

REACTIONS OF *closo*-1,5- $C_2B_3H_5$ WITH Cl_2 AND WITH BMe_3

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Summary

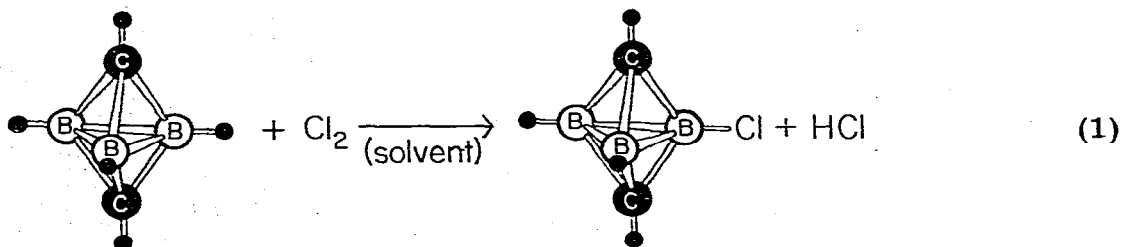
Reaction of *closo*-1,5- $C_2B_3H_5$ with Cl_2 under reduced temperatures in an inert solvent gives 2-Cl-1,5- $C_2B_3H_4$. Using a hot/cold reactor a mixture of BMe_3 and 1,5- $C_2B_3H_5$ is converted to a combination of *B*-mono-, di-, and tri-methyl derivatives of this smallest *closo* carborane. In addition, *B*-mono-, di-, tri-, and tetramethyl derivatives of 2,2'- $C_2B_3H_4-C_2B_3H_4$, as well as the parent dimer, are produced.

Introduction

In view of the reduced thermal [1] and hydrolytic [2] stability of 1,5- $C_2B_3H_5$ compared to the larger *closo*-carboranes [3], it is not surprising that very little derivative chemistry [4] of this smallest cage system of carbon and boron atoms has been reported. In the present study the preparations of boron-attached chloro and methyl derivatives involving the use of Cl_2 and BMe_3 , respectively, as reagents are discussed.

Results and discussion

Molecular chlorine reacts much more vigorously with $C_2B_3H_5$ than with the higher *closo*-carboranes [5]. Through the use of low temperatures and inert solvent the reaction can be moderated to give a small yield of the *B*-substituted derivative, 2-Cl-1,5- $C_2B_3H_4$, eq. 1.



Attempts to identify other boron-containing side products from this reaction were not successful; however, cage cleavage is indicated by singlet boron-11 resonances at low field with chemical shifts in the range $\delta -57$ and -60 ppm, corresponding to the general region expected for structures of the type RBCl_2 [6].

B-Monomethylation of $\text{C}_2\text{B}_3\text{H}_5$ with BMe_3 , eq. 2, can be effected at $50-90^\circ\text{C}$ if the reaction is not allowed to go beyond ca. 30% completion. Within experimental error the stoichiometry follows eq. 2 with dimethylborane (present as the dimeric tetramethyldiborane) produced in amounts equivalent to that of the

$$1,5\text{-C}_2\text{B}_3\text{H}_5 + \text{BMe}_3 \rightarrow 2\text{-Me-1,5-C}_2\text{B}_3\text{H}_4 + \frac{1}{2}\text{Me}_4\text{B}_2\text{H}_2 \quad (2)$$

2-Me-1,5- $\text{C}_2\text{B}_3\text{H}_4$. With additional heating time there is NMR evidence for the formation of both 2,3-Me₂-1,5- $\text{C}_2\text{B}_3\text{H}_3$ and 2,3,4-Me₃-1,5- $\text{C}_2\text{B}_3\text{H}_2$ but disappearance of all of the $\text{C}_2\text{B}_3\text{H}_5$ derivatives eventually occurs with the formation of a non-volatile oily material which exhibits a myriad of ^{11}B NMR resonances (in CH_2Cl_2 solvent) ranging from $\delta -30$ to $\delta -40$ ppm. Sublimation converts the residue into a volatile alkane mixture containing no boron and leaving behind an intractable nonvolatile residue. Fractionation of volatile reaction products prepared from $\text{BMe}_3/\text{C}_2\text{B}_3\text{H}_5$ (in ratios extending from 1 : 1 to 9 : 1) mixtures that are allowed to react until the starting carborane disappears usually gives some unreacted BMe_3 , $\text{Me}_4\text{B}_2\text{H}_2$, and a very small quantity of an unknown material of moderate volatility with a mass spectrum cutoff at m/e 156.

