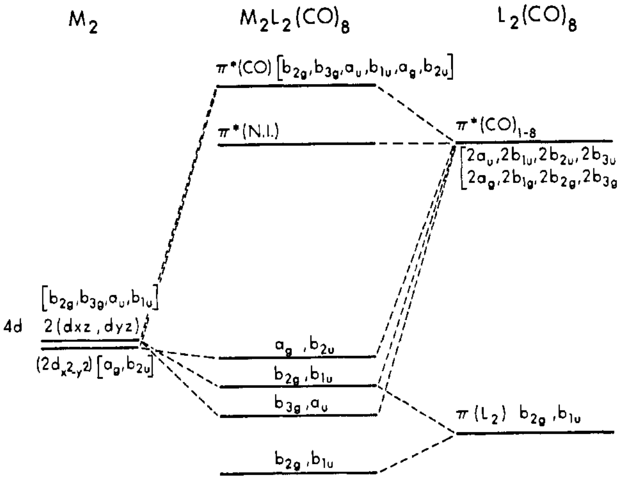

Figure 9.—Qualitative energy level diagram for the tetracarbonyl halide dimers of Mn. The symmetry labels are those for $L_2Mn_2(CO)_8$ (D_{2h}).

converts more slowly to the corresponding TCD in cyclohexane while the I monomer is stable. The decreasing *total* π interaction for the TCD compounds (since there are now only four carbonyls to accept π charge from each Mn) should result in a higher placement of the metal π levels. The a_g,b_{2u} level is placed highest since the $d_{x^2-y^2}$ orbitals interact with only two CO's each and the resulting orbital will have the least amount of *total* d–π* interaction. This accounts for the red shift of the low-energy band from monomer to dimer. The highest lying filled orbitals in the tetracarbonyl dimer compound should not interact with the halide orbitals of π symmetry, which may account for the greater intensity of the first observed band in the TCD compound as compared to the monomer. Increasing halide character in the highest filled e level in the monomer compounds appears to have a similar effect on the intensity of a similar band. Figure 9 gives a qualitative energy level diagram for the tetracarbonyl dimers, showing only the filled π levels and the antibonding π*(CO) levels. The assignments as proposed in Table III indicated a splitting of approximately 6000 cm^{-1} in the two uppermost filled π levels.

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Carboranes from Alkylboron Hydrides

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Both one-carbon and two-carbon carboranes have been prepared from the flow pyrolysis of several alkylboron hydrides. Carbahexaborane(7) and 2-carbahexaborane(9) have been prepared from methylpentaborane(9) and the corresponding *C*-methyl derivatives of these carboranes are obtained from ethylpentaborane(9). Pyrolysis of 1,2-dimethylpentaborane gives a modestly high yield of 1,5-$C_2B_3H_5$ and, surprisingly, no detectable quantity of *B*-methyl derivatives of CB_5H_7. The four-carbon carborane $C_4B_2H_6$ is obtained in low yield from 1,2-tetramethylenediborane(6). Temperature-dependent nuclear magnetic resonance studies on CB_5H_7 and its *C*-methyl derivative reveal a bridge hydrogen tautomerism with a $\Delta G^{\ddagger}$ of *ca.* 14 and 12 kcal, respectively.

Introduction

Nearly all previously known synthetic routes to the parent carboranes involve either a reaction of acetylene with boron hydrides or a degradation of a larger carborane. As one example, preparation of the trigonal-bipyramidal $C_2B_3H_5$ has been accomplished, variously, by the electric discharge or pyrolysis of acetylene with either pentaborane or diborane or by the decomposition of $C_2B_4H_8$.[1] The latter carborane compound, itself, is prepared by the thermal interaction of pentaborane and acetylene.[1]

A preliminary experiment involving methylpentaborane as a starting material indicated that a low-pressure pyrolysis produces small amounts of the carborane CB_5H_7.[2] This paved the way for the present study into the conversion of alkyl carbons (as ligands on boron hydrides) to cage carborane carbons.

Experimental Section

Materials.—1-Methyl-, 2-methyl-, 1,2-dimethyl-, and 1-ethylpentaboranes were prepared using previously known synthetic methods.[3] 1,2-Tetramethylenediborane(6) was prepared by the ether-catalyzed reaction between diborane and 1,3-butadiene.[4] All chemical manipulations were carried out in a standard high-vacuum apparatus. All compounds were purified using either a special low-temperature, high-vacuum distillation column[5] or a 30% Kel-F on firebrick glpc column and identified by mass, ir, and nmr spectroscopic data.

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[1] For references see R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, 1969, Chapter 2, p 51; and R. N. Grimes "Carboranes," Academic Press, New York, N. Y., 1970.

