Contribution from the Department of Chemistry, California State University, Los Angeles, California 90032,
and Chemical Systems, Inc., Irvine, California 92714

Boron Cage Expansion Studies: Conversion of *nido*-2,3-Dicarbahexaborane(8) to *B*-Methyl Derivatives of *closo*-1,7-Dicarbaoctaborane(8) and *closo*-2,4-Dicarbaheptaborane(7) and Formation of *B*-Dimethyl-*closo*-2,4-dicarbaheptaborane(7) from *closo*-1,6-Dicarbahexaborane(6)

ALEXANDER P. FUNG,[1a] EMMA W. DISTEFANO,[1a] KEITH FULLER,[1a] GOWIT SIWAPINYOYOS,[1a]
THOMAS ONAK,*[1a] and ROBERT E. WILLIAMS[1b]

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A two-boron cage expansion to give 2,3,4,5,6,8-Me_6-*closo*-1,7-$C_2B_6H_2$, as well as a previously observed one-boron expansion to give 1,3,5,6,7-Me_5-*closo*-2,4-$C_2B_5H_2$, is observed upon reacting trimethylborane with *nido*-2,3-$C_2B_4H_8$ at 220–230 °C. *closo*-2,4-$C_2B_5H_7$ and its *B*-methyl derivatives do not undergo *B*-methyl exchange with trimethylborane at the temperatures used for the cage expansion reaction which, along with the results from $^{10}B/^{11}B$ isotope studies on the cage expansion reaction, suggests that the per-*B*-methyl five-boron closo product from the reaction of 2,3-$C_2B_4H_8$ with trimethylborane may be produced via a six-boron intermediate. *closo*-1,6-$C_2B_4H_6$ reacts with excess trimethylborane in the temperature region 550–600 °C to give the cage expansion product *B*-Me_2-*closo*-2,4-$C_2B_5H_5$ along with minor amounts of mono- and trimethyl derivatives of this closo carborane.

Introduction

Alkylboron compounds such as methyldiborane have been widely used as alkylating agents for polyboranes; examples include the formation of methyltetraborane(10) and methylpentaborane(11) from the interaction of methyldiboranes with both the parent tetraborane(10) and pentaborane(11), respectively,[2a] and the formation of methyl derivatives of *closo*-1,5-$C_2B_3H_5$ from the interaction of trimethylborane with the parent $C_2B_3H_5$.[2b]

Also, boron cage expansion has been noted in reactions with alkylboranes with polyboranes, and examples of this include the formation of methyl derivatives of pentaborane(11) from a reaction of tetraborane(10) with methyldiborane[2a] and the production of an assortment of methylated pentaboranes and decaboranes from the pyrolysis of trimethylborane/diborane mixtures.[3] It is also known that at 300 °C *nido*-2,3-$C_2B_4H_8$ reacts with excess trimethylborane to give a small yield of *B*-Me_5-*closo*-2,4-$C_2B_5H_2$ as well as lesser amounts of mono-, di-, tri-, and tetramethyl derivatives of 2,4-$C_2B_5H_7$.[4] However, 2,3-$C_2B_4H_8$ is directly converted to 2,4-$C_2B_5H_7$ (as well as 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$[5]) under these same thermal conditions,[6] and thus it is not entirely clear that the presence of trimethylborane is essential for the cage expansion aspect of the reaction which gives the *B*-methyl derivatives of the *closo*-2,4-$C_2B_5H_7$ from *nido*-2,3-$C_2B_4H_8$.

Cage expansion reactions leading to *closo*-1,7-$C_2B_6H_8$, or derivatives of this carborane, are unknown. Previously, $C_2B_6H_8$ has been prepared from the ultraviolet irradiation of a mixture of *nido*-B_6H_{10} and dimethylacetylene (giving the *C,C'*-dimethyl derivative of $C_2B_6H_8$)[7] and from the thermolysis of *arachno*-$C_2B_7H_{13}$.[8-11] The cage structures of all of the polyboranes and carboranes mentioned in the present report have been confirmed by X-ray and/or electron diffraction and/or microwave studies and the primary references for these are cited in a recent review.[12]

Experimental Section

Materials and Handling of Chemicals. Trimethylamine–borane (Matheson), triphenylborane (Aldrich), and *tert*-butyl peroxide (Matheson Coleman and Bell) were used after vacuum distillation or sublimation. Glyme (i.e., $CH_3OCH_2CH_2OCH_3$; Matheson Coleman and Bell) and diethyl ether (Matheson Coleman and Bell) were vacuum distilled from $LiAlH_4$ prior to use. Trimethylborane (Alfa Chemicals), boron trifluoride (Union Carbide), boron trichloride (Union Carbide), and pentaborane(9) (Callery) were purified by a simple vacuum fractionation through traps at −78 and −190 °C. Diborane (Olin-Mathieson) and acetylene (Matheson) were purified by vacuum fractionation through a trap cooled with a pentane slush bath (−125 °C). Dicarba-*nido*-hexaborane(8), $C_2B_4H_8$, was prepared from the reaction between pentaborane(9) and acetylene by a previously described method.[13] 2,3-Dimethyl-2,3-dicarba-*nido*-hexaborane(8) was prepared from the thermal reaction of 2-butyne and pentaborane[6] followed by cold-column fractionation.[14] Dicarba-*closo*-heptaborane(7), $C_2B_5H_7$, and dicarba-*closo*-hexaborane(6), $C_2B_4H_6$, were prepared from the pyrolysis of 2,3-$C_2B_4H_8$[5a] and from the reaction of B_5H_9 and acetylene.[5b]

All materials were handled in conventional high-vacuum equipment or in a drybox under an atmosphere of dry nitrogen.[15]

Instrumentation. Nuclear Magnetic Resonance Spectra. Both the ^1H and ^{11}B NMR spectra were obtained on a Varian HA-100 NMR spectrometer operating at 100 and 32.1 MHz, respectively. Boron-decoupled ^1H spectra at 100 MHz were observed while irradiating at 32.1 MHz using a Fluka 6160B frequency synthesizer which is noise-modulated by a homemade pseudorandom noise generator. The noise bandwidth is controlled by a Hewlett-Packard 200CD wide range audio oscillator. The signal is amplified by an Electronic Navigation Industries 320L RF power amplifier and applied to the double-tuned transmitter coil of the HA-100.

