1,1,1-Trisborylalkanes as Precursors for Dicarbapentaboranes(5) − Synthesis, Reactivity, and Structures of *closo*-1,5-Bis(neopentyl)-2,3,4-trichloro-1,5-dicarbapentaborane and Its Derivatives

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Dedicated to Prof. Armin Berndt on the occasion of his 65th birthday

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The treatment of 3,3-dimethyl-1-butynyllithium with boron trichloride followed by double hydroboration with $HBCl_2$ afforded 1,1,1-tris(dichloroboryl)-3,3-dimethylbutane (**1a**), characterized as its catechol derivative **1b**. Analogously, three isomers (**3a**, **4a**, and **5a**) were obtained with trimethylsilylacetylide and identified as catechol derivatives **3b**, **4b**, and **5b**. On heating, **1a** formed 2,3,4-trichloro-1,5-dicarba-*closo*-pentaborane(5) (**6a**) with elimination of boron trichloride. Compound **6a** reacted with methyllithium and trimethylaluminium, and also with pentamethylsilazane and acetylides, to give the corresponding carborane derivatives **6c**, **6d**, **6e**, and **6f**. The compositions of the products followed from analytical data and X-ray structure analyses of **1b**, **4b**, **5b**, **6a**, and **6f**.

Introduction

The first synthesis of triborylmethane derivatives was reported in 1968, by Matteson and Castle,[1,2] who obtained methanetriboronic esters by treatment of dimethoxychloroborane and carbon tetrachloride with lithium in tetrahydrofuran. Subsequently, tris(dichloroboryl)methane was synthesized.[3] Köster et al.[4] described the preparation of pentaalkyl-1,5-dicarba-*closo*-pentaboranes(5) by hydroboration of dialkyl(1-alkynyl)boranes $R_2BC{\equiv}CR^1$ with tetraalkyldiboranes $(R_2BH)_2$. They obtained 1,1-bis(dialkylboryl)-1-alkenes, although detection of 1,1,1-tris(dialkylboryl)alkanes as precursors for the carboranes was unsuccessful.[4] In 1995 a new route to pentaethyl-1,5-dicarba-*closo*-pentaborane(5) was established, through the use of a large excess of $(Et_2BH)_2$ as a "hydride bath" to give a 1-carba-*arachno*-pentaborane(10) derivative[5] as precursor.[6] Its formation most probably occurred through [BH]-catalyzed condensation of two molecules of undetectable 1,1,1-tris(diethylboryl)propane.[6]

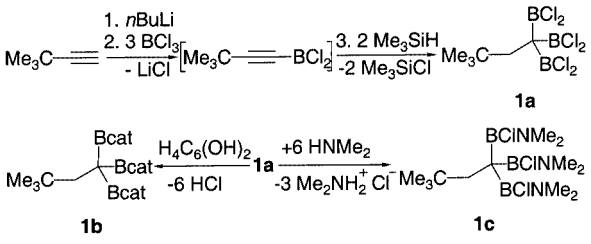
The *closo*-C_2B_3-carboranes warrant particular interest because their structure and bonding may be described as midway between classical and nonclassical. In the last decade, the structures of these smallest *closo*-carboranes have been elucidated by X-ray diffraction analyses of amino-substituted derivatives[7,8] and pentaethyl-1,5-dicarba-*closo*-pentaborane(5),[6,9] by electron density distribution,[9] and by ab initio computations.[10]

We report here on the synthesis and the characterization of 1,1,1-tris(dichloroboryl)-3,3-dimethylbutane and its transformation into 2,3,4-trichloro-1,5-dicarba-*closo*-pentaborane(5) (**6a**). Substitution reactions of **6a** and the syntheses of other tris(dichloroboryl)alkanes are also described.

Results and Discussion

1,1,1-Tris(dichloroboryl)-3,3-dimethylbutane (1a)

The synthesis of **1a** started with lithiation of 3,3-dimethyl-1-butyne by *n*-butyllithium, followed by boron/metal exchange with BCl_3 and a double hydroboration of the boryl alkyne with dichloroborane prepared in situ[11] (Scheme 1). This reaction sequence afforded a 42% yield of **1a**, a colorless and extremely air- and moisture-sensitive liquid. Its ^{11}B NMR spectrum showed a signal at $\delta = 58.7$,



Scheme 1

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and in the ^{1}H NMR spectrum signals for the *tert*-butyl group (δ = 0.94) and the methylene group (δ = 2.77) were observed. The ^{13}C NMR spectrum exhibited four resonances: at δ = 31.9 (CH_3), 33.8 (CMe_3), 55.2 (CH_2), and 59 (broad, CB_3). A NICI mass spectrum showed the molecular ion peak [M^+] at *m*/*z* = 328 as the base peak.

On treatment of **1a** with three equivalents of catechol in dichloromethane at −78 °C, compound **1b** was synthesized in 95% yield (Scheme 1). Compound **1b** is a colorless solid, soluble in dichloromethane, toluene, and THF. Its composition was determined by NMR spectroscopy, MS spectrometry, and an X-ray structure analysis, single crystals of **1b** being grown from a solution in dichloromethane at room temperature. The molecular structure of **1b** in the crystal is shown in Figure 1. The heterocycles are planar and the boron-bound carbon atom C1 is almost tetrahedral. For all distances and bonding angles, no significant differences from those in similar compounds[12] are observed.

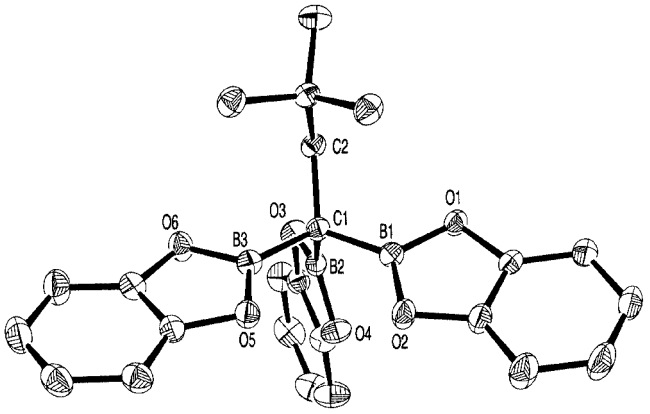
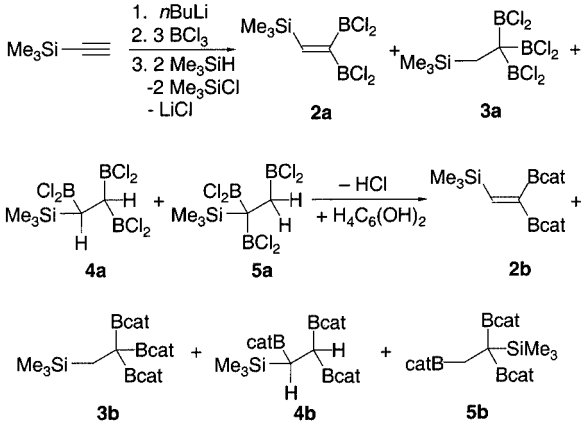