(2) T. Onak, P. Mattschei, and E. Groszek, *J. Chem. Soc. A*, 1990 (1969).

(3) For appropriate references consult P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, **9**, 1430 (1970).

(4) D. E. Young and S. G. Shore, *J. Amer. Chem. Soc.*, **91**, 3497 (1969).

(5) J. Dobson and R. Schaeffer, *Inorg. Chem.*, **9**, 2183 (1970).

Nuclear Magnetic Resonance.—Proton spectra were recorded on Varian A-60, HA-100,[6] and HR-220[7] spectrometers. The boron-11 spectra were obtained at 32.1 MHz using the Varian HA-100 instrument. Decoupled proton spectra at 100 Mc were observed while irradiating at 32.1 MHz using the Nuclear Magnetic Resonance Specialties Model HD-60 spin decoupler modified for use with the HA-100 and Hewlett-Packard Model 200 CD wide-range audio oscillators. Conversely, decoupled ^{11}B spectra at 32.1 MHz were observed while irradiating with the heteronuclear decoupling apparatus equipped with 100-MHz modules.

The chemical shift data for the protons were obtained using tetramethylsilane (τ 10.00) as an internal standard. The chemical shift data for the boron-11 were obtained using boron trichloride, δ −46.8 relative to boron trifluoride–ethyl etherate, as an external secondary standard.

The chemical shift data obtained from the ^{11}B nmr spectra were used to predict the relative double-irradiation frequencies used in obtaining boron-11 decoupled proton nmr spectra. The frequency band used for the decoupling experiments was broad enough with the available equipment to collapse the ^1H nmr multiplets into reasonably sharp singlets. Each kind of boron could be separately irradiated with an acceptable minimum effect on neighboring boron resonances as long as there is at least 5-ppm separation between such resonances.

Infrared spectra were recorded on Beckman IR 5 and Perkin-Elmer 137 spectrophotometers.

Mass spectra were recorded on a Hitachi RMU-6D instrument[8] and a CEC-20-620 instrument.

Apparatus for the Pyrolysis Experiments.—The high-temperature, low-pressure pyrolysis of a given alkylboron hydride was performed in a quartz reaction apparatus shown schematically in Figure 1. The furnace used was a 115-V, 422-W cylindrical furnace, Lindberg Co., Watertown, Wis., having a rated maximum temperature of 1000°. Since the quartz reaction tubes did not fit snugly into the heating cavity of the furnace, asbestos tape was wound around the tube at the exit parts of the furnace to minimize heat loss.

Trap A was kept at a suitably low temperature in order that the vapor pressure of the reactant was sufficiently low, *i.e.*, 1–10 Torr at equilibrium. This allowed the reactant to be bled very slowly into the high-temperature section while pumping with a high-vacuum system at the opposite end of the apparatus.

The pressure recorded at the exit end of trap B was usually about 0.1 Torr which was largely due to the production of noncondensable gases, H_2 and CH_4. After each run the inner surface of the reaction tube was glazed with dark solids which could be removed with boiling, concentrated sulfuric acid, followed with a water rinse before beginning another experiment.

Pyrolysis of 1-Methylpentaborane.—A considerable number of 1-methylpentaborane pyrolyses were executed at various reaction temperatures and flow concentrations. A representative number of these are summarized in Table I. At temperatures somewhat lower than 600° substantial amounts of the starting material could be recovered unchanged. By 600° most of the 1-methylpentaborane had reacted and therefore this was considered an optimum minimum temperature for the conversion.

TABLE I

SUMMARY OF 1-METHYLPENTABORANE(9) PYROLYSES EXPERIMENTS

Expt no.	Reaction temp, °C	Temp of trap A, °C	Approx duration of run, hr	Amt of $1\text{-}CH_3B_5H_8$, mmol: Start	Re-covered	CB_5H_7 yield, mmol (%)
1	450	−67	6	1.0	0.44	
2	515	−60	0.5	0.95	0.62	0.016 (1.7)
3	600	−67	3	0.75	0.07	0.019 (2.5)
4	600	−45	6	29.1	0.15	2.9 (10)[a]

[a] In addition 0.6 mmol (2%) of CB_5H_9 and 0.85 mmol (3%) of 2-methylpentaborane were also isolated.

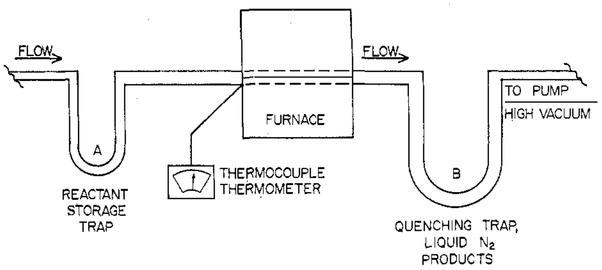

Figure 1.—Flow pyrolysis apparatus.