The proton chemical shifts were measured using tetramethylsilane (τ 10.00) as an external standard and 1,3,5,6,7-$Me_5C_2B_5H_2$ as an internal standard[16] when applicable. The ^{11}B chemical shifts were measured using boron trichloride, δ −46.8 (downfield) relative to boron trifluoride ethyl ether complex, as an external secondary standard.

Infrared Spectra. The infrared spectra were recorded on a Beckman Model Acculab 3 infrared spectrophotometer.

Mass Spectra. The mass spectral data were obtained from a Varian Massenspektrometer CH5 with an attached Varian Data Machine 620i.

Gas Chromatography–Mass Spectrometry. The GLC–mass spectra data were recorded using a Varian Mat 111 instrument, equipped with a 10% Kel F grease on a 60/80 mesh chrom W, 20 ft × 1/8 in., column.

General Procedure for the Reaction between Trimethylborane and $C_2B_4H_8$. In a typical reaction the measured quantities of $C_2B_4H_8$ and $(CH_3)_3B$ (Table I) were distilled into a glass reactor with an attached side-arm NMR tube. The mixture was then sealed off and heated between the temperatures 220 and 235 °C. After 1–16 h under these conditions (note: the reaction did not occur to any measurable extent at lower temperatures over this time span), a light yellow oily liquid and a small amount of milky white solid together with noncondensable gas were formed. The flask was opened into the vacuum apparatus, and the volatile contents were slowly fractionated through traps at −78 and −190 °C. The materials in the −190 °C trap were unreacted $(CH_3)_3B$ and/or $C_2B_4H_8$ (identified by ^1H and ^{11}B NMR). Analysis of the contents of the −78 °C trap by ^1H and ^{11}B NMR and GLC–MS indicated that the monomethyl, dimethyl, trimethyl, tetramethyl, and pentamethyl derivatives of $C_2B_5H_7$ as well as the higher *B*-methyl derivatives of $C_2B_6H_8$ were present (Table I). By cold column fractionation[14] the *B*-permethyl derivative of $C_2B_5H_7$ and *B*-permethyl

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Table I. Product Yields of $C_2B_4H_8/(CH_3)_3B$ Thermal Reactions

expt no	(1) initial amt of $C_2B_4H_8$, mmol	(2) initial amt of $(CH_3)_3B$, mmol	ratio of columns (2):(1)	(3) amt of $C_2B_4H_8$ consumed, mmol	(4) amt of $(CH_3)_3B$ consumed, mmol	ratio of columns (4):(3)	conditions	volatile carborane products, mol % of $C_2B_4H_8$ consumed									total carborane yield, %
								$Me_6C_2B_6H_2$	$Me_5C_2B_6H_3$	$Me_4C_2B_6H_4$	$Me_3C_2B_6H_5$	$Me_5C_2B_5H_2$	$Me_4C_2B_5H_3$	$Me_3C_2B_5H_4$	$Me_2C_2B_5H_5$	$MeC_2B_5H_6$	
1	0.52	0.51	0.98	0.26	0.38	1.46	220 °C, 1 h	2.1	5.1	7.9	6.6	19.6	26.4	19.5	7.1	3.2	97
2	0.50	0.50	1.00	0.28	0.36	1.30	220 °C, 5 h, + air (0.07 mmol)	0.9	4.1	5.1	1.8	25.0	27.1	9.2	6.8	0.01	80
3	0.49	0.49	1.00	0.31	0.49	1.59	220 °C, 16 h	^{11}B NMR of mixture similar to expt 1 and 2; GC-MS not run									82
4	0.48	1.09	2.27	0.32	0.65	2.03	220 °C, 9 h	3.5	4.5	6.4	trace	31.5	19.6	11.0	1.9	3.6	82
5	0.53	2.41	4.55	0.53	2.21	4.16	220 °C, 3 h	3.4	3.3	2.8	trace	14.8	6.8	3.3	0.6	0.3	35
6	0.47	2.44	5.20	0.46	1.49	3.24	240 °C, 16 h	9.3	1.9	0.6	trace	27.8	9.8	5.4	1.3	0.2	56
7	2.17	19.23	8.87	2.17	8.17	3.76	230 °C, 16 h	6.4	trace	trace	trace	26.3	7.6	5.3	trace	trace	46