Figure 1. Molecular structure of **1b** in the crystal; selected bond lengths [Å] and angles [°]: B1-C1 1.569(2), B2−C1 1.573(2), B3−C1 1.575(2), B1−O1 1.395(1), B1−O2 1.383(1), B2−O3 1.386(1), B2−O4 1.388 (1), B3−O5 1.388(1), B3−O6 1.391(1), C1−C2 1.570(1), B1−C1−B2 103.51(8), B2−C1−B3 102.44(9), B1−C1−B3 114.79(9), B1−C1−C2 113.27(9), B2−C1−C2 108.72(8), B3−C1−C2 112.86(9)

To obtain information on its reactivity, **1a** was treated with six equivalents of dimethylamine to form **1c** as a colorless, viscous liquid in 88% yield (Scheme 1). Its ^{11}B NMR spectrum showed a signal at δ = 38.5, confirming that each boryl group had one dimethylamino and one chlorine substituent. In the ^{1}H and ^{13}C NMR spectra, the signals of the *tert*-butyl group, the dimethylamino groups, and the methylene group were found in the expected regions. As in **1a** and **1b**, the resonance of the quaternary CB_3 carbon atom was broad (δ = 42). The EI mass spectrum of **1c** exhibited the molecular ion peak [M^+] at *m*/*z* = 353.

1,1-Bis(dichloroboryl)-2-trimethylsilylethene (2a), 1,1,1-Tris(dichloroboryl)-2-trimethylsilylethane (3a), 1,1,2-Tris(dichloroboryl)-2-trimethylsilylethane (4a), and 1,1,2-Tris(dichloroboryl)-1-trimethylsilylethane (5a)

Treatment of trimethylsilylacetylene with *n*-butyllithium, BCl_3, and two equivalents of $HBCl_2$ in the same manner as described above provided isomeric products (Scheme 2). On distillation of the reaction mixture, two fractions were obtained, these containing 1,1-bis(dichloroboryl)-2-trimethylsilylethene (**2a**), and a mixture of **3a**, **4a**, and **5a**.



Scheme 2

The ^{11}B NMR spectrum of **2a** showed signals at δ = 57.4 and 60.5, indicating two inequivalent boron atoms, while the ^{29}Si NMR spectrum exhibited a signal at δ = −3.2, in the range for trimethylalkenylsilanes.[13] In the ^{1}H NMR spectrum, the signals for the $SiMe_3$ group and the olefinic proton were detectable at δ = 0.22 and 7.12, respectively. The EI mass spectrum of **2a** showed the molecular ion peak [M^+] at *m*/*z* = 260. Treatment of **2a** with catechol gave the corresponding catechol derivative **2b** in 85% yield, and this was characterized by ^{1}H and ^{11}B NMR spectroscopy and EI mass spectrometry. The NMR spectroscopic data of the second fraction could not be interpreted; its ^{29}Si NMR spectrum indicated the presence of three saturated compounds. However, the NICI mass spectrum showed only one molecular ion peak [M^+] at *m*/*z* = 342, indicating the presence of constitutional isomers. In order to obtain evidence regarding the product mixture and to characterize the components, the mixture was treated with an excess of catechol. The NMR spectroscopic data of the catechol derivatives indicated the presence of **3b**, **4b**, and **5b** in the ratio 15:8.5:1. In the EI mass spectrum, the molecular ion peak [M^+] of the isomers **3b**, **4b**, and **5b** was found at *m*/*z* = 456.

Crystals of compounds **4b** and **5b** suitable for X-ray structure analysis were obtained from solutions of the catecholboryl isomers in dichloromethane at 4 °C. The structures are shown in Figure 2 and 3, respectively. All bond lengths and angles are normal, and the coordination of the boron atoms is almost trigonal planar.

For the formation of three isomeric compounds **3a**, **4a**, and **5a**, we propose the following mechanism. In the first step, hydroboration of [$Me_3Si-C\equiv C-BCl_2$] occurs regioselectively to give product **2a**. $HBCl_2$ then hydroborates **2a** in both directions, giving rise to the compounds **3a** and **4a**, with the former being favored. Moreover, the trimethylsilyl group has the tendency to migrate,[14] and the trimethylsilyl and one dichloroboryl group in **3a** change their positions, with formation of **5a** (Scheme 3).

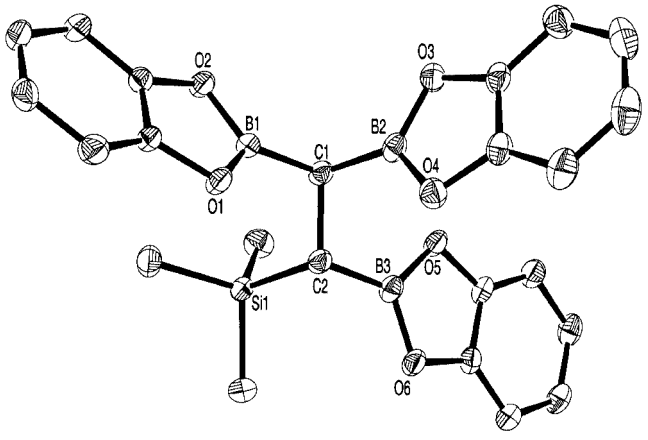


Figure 2. Molecular structure of **4b** in the crystal; selected bond lengths [Å] and angles [°]: B1−C1 1.564(3), B2−C1 1.560(3), B3−C2 1.548(3), B1−O1 1.388(3), B1−O2 1.392(2), B2−O3 1.391(3), B2−O4 1.393(3), B3−O5 1.395(3), B3−O6 1.393(3), C1−C2 1.579(3), C2−Si1 1.913(2), B1−C1−B2 109.5(2), B3−C2−C1 113.1(2), B1−C1−C2 111.8(2), B2−C1−C2 111.1(2), C1−C2−Si1 112.37(13), B3−C2−Si1 106.10(14)