Using a faster flow concentration, as implied by the higher temperature of trap A in Figure 1, and thus a shorter duration required for the disappearance of the starting material from the trap at 600° gave better yields of carboranes. A few experiments carried out slightly above 600° did not noticeably improve the yield of carboranes.

Pyrolysis of 1-Ethylpentaborane.—Two 27-mmol quantities of 1-ethylpentaborane were subjected in separate runs to a furnace temperature of 500° keeping trap A (Figure 1) at *ca.* −40 to −45°. The results are summarized in Table II. In addition to the cited products, there was some indication of trace amounts of 1-CH_3- and 3-$CH_3CB_5H_8$ in the mixture from run no. 2.

TABLE II

PYROLYSIS OF 1-ETHYLPENTABORANE (27 MMOL)

Products	Yield, mmol: Run 1	Run 2	Products	Yield, mmol: Run 1	Run 2
$1\text{-}CH_3CB_5H_6$	1.0	0.08	Alklydiboranes	~0.8	. . .
$2\text{-}CH_3CB_5H_8$	0.8	0.32	B_5H_9	0.7	0.2
$C_2B_3H_5$	2.2	0.13	$2\text{-}CH_3B_5H_8$	. . .	0.4
$C_2B_5H_7$	0.08	. . .	$2\text{-}C_2H_5B_5H_8$	. . .	10.5
C_2H_4	1.7	2.4	$1\text{-}C_2H_5B_5H_8$ (recovered)	. . .	3.1
B_2H_6	0.3	1.6			

Pyrolysis of 1,2-Dimethylpentaborane(9).—Using a furnace temperature of 550° and keeping trap A (Figure 1) at −45° a 19.3-mmol quantity of 1,2-dimethylpentaborane was pumped through the reaction zone over a period of 20 hr. The products (*ca.* 12.0 mmol) trapped at B (Figure 1) were separated by a combination of cold-column vacuum distillation and glpc. These are listed in Table III.

TABLE III

PRODUCTS ISOLATED FROM THE PYROLYSIS OF 1,2-DIMETHYLPENTABORANE(9) (19.3 MMOL)

Product	Yield, mmol	Yield based on initial reactant, %	Yield based on volatile product mixture, %
B_2H_6	2.43	12.6	20.3
$CH_3B_2H_5$	0.81	4.2	6.8
$(CH_3)_3B$	0.04	0.2	0.3
$1,2\text{-}(CH_3)_2B_2H_4$	0.12	0.6	1.0
$1,5\text{-}C_2B_3H_5$	5.0	26	42
$C_2B_4H_6$ + $2\text{-}CH_3\text{-}1,5\text{-}C_2B_3H_4$; or $3\text{-}CH_3\text{-}1,2\text{-}C_2B_3H_4$	0.10	0.5	0.8
$1,6\text{-}C_2B_4H_6$	0.19	1.0	1.6
$(CH_3)_3B_2H_3$	0.06	0.3	0.5
CB_5H_7	1.00	5.2	8.4
CB_5H_9	0.46	2.4	3.8
$2,4\text{-}C_2B_5H_7$	0.25	1.3	2.2
$2\text{-}CH_3B_5H_8$	0.14	0.7	1.1
$3\text{-}CH_3CB_5H_8$	0.15	0.8	1.3
$2,3\text{-}(CH_3)_2B_5H_7$	0.25	1.3	2.2
Carborane species isoelectronic with B_8H_{12}: $CH_3C_2B_5H_6$(?)	0.14	0.7	1.1
$C_2B_8H_{10}$ (?)	0.06	0.3	0.5
Unidentified Volatile Product	0.76	3.9	6.4

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(6) The Varian HA-100 at California State College, Los Angeles, Calif., was obtained through Grant GP-8347 from the National Science Foundation.

(7) The HR-220 nmr spectrometer at California Institute of Technology was available through National Science Foundation Grant GP-8540.

(8) West Coast Technical Service, San Gabriel, Calif.

Pyrolysis of 1,2-Tetramethylenediborane.—About 10 mmol of 1,2-tetramethylenediborane(6) was pumped from trap A (−45°) through the reaction tube (550°) into trap B. The volatile position of the pyrolysis product mixture (*ca.* 3.4 mmol) was subjected to a cold-column, high-vacuum distillation and a fraction was obtained at −92° which was nearly pure 2,3,4,5-tetracarbahexaborane(6). The impurities, as identified by mass, ir, and ^1H nmr spectra, appeared to be a mixture of alkanes. Three refractionations with 1–2° intervals between fractions removed all but a trace of these impurities giving 0.05 mmol of $C_4B_2H_6$. Other fractions obtained in very small amounts from the reaction mixture included $C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 3-CH_3-1,5-$C_2B_3H_5$. Spectroscopic properties gathered for the 2,3,4,5-$C_4B_2H_6$ are the ^{11}B nmr spectrum (Figure 2), ^1H nmr spectrum (Table IV), mass spectrum (Table V), and infrared spectrum (Table VI).

