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STUDIES OF BORANES

XXXVIII*. PREPARATION AND CHARACTERIZATION OF 1,2-DICARBADECABORANE(10) AND 1,2-DIMETHYL-1,2-DICARBADECABORANE(10)

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SUMMARY

The *closo*-carboranes, 1,2-$B_8C_2H_{10}$ and 1,2-$B_8C_2H_8(CH_3)_2$, are formed by pyrolyzing *nido*-5,6-$B_8C_2H_{12}$ and *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$, respectively Chemical and spectroscopic evidence support *closo*-bicapped Archimedian antiprism structures with vicinal carbon atoms in the 1,2-positons. A "twist-fold" mechanism for the *nido* → *closo* conversion is postulated. Further pyrolysis of 1,2-$B_8C_2H_{10}$ or 1,2-$B_8C_2H_8(CH_3)_2$ produces the known 1,6- and 1,10-$B_8C_2H_{10}$ or 1,6- and 1,10-$B_8C_2H_8(CH_3)_2$ species, respectively.

Closo-1,2-$B_8C_2H_{10}$ and *closo*-1,2-$B_8C_2H_8(CH_3)_2$ are also recovered as products from the disproportionation of *nido*-$B_7C_2H_{11}$ and *nido*-$B_7C_2H_9(CH_3)_2$, respectively

INTRODUCTION

Members of the $B_nC_2H_{n+2}$ series of *closo*-carboranes are known[2] for $n = 3$ to $n = 10$. Although at least two (and usually more) isomers are possible for each geometry, mainly the "most stable" isomers with non-adjacent carbon atoms have been isolated and studied[2]. Several molecular orbital studies[3-6] have predicted structures containing vicinal carbon atoms to be thermodynamically unstable with respect to those containing non-adjacent carbon atoms. The thermal isomerizations of $B_4C_2H_6$[7], $B_{10}C_2H_{12}$[8], and now $B_8C_2H_{10}$ substantiate these predictions.

Prior to 1970 only two "least stable" isomers of smaller *closo*-carboranes were known, *viz* C,3-$(CH_3)_2$-1,2-$B_3C_2H_3$[9] and 1,2-$B_4C_2H_6$[10] At that time we reported 2,3-$B_5C_2H_5(CH_3)_2$ as a minor product in the reaction of 2-butyne with octaborane(12)[11,12]. We also noted an intermediate size *closo*-carborane that also contained adjacent carbon atoms, *i.e.* 1,2-$B_8C_2H_8(CH_3)_2$, as one of several carboranes formed by the disproportionation of *nido*-1,2-$B_7C_2H_9(CH_3)_2$[11-14]. 1,2-$B_8C_2H_8(CH_3)_2$ can also be made in low yield by heating *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$. Similarly, 1,2-$B_8C_2H_{10}$

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* For Part XXXVII see ref 1

is obtained not only from the disproportionation of *nido*-$B_7C_2H_{11}$, but also from the direct pyrolysis of *nido*-5,6-$B_8C_2H_{12}$[13]. 1,2-$B_8C_2H_{10}$ has also been generated by the heating of *nido*-5,6-$B_8C_2H_{12}$ with (*N*-ethylpiperdine)borane[15] and by the disproportionation of Na $(B_8C_2H_{11})$[16].

In light of the paucity of *closo*-carboranes containing vicinal carbon atoms, we here summarize our syntheses and detail the characterization of *closo*-1,2-$B_8C_2H_{10}$ and *closo*-1,2-$B_8C_2H_8(CH_3)_2$.

RESULTS AND DISCUSSION

Closo-1,2-$B_8C_2H_{10}$ is a white, crystalline solid (m.p 173–174°, sealed tube) with a volatility slightly below decaborane(14). The retention time of 1,2-$B_8C_2H_{10}$ is far longer than that of the 1,6- or 1,10-isomers (see Table 1) and, unfortunately, elutes at nearly the same R_f value as *nido*-5,6-$B_8C_2H_{12}$ These two compounds are separated only with great difficulty by repeated fractionation.