The formation of the ill-defined nonvolatile oily materials is minimized by the use of a hot/cold reactor [4,7] for the methylation. With this technique a host of methylated products is obtained including *B*-mono-, di-, and tri-methyl derivatives of 1,5- $\text{C}_2\text{B}_3\text{H}_5$ and *B*-methyl and *B*-polymethyl derivatives of the carborane dimer, $\text{C}_2\text{B}_3\text{H}_4\text{-C}_2\text{B}_3\text{H}_4$ [4], as well as the parent dimer, eq. 3. In total, about 60 to 65% of the $\text{C}_2\text{B}_3\text{H}_5$ was converted to identifiable carborane derivatives.

Because methylation of the parent carborane takes place under milder conditions than dimerization, the methylated dimers probably arise from the dimerization of $\text{Me}_x\text{C}_2\text{B}_3\text{H}_{5-x}$ rather than by way of parent dimer methylation.

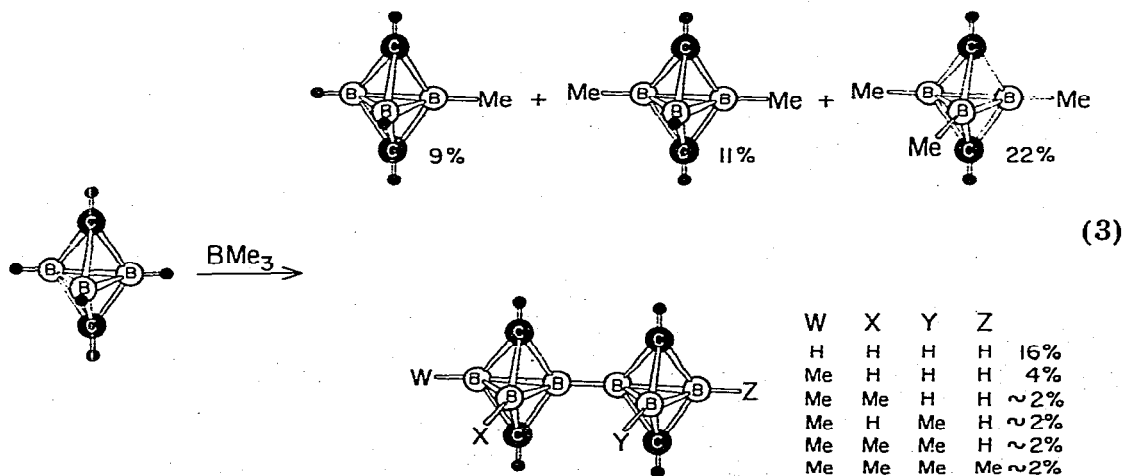


TABLE 1
NUCLEAR MAGNETIC RESONANCE DATA

	δ (^{11}B) ^a (ppm)	J (Hz)	τ (^1H) ^b (ppm)	J (Hz)
2-Cl-1,5-C ₂ B ₃ H ₄				
B-Cl	-11.6			
B-H	-12.2	186	6.77	190
C-H			6.24	
2-Me-1,5-C ₂ B ₃ H ₄				
B-Me	-8.8		9.27	
B-H	-7.0 ^c	184	5.94	184
C-H			4.83	
2,3-Me ₂ -1,5-C ₂ B ₃ H ₃				
B-Me	-12.8 ^d		9.66 ^d	
B-H	-10.8	170	5.79	170
C-H			5.18	
2,3,4-Me ₃ -1,5-C ₂ B ₃ H ₂				
B-Me	-16.3 ^e		9.61 ^e	
C-H			5.52	
2,2'-C ₂ B ₃ H ₄ -C ₂ B ₄ H ₄				
B-B	-8.3			
B-H	-2.1	186	6.19	189
C-H			4.35	

^a Relative to $\text{BF}_3 \cdot \text{Et}_2\text{O} = 0.00$. ^b δ (in TMS) 10.00 ppm; internal standard except for Cl-C₂B₃H₄.
^c δ (^{11}B) -8.5 and -6.6 ppm and τ 10.13, 6.25, and 5.02 ppm (ext. TMS?) reported earlier [12]. ^d An authentic sample provided by R.E. Williams gives δ (^{11}B) -14 (singlet), δ -12 (doublet); ^1H , (τ (B-Me) - τ (C-H)) \sim 4.43. ^e An authentic sample provided by R.E. Williams gave δ (^{11}B) -16.2; ^1H , (τ (B-Me) - τ (C-H)) 4.12. Brown et al. [13] report (τ (B-Me) - τ (C-H)) 4.06 ppm for the ^1H spectrum.

