above, rather than



(1)

at −78 °C. The use of only a slight excess of Et_2BH (2.1 equivalents) results in mainly polymeric material containing just traces (< 1%, according to ^{11}B-NMR spectra) of carboranes, but the presence of a small amount of trimethyl- or tributyltin chloride leads to the formation of interesting products. Examination of the ^{11}B-NMR spectra of such reaction mixtures, after removing readily volatile material, shows not only the presence of polymers (ca. 60%), but also new types of carboranes **6** (ca. 15%) and **7** (ca. 10%) along with the known carboranes **3** (ca. 10%) and **4** (ca. 5%). Unlike **7**, pure carborane **6** could not be isolated. However, **6** was readily identified by its characteristic[8] ^{11}B-NMR data

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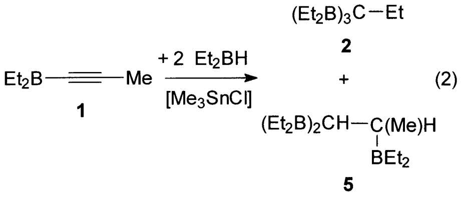
[$\delta^{11}B(1) = -36.4$ and $\delta^{11}B(4,6) = 21.9$] as a 2,3,5-tricarba-*nido*-hexaborane(7) derivative. **6** is not stable to oxidation or hydrolysis but **7** is, meaning the latter can be separated and isolated. The compounds **7** do not react with Na[Et_3BH] after prolonged heating at 60°C in hexane, with Et_3Al in hexane at room temperature, or with bases such as pyridine.