derivative of $C_2B_6H_8$ were obtained in reasonably good purity. The identity of B-$(CH_3)_5$-$C_2B_5H_2$ (collected from −45 to −39 °C on the cold column) was established by (a) ^1H NMR containing three B-methyl peaks at τ 9.19, 9.48, and 10.50 with an area ratio of 1:2:2, respectively, and a cage C–H peak at τ 5.3,[16] (b) the ^{11}B NMR exhibiting peaks at δ +15.1 [B(1) and B(7)], −9.7 [B(5), B(6)], and −14.4 [B(3)] in an area ratio of 2:2:1, respectively,[16] and (c) a mass spectrum with P = m/e 156.[17] The B-$(CH_3)_6$-$C_2B_6H_2$ (collected from −34 to −28 °C on the cold column) was identified by (a) ^1H NMR containing three peaks at τ 6.22 (cage C–H), 9.65 (CH_3–B), 9.91 (CH_3–B) with area ratio 2:12:6, (b) the ^{11}B NMR spectrum exhibiting singlet peaks at δ −12.5 and +7.0 with an area ratio of 4:2, respectively, and (c) the following m/e values: m/e 183, 4.1% of base peak; m/e 182, 52.8% (parent peak for $^{12}C_8\,^{11}B_6\,^1H_{20}$); m/e 181, 100.0% (base peak); m/e 180, 87.4%; m/e 179, 42.5%; m/e 178, 12.8%; m/e 177, 2.8%. Monoisotopic mass spectrum, relative intensities: P = 100.0, P − 1 = 56.8, P − 2 = 8.0. The nonvolatile residues formed in small quantities from reactions 1–7, Table I, dissolved in various deuterated solvents (i.e., benzene, ether, and chloroform), and each solution exhibited a very broad peak centered at approximately δ +13 ppm in the ^{11}B NMR spectra. Both the low volatility of the residues and the broadness and position of the NMR signals suggest polymers containing carborane units.

Analysis of the Noncondensable Gases (Hydrogen and Methane). The reaction flask of reaction 5 (Table I) was opened on the vacuum line utilizing a Sprenkel pump.[18] The noncondensable gas (1.20 mmol, passed through a −190 °C trap) from the reaction mixture was allowed to circulate over CuO at 400 °C for 1.5 h. The material was subsequently passed through a −78 °C trap which collects the water produced from H_2; the CO_2 produced from the oxidation of methane, as well as any unreacted methane, passed through this trap and was measured (0.24 mmol). From these results the ratio of H_2 to CH_4 is (1.20 − 0.24):0.24 = 4:1.

Photolysis of 2,3-Dicarba-*nido*-hexaborane and Trimethylborane. A sample with a 1:1 ratio of 2,3-dicarba-*nido*-hexaborane and trimethylborane (0.50 mmol each) was condensed into a 13.5 cm × 1.2 cm quartz tube and irradiated with a 360-W quartz, medium-pressure, mercury arc lamp for 18 h. ^{11}B NMR studies showed that neither substituted $C_2B_5H_7$ nor substituted $C_2B_6H_8$ was obtained; instead, the mixture exhibited a triplet at δ −25 ppm due to $Me_4B_2H_2$.[19] In addition to the presence of some unreacted starting materials, the ^{11}B NMR also indicated that trace amounts of the parent carboranes $C_2B_4H_6$, $C_2B_3H_5$, and $C_2B_5H_7$ were also formed.[20]

Photolysis of a 2,3-Dicarba-*nido*-hexaborane, Trimethylborane, and *tert*-Butyl Peroxide Mixture. A sample of $C_2B_4H_8$ (0.52 mmol), $B(CH_3)_3$ (1.06 mmol), and $(Me_3CO)_2$ (0.25 mmol) in a quartz vessel was irradiated (see above) for 2 h. ^{11}B and ^1H NMR of the mixture indicated results similar to that of the above reaction, and it was noted that *tert*-butyl peroxide did not disappear.

Attempted Reaction of Dicarba-*closo*-heptaborane and Trimethylborane. Into a 30-mL reaction flask were condensed $(CH_3)_3B$ (1.09 mmol) and $C_2B_5H_7$ (1.01 mmol). The flask was sealed and heated to 300 °C for 2 days. Both the ^1H and ^{11}B NMR spectra of the reaction mixture gave no evidence for the formation of methyl derivatives of $C_2B_5H_7$. The starting materials were found unchanged.

Reaction of Pentaborane, Acetylene, and Trimethylborane. Acetylene (2.10 mmol), B_5H_9 (0.52 mmol), and $B(CH_3)_3$ (2.13 mmol) were sealed in a 30-mL reaction bulb, and the sample was then heated to 235 °C for 16 h. The flask was opened into the vacuum line, and its contents were slowly vacuum fractionated through traps at −78 and −190 °C. Analysis of the contents in the −78 °C trap (0.11 mmol) by NMR and GLC–MS indicated results similar to that of the reaction between $C_2B_4H_8$ and Me_3B: $Me_5C_2B_5H_2$, 31.8% of the volatile carborane fraction; $Me_4C_2B_5H_3$, 14.6%; $Me_3C_2B_5H_4$, 9.5%; $Me_2C_2B_5H_5$, 4.9%; $MeC_2B_5H_6$, 2.7%; $Me_6C_2B_6H_2$, 20.7%; $Me_5C_2B_6H_3$, 9.7%; $Me_4C_2B_6H_4$, 6.0%; $Me_3C_2B_6H_5$, trace. Both acetylene and pentaborane were entirely consumed, and 0.81 mmol of Me_3B was recovered from the reaction.

Reaction between Trimethylborane and Acetylene. Acetylene (2.10 mmol) and $(CH_3)_3B$ (2.10 mmol) were sealed in a 30-mL reaction bulb, and the mixture was then heated to 235 °C for 17 h. ^{11}B NMR studies showed the only products to be trace amounts of a trialkenylborane (δ −54.5) and methyldialkenylborane (δ −64.4).[21] No carboranes were found.

Reaction of 2,3-Dimethyl-2,3-dicarba-*nido*-hexaborane and Trimethylborane; Formation of Me_7-*closo*-C_2B_5 and Related Compounds.