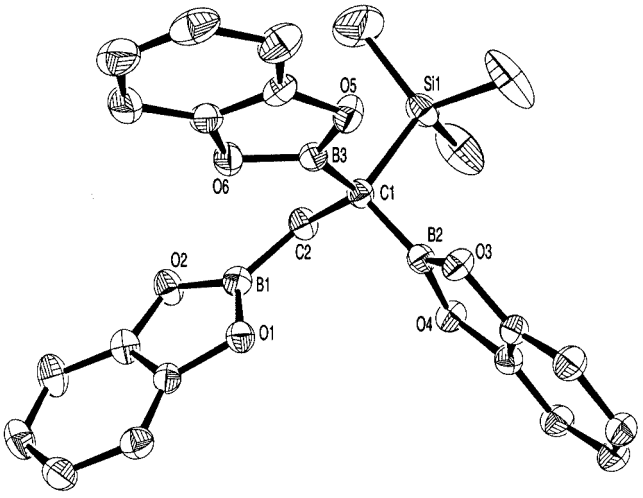
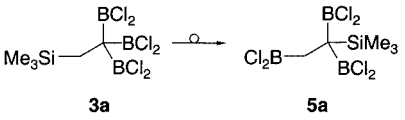


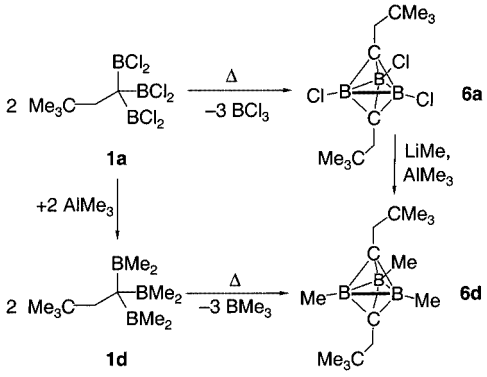
Figure 3. Molecular structure of **5b** in the crystal; selected bond lengths [Å] and angles [°]: B1−C2 1.555(3), B2−C1 1.556(3), B3−C1 1.551(3), B1−O1 1.388(3), B1−O2 1.383(2), B2−O3 1.392(2), B2−O4 1.395(2), B3−O5 1.391(2), B3−O6 1.389(2), C1−C2 1.566(2), C1−Si1 1.925(2), B2−C1−B3 110.98(15), B2−C1−C2 112.88(15), B3−C1−C2 111.30(15), B1−C2−C1 115.75(15), B2−C1−Si1 105.89(12), B3−C1−Si1 108.18(12)



Scheme 3

2,3,4-Trichloro-1,5-dicarba-*closo*-pentaborane(5) (6a) and Its Substitution

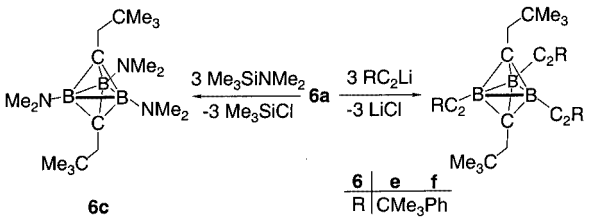
On heating neat **1a** at 170 °C for two hours, elimination of BCl_3 occurred with formation of the *closo*-C_2B_3 carborane **6a**, which was obtained by distillation as a colorless, air-sensitive solid in 25% yield (Scheme 4). A signal at δ = 22.1 in its ^{11}B NMR spectrum supported the carborane structure. The ^1H NMR spectrum showed two singlets for the methyl and the methylene protons, at δ = 1.02 and 2.09, respectively, and the ^{13}C NMR spectrum exhibited four signals for CH_3 (δ = 29.7), the quaternary carbon atom (δ = 31.6), CH_2 (δ = 38.5), and the apical carbon atoms of the cluster (δ = 94, br.). The highest peak observed in an EI mass spectrum of **6a** was found at *m*/*z* = 289 [$M^+ - CH_3$], but the PICI mass spectrum showed [M^+] at *m*/*z* = 303 as the base peak. The composition of **6a** was confirmed by an X-ray structure analysis. The trimethyl derivative **6d** may be obtained by two routes (Scheme 4). Firstly, methylation of **1a** gave **1d**, which on heating was transformed into **6d** with elimination of trimethylborane. Compound **1d** was characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy and by PICI mass spectrometry.



Scheme 4

The second route is of general interest, because **6d** was formed by direct methylation of **6a** with MeLi or $AlMe_3$ at low temperature. Substitution reactions of *closo*-C_2B_3 carboranes have not previously been investigated. In general, substitution reactions at boron atoms in carboranes are difficult[15] and not as developed as those at carbon atoms. The first successes were achieved with *closo*-C_2B_{10} carboranes.[15,16] The ^{11}B NMR signal for **6d** was shifted to higher field (δ = 17.3) relative to that of **6a**. In the ^1H NMR spectrum, the expected signals for *tert*-butyl (δ = 0.99) and the methylene group (δ = 2.17) were observed, whilst the signal of the methyl group at boron was located at δ = 1.23. The ^{13}C NMR spectrum exhibited the resonances of the *tert*-butyl substituent at δ = 29.7 for the methyl groups and at δ = 31.6 for the quaternary carbon atom. The signal of the methylene carbon atom appeared at δ = 39.6, while the signal for the methylboron group was broad at δ = 14. No signal was found for the apical carbon atoms. An EI mass spectrum of **6d** showed the molecular ion peak [M^+] at *m*/*z* = 244. When **6a** was treated with pentamethylsilazane at −30 °C (Scheme 5), colorless **6c** was formed as a solid in good yields. Its ^{11}B NMR spectrum showed a signal at δ = 21.3, in agreement with the reported[7,8] amino-substituted *closo*-$(RC)_2(BN\mathit{i}Pr_2)_3$. In the ^1H and ^{13}C NMR spectra, the expected signals for the *tert*-butyl, dimethylamino, and methylene groups were found, although no resonance was detected for the quaternary CB_3 carbon atom. The EI mass

spectrum of **6c** showed the molecular ion peak [M^+] at *m*/*z* = 331.



Scheme 5

Treatment of **6a** with 3,3-dimethyl-1-butynyllithium and 2-phenylethynyllithium afforded **6e** and **6f**, respectively (Scheme 5). Compound **6e** is a colorless solid and **6f** a yellow solid. Their compositions were determined by NMR spectroscopy, MS spectrometry, and X-ray structure analysis.