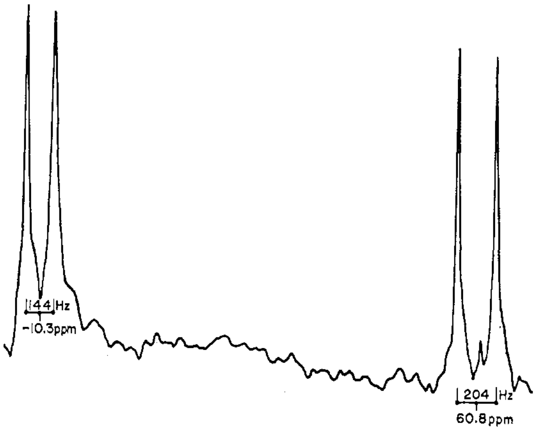


Figure 2.—Boron-11 nmr spectrum (32.1 MHz) of $C_4B_2H_6$.

TABLE IV

^1H NMR DATA OF 2,3,4,5-TETRACARBA-*nido*-HEXABORANE(6)[a]

Assignment	Chem shift,[b] ppm	J, Hz	Comments
B(1)–H	10.59	205	1:1:1:1 quartet (area 1) which decouples to a singlet when ^{11}B is irradiated.
B(6)–H	6.08	141	1:1:1:1 quartet (area 1) which decouples to a singlet when ^{11}B is irradiated.
C(2,5)–H or C(3,4)–H	5.38	...	Slightly broad singlet (area 2) not appreciably affected by ^{11}B irradiation
C(3,4)–H or C(2,5)–H	4.24	...	Slightly broad singlet (area 2) not appreciably affected by ^{11}B irradiation

[a] Data gathered from a composite of 220-MHz spectra, 100-MHz spectra, and ^{11}B decoupled 100-MHz spectra. [b] Chemical shifts were measured relative to internal tetramethylsilane, τ 10.00.

TABLE V

THE RELATIVE INTENSITIES OF THE PARENT GROUP OF THE MASS SPECTRUM OF 2,3,4,5-TETRACARBA-*nido*-HEXABORANE(6)

m/e	Intens	m/e	Intens	m/e	Intens
66	0.34	70	4.22	74	100.00
67	0.68	71	12.16	75	91.55
68	1.01	72	26.35	76	98.99
69	2.36	73	97.64	77	5.33

TABLE VI

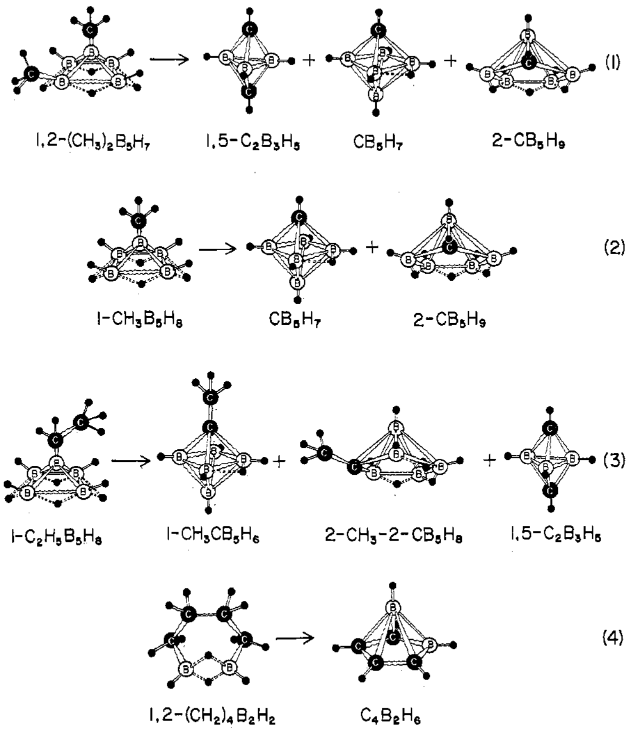
THE INFRARED DATA (CM^{-1}) FOR 2,3,4,5-TETRACARBA-*nido*-HEXABORANE(6)

3100 w[a]	1285 m, b	990 m–s	840 m	706 w, sp
2900 w[a]	1130 w, b	950 m	780 m	653 m, sp
2580 vs, sp[b]	1020 s	953 m	768 m, b	620 w, b
1340 m, b	1000 vs–s, sp	850 ms, sp	746 m, sp	

[a] C–H stretch. [b] B–H stretch.