Trimethylborane (2.58 mmol) and 2,3-$(CH_3)_2$-*nido*-2,3-$C_2B_4H_6$ (0.537 mmol) were sealed in a 30-mL reaction bulb and the contents of the flask were then heated to 225 °C for 10 h (heating the mixture at lower temperatures did not effect a reaction within the same time period). The product mixture was subsequently vacuum fractionated through traps at −42, −78, and −190 °C over a 2-h period. The contents of the −190 °C trap were found to be unreacted $(CH_3)_3B$ (1.68 mmol) which was identified by ^{11}B and ^1H NMR. The contents of the −42 and −78 °C traps were combined (0.30 mmol) and identified using ^{11}B NMR and GLC-MS: $Me_7C_2B_5$, 69.7%; $Me_6C_2B_5H$, 10.1%; $Me_5C_2B_5H_2$, 6.3%; $Me_4C_2B_5H_3$, 2.9%; $Me_3C_2B_5H_4$, 2.7%; $Me_2C_2B_5H_5$, 1.2%; $Me_7C_2B_6H$, trace; $Me_6C_2B_6H_2$, 3.5%; and trace quantities of polyborane compounds with parent peaks at *m/e* 116 and 144.

Reaction of 2,3-Dicarba-*nido*-hexaborane and Triphenylborane. A mixture of $B(C_6H_5)_3$ (0.50 mmol) and $C_2B_4H_8$ (0.55 mmol) was sealed in a 30-mL reaction bulb. $(C_6H_5)_3B$ dissolves in $C_2B_4H_8$ at 90 °C. The ^{11}B NMR spectrum showed that a reaction occurred after heating the reactants to 220 °C for 16 h. The volatile material was condensed into a −190 °C trap and was identified as unreacted $C_2B_4H_8$, 0.10 mmol. The solid dissolved slowly in $CHCl_3$ and in benzene and gave a very broad peak in the ^{11}B NMR centered at δ +13 which suggests that a high molecular weight compound with at least one carborane unit was produced. Attempts at purification were unsuccessful.

Attempted Reaction between 2,3-Dicarba-*nido*-hexaborane and Diborane. Diborane (2.30 mmol) and $C_2B_4H_8$ (0.47 mmol) were both sealed in a 30-mL glass bulb, and the mixture was heated to 220 °C for 16 h during which time white solids, together with noncondensable gas, were formed. Vacuum fractionation through traps at −78 and −190 °C gave only $C_2B_4H_8$ (identified by ^1H and ^{11}B NMR) in both traps, 0.43 mmol total. The solid left in the reactor did not dissolve in glyme or chloroform. No diborane was recovered indicating that it probably is primarily responsible for the formation of the white solids under these conditions.

Reaction between 2,3-Dicarba-*nido*-hexaborane and Trichloroborane. Trichloroborane (1.77 mmol) and $C_2B_4H_8$ (0.46 mmol) were sealed in a 30-mL glass flask and, after heating the mixture to 236 °C for 3 h, a small amount of yellow-brown solid was formed. The volatile materials from the reaction were vacuum pumped out of the flask through traps at −43, −78, and −190 °C. The material in the −190 °C trap was found to be BCl_3 (1.55 mmol) by ^{11}B NMR. The mixture in the −78 °C trap (0.06 mmol) contained about 80% BCl_3 and 20% material with ^{11}B NMR peaks in the "carborane region".[22] Using glyme as a solvent for the contents in the −43 °C trap gave a broad peak at δ +13 ppm in the ^{11}B NMR spectrum. All $C_2B_4H_8$ was consumed. It is suggested that the formation of a polychloro derivative of *closo*-$C_2B_5H_7$ did occur but further work to characterize the carborane fraction has not yielded conclusive results.

Reaction of Trifluoroborane and 2,3-Dicarba-*nido*-hexaborane. Trifluoroborane (2.44 mmol) and $C_2B_4H_8$ (0.52 mmol) were sealed in a NMR tube, and the mixture was heated to 260 °C for 2 days. Both ^1H and ^{11}B NMR spectra gave no evidence that a reaction had occurred. Further heating to 292 °C for 17 h gave a ^{11}B NMR spectrum with resonances at δ −7.2 B(3), −3.9 B(5,6), and +21.2 B(1,7),[16] area ratio 1:2:2. This indicated the conversion of *nido*-$C_2B_4H_8$ to *closo*-$C_2B_5H_7$ has been achieved[6,13] without the involvement of BF_3.

Preparation of $^{10}BMe_3$. $^{10}BMe_3$ was prepared from elemental ^{10}B via $^{10}BCl_3$ using the following sequence of reactions

$$2\,^{10}B + 3Cl_2 \rightarrow 2\,^{10}BCl_3;\ ^{10}BCl_3 \xrightarrow{PbMe_4} {}^{10}BMe_3$$

Boron-10-enriched elemental boron (obtained from Union Carbide Corp., with 92% of ^{10}B isotope and 8% ^{11}B isotope, 56.8 mg, 5.25 mmol) was placed into a 500-mL quartz reaction flask with a break-tip attached to it. After the flask was evacuated for 2 h, 10 mmol of chlorine (Matheson Co.) was added, the flask sealed, and the contents heated to 650 °C for a 5-h period; cold column distillation of the mixture gave $^{10}BCl_3$ (4.4 mmol, 84% yield) collected from −110 to −100 °C and identified by ^{11}B NMR and IR.