Spectral evidence strongly favors a molecular structure for 1,2-$B_8C_2H_{10}$ of a bicapped Archimedian antiprism with carbon atoms at the adjacent 1,2-positions (Fig. 1A) This kind of geometry has been verified crystallographically for the isomeric 1,6-$B_8C_2H_8(CH_3)_2$ species[17] and for the isoelectronic $B_{10}H_{10}^{2-}$ ion[18]. Such a geometry (Fig. 1A) would possess a mirror plane through C(1,2) and B(4,10) and would be expected to give to a 1/2/2/2/1 pattern of doublets in the ^{11}B NMR spectrum. The actual spectrum is shown in Fig. 2A. The expected pattern is realized if one considers doublet (d) to arise from the accidental overlap of two doublets of intensity two. No increase in resolution of the spectrum is obtained by proton decoupling, artificial line narrowing[19], or partial relaxation techniques[20]. This spectral ambiguity is resolved for the dimethyl derivative (*vide infra*).

TABLE 1

PRODUCTS FROM PYROLYSES OF *nido*-CARBORANES

	R_f[a]	Yield (%) $B_8C_2H_{12}$ (180°)[b]	 $B_8C_2H_{12}$ (260°)[c]	 $B_7C_2H_{11}$ (150°)[c]
2,3-$B_5C_2H_7$	2 2			Trace[d]
1,6-$B_6C_2H_8$	5 5			Trace[d]
1,6-$B_7C_2H_9$	11 8	11 2	5 7	1 5
1,10-$B_8C_2H_{10}$	14 1	3 8	5 7	0 7
1,6-$B_8C_2H_{10}$	18 6	29 4	60 8	10 2
2,3-$B_9C_2H_{11}$	33.7		3 8	Trace[d]
5,6-$B_8C_2H_{12}$	41 6	10 0		6 0
1,2-$B_8C_2H_{10}$	47 7	22 2		1 0
1,7-$B_{10}C_2H_{10}$	55 1		Trace[d]	Trace[d]
1,2-$B_{10}C_2H_{12}$	84 0		Trace[d]	Trace[d]

[a] Relative to n-pentane = 1 00 on 1/4″ × 10′ SF-96 on firebrick column at 160°, 60 ml/min [b] Yields determined by weighing recovered carboranes [c] Yields determined by GLC integrals and total weight of products [d] I D by mass spectra and R_f value

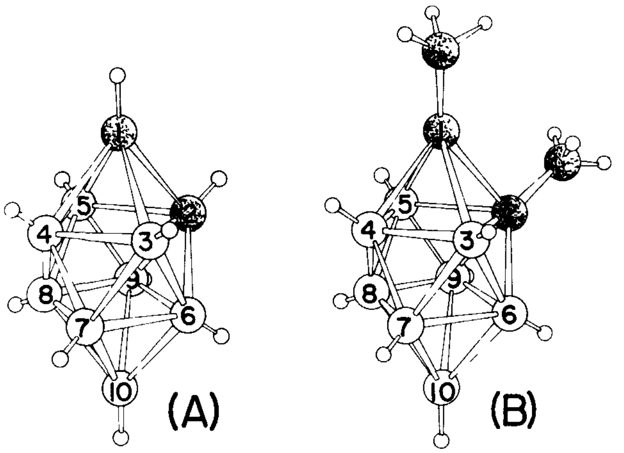

Fig 1 Proposed structures for (A) $1,2\text{-}B_8C_2H_{10}$ and (B) $1,2\text{-}B_8C_2H_8(CH_3)_2$

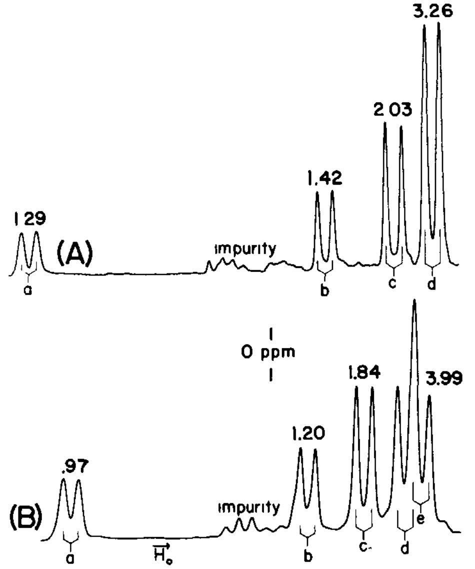

Fig 2 70 6 MHz ^{11}B NMR spectra obtained by the Fourier transform method, with 2048 points in the time domain and 5000 Hz sweep width Each spectrum is the result of 1024 accumulations with a recycle time of 0 11 sec (total time about 2 min). Chemical shifts [δ, ppm relative to external $BF_3 \cdot O(C_2H_5)_2$] and coupling constants (Hz) for (A) $1,2\text{-}B_8C_2H_{10}$ in n-pentane solution are (a) −38 4, 178, (b) +8 5, 170, (c) +19 3, 185, and (d) +25 4, 162 The impurity peaks arise from *nido*-5,6-$B_8C_2H_{12}$ Chemical shifts and coupling constants for (B) $1,2\text{-}B_8C_2H_8(CH_3)_2$ are (a) −32 0, 168, (b) +5 3, 165, (c) +14 2, 178, (d) +20 7, 182, and (e) +23 2, 175 The impurity peaks arise from *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$. Computer integrated areas are given above the peaks