Discussion

The present study clearly demonstrates that a fully saturated carbon-containing substituent of a boron hydride can be persuaded to lose hydrogen with consequent incorporation of the carbon atom(s) into the polyhedral framework of a carborane system. For the compounds examined, the major carboranes formed are summarized in eq 1–4.



Except for the reaction summarized by eq 1 the yields (consult Experimental Section) of product(s) are not, in the absolute sense, very high. However, for most of the one-carbon carboranes the described pyrolyses represent, to date, the best and/or easiest routes to those compounds. For the parent four-carborane, 2,3,4,5-$C_4B_2H_6$, eq 4 represents the only known route of preparation.[9]

It should be mentioned that the yields of carborane products may well be improved over those reported in this work should a more detailed study be made on the effect of each of the following experimental variables: (a) reaction zone temperature, (b) residence time of reactant in the reaction zone, (c) the effect of diluents on yields, and (d) the effect of exposed surface area and the type of surface area on the yield of products. In our attempts we were able to find a reasonable minimum temperature for each conversion; however, a trial and error encompassing all of the variables cited above is well beyond the scope of the present work.

The modestly high-yield conversion of 1,2-dimethylpentaborane(9) to 1,5-dicarba-*closo*-pentaborane(5) is accompanied by the production of many other carboranes. Together, the combined yield of carborane products approaches 40% which is strikingly high when the drastic temperatures needed for the conversion are considered. Certainly under static, rather than the adopted flow, reaction conditions, not one of the products would be expected to survive much longer

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(9) For a preliminary communication of this work see T. P. Onak and G. T. F. Wong, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).

than the alkylborane reactant at 550°. The formation of a two-boron-containing product, diborane, as the second most important product to the three-boron carborane does tend to suggest that a significant fraction of the pyrolysis can be summarized by

$$1,2\text{-}(CH_3)_2B_5H_7 \longrightarrow 1,5\text{-}C_2B_3H_5 + B_2H_6 + H_2 \qquad (5)$$

The side product methyldiboranes might simply be formed from a *B*-methyl exchange between methylpentaborane(s) and diborane or may be the result of an extension of eq 5 incorporating the loss of a diborane fragment with an attached methyl group. Certainly further speculation on this point, in the absence of appropriate control experiments, is unwarranted.

The presence of the basal methyl-substituted pentaborane $2,3\text{-}(CH_3)_2B_5H_7$ in the product mixture is not unduly surprising, for its formation is analogous to the thermal rearrangement of 1-methylpentaborane to the 2-methyl derivative.[10] It was hoped that pyrolysis of $1,2\text{-}(CH_3)_2B_5H_7$ would lead to the formation of, as yet, unknown *B*-methyl derivatives of the one-carbon carboranes, *i.e.*, 2-, 4-, and/or $6\text{-}CH_3CB_5H_6$. However, only a very small quantity of the known $3\text{-}CH_3CB_5H_8$ was found.

The pyrolyses both of 1-methyl- and of 1-ethylpentaborane gives, as major carborane products, one-carbon carboranes. With ethylpentaborane as the starting material, it is not surprising to find the *C*-methyl derivatives of the product carboranes as well as some of the already known two-carbon carboranes in the product mixture. It is difficult to obtain consistent product yields with the ethylpentaborane. It is thought that ethylboron chlorides, present as minor impurities from the modified Friedel–Crafts preparation of this material, may be affecting the inconsistent outcome of this reaction.

It is tempting to think of the CB_5H_9 carborane as an intermediate in the formation of CB_5H_7.

$$CH_3B_5H_8 \longrightarrow CB_5H_9 + H_2 \qquad (6)$$

$$CB_5H_9 \longrightarrow CB_5H_7 + H_2 \qquad (7)$$

This is partially supported by an experiment in which an ethyl derivative of the nido carborane $2\text{-}C_2H_5\text{-}2\text{-}CB_5H_8$, pyrolyzed at 575°, gives a small yield of a product with a sharp cutoff in the mass spectrum at *m/e* 102. This, coincidentally, is the cutoff expected for the ethyl derivative of the octahedral CB_5H_7, *i.e.*, $C_2H_5CB_5H_6$. Unfortunately, however, there is not enough of the material present in the reaction products for further identification.