Tetramethyllead, $PbMe_4$ (5.5 mL, Alfa Inc.), was syringed into a 500-mL glass reactor, and the contents were cooled to −190 °C. The above $^{10}BCl_3$ (4.0 mmol) was then vacuum transferred into the flask. The reaction mixture was warmed to −78 °C at which temperature a brown solid was initially formed which subsequently turned yellowish and finally became a white crystalline material over a 1-h period. The mixture was allowed to warm to room temperature over a 15-h period. Use of cold trap fractionation gave $^{10}BMe_3$ (2.2 mmol, 55% yield) which passed through a −78 °C trap and collected at −190 °C.

Reaction between $^{10}BMe_3$ and 2,3-Dicarba-*nido*-hexaborane. Both $^{10}BMe_3$ (with 92% ^{10}B isotope and 8% ^{11}B isotope) (1.74 mmol) and $C_2{}^nB_4H_8$ (0.83 mmol) were condensed into a 30-mL reaction flask with an attached side-arm NMR tube. After the mixture was heated to 244 °C for 20 h, a yellowish oily liquid was formed. The volatile fraction of the reaction products was separated by fractional condensation followed by cold column distillation (vide supra). The ^1H and ^{11}B NMR spectra of reaction products are very similar to those of the corresponding reaction involving $^nBMe_3$; however, the area for the B(3) peak of 1,3,5,6,7,-Me_5-2,4-$C_2B_5H_2$ in the ^{11}B NMR spectrum is perhaps slightly enhanced relative to the other resonances. This suggests that the incorporation of the additional boron atom from $^{10}BMe_3$ in the cage expansion reaction, at best, very slightly favors positions 5,6 and 1,7 of the dicarbaheptaborane. A comparison of the mass spectrum of *B*-Me_6-$C_2B_6H_2$, obtained from the $^{10}BMe_3$/$C_2B_4H_8$ reaction, with *B*-Me_6-$C_2{}^nB_6H_2$ (n is natural abundance $^{11}B/^{10}B$ ratio = 4.0) indicated a ratio of 43/57 for $^{10}B/^{11}B$ in the ^{10}B-enriched compound. Similarly, the *B*-Me_5-$C_2B_5H_2$ obtained from the $^{10}BMe_3/C_2B_4H_8$ reaction gave a 44/56 $^{10}B/^{11}B$ ratio. Theoretically if a 2:1 ratio of $BMe_3/C_2B_4H_8$ is required for the formation of the cage expansion product, i.e., the C_2B_6 cage moiety, a 44/56 $^{10}B/^{11}B$ ratio is expected; if a 1:1 ratio of $BMe_3/C_2B_4H_8$ is required, a 34/66 $^{10}B/^{11}B$ ratio is expected for the cage-expansion product, i.e., the C_2B_5 cage moiety.

Preparation of Diborane from BCl_3 and $(CH_3)_3NBH_3$. Trimethylamine–borane (10.6 mmol) was placed into a 250-mL reaction flask. After evacuation, BCl_3 (2.71 mmol) was condensed into the flask which was then sealed and the mixture allowed to warm to room temperature. The mixture was kept at room temperature for 3 h during which time a new type of white solid formed (similar to a "wet" white powder in appearance, as compared to the fairly large crystals of the starting material, trimethylamine–borane), and then the mixture was heated to 62 °C for 16 h. The reaction flask was connected and opened to the vacuum apparatus, and the contents were separated by cold trap fractionation at −120 and −190 °C. The trap at −190 °C contained 1.25 mmol of B_2H_6 (92% yield based on the limiting reagent BCl_3) which was identified from its infrared spectrum.[23] The reaction proceeded according to the equation

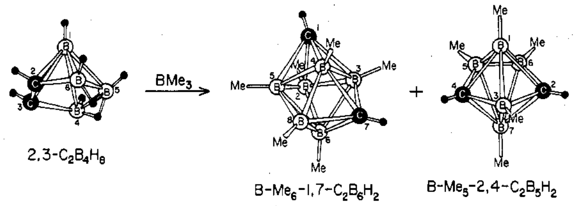
$$BCl_3 + (CH_3)_3NBH_3 \rightarrow {}^1/_2B_2H_6 + (CH_3)_3NBCl_3$$

Purification of 1,6-$C_2B_4H_6$. The 1,6-$C_2B_4H_6$ given to us contained about 10% 2-CH_3-1,5-$C_2B_3H_4$ which was difficult to remove using conventional high-vacuum fractionation techniques. But upon combining the carborane mixture with a 10% mole fraction of tetramethylethylenediamine at −190 °C and warming to room temperature with stirring for 0.5 h, the 2-$CH_3C_2B_3H_4$ formed a very low volatility complex from which the 1,6-$C_2B_4H_6$ could be removed by vacuum fractionation through traps at −50 and −190 °C. The purified 1,6-$C_2B_4H_6$ was found in the latter trap.