With sterically demanding lithium reagents (*t*BuLi, LiN*i*Pr$_2$, *n*BuLi, PhLi), only product mixtures were obtained. NMR spectroscopic and MS spectrometric data indicated the presence of the expected products; isolation of them failed, however. Attempts to substitute the chloro atoms with OH, OMe, O*t*Bu, and catechol were unsuccessful. In all cases the ^{11}B NMR spectra showed low-field signals at about δ = 32, indicating the decomposition of the carborane framework and the formation of dialkoxyboranes.

Discussion of the Structure of 6

The structure of **6a** was obtained by performing a single-crystal X-ray analysis. Colorless crystals of **6a** were grown from a solution in pentane at 4 °C; its molecular structure is shown in Figure 4. In the C_2B_3 framework, the B−B [1.842(3)−1.855(3) Å] and B−C distances [1.541(3)−1.586(3) Å] are in the range of the corresponding values for the parent *closo*-$C_2B_3H_5$, determined by electron diffraction.[17] The B−B bond lengths are substantially shorter than the structure data [1.965(8) Å] published by Meller et al.,[7,8] who classified their molecules as bicycles. The B−B distances in **6a** are somewhat shorter than those in the carborane $C_2B_3Et_5$ reported by Köster et al.[6] [1.876(4) Å]. Nevertheless, the B−B bond in **6a** is long and the B−C bond short in comparison with data relating to octahedral carboranes [B−B: 1.72 Å, C−B: 1.62 Å in 1,6-$C_2B_4H_6$].[17] The C_2B_3 carborane may be described as a classically bonded structure in which the trigonal bipyramid is bonded through 2c,2e C−B bonds, but involves no strong B−B overlap.[17,18] This was confirmed by measurements of the electron density distribution of the *closo*-cluster $C_2B_3Et_5$, which gave no electron density in the B−B−B plane of the molecule;[9] electron density was, however, found above each triangular CB_2 face. This indicates that the contribution of nonclassical multicenter bonds is as important as that of the conventional 2c,2e bonds.[9]

As far as the X-ray data are concerned, the classification of the C_2B_3 framework is ambiguous. In the light of ^{11}B NMR spectra of several dialkylchloroboranes in cyclic or

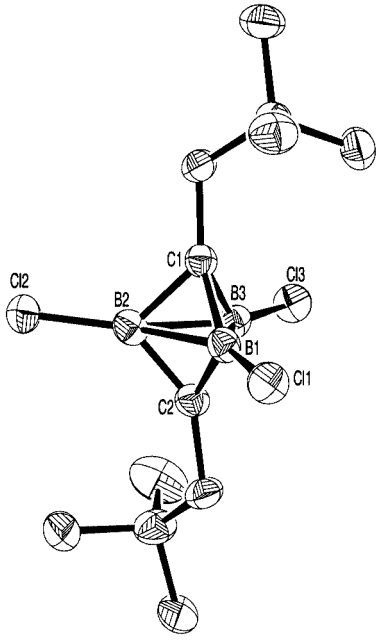


Figure 4. Molecular structure of **6a** in the crystal; selected bond lengths [Å] and angles [°]: C1−B1 1.541(3), C1−B2 1.580(3), C1−B3 1.569(3), C2−B1 1.586(3), C2−B2 1.546(3), C2−B3 1.550(3), B1−B2 1.842(3), B1−B3 1.853(3), B2−B3 1.855(4), B1−Cl1 1.746(2), B2−Cl2 1.742(2), B3−Cl3 1.742(3), C1−B1−C2 93.6(2), C1−B2−C2 93.6(2), C1−B3−C2 93.9(2), B2−B1−B3 60.28(12), B1−B2−B3 60.15(12), B1−B3−B2 59.57(13), B1−C1−B2 72.3(2), B1−C1−B3 73.1(2), B2−C1−B3 72.2(2), B1−C2−B2 72.1(2), B1−C2−B3 72.4(2), B2−C2−B3 73.7(2)

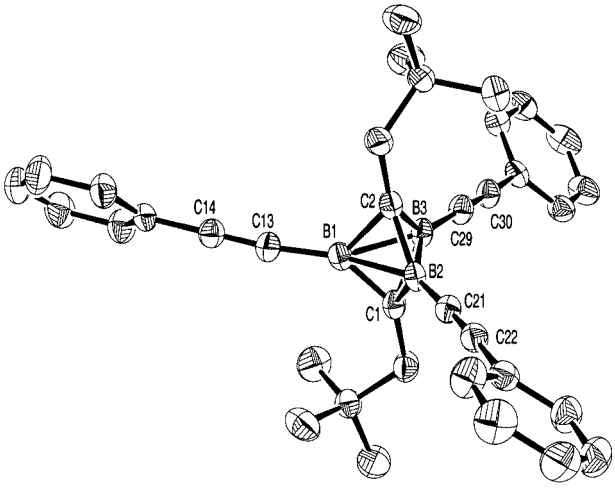


Figure 5. Molecular structure of **6f** in the crystal; selected bond lengths [Å] and angles [°]: C1−B1 1.536(3), C1−B2 1.567(3), C1−B3 1.594(3), C2−B1 1.596(3), C2−B2 1.557(3), C2−B3 1.539(3), B1−B2 1.855(3), B1−B3 1.852(3), B2−B3 1.849(3), B1−C13 1.511(3), B2−C21 1.508(3), B3−C29 1.509(3), C13−C14 1.208(3), C21−C22 1.206(3), C29−C30 1.206(3), C1−B1−C2 93.7(2), C1−B2−C2 94.1(2), C1−B3−C2 93.7(2), B2−B1−B3 59.83(12), B1−B2−B3 59.99(13), B1−B3−B2 60.19(13), B1−C1−B2 73.4(2), B1−C1−B3 72.5(2), B2−C1−B3 71.6(2), B1−C2−B2 72.1(2), B1−C2−B3 72.4(2), B2−C2−B3 73.3(2)

acyclic organoboranes, one would expect a signal at about δ = 74 for **6a** as a bicycle.[19] In fact, the resonance for **6a** is at higher field (δ = 22.1), which is compatible with a nonclassical description of the bonding situation and supports the carborane character of **6a**.

Crystals of compounds **6e** and **6f** suitable for X-ray structure analyses were obtained from toluene at 4 °C. As **6e** is disordered in the crystal, only the structure of **6f** is discussed here, because of its better crystallographic data. The molecular structure is shown in Figure 5. The B−B [1.848(3)−1.855(3) Å] and B−C [1.536(3)−1.596(3) Å] distances are in the same range as those in the chloro-substituted compound **6a**. As no elongations of the B−B bond lengths relative to those in **6a** are observed and the ^{11}B NMR spectra of **6e** and **6f** showed signals at δ = 11.4 (expected resonances for dialkylalkynylboranes lie at about δ = 72[20]) both compounds are regarded as carboranes.