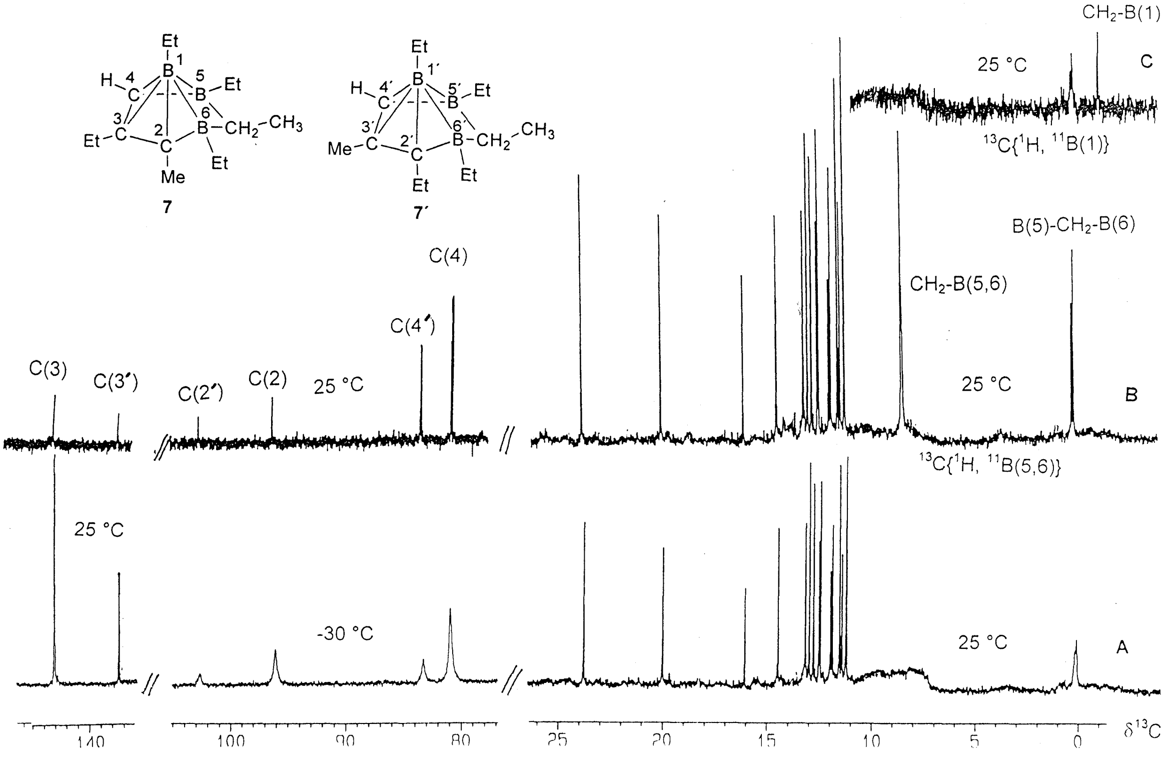


(2)

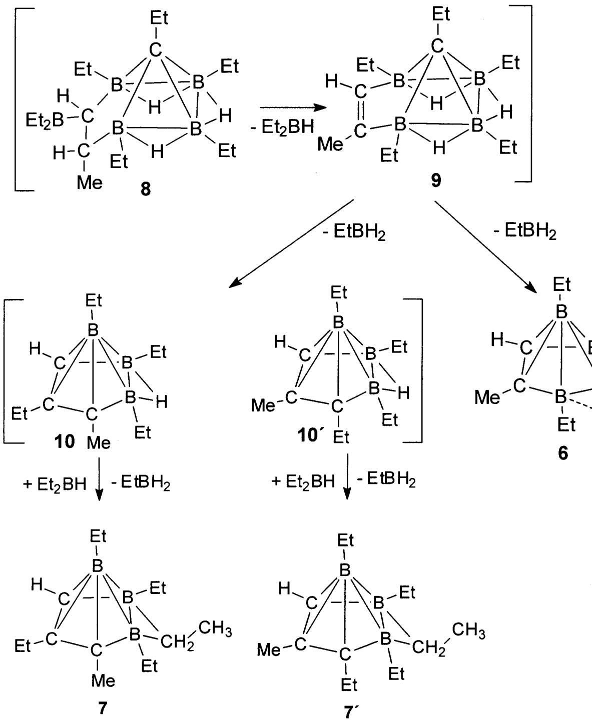
Potential intermediates prior to the formation of the carboranes **6** and **7** are shown in Scheme 1. It is suggested that the C_2-bridged compound **8** is formed in a similar way to **3**.[7] The C_2-bridged *arachno*-carborane **9** is comparable with a benzo derivative that has already been characterized.[9] The intermediacy of **9** (prior to elimination of $EtBH_2$[10][11] and rearrangement) has been proposed in order to explain the formation of 2,3,5-tricarba-*nido*-hexaborane(7) derivatives analogous to **6**.[8b] Although other rearrangements of **9** have not been observed before,[8b] it is conceivable that insertion of the formerly apical CEt group takes place not only into B−H−B bonds but also into B−C or C−C bonds, accompanied or followed by elimination of $EtBH_2$. This explains the formation of **10** and **10′** which, under the reaction conditions, can undergo irreversible H/Et exchange to give the isomers **7** and **7′** (in repeated experiments the ratio of **7**/**7′** varied from 3:1 to 2:3). The B(5)−Et−B(6) bridge in **7** is an unprecedented structural feature in borane and carborane chemistry. Bridging triorganosilyl, -germyl, and -stannyl groups have been observed previously, e.g. in the case of *nido*-pentaborane(9) derivatives.[12]

NMR Spectroscopic Results: The ^{1}H-, ^{11}B- and ^{13}C-NMR data of **7** (Table 1 and Experimental Section) are fully consistent with a 2,3,4-tricarba-*nido*-hexaborane(7) cage bearing terminal ethyl groups at all boron atoms, a hydrogen at C(4) and a methyl or a ethyl group at C(2) or C(3). There was no indication of the initially expected B−H−B group, either in the ^{1}H-NMR spectra (with or without ^{11}B decoupling) or in the ^{11}B-NMR spectra (with and without ^{1}H decoupling); this evidence definitely precludes the structures **10** and **10′**. However, there were additional signals due to an ethyl group for each isomer in the ^{1}H- and ^{13}C-NMR spectra. ^{13}C-NMR spectra of a mixture of **7** and **7′**, recorded under various conditions, are shown in Figure 1. The aliphatic region displays fourteen sharp ^{13}C resonances (two CH_2 and twelve CH_3 groups with carbon atoms not linked to boron), and in the region for the cage carbon atoms two sharp signals [$^{13}C(3,3')$] and four