Returning to an analysis of the $1,2\text{-}(CH_3)_2B_5H_7$ pyrolysis, it is somewhat surprising that a *B*-methyl derivative of CB_5H_7 is not formed. The only *B*-methyl monocarbon carborane in the product mixture, as previously mentioned, is the 3-methyl derivative of CB_5H_9. At the moment it appears significant that this latter carborane may also be the product of a reaction between $C_2B_3H_5$ and B_2H_6 at 300°.[11] Because both $C_2B_3H_5$ and diborane are present in copious quantities in the dimethylpentaborane pyrolysis, it may be possible that the *B*-methyl derivative of CB_5H_9 found in the reaction mixture may be merely the result of the sequence

$$1,2\text{-}(CH_3)_2B_5H_7 \overset{\text{as yet unknown pathway}}{\longrightarrow \longrightarrow \longrightarrow} C_2B_3H_5 + B_2H_6 + H_2 \qquad (8)$$

$$C_2B_3H_5 + B_2H_6 \longrightarrow 3\text{-}CH_3CB_5H_8 \qquad (9)$$

If, however, eq 9 is reversible, then it is possible to consider that the $3\text{-}CH_3CB_5H_8$ may be an important intermediate in the pyrolysis, eq 8. In the many reaction products isolated, it is important to note that none of the nido carborane $C_2B_4H_8$ is found. Furthermore, this carborane can most probably be excluded as an important intermediate in any mechanistic scheme to produce $C_2B_3H_5$[12] on the basis that very little $C_2B_5H_7$ is formed, for it is known that $C_2B_5H_7$ is a major product in the pyrolysis of $C_2B_4H_8$.[12,13]

The pyrolysis of 1,2-tetramethylenediborane gave, in addition to small quantities of several known two-carbon carboranes, the parent 2,3,4,5-tetracarbahexaborane(6), $C_4B_2H_6$. Consistent with structural theory[14] and with the proposed structures for alkyl derivatives[15] the framework of the parent four-carbon carborane most probably assumes a pentagonal-pyramidal arrangement of carbon and boron atoms. Of three possible isomers within this framework geometry the ^{11}B nmr and ^1H nmr data exclude two of these (*e.g.*, $1,2,3,4\text{-}C_4B_2H_6$ and $1,2,4,5\text{-}C_4B_2H_6$) in that two kinds of boron and two kinds of boron-attached hydrogens are observed. Furthermore, the chemical shift data (Figure 2 and Tables VII and VIII) and coupling constants strongly indicate one boron in an apical environment and another in a basal environment of the proposed pyramid. Also, the chemical shift differences $\delta_{^{11}B_{apex}} - \delta_{^{11}B_{base}}$ and $\tau_{^1H_{apex}} - \tau_{^1H_{base}}$ are consistent with ring current computations[16] applied to related pyramidal systems.

TABLE VII

^{11}B NMR DATA FOR THE PARENT MEMBERS OF THE HEXABORANE(10) FAMILY OF COMPOUNDS

	B_{apex}		B_{base}		
Compd	δ,[a] ppm	*J*(B–H), Hz	δ, ppm	*J*(B–H), Hz	Ref
$C_4B_2H_6$	60.8	202	−10.4	144	This work
$C_3B_3H_7$					*b*
$C_2B_4H_8$	50.5	181	0.6	160	*c*
			3.3	154	
CB_5H_9	51.9	160	4.2	164	This work[d]
			−16.6	161	
B_6H_{10}	51.8	155	−14.1	158	*e*

[a] Relative to $BF_3\cdot(C_2H_5)_2O$ = 0.0 ppm. [b] Not yet known. [c] T. Onak and G. B. Dunks, *Inorg. Chem.*, **5,** 439 (1966). [d] The cited values are within ±1.5 ppm and ±5 Hz of those reported by G. B. Dunks and M. F. Hawthorne, *ibid.*, **8,** 2667 (1969). [e] J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **9,** 2170 (1970).

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TABLE VIII
PROTON NMR DATA[a]

Compd	τ (J)		τ		Ref
	H_t(apex)	H_t(base)	H_{bridge}	H_c	
$C_4B_2H_6$	10.59 (205)	6.08 (141)	. . .	5.38 4.24	This work
$C_3B_3H_7$					*b*
$C_2B_4H_8$	11.13 (181)	6.56 (158)	12.4	4.68	*c*
CB_5H_9	11.1 (170)	5.5 (165) ($H_{3,6}$) 6.5 (162) ($H_{4,5}$)	12.4 ($H_{3,5}$) 10.4 (H_4)	4.6[d]	This work
B_6H_{10}	11.22 (155)	5.82 (158)	11.1	. . .	*g*
CB_5H_7	7.8 (173) 7.9 (183)		13.9	7.2	This work
1-$CH_3CB_5H_6$	8.1 (180)		13.9	8.6 (CH_3)	This work
1,2-$C_2B_4H_6$	8.2 (178)			7.1	*e*
1,6-$C_2B_4H_6$	8.1 (187)			6.9	*e*
1,6-$(CH_3)_2$-1,6-$C_2B_4H_4$	8.2 (184)			8.7 (CH_3)	*f*