Conclusion

In this paper we report on the treatment of alkynyllithium with boron trichloride, followed by double hydroboration with $HBCl_2$. 3,3-Dimethyl-1-butynyllithium as starting material afforded 1,1,1-tris(dichloroboryl)-3,3-dimethylbutane (**1a**), which was transformed into the chloro-substituted 1,5-dicarba-*closo*-pentaborane(5) **6a**. Furthermore, it was shown that substitution reactions at **6a** occurred in good yields. Substitution of **6a** with small groups (methyl in **6d**, dimethylamino in **6c**, or rod-like acetylides in **6e** and **6f**) was successful, while bulky substituents produced inseparable product mixtures of unknown composition. Treatment with oxygen-containing reagents decomposed the carborane framework. In the case of lithium trimethylsilylacetylide as starting material, a mixture of three constitutional isomers was formed.

Experimental Section

General: Reactions were carried out under dry argon or nitrogen, by standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. Glassware was dried with a heat gun under high vacuum. ^1H, ^{11}B, and ^{13}C NMR: Bruker DRX 200 spectrometer, $Et_2O{\cdot}BF_3$ was used as the external standard for ^{11}B NMR. The signals of the deuterated solvents were used as internal references for ^1H and ^{13}C NMR spectra, and calculated relative to TMS. The mass spectra were measured on a ZAB-2F VH Micromass CTD spectrometer (EI and HR-EI techniques) and on a Jeol MS station JMS 700 (NICI, PICI, EI, and HR-EI techniques). Melting points (uncorrected) were measured with a Büchi apparatus in capillaries that were filled under argon or nitrogen, and sealed.

1,1,1-Tris(dichloroboryl)-3,3-dimethylbutane (1a): 3,3-Dimethyl-1-butyne (8.22 g, 0.1 mol) was added at −15 °C to a solution of *n*BuLi (0.1 mol) in 230 mL of pentane. The mixture was allowed to warm to room temp. and stirred for 2 h. The suspension was then cooled to −78 °C and added at −78 °C to a solution of BCl_3 (37.5 g, 0.32 mol) in 50 mL of pentane. After the mixture had stirred for 1 h, a solution of Me_3SiH (14.9 g, 0.2 mol) in 20 mL of pentane was added over 30 min from a dropping funnel cooled to − 30 °C. The reaction mixture was allowed to warm slowly to room temp. and was stirred for 10 h. After separation of the solution from the precipitate, the solvent was evaporated and the residue was distilled at 63 °C/0.057 mbar to yield **1a** (13.67 g, 41.6% yield) as a colorless and extremely air-sensitive liquid. ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.94 [s, 9 H, $C(CH_3)_3$], 2.77 (s, 2 H, CH_2). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 58.7. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 31.9 [$C(CH_3)_3$], 33.8 [$C(CH_3)_3$], 55.2 (CH_2), 59 [br., $C(BCl_2)_3$]. EI-MS: *m*/*z* (%) = 313 (1) [$M^+ - CH_3$], 246 (1) [$M^+ - BCl_2$], 231 (4) [$M^+ - CH_3 - BCl_2$], 195 (1) [$M^+ - CH_3 - BCl_2 - HCl$], 128 (15) [$M^+ - 2BCl_2 - HCl$], 115 (51) [$M^+ - 2BCl_2 - HCl - CH_3$], 81 (63) [$BCl_2^+$], 57 (100) [$C_4H_9^+$], 41 (62) [$C_3H_5^+$]. NICI-MS: *m*/*z* (%) = 328 (100) [M^+].

1,1,1-Tris(catecholboryl)-3,3-dimethylbutane (1b): Catechol (660 mg, 6 mmol) was dissolved in CH_2Cl_2 (40 mL), and the solution was cooled to −60 °C. Compound **1a** (660 mg, 2 mmol) was then added dropwise to the reaction mixture, and the solution was allowed to warm to room temp. The CH_2Cl_2 was removed under vacuum to give colorless **1b** (840 mg, 95.0%, m.p. 163 °C). ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.83 [s, 9 H, $C(CH_3)_3$], 2.62 (s, 2 H, CH_2), 7.03−7.27 (m, 12 H, C_6H_4). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 34.7. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 30.0 [$C(CH_3)_3$], 32.6 [$C(CH_3)_3$], 43.3 (CH_2), 112.7, 122.7, 148.2 (C_6H_4). EI-MS: *m*/*z* (%) = 440 (21) [M^+], 425 (5) [$M^+ - CH_3$], 383 (42) [$M^+ - C_4H_9$], 320 (4) [$M^+ - C_6H_4O_2BH$], 305 (1) [$M^+ - CH_3 - C_6H_4O_2BH$], 120 (4) [$C_6H_4O_2BH^+$], 57 (100) [$C_4H_9^+$]. HR-MS (EI): *m*/*z* = 440.1797 [M^+]; calcd. for $^{12}C_{24}{}^1H_{23}{}^{11}B_3{}^{16}O_6$: 440.1820 (Δ = 2.3 mmu).

1,1,1-Tris[chloro(dimethylamino)boryl]-3,3-dimethylbutane (1c): Compound **1a** (2.38 g, 7.25 mmol) was added to a solution of dimethylamine (1.96 g, 43.5 mmol) in 40 mL of hexane at −60 °C. The mixture was allowed to warm to room temp., the solution was separated from the precipitate, the solvent was evaporated, and the colorless oil **1c** was dried under vacuum. Yield: 2.27 g (88.4%). ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.93 [s, 9 H, $C(CH_3)_3$], 2.20 (s, 2 H, CH_2), 2.86 [s, 9 H, $N(CH_3)_2$], 2.87 [s, 9 H, $N(CH_3)_2$]. ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 38.5. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 31.0 [$C(CH_3)_3$], 33.0 [$C(CH_3)_3$], 40.0, 40.6 [$N(CH_3)_2$], 42 (br., CB_3), 48.3 (CH_2). EI-MS: *m*/*z* (%) = 353 (2) [M^+], 296 (10) [$M^+ - C_4H_9$], 262 (2) [$M^+ - HBClN(CH_3)_2$], 251 (4) [$M^+ - C_4H_9 - HN(CH_3)_2$], 228 (11) [$M^+ - BClN(CH_3)_2 - Cl$], 207 (9) [$M^+ - C_4H_8 - BClN(CH_3)_2$], 171 (100) [$M^+ - 2HBClN(CH_3)_2$], 90 (61) [$BClN(CH_3)_2^+$], 57 (48) [$C_4H_9^+$]. HR-MS (EI): *m*/*z* = 296.1006 [$M^+ - C_4H_9$]; calcd. for $^{12}C_8{}^1H_{20}{}^{11}B_3{}^{35}Cl_3{}^{14}N_3$: 296.1002 (Δ = 0.4 mmu).