Figure 1. 125.8-MHz ^{13}C-NMR spectra of a mixture of **7** and **7′** (ca. 10 mg in 0.5 ml of $CDCl_3$). **A**: Normal $^{13}C\{^1H\}$-NMR spectrum; the region of the boron bonded cage carbon atoms has been taken from a spectrum recorded at −30°C in order to show the broadened ^{13}C-NMR signals which are exceedingly broad in the spectrum at 25°C. **B**: The selective heteronuclear $^{13}C\{^1H, ^{11}B(5,6)\}$ triple-resonance experiment shows sharpening of the $B(5)-^{13}CH_2-B(6)$, $^{13}CH_2-B(5,6)$, and $^{13}C(2, 2', 4, 4')$ signals. **C**: The selective heteronuclear $^{13}C\{^1H,^{11}B(1)\}$ triple-resonance experiment only gives rise to sharpening of the $^{13}CH_2-B(1)$ signal.



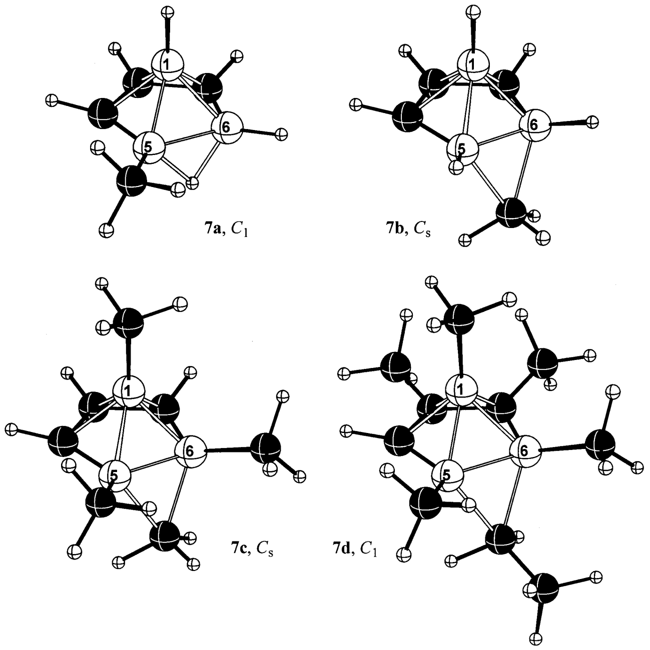
Scheme 1



broad signals [^{13}C(2,2′) and 13C(4,4′)] are observed, as required for the two isomers **7** and **7′**. The unique µ-^{13}C(CH$_2$) signals (Figure 1, A and C) are significantly broadened [although less than the ^{13}C(CH$_2$) resonance of terminal BEt groups] as a result of scalar relaxation of the second kind[13][14] (partially relaxed scalar ^{13}C-^{11}B spin-spin coupling). This was proved by selective ^{11}B(5,6) decoupling (Figure 1, B) which, as expected, causes sharpening of the ^{13}C(2, 2′, 4, 4′) and ^{13}C(CH$_2$) signals of the terminal B(5,6)Et groups, and also the µ-^{13}C(CH$_2$) signal of the ethyl group in the B(5)−Et−B(6) bridge. Decoupling of B(1) (Figure 1, C) has no appreciable effect on the appearance of the ^{13}C-NMR spectrum except for sharpening of the ^{13}C(CH$_2$) resonance of the apical BEt group. The greater broadening of the terminal ^{13}C(CH$_2$) signal of the BEt groups with respect to that of the bridging B−Et−B [i.e. $^{1}J(^{13}C_{terminal},^{11}B) > {}^{1}J(^{13}C_{bridging},^{11}B)$] is reminiscent of the $^{1}J(^{11}B,^{1}H)$ in diborane(6) where the magnitude of the coupling constant of the terminal ^{1}H nucleus is approximately three times greater than that of the bridging ^{1}H nucleus.