[a] τ 10.00 ppm (tetramethylsilane); TMS used as internal standard; *J* is given in hertz. [b] Not yet known. [c] T. Onak and G. B. Dunks, *Inorg. Chem.*, **5,** 439 (1966). [d] This compares favorably with the value of τ 4.62 for H_c reported by G. B. Dunks and M. F. Hawthorne, *ibid.*, **8,** 2667 (1969). [e] T. Onak, R. Drake, and G. B. Dunks, *ibid.*, **3,** 1686 (1964). [f] T. Onak, F. J. Gerhart, and R. E. Williams, *J. Amer. Chem. Soc.*, **85,** 3378 (1963). [g] J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **9,** 2170 (1970).

alkylboron hydride pyrolysis reactions several observations warrant discussion.

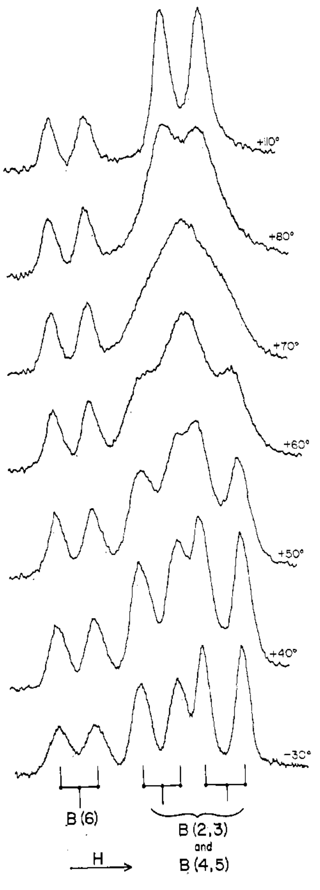

Figure 3.—Temperature-dependent boron-11 nmr spectra of CB_5H_7.

TABLE IX
^{11}B NMR DATA FOR CB_5H_7 AND ITS 1-METHYL DERIVATIVE

	$CH_3CB_5H_6$, −30°		CB_5H_7, 25°	
	δ,[a] ppm	*J*, Hz	δ,[a] ppm	*J*, Hz
B(2,3 or 4,5)	+7.9	~170	+9.8	168
B(4,5 or 2,3)	+17.6	~170	+19.0	186
B(6)	+4.6	~170	−2.7	176

[a] Relative to $BF_3 \cdot (C_2H_5)_2O$ = 0.0 ppm.

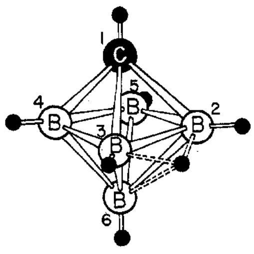

Figure 4.—Ball and stick model of CB_5H_7.

The ^{11}B nmr patterns for both CB_5H_7 and 1-$CH_3CB_5H_6$ were found to be temperature dependent. The spectra recorded for CB_5H_7 at various temperatures are reproduced in Figure 3, and the data gathered at the lowest temperature tabulated in Table IX. It is clear from the change in spectral pattern for CB_5H_7 that two of the B–H$_{\text{terminal}}$ doublets (area 2 each) seen at the lower temperatures coalesce into one B–H$_{\text{terminal}}$ doublet at 100°. This is interpreted in terms of a bridge hydrogen exchange which is equivocating positions 2, 3, 4 and 5 (Figure 4). An estimate for T_c of 70 ± 10° can be made from the observed spectra and, when used with a calculated rate constant,[17] an approximate $\Delta G^{\ddagger}$ of 14 ± 0.5 kcal can be computed for the exchange process. The coalescence temperature for the 1-methyl derivative $CH_3CB_5H_6$ was lower than that for the parent compound by about 50°. It was very difficult to obtain clean spectra to illustrate this, however, for the carborane could not be obtained free from a pentaborane impurity. The coalesced doublet fell nearly on the low-field doublet of pentaborane and therefore a comparison of ΔT_c ($T_c(CB_5H_7) - T_c(CH_3CB_5H_6)$) is difficult to make. Using an estimate of two extremes for T_c, a $\Delta G^{\ddagger}$ of 12 ± 1 kcal was calculated for the bridge hydrogen tautomerization process in 1-$CH_3CB_5H_6$.