Nuclear magnetic resonance

The B-Cl signal of ClC₂B₃H₄ in the ^{11}B NMR (Table 1) is very sensitive to saturation and only gives reasonably acceptable peaks for area comparisons at very low rf power-settings. The downfield shift of about 10 ppm upon chlorine substitution of the parent carborane is about the same as observed upon similar substitution in the other small carboranes, C₂B₄H₆ and C₂B₅H₇ [8]. In the case of the smallest carborane, however, there is also a considerable downfield shift of neighbouring borons which is not observed in the other two compounds.

A downfield shift of the ^{11}B resonance upon *B*-methyl substitution of C₂B₃H₅ also follows the trend found in other boron compounds [3]. But again, neighbouring borons also shift much further downfield than observed in the higher cage compounds. A sensitive indicator of *B*-methyl substitution in the C₂B₃H₅ system is provided by the ^1H NMR spectrum where the H-C(cage) proton systematically shifts 0.33 to 0.35 ppm to higher field upon each new methyl attached to a neighbouring boron. This trend is of considerable help in making ^1H assignments for the various polymethylated derivatives of the dimer, C₂B₃H₄-C₂B₃H₄.

Experimental

Materials

A sample of the 1,5-C₂B₃H₅ was a gift from R.E. Williams and J. Ditter,

Chemical Systems, Santa Ana, California. A simple vacuum fractionation of the sample through a -80°C trap removed a small amount of less volatile impurities. Trimethylborane was obtained from Alfa Inorganics, Ventron, Beverly, Massachusetts, and was passed through a -78°C trap before use. Molecular chlorine (Matheson) was purified prior to use by trapping at -126°C to rid the sample of HCl. All materials were handled using conventional high vacuum techniques.

Spectroscopic data

Both the ^1H (τ (in TMS) 10.00 ppm) and ^{11}B (δ in $(\text{BF}_3 \cdot \text{Et}_2\text{O})$ 0 ppm) nuclear magnetic resonance spectra were obtained from a Varian HA-100 spectrometer operating at 100 and 32.1 MHz, respectively. Heteronuclear decoupling was carried out in a manner described earlier [9]. Mass spectroscopic data were recorded using a Varian CH5 Massenspektrometer equipped with a Data-Machine 6201 printout. Infrared spectra were obtained from a Beckman Acculab-3 instrument.

Preparation of 2-Cl-1,5-C₂B₃H₄

Using CF_2Cl_2 (2.75 mmol) as a solvent, 1,5-C₂B₃H₅ (0.52 mmol) and Cl₂ (1.5 mmol) were allowed to warm slowly from -70°C to ambient temperature over a 16 h period. Cold-column fractionation [10] gave HCl (1.2 mmol, -170 to -150°C), unreacted Cl₂ (-140 to -130°C), 1,5-C₂B₃H₅ (-130 to -105°C) and 2-Cl-1,5-C₂B₃H₄ (0.03 mmol, -105°C and up). (Because the solvent CF_2Cl_2 also came off the column between the temperatures of -140 to -105°C it was difficult to assess the quantities of unreacted carborane and chlorine). An involatile oily fraction showed two intense ^{11}B NMR singlet resonances at δ -57 and -60 ppm.

The infrared spectrum of 2-Cl-1,5-C₂B₃H₄ exhibited absorption peaks at 2985w (CH), 2640s (B-H), 1300s(br), 1160–1220s(br), 1100s, 1000w, 960m, 905m, 775ms cm^{-1} .

The polyisotopic mass spectrum gave positive ions at m/e 98 ($^{37}\text{Cl}^{12}\text{C}_2^{11}\text{B}_3^1\text{H}_4^+$) 17% of base peak; m/e 97, 33%; m/e 96, 70%; m/e 95, 100%, base peak; m/e 94, 60%; m/e 93, 24%; m/e 92, 9%; m/e 91, 3% as well as a few ions of weak intensity at lower masses; the monoisotopic spectrum conformed reasonably well to $\text{ClC}_2\text{B}_3\text{H}_4^+$ (83%), $\text{ClC}_2\text{B}_3\text{H}_3^+$ (100%). NMR data are given in Table 1.