MO Calculations: We applied the ab initio/GIAO/NMR method,[15][16] a powerful computational tool for the determination of polyhedral borane and carborane structures, to establish, in the absence of X-ray determinations the structural assignment for **7**.[17] The chemical shifts, computed for various optimized models, are compared with experimental NMR data. The methyl-bridged µ-Me-2,3,4-C$_3$B$_3$H$_6$ model compound **7b** not only allows the investigation of the chemical shifts of a bridging alkyl group (the new feature in **7** and **7′**, which is represented in **7b**) but also a thermodynamic stability assessment in comparison with the hydrogen bridge isomer (5-Me-2,3,4-C$_3$B$_3$H$_6$, **7a**, Figure 2). The 18.3 kcal mol^{-1} lower energy of **7a** than **7b** quantifies the extend to which methyl bridging is normally unfavourable. However, the methyl bridge has no large effect on the chemical shifts (compare **7b** to **7a**): The differences are ca. −10 ppm for C(2,4), +8 ppm for C(3), and ca. −5 ppm for B(6) (Table 1).[18] In particular, the apical B(1) has almost the same d^{11}B value of δ = −52 in **7a** and **7b**.

Figure 2 Geometries (bond lengths in pm) of model compounds **7a−d**, optimized at MP2(fc)/6-31G*[a]



7a, C_1 **7b**, C_s **7c**, C_s **7d**, C_1

[a] **7a**: B1−C2 172.0, B1−C3 173.0, B1−C4 172.1, B1−B5 176.8, B1−B6 175.4, C2−C3 142.7, C3−C4 142.9, C2−B6 153.6, C4−B5 153.8, B5−B6 177.6, B5−µH 133.3, B6−µH 130.9. − **7b**: B1−C2 170.6, B1−C3 173.1, B1−B5 176.4, C2−C3 142.9, C2−B6 154.5, B5−B6 176.3, B5−µCH$_3$ 179.5. − **7c**: B1−C2 171.2, B1−C3 173.7, B1−B5 176.9, C2−C3 142.9, C2−B6 154.9, B5−B6 177.4, B5−µCH$_3$ 1.802. − **7d**: B1−C2 170.5, B1−C3 174.9, B1−C4 169.7, B1−B5 177.0, B1−B6 176.1, C2−C3 143.2, C3−C4 143.7, C2−B6 156.2, C4−B5 154.6, B5−B6 176.2, B5−µCH$_2$ 185.1, B6−µCH$_2$ 180.4.

Because of the large size of **7** and **7′** and the many possible orientations of the ethyl groups, model compounds were computed instead. The addition of methyl substituents to **7b** at B(1) and B(5,6) to give **7c** results in the expected d^{11}B increase of ca. 10 ppm but has no significant influece on the geometry (compare **7b** and **7c**, Figure 2). While the chemical shifts computed for **7c** correspond reasonably well with the measured values for **7** and **7′**, our best model, a 1,2,3,5,6-pentamethyl tricarbahexaborane(7) with a bridging ethyl group, gives better agreement with almost all the data in Table 1. The differences between **7c** and **7d** can be ascribed to electronic effects of the additional alkyl substituents to the cage in **7d**.[19] The constitution of **7** and **7′** with their unique B−alkyl−B bridge is supported by the above computations.