It is considered unlikely that a mechanistic interpretation of the ^{11}B nmr observations involves intermolecular exchange of the bridge hydrogen. A temperature-dependent study of the broad bridge region of the ^{1}H nmr indicates that the resonance is not

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(17) A. Ratajczak, F. A. L. Anet, and D. J. Cram, *J. Amer. Chem. Soc.*, **89,** 2072 (1967).

sharpened above the ^{11}B nmr determined coalescence temperature. It can be demonstrated by separate ^{11}B decoupling experiments carried out from 25 to 110° that the bridge proton resonance can be narrowed considerably, indicating that bridge hydrogen–boron coupling is largely responsible for the broadness of the undecoupled peak. Therefore, the bridge hydrogen cannot be undergoing significant intermolecular exchange within this temperature range, for such an exchange process, alone, should sharpen the bridge resonance. An intramolecular bridge tautomerism in which the hydrogen migrates from the 2,3 position to the 3,4, etc., appears to be a reasonable mechanism. However, in moving from one position to another equivalent position it must skirt an equatorial $B-H_{terminal}$ group. It is considered likely that this occurs with an intermediate positioning of the hydrogen along the B(3)–B(6) edge rather than the B(3)–C(1) edge. This is justified on the basis that B–H–B bridge bonds are commonplace in boron hydride–carborane chemistry whereas B–H–C bridge bonds are unknown and thus expected to be much less stable (*i.e.*, note the positional preference of bridge hydrogens in the carborane $C_2B_4H_8$[18]).

From a quick inspection of such a mechanistic model it is tempting to conclude that the initial position of the bridge hydrogen may be closer to the B(6) boron (Figure 4) than heretofore depicted. This would allow the tautomeric hydrogen to follow a path with little deviation from an appropriately placed imaginary plane just below the equatorial boron atoms. Such a position is considered more consistent with two other observations.

(1) No distinct bridge hydrogen–boron coupling pattern is observed in either the boron-11 or the proton nmr spectra. A bridge proton situated midway between two equivalent boron-11 atoms and thus coupled equally to both of them should be visually observed as a distinct 1:2:3:4:3:2:1 heptet whereas, in fact, only a broad peak is observed. Should that same bridge proton be also weakly coupled to a third boron (*i.e.*, B(6)), each of these peaks will be split into a 1:1:1:1 quartet. This should raise the probability of observing only a single diffuse peak. Such coupling is obviously enhanced by invoking a certain degree of bonding between the bridge hydrogen and B(6). In this respect the proposed four-center bond in the ground-state static structure is not unlike the anomalous hydrogen in pentaborane(11).[19]

(2) A methyl group attached to the skeletal carbon shifts B(6) upfield (Table IX) in a manner analogous to long-range effects observed in other electron-delocalized boron hydride[20a] and carborane systems.[20b] Also this substitution enhances the tautomerism of the bridge hydrogen, as mentioned above. It could be sensibly argued that the upfield shift of B(6) by the distant methyl group is partially or totally a result of increased electron density about B(6). If this is correct, the bonding of B(6) to the bridge hydrogen may be enhanced which, in turn, pulls the bridge hydrogen away from the equatorial B–H plane and allows the tautomerization pathway to be less obstructed.

Many of the ^{11}B and ^{1}H chemical shift and coupling values in CB_5H_7 and $CH_3CB_5H_6$ (Tables VIII and IX) are remarkably similar to the isoelectronic and isostructural $C_2B_4H_6$. For the known two isomers of $C_2B_4H_6$ (1,2 and 1,6) a range of δ +1 to +19 has been found for the various boron-11 environments.[21] This compares favorably with the δ −2 to +19 range in the CB_5H_7 framework. Also an inspection of H_t and H_c of CB_5H_7 and its carbon-attached methyl derivative with $C_2B_4H_6$ and a carbon-attached methyl derivative (Table VIII) reveals a number of close correlations. Thus it appears that the common octahedral geometry decides many of the nmr values. This conclusion is supported when making comparisons with the corresponding nmr data of the pentagonal bipyramid of $C_2B_5H_7$ and the trigonal bipyramid $C_2B_3H_5$,[21] especially the proton τ values where one finds that these latter two compounds show H–B and/or H–C chemical shifts significantly different from those of the octahedral $C_2B_4H_6$ and CB_5H_7 compounds and methyl derivatives.

Acknowledgment.—This project was supported, in part, by the Office of Naval Research.

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(18) F. P. Boer, W. E. Streib, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1999 (1964).

(19) For example, $H_{\mu 3,4}$ of B_5H_{11}: J. B. Leach, T. Onak, J. Spielman, R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *ibid.*, **9**, 2170 (1970).

(20) (a) P. M. Tucker, T. Onak, and J. B. Leach, *ibid.*, **9**, 1430 (1970); (b) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *ibid.*, **9**, 2285 (1970).

(21) Consult primary references cited in G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.