Reaction of BMe₃ with 1,5-C₂B₃H₅

Using a hot/cold apparatus similar to that described earlier [4,7] a mixture of 1,5-C₂B₃H₅ (1.0 mmol) and BMe₃ (4.0 mmol) was subjected to hot and cold temperatures of $240/-30^{\circ}\text{C}$. After 5 h under these conditions 0.12 mmol of noncondensables were formed; cold-column fractionation of the condensable product mixture gave Me₄B₂H₂ (ca. 0.11 mmol, -91 to -76°C), 2-Me-1,5-C₂B₃H₄ (0.082 mmol, -112 to -95°C), 2,3-Me₂-1,5-C₂B₃H₃ (0.10 mmol, -91 to -80°C), 2,3,4-Me₃-1,5-C₂B₃H₂ (0.20 mmol, -76°C), 2,2'-C₂B₃H₄-C₂B₃H₄ (0.07 mmol, -58 to -54°C , mass spectrum cutoff m/e 122) [4], 3-Me-2,2'-C₂B₃H₃-C₂B₃H₄ (0.02 mmol, -47 to -35°C , mass spectrum cutoff at m/e 136) and a 0.04 mmol mixture (-35°C and up) of polymethyl derivatives of the dimer with mass spectrum cutoffs corresponding to all B-substituted polymethyl

derivatives, e.g., m/e 150 for $\text{Me}_2\text{C}_4\text{B}_6\text{H}_6$ and additional cutoffs at increments of m/e 14. The ^{11}B NMR of the mixture was composed of three broad peaks at δ -23, -16 and -6.4 ppm; the ^1H NMR exhibited a number of broad overlapping B-Me resonances, τ 9.32, 9.64, 9.93 and 10.38 ppm and three well defined low field peaks at τ 4.35, 4.67 and 5.01 ppm assigned to the cage CH resonances in an area ratio of approximately 2 : 1 : 1.5. Also, some $\text{C}_2\text{B}_3\text{H}_5$ (0.09 mmol) and BMe_3 (3.16 mmol) were recovered, and there was ^{11}B NMR evidence of small quantities of low volatility compound(s) with broad singlets at δ -40 and δ -33 ppm.

In a separate series of experiments 0.50 mmol portions of $\text{C}_2\text{B}_3\text{H}_5$ were sealed off in a set of three NMR tubes containing (a) 0.50, (b) 1.00, and (c) 3.00 mmol of BMe_3 , respectively. With tube (a) left at room temperature for 5 days the ^{11}B NMR exhibited very weak peaks attributed to $\text{B-MeC}_2\text{B}_3\text{H}_4$ (doublet, area 2, δ -5.3 ppm, J 155 Hz; singlet, area 1, δ -7.0 ppm) and $\text{Me}_4\text{B}_2\text{H}_2$ [11] in roughly a compound ratio of 1 : 1, respectively. After heating to 50°C for 5 h, these products grew together in intensity at the expense of the starting materials. An area comparison indicated that the reaction was about 30% complete. Further heating at 60°C for 4 h and then at 90° for 10 h resulted in the gradual disappearance of $\text{B-MeC}_2\text{B}_3\text{H}_4$, and remaining BMe_3 and $\text{C}_2\text{B}_3\text{H}_5$. After heating for another 30 h at 90°C all of the resonances attributed to the above compounds disappeared leaving only broad resonances at δ -23, -6, +10, +19, and +38 ppm. Fractionation of the mixture showed that very little volatile material (mostly $\text{Me}_4\text{B}_2\text{H}_2$) was present. The residue (in CH_2Cl_2) exhibited broad resonances at δ -25, -15, -5, +12, +21 and +38 ppm. Tube (b) was heated to 90°C for 1.3 h after which the ^{11}B NMR showed an approximately 20% conversion to $\text{B-MeC}_2\text{B}_3\text{H}_4$ and $\text{Me}_4\text{B}_2\text{H}_2$ the only other peaks present being unreacted starting materials. After heating at 90°C for an additional 17 h the ^{11}B NMR pattern indicated that all of the $\text{C}_2\text{B}_3\text{H}_5$ as well as the B-Me derivative had disappeared with the formation of more $\text{Me}_4\text{B}_2\text{H}_2$ and the appearance of a number of resonances extending from δ -53 to +41 ppm. Fractionation of the sample through -78 and -190°C traps gave 0.42 mmol BMe_3 in the last trap and a mixture of $\text{Me}_4\text{B}_2\text{H}_2$ (0.23 mmol) (δ -25 ppm in the ^{11}B NMR) and a small amount of material with resonances at δ -32, -14, -4, and +40 ppm. Tube (c) was heated to 90°C for 1.3 h after which the ^{11}B NMR indicated that ca. 20% of the starting materials was converted to $\text{B-MeC}_2\text{B}_3\text{H}_4$ and $\text{Me}_4\text{B}_2\text{H}_2$. Another 3 h of heating at this temperature showed some decomposition of the carboranes and after an additional 20 h the NMR pattern was that of a mixture of BMe_3 (δ -85 ppm) and $\text{Me}_4\text{B}_2\text{H}_2$ (δ -24 ppm) with very weak peaks at δ -76, -65, -55, -15, -5, +11, +20, +26 and +38 ppm. A fractionation of the mixture through -78 and -190°C traps gave 2.07 mmol of BMe_3 and 0.23 mmol of $\text{Me}_4\text{B}_2\text{H}_2$ in the -190°C trap and a very small quantity of material in the -78°C trap with broad ^{11}B resonances at δ -61, -54, -33, -23.5, -15.5, -5, +4, +8, +12, +14, +17, +21 and +39 ppm. A mass spectrum of this fraction gave a cutoff at m/e 156. No uncondensed gas was found. An involatile material left behind in the original NMR tube was a clear viscous oily substance with a slight greenish cast and with a very broad ^{11}B NMR pattern that sharpened somewhat to give peaks at δ -16, -14, -7, +11, +19 and +36 ppm when CH_2Cl_2 was used as a solvent. After evaporating the solvent in vacuo, sublimation of the residue