1,1,1-Tris(dimethylboryl)-3,3-dimethylbutane (1d): Compound **1a** (1.00 g, 3.1 mmol) was dissolved in hexane (20 mL), and a solution of $AlMe_3$ (2 mL, 20.8 mmol) in 10 mL of hexane was added at −78 °C. The mixture was allowed to warm to room temp., the solution was separated from the precipitate, and all volatile components were removed under vacuum to give **1d** (520 mg, 83.0%) as a pale yellow oil. ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.78 [s, 18 H, $B(CH_3)_2$], 0.82 [s, 9 H, $C(CH_3)_3$], 2.54 (s, 2 H, CH_2). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 82.6. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 16.5 [$B(CH_3)_2$], 30.9 [$C(CH_3)_3$], 32.6 [$C(CH_3)_3$], 46 (br.,CB_3), 50.7 (CH_2). EI-MS: *m*/*z* (%) = 150 (25) [$M^+ - B(CH_3)_3$], 149 (12) [$M^+ - C_4H_9$], 93 (64) [$M^+ - B(CH_3)_3 - C_4H_9$], 57 (100) [$C_4H_9^+$], 41 (97) [$C_3H_5^+$]. PICI-MS: *m*/*z* (%) = 207 (30) [$M^+ + H$], 57 (100) [$C_4H_9^+$]. HR-MS (EI): *m*/*z* = 150.1742 [$M^+ - B(CH_3)_3$]; calcd. for $^{12}C_9{}^1H_{20}{}^{11}B_2$: 150.1733 (Δ = 0.9 mmu): *m*/*z* = 149.1786 [$M^+ - C_4H_9$]; calcd. for $^{12}C_8{}^1H_{20}{}^{11}B_3$: 149.1727 (Δ = 5.9 mmu): *m*/*z* =

93.1045 [$M^+ - B(CH_3)_3 - C_4H_9$]; calcd. for $^{12}C_5{}^1H_{11}{}^{11}B_2$: 93.1044 ($\Delta$ = 0.1 mmu).

1,1-Bis(dichloroboryl)-2-trimethylsilylethene (2a), 1,1,1-Tris(dichloroboryl)-2-trimethylsilylethane (3a), 1,1,2-Tris(dichloroboryl)-2-trimethylsilylethane (4a), and 1,1,2-Tris(dichloroboryl)-1-trimethylsilylethane (5a): Trimethylsilylacetylene (9.82 g, 0.1 mol) was added at −15 °C to a solution of *n*BuLi (0.1 mol) in 230 mL of pentane. The mixture was allowed to warm to room temp. and stirred for 2 h. The suspension was then cooled to −78 °C and added at −78 °C to a solution of BCl_3 (37.5 g, 0.32 mol) in 50 mL of pentane. After the mixture had stirred for 1 h, a solution of Me_3SiH (14.9 g, 0.2 mol) in 20 mL of pentane was added over 30 min from a dropping funnel cooled to −30 °C. The reaction mixture was allowed to warm slowly to room temp. and stirred for 10 h. The solution was separated from the precipitate, the solvent was evaporated, and the residue was distilled to yield two fractions of colorless, extremely air-sensitive liquids: **2a** (43 °C/0.065 mbar, 6.00 g, 22.9%), and a mixture of **3a**, **4a**, and **5a** (65 °C/0.065 mbar, 5.23 g, 15.2%).

Compound 2a: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 7.12 (s, 1 H, CH). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 60.5 (s, 1B), 57.4 (s, 1B). ^{29}Si NMR ($CDCl_3$, 40 MHz): δ = −3.3. EI-MS: *m*/*z* (%) = 260 (6) [M^+], 245 (58) [$M^+ - CH_3$], 225 (10) [$M^+ - Cl$], 163 (34) [$M^+ - H - CH_3 - BCl_2$], 73 (100) [$Si(CH_3)_3{}^+$].

Mixture 3a, 4a, 5a: ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 63.4 (s, 1B), 61.0 (s, 1B). ^{29}Si NMR ($CDCl_3$, 40 MHz): δ = 4.2, 4.3, 4.7. EI-MS: *m*/*z* (%) = 327 (12) [$M^+ - CH_3$], 272 (1) [$M^+ - HCl - Cl$], 245 (2) [$M^+ - H - BCl_2 - CH_3$], 73 (100) [$Si(CH_3)_3{}^+$], 36 (82) [HCl^+]. NICI-MS: *m*/*z* (%) = 342 (29) [M^+].

1,1-Bis(catecholboryl)-2-trimethylsilylethene (2b): Catechol (440 mg, 4 mmol) was dissolved in CH_2Cl_2 (40 mL) and cooled to −60 °C. Compound **2a** (520 mg, 2 mmol) was then added dropwise to the reaction mixture, and the solution was allowed to warm to room temp. The CH_2Cl_2 was removed under vacuum to give **2b** (750 mg, 84.6% yield) as a pale beige solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.31 [s, 9 H, $Si(CH_3)_3$], 6.99−7.36 (m, 8 H, C_6H_4), 7.95 (s, 1 H, CH). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 32.1. EI-MS: *m*/*z* (%) = 336 (25) [M^+], 321 (82) [$M^+ - CH_3$], 262 (4) [$M^+ - H - Si(CH_3)_3$], 229 (3) [$M^+ + H -$ Bcat], 203 (12) [$M^+ + H - CH_3 -$ Bcat], 92 (16) [$C_6H_4O^+$], 73 (100) [$Si(CH_3)_3{}^+$]. HR-MS (EI): *m*/*z* = 336.1187 [M^+]; calcd. for $^{12}C_{17}{}^1H_{18}{}^{11}B_2{}^{16}O_4{}^{28}Si$: 336.1161 ($\Delta$ = 2.6 mmu).