The 220 MHz PMR spectrum of $1,2\text{-}B_8C_2H_{10}$ in TMS consists of two singlets of equal intensity at −5.38 and −3.23 ppm. These resonances are easily assigned to the apical C(1) and equitorial C(2) protons, respectively, by comparison to chemical

TABLE 2

IR SPECTRA
Thin film on IRTRAN-2 window at −196° (ref 33)

1,2-$B_8C_2H_{10}$	2900 (w), 2550 (sb), 1530 (wb), 1465 (w), 1295 (vw), 1220 (m), 1150 (vw), 1130 (m), 1105 (s), 1090 (msh), 1040 (m), 1205 (m), 1010 (m), 970 (s), 940 (sb), 912 (mb), 865 (w), 845 (w), 803 (w), 755 (w), 740 (wsh), 712 (w)
1,2-$B_8C_2H_8(CH_3)_2$	2950 (w), 2830 (w), 2550 (s), 1445 (s), 1430 (s), 1250 (wb), 1025 (vw), 975 (w), 960 (w), 945 (m), 925 (w), 918 (w), 905 (w), 895 (w), 885 (m), 875 (msh), 825 (w), 765 (w), 755 (w), 710 (w)

shift values for known C-substituted derivatives of 1,6- and 1,10-$B_8C_2H_{10}$[21,22]. The IR spectrum (Table 2) displays characteristic C–H and B–H stretching modes at 2900 and 2550 cm^{-1} respectively; however, there are no absorptions in the range normally associated with hydrogen bridging vibrations ($\approx$1800–2300 cm^{-1}). The mass spectrum at 70 eV of 1,2-$B_8C_2H_{10}$ exhibited a typical *closo*-carborane pattern[23] with a very intense molecular envelope at *m/e* 115 to 122 (highest intensity *m/e* 120) An exact mass matching experiment on the molecular ion gave 122.1536; calcd. for $^{11}B_8{}^{12}C_2{}^{1}H_{10}{}^{+\cdot}$ 122.1527.

Closo-1,2-$B_8C_2H_8(CH_3)_2$ is a white, crystalline solid (m.p. 97°, sealed tube) of low volatility. It is slightly less volatile than *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$, and the two compounds can easily be separated on a low temperature fractionation column[24] As with the parent species, 1,2-$B_8C_2H_8(CH_3)_2$ elutes after the 1,10- and 1,6-isomers (see Table 3)

The proposed structure of 1,2-$B_8C_2H_8(CH_3)_2$ (Fig. 1B) is in complete accord with the observed ^{11}B NMR spectrum (Fig. 2B). The expected 1/2/2/2/1 pattern of doublets is readily apparent. The 220 MHz PMR spectrum of 1,2-$B_8C_2H_8(CH_3)_2$ in CS_2 consists of two singlets of equal intensity at −2.36 and −1.96 ppm These resonances may be assigned to the apical C(1) and equitorial C(2) methyl groups, respectively, by comparison to known values of C-substituted derivatives of 1,6- and 1,10-$B_8C_2H_{10}$[21,22]. Again, the IR spectrum (Table 2) shows no evidence of B–H–B groups. The mass spectrum of 1,2-$B_8C_2H_8(CH_3)_2$ at 70 eV exhibits a strong molecular