resulted in decomposition into an intractable nonvolatile substance and a volatile material (50% of original material) containing no boron and giving a strong broad ^1H resonance around τ 9.0 ppm.

In another NMR tube was sealed 1.66 mmol BMe_3 and 0.19 mmol $\text{C}_2\text{B}_3\text{H}_5$. After heating to 55°C for 3 days about one-third of the carborane was converted to $\text{B-MeC}_2\text{B}_3\text{H}_4$ along with the concomitant formation of $\text{Me}_4\text{B}_2\text{H}_2$. With an additional 5 h at 65°C the ^{11}B NMR spectrum exhibited the combined spectra of $\text{Me}_4\text{B}_2\text{H}_2$, $2\text{-MeC}_2\text{B}_3\text{H}_4$, $2,3\text{-Me}_2\text{C}_2\text{B}_3\text{H}_3$ and $2,3,4\text{-Me}_3\text{C}_2\text{B}_3\text{H}_2$ (Table 1) as well as the resonances attributable to unreacted $\text{C}_2\text{B}_3\text{H}_5$ (approx. ratio of the five compounds, respectively, 10 : 8 : 4 : 1 : 10) and a large quantity of BMe_3 . With an additional 15 h at 90°C no $\text{C}_2\text{B}_3\text{H}_5$ remained and only $\text{Me}_4\text{B}_2\text{H}_2$ and some $\text{Me}_3\text{C}_2\text{B}_3\text{H}_2$ as well as a number of weak broad resonances scattered across the ^{11}B spectrum were present in addition to the strong BMe_3 peak. Fractionation of the sample through -80 and -190°C traps was carried out after it was assessed that no noncondensables were formed. The -80°C trap contained only a trace of material with several C-H vibrations and a B-H(bridge) (?) vibration at 1590 cm^{-1} but no B-H_i absorptions in the infrared. The ^{11}B NMR exhibited broad peaks at δ -23.3, -15.3, -4.3, +13, +21 and +38 ppm. The PMR exhibited a strong broad resonance at ca. τ 10.5 ppm (external TMS) with a much weaker resonance appearing at τ 7.3 ppm. The -190°C trap contained mostly BMe_3 with a trace of $\text{Me}_4\text{B}_2\text{H}_2$. A nonvolatile greenish-yellow residue in the original NMR reaction tube gave a very broad peak (half-width ~ 20 ppm) centered ca. δ +4 ppm.

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