Reaction of 1,6-$C_2B_4H_6$ and $(CH_3)_3B$. One end of a sealed quartz tube containing a mixture of $(CH_3)_3B$ (8.0 mmol) and 1,6-$C_2B_4H_6$ (2.0 mmol) was immersed in a −30 °C bath while subjecting the other end to a series of high-temperature settings. With a high-temperature setting of less than 550 °C no significant reaction occurred and at this temperature there was only trace evidence of oily products. After a 17-h heating period at 590 °C, the mixture was vacuum fractionated through traps at 0 °C (trace quantity), −40 °C (small quantity of white solids which when dissolved in CS_2 exhibited peaks at δ −86 and −53 in the ^{11}B NMR), −95 °C (ca. 0.5 mmol), −125 °C (0.95 mmol of recovered 1,6-$C_2B_4H_6$ and 0.05 mmol of $Me_4B_2H_2$), and −190 °C (5.0 mmol of recovered Me_3B). Fractionation of the 0.5 mmol product trapped at −95 °C through a cold column[14] gave the following: at −126 to −125 °C, 0.03 mmol of unidentified material; at −90 to −84 °C, 0.03 mmol of $Me_4B_2H_2$; at −67 to −63 °C, 0.20 mmol of compound mixture A; at −62 to −57 °C, 0.16 mmol of compound mixture B; at −45 °C to room temperature, 0.02 mmol of C. The nonvolatiles of the reaction tube partially dissolved in chloroform and exhibited a broad band in the ^{11}B NMR from δ −10 to +13 ppm. Mass spectra of the cold-column fractions A, B, and C indicated that all contained mostly $Me_2C_2B_5H_5$ and a minor amount of $Me_3C_2B_5H_4$. A GLC-MS of fraction B gave three GLC peaks in an approximate area ratio of 2:16:1 with all three exhibiting the mass spectra expected of $Me_2C_2B_5H_5$[17] and the last of these three GLC peaks containing some (an estimated 10%) $Me_3C_2B_5H_4$. A GLC–MS of fraction A exhibits three peaks in an area ratio of 8:7:1, and again the mass spectral patterns of all three GC peaks were those of $Me_2C_2B_5H_5$ with the last peak containing some $Me_3C_2B_5H_4$. The presence of a very weak intensity mass spectral peak at *m/e* 100 in the first GLC–MS fraction may indicate the presence of a small amount of $CH_3C_2B_5H_6$. A ^{11}B and ^1H NMR analysis[16] gave the approximate ratios of Me_2-2,4-$C_2B_5H_5$ isomers: 45–60% 1,3-, 18–30% 3,5-, 9–11% 1,7-, 0–12% 5,6-, and 0–12% 1,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ for fraction A and 16–46% 1,3-, 16–47% 1,5-, 7–8% 1,7-, 0–31% 5,6-, and 0–31% 3,5-$(CH_3)_2$-2,4-$C_2B_5H_5$ for fraction B. The ^1H NMR data for both $(CH_3)_2C_2B_5H_5$ fractions gave a relative intensity of 38:30:32 for the three methyl regions, 1-CH_3-, 3-CH_3-, and 5-CH_3-, respectively.

Discussion

A two-boron cage expansion giving *B*-Me_6-*closo*-$C_2B_6H_2$ occurs upon reacting *nido*-2,3-$C_2B_4H_8$ with trimethylborane at 220–240 °C, eq 1. The highest yield product, however, is *B*-Me_5-*closo*-2,4-$C_2B_5H_2$, as previously observed when the reaction is carried out at the higher temperature of 300 °C.[4] In contrast to the higher temperature reaction, the 220–240 °C reaction products do not contain substantial quantities of amorphous nonvolatile tan-colored solids but instead have the appearance of a slightly milky oil which consists largely of the volatile products listed in Table I. Total combined yields of volatile cage expansion products, $Me_xC_2B_6H_{8-x}$ and $Me_xC_2B_5H_{7-x}$, vary somewhat, ranging over a series of reactions from 35 to 97% of theoretical based upon $C_2B_4H_8$ consumed. The ratio of the per-*B*-methylated/less-*B*-methylated products as well as the ratio of $Me_xC_2B_6H_{8-x}$/$Me_xC_2B_5H_{7-x}$ carboranes improves upon increasing the $BMe_3/C_2B_4H_8$ ratio of reactants.



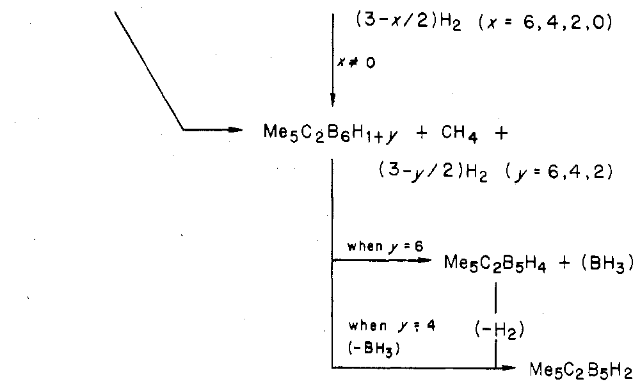
(1)

The reaction rate does not appear to follow a consistent pattern and attempts to measure the rate dependence on trimethylborane and $C_2B_4H_8$ were not productive. Varying the $BMe_3/C_2B_4H_8$ concentration ratio did not give a systematic change in reaction rate although all mixtures react to near completion within 16 h. The course of the reaction was reminiscent of radical-type reactions in that no observable reaction after a given time period was often followed by a shorter period at the same temperature in which a reaction hurried to completion. Attempts to encourage a shorter initiation time by introducing small amounts of oxygen or by ultraviolet irradiation of the reaction mixture or UV irradiation of a *tert*-butyl peroxide solution of the reaction mixture did not prove successful. Although ultraviolet irradiation of the $BMe_3/C_2B_4H_8$ mixture does not result in the formation of the thermal cage-expansion products, tetramethyldiborane is formed and is attributed to the photolytic formation of diborane from $C_2B_4H_8$[20] followed by the transmethylation of B_2H_6 by BMe_3.[24]