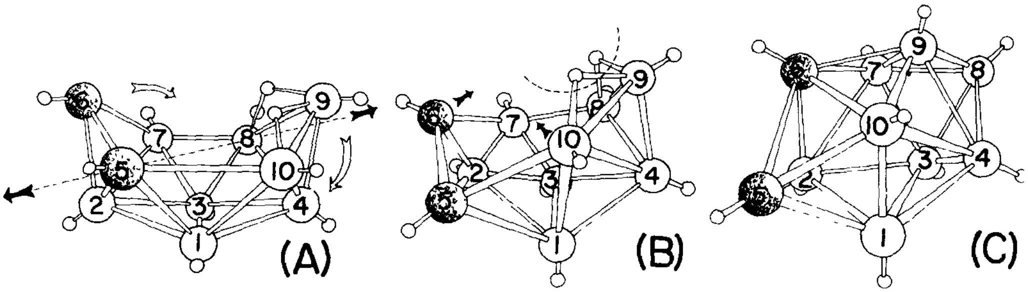

Fig 3 A "twist-fold" mechanism for 1,2-$B_8C_2H_{10}$ formation from *nido*-5,6-$B_8C_2H_{12}$ (A) B(6 7) and B(9 10) are twisted clockwise (open arrows) while the molecule is elongated along the B(5,8) axis (solid arrows) (B) Hydrogen is eliminated and the molecule is folded up by forming B(6,10) and B(7,9) bonds to give the bicapped Archimedian antiprism structure (C) The correct numbering is given in Fig 1

envelope at *m/e* 143 to 150 (highest intensity, *m/e* 147) An exact mass matching experiment on the molecular ion gave 150.1838; calcd. for $^{11}B_8{}^{12}C_4{}^{1}H_{14}$: 150.1840

A suggested mechanism to explain the conversion of *nido*-5,6-$B_8C_2H_{12}$ into *closo*-1,2-$B_8C_2H_{10}$ is shown in Fig. 3. This "twist-fold" process has been shown[25] to occur for the isostructural conversion, $B_{10}H_{12}[N(C_2H_5)_3]_2$ to $B_{10}H_{10}{}^{2-}$. It is also believed to account for the novel structure[26] of *nido*-1,2-$B_7C_2H_9(CH_3)_2$[14] The process involves simple hydrogen elimination (eqn 1).

$$B_8C_2H_{12} \xrightarrow[-H_2]{(1)} 1{,}2\text{-}B_8C_2H_{10} \xrightarrow{(2)} 1{,}6\text{-}B_8C_2H_{10} \xrightarrow{(3)} 1{,}10\text{-}B_8C_2H_{10}$$

$$\xrightarrow[-2H_2]{(4)} B_7C_2H_9 + B_9C_2H_{11}$$

Above 180°, 1,2-$B_8C_2H_{10}$ begins to rearrange to the known 1,6-isomer which, in turn, rearranges to the 1,10-isomer[22]. This "double diamond-square-diamond" rearrangement has been described elsewhere[27].

To a lesser extent, a disproportionation of *nido*-5,6-$B_8C_2H_{12}$ (eqn. 4) appears to occur above 200° This process is well known for the systems in eqns. (5)[7,28] and (6)[22,29].

$$B_4C_2H_8 \xrightarrow{(5)} B_3C_2H_5 + B_5C_2H_7 \quad (\text{also } B_4C_2H_6)$$

$$B_7C_2H_{13} \xrightarrow{(6)} B_6C_2H_8 + 1{,}6\text{-}B_8C_2H_{10} \quad (\text{also } B_7C_2H_9)$$

In the case of the *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$, the dominant mechanism upon pyrolysis appears to be the "twist-fold", direct hydrogen elimination process (Fig. 3). The reaction proceeds far slower than in the case of the parent carboranes. Attempts to raise the temperature resulted in the 1,2- → 1,6-$B_8C_2H_8(CH_3)_2$ isomerization; however, addition of diborane appreciably raised the yield of 1,2-$B_8C_2H_8(CH_3)_2$.

The disproportionation of *nido*-$B_7C_2H_{11}$ (eqn. 8) was also explored as a route

$$B_7C_2H_{11} \xrightarrow[-H_2]{(7)} B_7C_2H_9$$

$$\xrightarrow[-2H_2]{(8)} B_6C_2H_8 + 1{,}2\text{-}B_8C_2H_{10}$$

to 1,2-$B_8C_2H_{10}$, but the yields were disappointingly low (see Table 1). Surprisingly, both 1,2-$B_8C_2H_{10}$ and *nido*-5,6-$B_8C_2H_{12}$ were identified.

This experiment was repeated using *nido*-1,2-$B_7C_2H_9(CH_3)_2$. Both 1,2-$B_8C_2H_8(CH_3)_2$ and *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$ were isolated*. Addition of diborane to the reaction greatly increased the yield of the *nido*-B_8C_2 carborane, suggesting that a *nido*-carborane to *nido*-carborane expansion was occurring. This process is already known for *closo*-carboranes[21]. Our experiments also imply that the *nido*-5,6-B_8C_2 framework can be expanded to the *closo*-$B_{10}C_2$ framework.