The B−µ-C and B(5)−B(6) distances computed for **7b−d** (Figure 2) show that the bridging alkyls are involved in deltahedral (three-centre) bonding. Corner protonated cyclopropane (a CH_3^+ π complex of ethylene) provides an anology in carbon chemistry.[20]

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

Experimental Section

All synthetic work (except for the purification of **7** and **7′**) and handling of samples was carried out in an atmosphere of N_2 or Ar, observing all necessary precautions to exclude traces of oxygen or moisture. The starting materials were commercial samples (Me_3SnCl or nBu$_3$SnCl) or were prepared as described [Et$_2$BH[4], Et$_2$B−C≡CMe[6b]]. − NMR spectra: Bruker ARX 250 and DRX 500 spectrometers; the latter was equipped with a triple resonance probe head for the ^{13}C{^{1}H, ^{11}B} experiments; chemical shifts are reported with respect to Me$_4$Si [δ^1H (CHCl$_3$/CDCl$_3$) = 7.24; δ^1H (C$_6$C$_5$CD$_2$H) = 2.03; δ^{13}C (CDCl$_3$) = 77.0; δ^{13}C (C$_6$D$_5$CD$_3$) = 20.4] and Et$_2$O−BF$_3$ [δ^{11}B = 0 for Ξ(^{11}B) = 32.083971 MHz]. − Electron impact (EI) mass spectra (70 eV): VARIAN MAT CH 7 with direct inlet.

5,6-μ-Ethyl-1,3,5,6-tetraethyl-2-methyl-2,3,4-tricarba-nido-hexaborane(7) (**7**) *and 5,6-μ-Ethyl-1,2,5,6-tetraethyl-3-methyl-2,3,4-tricarba-nido-hexaborane(7)* (**7′**): Et$_2$BH (1.326 g, 16.7 mmol hydride) was added at −78 °C to diethyl(1-propynyl)borane **1** (1.799 g, 16.7 mmol) containing trimethyltin chloride (0.2 g) within 10 min. The reaction mixture was allowed to warm to room temperature and heated to 50 °C. A further quantity of Et$_2$BH (1.344 g, 16.8 mmol hydride) diluted with BEt$_3$ (20 ml) was added over a period of 90 min, and the mixture was stirred at 50 °C for a further 4 h. All volatile material was removed in vacuo, and fractional distillation of the residue gave a mixture (0.326 g; b.p. 70−80 °C/10^{-3} Torr) of the carboranes **6** (55%), **7** and **7′** (35%) together with small amounts of unidentified products. The distillate was diluted with hexane (10 ml) and stirred in the presence of air for 10 h. The resulting solution was filtered, the solvent was removed in vacuo, and the residue was redistilled. The distillate [0.134 g (7%) of a colorless liquid; b.p. 74−77 °C / 10^{-3} Torr] contained the carboranes **7** and **7′** in a ratio varying from 3:1 to 2:3 in repeated experiments, always in approximately the same yield.

7: ^{1}H NMR (500.1 MHz, 25 °C, CDCl$_3$): δ = 4.03 [s, 1 H, C(4)H], 2.21 (m, 1 H), 2.01 (m, 1 H), 1.02 [t, 3 H, C(3)Et], 1.66 [s, 3 H, C(2)Me], 1.48 (m, 2 H), 0.18 (t, 3 H, μ-Et), 0.23 (m, 2 H), 0.68 [t, 3 H, B(1)Et], 0.88 (m, 2 H), 0.85 (m, 2 H), 1.18 (t, 3 H), 1.13 [t, 3 H, B(5,6)Et]. − ^{11}B NMR (160.6 MHz, 25 °C, CDCl$_3$): δ = −34.4 [B(1)], 3.0, 5.4 [B(5,6)]. − ^{13}C NMR (125.8 MHz, 25 °C, [D$_8$]toluene): δ = 143.3 [C(3)], 96.0 [broad, C(2)], 80.9 [broad, ^1J(^{13}C^{1}H) = 163.0 Hz, C(4)], 11.4 [C(3)*Me*], 24.0, 12.2 [C(2)*Et*], −0.3 (broad), 13.0 (μ-Et), −1.0 (broad), 11.8 [B(1)Et], 8.8 (broad), 8.7 (broad), 13.4, 11.7 [B(5,6)Et]. − EI-MS (70 eV): *m/z* (%) = 230 (5) [M$^+$], 201 (50) [M$^+$ − Et].