When the thermal cage-expansion reaction was effected using ^{10}B-enriched trimethylborane, the ^{10}B enrichment of $Me_6C_2B_6H_2$ is nearly exactly that predicted by the simple overall eq 2. The isotope study then appears to eliminate

$$2BMe_3 + C_2B_4H_8 \rightarrow Me_6C_2B_6H_2 + 3H_2 \qquad (2)$$

mechanistic reaction schemes involving an intermolecular boron–boron exchange between any expected intermediate nido, arachno, or hypho carboranes, a phenomenon not uncommon in reactions of some polyboranes.[12] A little surprisingly, the $^{10}B/^{11}B$ ratio found in the $Me_5C_2B_5H_2$ produced from the isotope study is the same as found in the $Me_6C_2B_6H_2$. This suggests that a C_2B_6 carborane is a precursor to the C_2B_5 carborane system and loses a boron in a random fashion. Since we have not found any indication that the *closo*-$C_2B_6H_8$ (and its known *B*-methyl derivatives) converts to *closo*-$C_2B_5H_7$ (and its *B*-methyl derivatives) under the conditions of the above reaction, it is likely that loss of a borane unit from a higher order (i.e., nido, arachno, or hypho) C_2B_6 intermediate occurs, eq 3. Although none of the higher order C_2B_6 carboranes were isolated in a pure state, there was GLC–MS evidence for a *nido*-$Me_5C_2B_6H_5$ in several of the product mixtures. Elimination of a BH_3 unit from a compound of this composition could well be responsible for the obtained $Me_5C_2B_5H_2$. The ^{11}B NMR spectra of the reaction products of $^{10}BMe_3$ and $C_2B_4H_8$ show that there is no significant positional preference of the additional borons in the cage expansion.



(3)

Both methane and molecular hydrogen are formed during the cage-expansion reaction. The formation of methane may occur in one of the steps leading to the formation of the various methylated derivatives of $C_2B_5H_7$ as indicated in eq 3 and in the net equation (4). Since the moles of hydrogen liberated

$$2BMe_3 + C_2B_4H_8 \rightarrow Me_xC_2B_5H_{7-x} + (6-x)CH_4 + (x-2.5)H_2 \qquad (4)$$

cannot be negative, unit values of *x* in eq 4 cannot be less than 3 which is consistent with the observation that the mono- and dimethyl derivatives of $C_2B_5H_7$ are produced in low yields relative to higher methylated derivatives of the same carborane system. A more elaborate scheme undoubtedly accounts for the almost insignificant presence of the mono- and dimethyl derivatives of $C_2B_5H_7$.

It is known that two molecules of *nido*-$C_2B_4H_8$ can thermally disproportionate at 300 °C to give the closo products 2,4-$C_2B_5H_7$ and 1,5-$C_2B_3H_5$ with loss of 2 H_2[5,6,13] suggesting the possibility that the *B*-permethyl derivatives of $C_2B_5H_7$ obtained in the above cage expansion reaction might arise from a methyl–hydrogen exchange of the parent $C_2B_5H_7$ with $(CH_3)_3B$; however, control experiments show that $C_2B_5H_7$ cannot be methylated with BMe_3 at 300 °C or below. Also, no B-methylated derivatives of *nido*-$C_2B_4H_8$, *closo*-$C_2B_4H_6$, nor *closo*-$C_2B_3H_5$ (nor the parent of the last two) were detected in the product mixture from the thermal cage expansion reaction. It is improbable that the two closo carboranes 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ are intermediates leading to the observed methylated C_2B_5 and C_2B_6 carboranes, for we have found that the reaction of trimethylborane with 1,5-$C_2B_3H_5$ gives methylated derivatives of $C_2B_3H_5$ and $C_2B_3H_4$–$C_2B_3H_4$ with no evidence that these in turn convert to *closo*-$C_2B_5H_7$ or *closo*-$C_2B_6H_8$ derivatives.[2b] And trimethylborane does not react with 1,6-$C_2B_4H_6$ until well above the temperatures used in the cage expansion of $C_2B_4H_8$, and then the major products are various isomers of *B*-$(CH_3)_2$-2,4-$C_2B_5H_5$ with only small quantities of *B*-CH_3-2,4-$C_2B_5H_6$ and *B*-$(CH_3)_3$-2,4-$C_2B_5H_4$

also produced, even though trimethylborane was present in large excess.

In an attempt to make chloro, phenyl, and fluoro derivatives of $C_2B_5H_7$ and $C_2B_6H_8$, a number of reactions between $C_2B_4H_8$ and BR_3 (where R = Cl, C_6H_5, or F, respectively) were tried. In the cases of BCl_3 and $B(C_6H_5)_3$ some reaction was noted giving some unsubstantiated evidence of cage expansion products, while BF_3 did not appear to react with the carborane.

The preferred route to the parent *nido*-2,4-$C_2B_4H_8$ is the reaction between pentaborane and acetylene at 220 °C, eq 5.[13]

$$B_5H_9 + HC{\equiv}CH \xrightarrow{220\ ^\circ C} \underset{30\text{–}50\%\ \text{yield}}{C_2B_4H_8 + \text{polymeric materials}} \qquad (5)$$

We therefore attempted to synthesize the *B*-methyl derivatives of *closo*-2,4-$C_2B_5H_7$ and *closo*-1,7-$C_2B_6H_8$ directly from B_5H_9, eq 6, by the combination of eq 1 and 5.

$$B_5H_9 + HC{\equiv}CH + B(CH_3)_3 \xrightarrow{235\ ^\circ C} B\text{-}(CH_3)_6\text{-}1,7\text{-}C_2B_6H_2 + B\text{-}(CH_3)_5\text{-}C_2B_5H_2,\ \text{etc.} \qquad (6)$$

The observed combined yield of all obtained closo carboranes is 21–22% from eq 6, as compared to an approximate 25% overall yield when carrying out the two steps separately. It is noted in a control experiment that $(CH_3)_3B$ does not react with acetylene at 235 °C and therefore it is considered unlikely that a reaction sequence other than eq 1 followed by eq 5 could be responsible for the products found in eq 6.