1,1,1-Tris(catecholboryl)-2-trimethylsilylethane (3b), 1,1,2-Tris(catecholboryl)-2-trimethylsilylethane (4b), and 1,1,2-Tris(catecholboryl)-1-trimethylsilylethane (5b): Catechol (660 mg, 6 mmol) was dissolved in CH_2Cl_2 (40 mL) and cooled to −60 °C. The mixture of **3a**, **4a**, and **5a** (690 mg, 2 mmol) was then added dropwise to the catechol, and the solution was allowed to warm to room temp. The CH_2Cl_2 was removed under vacuum to give a beige solid. Yield: 810 mg **3b**, **4b**, **5b** (88.7%), product ratio **3**:**4**:**5** = 15:8.5:1 (determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$, 200 MHz): **3b:** δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 1.99 (s, 2 H, CH_2), 6.93−7.30 (m, 12 H, C_6H_4); **4b:** δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 1.82 [d, $^3J_{H,H}$ = 9.5 Hz, 1 H, $(CH_3)_3SiCH$Bcat], 2.18 [d, $^3J_{H,H}$ = 9.5 Hz, 1 H, $CH(Bcat)_2$], 6.93−7.30 (m, 12 H, C_6H_4); **5b:** δ = 0.01 [s, 9 H, $Si(CH_3)_3$], 1.75 (s, 2 H, CH_2), 6.93−7.30 (m, 12 H, C_6H_4). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 35.8. ^{29}Si NMR ($CDCl_3$): δ = 4.0, 5.6, 8.1. EI-MS: *m*/*z* (%) = 456 (9) [M^+], 441 (7) [$M^+ - CH_3$], 383 (1) [$M^+ - Si(CH_3)_3$], 322 (7) [$M^+ - CH_3 -$ Bcat], 203 (1) [$M^+ - CH_3 -$ 2Bcat], 92 (7) [$C_6H_4O^+$], 73 (100) [$Si(CH_3)_3{}^+$]. HR-MS (EI): *m*/*z* = 456.1551 [M^+]; calcd. for $^{12}C_{23}{}^1H_{23}{}^{11}B_3{}^{16}O_6{}^{28}Si_1$: 456.1543 ($\Delta$ = 0.8 mmu).

2,3,4-Trichloro-1,5-dicarba-*closo*-pentaborane(5) (6a): Neat **1a** (5.30 g, 11.8 mmol) was heated for 2 h at 170 °C and elimination of BCl_3 was observed. The brown product mixture was distilled at 54 °C/0.02 mbar to give colorless, air-sensitive **6a** (606 mg, 24.6%), m.p. 61 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.02 [s, 9 H, $C(CH_3)_3$], 2.09 (s, 2 H, CH_2). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 22.1. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.7 [$C(CH_3)_3$], 31.6 [$C(CH_3)_3$], 38.5 (CH_2), 94 (br., CB_3). EI-MS: *m*/*z* (%) = 289 (87) [$M^+ - CH_3$], 247 (21) [$M^+ - C_4H_9$], 57 (100) [$C_4H_9{}^+$]. PICI-MS: *m*/*z* (%) = 303 (100) [$M^+ - H$], 289 (11) [$M^+ - CH_3$], 261 (5) [$M^+ - C_3H_7{}^+$]. HR-MS (EI): *m*/*z* = 304.1034 [M^+]; calcd. for $^{12}C_{12}{}^1H_{22}{}^{11}B_3{}^{35}Cl_3$: 304.1001 ($\Delta$ = 3.3 mmu).

2,3,4-Tris(dimethylamino)-1,5-dicarba-*closo*-pentaborane(5) (6c): Pentamethylsilazane (310 mg, 2.20 mmol) was added at −30 °C to a solution of **6a** (224 mg, 0.73 mmol) in 15 mL of pentane. The solution was allowed to warm to room temp. and after 4 h stirring all volatile components were removed. Compound **6c** was obtained as a colorless oil. Yield: 193 mg (79.4%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.00 [s, 18 H, $C(CH_3)_3$], 2.16 (s, 4 H, CH_2), 2.77 [s, 18 H, $N(CH_3)_2$]. ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 21.3. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 32.1 [$C(CH_3)_3$], 34.9 [$C(CH_3)_3$], 38.9 (CH_2), 42.5 [$N(CH_3)_2$]. EI-MS: *m*/*z* (%) = 331 (45) [M^+], 316 (1) [$M^+ - CH_3$], 260 (1) [$M^+ - C_5H_{11}$], 57 (100) [$C_4H_9{}^+$], 44 (73) [$N(CH_3)_2{}^+$]. HR-MS (EI): *m*/*z* = 331.3499 [M^+]; calcd. for $^{12}C_{18}{}^1H_{40}{}^{11}B_3{}^{14}N_3$: 331.3497 ($\Delta$ = 0.2 mmu).

2,3,4-Trimethyl-1,5-dicarba-*closo*-pentaborane(5) (6d):
a) Compound **1d** (500 mg, 2.43 mmol) was dissolved in 5 mL of toluene, and this was heated under reflux for 2 h. The solvent and volatile compounds were removed under vacuum to yield a brown, viscous residue, consisting of **6d** and some by-products.
b) Compound **6a** (124 mg, 0.4 mmol) was dissolved in 10 mL of hexane and treated at −78 °C with a solution of $AlMe_3$ (0.4 mL, 4 mmol) in 5 mL of hexane. The reaction mixture was allowed to warm slowly to room temp. After filtration of a solid, the solvent was removed and **6d** was dried under vacuum to afford a pale yellow, viscous oil. Yield: 71 mg (71.6%).

c) Compound **6a** (170 mg, 0.56 mmol) was dissolved in 15 mL of diethyl ether and treated at −70 °C with a solution of methyllithium in diethyl ether (1.6 M, 1.1 mL, 1.7 mmol). The reaction mixture was allowed to warm slowly to room temp. After the solution had been separated from the precipitate, the solvent was removed and the pale yellow, viscous oil **6d** was dried under vacuum. Yield: 101 mg (74.3%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.99 [s, 18 H, $C(CH_3)_3$], 1.23 (s, 9 H, BCH_3), 2.17 (s, 4 H, CH_2). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 17.3. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.1 (BCH_3), 29.7 [$C(CH_3)_3$], 31.6 [$C(CH_3)_3$], 39.6 (CH_2). EI-MS: *m*/*z* (%) = 244 (7) [M^+], 229 (7) [$M^+ - CH_3$], 187 (17) [$M^+ - C_4H_9$], 173 (8) [$M^+ - C_5H_{11}$], 131 (23) [$M^+ - C_4H_9 - C_4H_8$], 57 (100) [$C_4H_9{}^+$], 41 (80) [$C_3H_5{}^+$]. HR-MS (EI): *m*/*z* = 244.2715 [M^+]; calcd. for $^{12}C_{15}{}^1H_{31}{}^{11}B_3$: 244.2725 ($\Delta$ = 1.0 mmu).