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* The pyrolysis of *nido*-1,2-$B_7C_2H_9(CH_3)_2$ also provides the best known preparation of *closo*-2,3-$B_5C_2H_5(CH_3)_2$ (see refs. 13 and 14) In addition, a clear liquid was noted with R_{f_a} 9 0 and parent *m/e* 126 which may be *closo*-1,2-$B_6C_2H_6(CH_3)_2$

TABLE 3

PRODUCTS FROM THE PYROLYSES OF DIMETHYL- *nido*-CARBORANES

	R_f[a]	R_f[b]	Yields (%)				
			$B_8C_2H_{10}(CH_3)_2$ (120°)[c]	$B_8C_2H_{10}(CH_3)_2$ (260°)[c]	$B_8C_2H_{10}(CH_3)_2 + B_2H_6$[c]	$B_7C_2H_9(CH_3)_2$ (100°)[c]	$B_7C_2H_9(CH_3)_2 + B_2H_6$[c]
2,4-$B_5C_2H_5(CH_3)_2$	1.6					Trace	
1,6-$B_6C_2H_6(CH_3)_2$	2.7		Trace			2	
2,3-$B_5C_2H_5(CH_3)_2$	3.6		Trace			13	
1,6-$B_7C_2H_7(CH_3)_2$	5.5					Trace	
1,10-$B_8C_2H_{10}(CH_3)_2$		5.8		7	Trace		
1,6-$B_8C_2H_{10}(CH_3)_2$		7.1	1	81	12	Trace	
1,8-$B_9C_2H_9(CH_3)_2$	18.0	9.4			Trace	4	
1,2-$B_8C_2H_8(CH_3)_2$	21.5	10.5	3		36	17	
5,6-$B_8C_2H_8(CH_3)_2$	23.0	11.2	96		36	9	35
1,7-$B_{10}C_2H_{10}(CH_3)_2$	49.0	13.7			4	2	42

[a] Relative to n-hexane = 1.00, 1/8" × 10' SF-96 on firebrick column at 130°, 30 ml/min [b] Relative to n-pentane = 1.00, 1/8" × 10' SF-96 on firebrick column at 120°, 30 ml/min [c] Yields determined by GLC integrals and total weight of products

The exact manner in which either *nido*-$B_7C_2H_{11}$ or *nido*-1,2-$B_7C_2H_9(CH_3)_2$ disproportionates is unclear at this time We note that when no diborane is present upon pyrolysis, a large number of different carboranes results, perhaps indicative that the *nido*-B_7C_2 framework may break apart in several competing ways. In contrast to the *nido*-B_8C_2 system, the direct elimination of H_2 to form *closo*-B_7C_2 species (eqn. 7) does not appear to be dominant.

EXPERIMENTAL SECTION

Gas chromatography

Preparative VPC was performed on a F&M Model 700 gas chromatograph using a 1/4″ × 10′ 30% SF-96 on NAW Firebrick column, a thermal conductivity detector, and a He flow rate of 60 ml/min. Fractions were collected in an all glass trapping system[30] at −196°

Analytical VPC was performed on a Varian Model 1200 gas chromatograph connected directly to a Varian Model CH-7 mass spectrometer. A 1/8″ × 10′ 10% SF-96 on NAW Firebrick column was employed at 120° with a He flow rate of 30 ml/min.

Relative retention times are given in Tables 1 and 3.

Spectroscopic data

The ^1H NMR spectra were obtained on a Varian Associates HR-220 spectrometer. The ^{11}B NMR spectra were obtained by the Fourier transform method using a "home-built" pulsed NMR apparatus operating at 70.6 MHz, a Varian 51.7 kG superconducting magnet, and a Nicolet 1086 20K/20 bit computer[31] Both signal averaging and Fourier transformation of the time domain signals were performed directly in the computer. Chemical shifts for ^{11}B and ^1H spectra were measured relative to external samples of $BF_3 \cdot O(C_2H_5)_2$ and TMS, respectively.

Exact mass measurements were made on an Associated Electrical Industries Model MS-9 mass spectrometer by measuring mass ratios to known peaks of perfluorotributylamine.

Infrared spectra were recorded on a Perkin–Elmer Model 621 grating spectrophotometer.