The C-methylated 2,3-$(CH_3)_2$-*nido*-2,3-$C_2B_4H_6$, prepared from B_5H_9 and MeC≡CMe at 160 °C, reacts with BMe_3 to give results similar to the above with *closo*-$Me_7C_2B_5$ as the primary cage expansion product. Because $Me_5C_2B_5H_2$ is formed from Me_3B and $C_2B_4H_8$ at 80 °C lower than the parent $C_2B_5H_7$ is formed from the disproportionation of $C_2B_4H_8$, it was an unrealized possibility that $Me_7C_2B_5$ might be formed from 2,3-$Me_2C_2B_4H_6$ and Me_3B at a temperature significantly lower than the 220 °C needed to form the heptamethyl-*closo*-carborane from a disproportionation of 2,3-$Me_2C_2B_4H_6$. Instead, the same temperature range as used for the parent *nido*-carborane/trimethylborane reaction was required when the 2,3-Me_2-2,3-$C_2B_4H_6$ was used.

Two intermediate-size closo carboranes are known to react with diborane to form the next higher closed polyhedron, equations 7 and 8, and it is suggested that the *arachno*-1,3-$C_2B_7H_{13}$ may react directly with diborane to give the next higher closo carborane, eq 9.[8-11] Based on the above, it was predicted that a reaction according to eq 10 might occur, but our results showed that closo carboranes are not produced in any appreciable quantities by the incorporation of boron from diborane. This may be attributed, in part, to the degradation of B_2H_6 prior to reaction with $C_2B_4H_8$ under these conditions. Alternatively, one notices the absence of a (reactive?) vacant p orbital in B_2H_6 in contrast to BMe_3, and an insufficient equilibrium quantity of a possibly reactive "BH_3" species may account for the inability to effect a reaction with $C_2B_4H_8$.

$$1,7\text{-}C_2B_6H_8 + 0.5B_2H_6 \rightarrow 1,6\text{-}C_2B_7H_9 + H_2 \qquad (7)$$

$$1,6\text{-}C_2B_7H_9 + 0.5B_2H_6 \rightarrow 1,6\text{-}C_2B_8H_{10} + H_2 \qquad (8)$$

$$1,3\text{-}C_2B_7H_{13} + 0.5B_2H_6 \rightarrow 1,6\text{-}C_2B_8H_{10} + 3H_2 \qquad (9)$$

$$2,3\text{-}C_2B_4H_8 + 0.5B_2H_6 \rightarrow 2,4\text{-}C_2B_5H_7 + 2H_2 \qquad (10)$$

The ^{11}B NMR of $Me_6C_2B_6H_2$ consists of two singlets at δ −12.5 and +7.0, relative to $(C_2H_5)_2O{\cdot}BF_3$, in an area ratio of 2:1. The downfield shifts caused by *B*-methyl attachment to the parent *closo*-$C_2B_6H_8$[25] are 5.2 and 1.9 ppm, respectively, for the two types of resonances. These downfield shifts are slightly less in magnitude to similar shifts seen in several methyl derivatives of *closo*-$C_2B_5H_7$.[16]

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Registry No. *nido*-2,3-$C_2B_4H_8$, 21445-77-2; $(CH_3)_3B$, 593-90-8; *B*-Me_6-*closo*-1,7-$C_2B_6H_2$, 68238-13-1; *B*-Me_5-*closo*-1,7-$C_2B_6H_3$, 68238-04-0; *B*-Me_4-*closo*-1,7-$C_2B_6H_4$, 68238-05-1; *B*-Me_3-*closo*-1,7-$C_2B_6H_5$, 68238-06-2; *B*-Me_5-*closo*-2,4-$C_2B_5H_2$, 18972-11-7; *B*-Me_4-*closo*-2,4-$C_2B_5H_3$, 68238-07-3; *B*-Me_3-*closo*-2,4-$C_2B_5H_4$, 68238-08-4; *B*-Me_2-*closo*-2,4-$C_2B_5H_5$, 29294-50-6; *B*-Me-*closo*-2,4-$C_2B_5H_6$, 68238-09-5; 2-3-$(CH_3)_2$-*nido*-2,3-$C_2B_4H_6$, 20741-68-8; Me_7-*closo*-2,4-C_2B_5, 68297-90-5; Me_6-*closo*-2,4-C_2B_5H, 68238-14-2; Me_7-*closo*-1,7-C_2B_6H, 68238-15-3; *closo*-1,6-$C_2B_4H_6$, 20693-67-8; 1,3-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68297-89-2; 3,5-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68238-16-4; 1,7-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 23753-78-8; 1,5-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 68238-17-5; 5,6-$(CH_3)_2$-*closo*-2,4-$C_2B_5H_5$, 58548-76-8; $B(C_6H_5)_3$, 960-71-4; BCl_3, 10294-34-5; $^{10}BMe_3$, 5943-12-4; $(CH_3)_3NBH_3$, 75-22-9; acetylene, 74-86-2; B_5H_9, 19624-22-7.

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(25) G. Dunks, Ph.D. Thesis, UCLA, 1970; University Microfilms No. 71-3880; G. Dunks, private communication. ^{11}B NMR chemical shift values found for the parent *closo*-$C_2B_6H_8$ are δ −7.3 (area 4) and +8.9 (area 2).