2,3,4-Tris(3,3-dimethyl-1-butynyl)-1,5-dicarba-*closo*-pentaborane(5) (6e): 3,3-Dimethyl-1-butyne (172 mg, 2 mmol) was added at −15 °C to a solution of *n*BuLi (2 mmol) in 20 mL of hexane. The mixture was allowed to warm to room temp. and stirred for 30 min. The suspension was then cooled to −78 °C and added to a solution of **6a** (212 mg, 0.69 mmol) in 5 mL of hexane. The reaction mixture was allowed to warm slowly to room temp. After the solution had been separated from the precipitate, the solvent was removed, and the yellow, solid **6e** was dried under vacuum. Yield: 236 mg

Table 1. Crystal data and details of the structure determinations

	1b	**5b**	**5b**	**6a**	**6f**
Formula	$C_{24}H_{23}B_3O_6$	$C_{23}H_{23}B_3O_6Si$	$C_{23.5}H_{24}B_3ClO_6Si$	$C_{12}H_{22}B_3Cl_3$	$C_{36}H_{37}B_3$
M	439.85	455.93	498.40	305.08	502.09
Temperature [K]	173(2)	173(2)	173(2)	190(2)	190(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	9.3558(2)	6.3424(1)	10.0111(3)	13.0672(13)	11.5657(12)
b [Å]	9.5761(2)	10.6553(2)	10.1299(3)	11.0691(11)	12.2601(13)
c [Å]	14.2103(2)	17.5659(4)	14.8106(4)	11.7038(11)	12.3944(13)
α [°]	96.423(1)	104.320(2)	74.219(2)	90	76.116(2)
β [°]	104.096(1)	97.559(2)	74.551(2)	100.488(2)	89.685(2)
γ [°]	113.380(1)	99.214(2)	60.980(2)	90	65.234(2)
V [Å^3]	1101.88(4)	1117.05(4)	1247.65(6)	1664.6(3)	1540.2(3)
Z	2	2	2	4	2
d_{calc} [g cm^{-3}]	1.326	1.356	1.327	1.217	1.083
μ (Mo-K_α) [mm]	0.092	0.144	0.239	0.530	0.059
F_{000}	460	476	518	640	536
Crystal size [mm]	0.42 × 0.28 × 0.26	0.27 × 0.25 × 0.16	0.42 × 0.35 × 0.08	0.40 × 0.19 × 0.19	0.60 × 0.12 × 0.07
Θ_{max} [°]	28.34	27.88	28.35	28.30	25.00
Measured reflections	14849	14501	16805	10523	17345
Independent (R_{int})	5381 (0.033)	5279 (0.036)	6100 (0.036)	3853 (0.035)	5423 (0.087)
No. of parameters	390	390	386	252	500
GooF	1.048	1.071	1.076	1.023	1.057
*R*1 ($I > 2\sigma I$)	0.0419	0.0481	0.0552	0.0398	0.0512
*wR*2	0.1196	0.1336	0.1614	0.1109	0.1429
Resid. electron dens. [e Å^{-3}]	0.363/−0.227	0.830/−0.335	0.899/−0.555	0.316/−0.213	0.224/−0.197

(76.8%), m.p. 83 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): 1.04 [s, 18 H, $C(CH_3)_3$], 1.20 [s, 27 H, $C(CH_3)_3$], 2.27 (s, 4 H, CH_2). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 11.4. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.9 [$C(CH_3)_3$], 30.8 [$C(CH_3)_3$], 32.0 [$C(CH_3)_3$], 32.3 [$C(CH_3)_3$], 39.6 (CH_2). EI-MS: *m*/*z* (%) = 442 (100) [M^+], 427 (10) [$M^+ - CH_3$], 385 (43) [$M^+ - C_4H_9$], 329 (37) [$M^+ + H - 2C_4H_9$], 57 (49) [$C_4H_9^+$]. HR-MS (EI): *m*/*z* = 442.4151 [M^+]; calcd. for $^{12}C_{30}{}^1H_{49}{}^{11}B_3$: 442.4188 (Δ = 3.7 mmu).

2,3,4-Tris(2-phenyl-1-ethynyl)-1,5-dicarba-*closo*-pentaborane(5) (6f): Phenylacetylene (124 mg, 1.21 mmol) was added at −15 °C to a solution of *n*BuLi (1.21 mmol) in 15 mL of hexane. The mixture was allowed to warm to room temp. and stirred for 30 min. The suspension was then cooled to −78 °C and added to a solution of **6a** (123 mg, 0.4 mmol) in 5 mL of hexane. The reaction mixture was allowed to warm slowly to room temp. After the solution had been separated from the precipitate, the solvent was removed and the brown, viscous oil **6f** was dried under vacuum. Yield: 127 mg (62.7%), m.p. 94 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): 1.19 [s, 18 H, $C(CH_3)_3$], 2.53 (s, 4 H, CH_2), 7.30−7.51 (m, 15 H, C_6H_5). ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 11.4. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.9 [$C(CH_3)_3$], 32.4 [$C(CH_3)_3$], 39.9 (CH_2), 108.1 (CB_3) 122.9 (*ipso*-C_{Ph}), 128.3 (*m*-C_{Ph}), 129.1 (*p*-C_{Ph}), 132.1 (*o*-C_{Ph}). EI-MS: *m*/*z* (%) = 502 (55) [M^+], 446 (13) [$M^+ + H - C_4H_9$], 402 (9) [$M^+ + H - C_8H_5$], 389 (16) [$M^+ + H - 2C_4H_9$], 57(100) [$C_4H_9^+$]. HR-MS (EI): *m*/*z* = 502.3191 [M^+]; calcd. for $^{12}C_{36}{}^1H_{37}{}^{11}B_3$: 502.3207 (Δ = 1.6 mmu).

Crystal Structure Determinations of 1b, 4b, 5b, 6a, and 6f: A summary of the crystal data and details of the structure determinations is given in Table 1. Data were collected on a Bruker AXS Smart 1000 area detector (Mo-K_α radiation, λ = 0.71073 Å, ω-scans) at low temperature. Data were corrected for Lorentz polarisation and absorption effects (semiempirical, SADABS[21]). The structures were solved by direct methods and refined by full-matrix, least-squares methods based on F^2 (SHELXTL).[22] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier syntheses and refined with isotropic displacement parameters [with the exception of the methyl groups in **5b** and those at the disordered $CH_2C(CH_3)_3$ group in **6a**, which were inserted in calculated positions and refined using a riding model].

CCDC-175653 (**1b**), -175654 (**4b**), -175655 (**5b**), -175656 (**6a**) and -175656 (**6f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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