Preparation of starting materials

The preparation and purification of the *nido*-carboranes: $B_7C_2H_{11}$, $B_7C_2H_9(CH_3)_2$, $B_8C_2H_{12}$, and $B_8C_2H_{10}(CH_3)_2$, have been described elsewhere[12–14] Diborane(6) was prepared from KBH_4 and polyphosphoric acid[32] and purified by fractional distillation

Pyrolyses

Pyrolysis of nido-5,6-$B_8C_2H_{12}$ at 180°. 0.394 g $B_8C_2H_{12}$ (3 22 mmole) was sealed in a 100 ml Pyrex bulb and heated at 180° for 6 days. H_2 evolved, 3.94 mmoles The volative products (0.234 g) were separated by preparative GLC. (see Table I) 0.086 g 1,2-$B_8C_2H_{10}$ (0 715 mmole, 22.2%) was recovered

Pyrolysis of nido-5,6-$B_8C_2H_{12}$ at 260° 0 176 g $B_8C_2H_{12}$ (0 948 mmole) was sealed in a 20 ml Pyrex bomb and heated at 260° for 14 h. H_2 evolved, 1 25 mmoles

0.88 g white crystals were purified by GLC (Table 1).

Pyrolysis of nido-$B_7C_2H_{11}$. 0.0539 g $B_7C_2H_{11}$ (0.487 mmole) was sealed into a 5 ml Pyrex bomb and heated to 155° for 15 h H_2 evolved, 0.963 mmole. 0.011 g white crystals were further purified by GLC (Table 1).

Pyrolysis of nido-5,6-$B_8C_2H_{10}(CH_3)_2$ at 260°. 0.249 g $B_8C_2H_{10}(CH_3)_2$ (1.65 mmoles) was sealed into a 20 ml Pyrex bomb and heated at 260° for 36 h H_2 evolved, 1.76 mmoles. 0.22 g of a clear liquid distilled from the bomb was further purified by VPC (see Table 3)

Pyrolysis of nido-5,6-$B_8C_2H_{10}(CH_3)_2$ at 120°. 0.138 g $B_8C_2H_{10}(CH_3)_2$ (0.917 mmole) was sealed into a 200 ml Pyrex bulb and heated at 120° for 24 h 0.069 g of a clear liquid (50% recovery) was partially separated by preparative GLC (see Table 3). Identification was done by mass spectra, R_f values, and ^{11}B NMR spectra.

Pyrolysis of nido-5,6-$B_8C_2H_{10}(CH_3)$ in presence of diborane(6). 0.3260 g $B_8C_2H_{10}(CH_3)_2$ (2.16 mmoles) and 3.80 mmoles B_2H_6 were sealed into a 250 ml Pyrex bulb and heated at 115° for 18 h. H_2 evolved, 6 mmoles. B_2H_6 recovered, 0.36 mmole. 0.26 g of a liquid and solid were purified by VPC (see Table 3).

Pyrolysis of nido-1,2-$B_7C_2H_9(CH_3)_2$. 0.232 g 1,2-$B_7C_2H_9(CH_3)_2$ (1.67 mmoles) was sealed in a 100 ml Pyrex bulb and heated at 100° for 30 h. H_2 evolved, 1.48 mmoles The volative liquids and solids (0.12 g) were partially fractionated on a low temperature distillation column[24] and further purified by VPC. Identifications were done by both R_f values, mass spectra, and ^{11}B NMR spectra (see Table 3)

Pyrolysis of nido-1,2-$B_7C_2H_9(CH_3)_2$ in presence of diborane(6). 0.0306 g 1,2-$B_7C_2H_9(CH_3)_2$ (0.22 mmole) and 0.122 mmole B_2H_6 were sealed into a 5 mm NMR tube to allow observation of the reaction by ^{11}B NMR. Although the liquid yellowed, the ^{11}B NMR spectrum remained unchanged after one week at 30° and also after heating the sample to 80° for 6½ h. After the sample was heated for 8 days at 80°, the spectrum of 1,2-$B_7C_2H_9(CH_3)_2$ had disappeared, and new ^{11}B NMR resonances were apparent. The tube was opened and 0.357 mmoles H_2 removed. No B_2H_6 was found. 0.0272 g solid and liquid were separated by fractional distillation and identified by their VPC R_f values and characteristic ^{11}B NMR spectra (Table 3).

Pyrolysis of closo-1,2-$B_8C_2H_{10}$. 0.0052 g 1,2-$B_8C_2H_{10}$ (0.043 mmoles) was sealed into a 20 ml Pyrex bomb and heated at 200° for 48 h. No hydrogen was detected. The 0.0040 g (77% recovery) of white crystalline products was subject to GLC 1,6-$B_8C_2H_{10}$ (40%) and unchanged 1,2-$B_8C_2H_{10}$ (60%) were identified by their R_f values and ^{11}B NMR spectra.

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