7′: ^{1}H NMR (500.1 MHz, 25 °C, CDCl$_3$): δ = 4.12 [s, 1 H, C(4)H], 2.04 (m, 2 H), 1.09 [t, 3 H, C(2)Et], 1.81 [s, 3 H, C(3)Me], 1.60 (m, 2 H), 0.21 (t, 3 H, μ-Et), 0.15 (m, 2 H), 0.70 [t, 3 H, B(1)Et], 0.98 (m, 2 H), 0.86 (m, 2 H), 1.16 (t, 3 H), 1.12 [t, 3 H, B(5,6)Et]. − ^{11}B NMR (160.6 MHz, 25 °C, CDCl$_3$): δ = −34.5 [B(1)], 2.9, 5.7 [B(5,6)]. − ^{13}C NMR (125.8 MHz, 25 °C, [D$_8$]toluene): δ = 137.7 [C(3)], 102.7 [broad, C(2)], 83.2 [broad, ^1J(^{13}C^{1}H) = 161.1 Hz, C(4)], 15.7 [C(3)*Me*], 20.1, 15.0 [C(2)*Et*], −0.2 (broad), 13.4 (μ-Et), −1.1 (broad), 11.3 [B(1)Et], 8.9 (broad), 8.8 (broad), 11.7, 12.5 [B(5,6)Et].

Table 1. Experimental chemical shifts [ppm] of the cage nuclei of **7** and **7′** compared with computed values for model compounds **7a** to **7d** (compare Figure 1) at GIAO-SCF/6-31G*//MP2(fc)/6-31G* [a]

	7	**7′**	**7a**	**7b**	**7c**	**7d**
δ[^{11}B(1)]	−34.5	−34.4	−52.1	−52.3	−43.9	−39.4
δ[^{11}B(5,6)]	5.7, 2.9	5.4, 3.0	7.8, −0.4	−5.1	1.5	4.7, −2.2
δ[^{13}C(2)]	102.7	96.0	86.4	76.1	80.1	88.5
δ[^{13}C(3)]	137.7	143.3	119.5	127.5	132.3	140.0
δ[^{13}C(4)]	83.2	80.9	86.8	76.1	80.1	75.3
δ[^{13}C(μ-CH$_2$)]	−0.2	−0.3	−	−19.7	−8.5	−6.3

[a] Absolute energies [hartree]: **7a**: HF = −230.74721, MP2 = −231.53436; **7b**: HF = −230.71055, MP2 = −231.50560; **7c**: HF = −347.84152, MP2 = −349.04143; **7d**: HF = −464.94023, MP2 = −466.54612

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[18] For the parent 2,3,4-$C_3B_3H_7$ we get IGLO/DZ/MP2(fu)/6-31G* chemical shifts of −52.9 (B1), 0.7 (B5,6), 87.6 (C2,4) and 120.0 (C3); experimental $\delta^{11}B$ data :[2b] −57.9 [B(1)), −0.3 (B(5,6)].

[19] Geometric effects can be shown to be less important: A structure based on **7d** but with the methyl groups at C(2), C(3) and the bridging methylene group replaced by H (i.e. **7c** in the geometry of **7d**) gave computed chemical shifts [B(1): −42.3, B(5): 4.0, B(6): −3.1, C(2): 88.4, C(3): 138.0, C(4): −75.1, C(μ-CH_2): −9.7] close to those for the optimized **7c** geometry.

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