The Polyhedral $B_9C_2H_{11}$, $B_8C_2H_{10}$, $B_7C_2H_9$, and $B_6C_2H_8$ Carboranes and the $B_7C_2H_{13}$ System

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Abstract: Protonation of $B_9C_2H_{12}^-$ salts followed by pyrolysis of the $B_9C_2H_{13}$ intermediates yields $B_9C_2H_{11}$ carboranes. Subsequent oxidation of the $B_9C_2H_{11}$ system produces a $B_7C_2H_{13}$ series which when pyrolyzed at 215° yields $B_6C_2H_8$, $B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ derivatives. The latter carborane may be isomerized to the 1,10-$B_8C_2H_{10}$ isomer at 350°. These studies have completed the polyhedral $B_{n-2}C_2H_n$ carborane series from $n = 5$ to 12.

During the past few years a great deal of interest has developed in the general area of polyhedral borane chemistry. Thus, one finds innumerable studies related to the preparation, characterization, structural examination, and theoretical treatments of the $B_nH_n^{-2}$ ions and their isoelectronic $B_{n-2}C_2H_n$ analogs, and these topics have been recently reviewed.[1,2] It is the purpose of this paper to describe the preparation and characterization of the carboranes (polyhedral $B_{n-2}C_2H_n$ species) which complete the carborane series from $n = 5$ to $n = 12$. Specifically, the species under discussion are $B_9C_2H_{11}$, two isomers of $B_8C_2H_{10}$, $B_7C_2H_9$, and $B_6C_2H_8$ carboranes, and the precursor of the latter three carboranes, the $B_7C_2H_{13}$ system. Heretofore, this work was only available in the form of brief communications.[3-7] Critical structural determinations have been completed,[8,9] and a full presentation of the initial results appears to be warranted at this time.

The $B_9C_3H_{11}$ Carborane

Previous work[10] proved that the protonation of the (3)-1,2-dicarbadodecahydroundecaborate(−1) ion ((3)-1,2-$B_9C_2H_{12}^-$)[11] produced a sublimable, water-soluble acid,

$$B_9C_2H_{12}^- + H_3O^+ \rightleftharpoons B_9C_2H_{13} + H_2O$$

(3)-1,2-dicarbaundecaborane(13)[11] ((3)-1,2-$B_9C_2H_{13}$). Similar treatment of the (3)-1,7-dicarbadodecahydroundecaborate(-1) ion ((3)-1,7-$B_9C_2H_{12}^-$)[11] produced an analogous (3)-1,7-$B_9C_2H_{13}$[11] which was not sufficiently stable to allow chemical characterization.[4] The (3)-1,2-$B_9C_2H_{13}$ could be titrated as a strong monoprotic acid to yield quite acceptable equivalent weight values.[10] The carbon-substituted derivatives (alkyl and aryl substituents) of the $B_9C_2H_{13}$ isomers displayed analogous reactions.

Pyrolysis of the (3)-1,2- and (3)-1,7-$B_9C_2H_{13}$ species and their C-substituted derivatives at 100 and 75°, respectively,[3,4] proceeded to yield hydrogen and one major product, the $B_9C_2H_{11}$ carborane bearing the carbon substituents of the starting material $B_9C_2H_{13}$. The

$$B_9C_2H_{13} \longrightarrow B_9C_2H_{11} + H_2$$

(3)-1-phenyl-1,2- and (3)-1-phenyl-1,7-$B_9C_2H_{12}$ derivatives generated *in situ* from the correspondingly substituted and optically active $B_9C_2H_{12}^-$ ions produced the C-phenyl-substituted $B_9C_2H_{11}$ carborane having no optical activity.[5] The apparent relationship of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions shown in Figure 1 and the results of the above experiments suggested that the formation of the $B_9C_2H_{11}$ carborane from the (3)-1,2-$B_9C_2H_{12}^-$ ion proceeds by way of carbon–boron position interchange and that the (3)-1-phenyl-1,2- and (3)-1-phenyl-1,7 derivatives of $B_9C_2H_{12}^-$ underwent racemization during $C_6H_5B_9C_2H_{10}$ formation or that the phenyl group of the $C_6H_5B_9C_2H_{10}$ product lies upon a plane of molecular symmetry. The observations described above are illustrated in a schematic diagram (eq 1). The thermal rearrangement of the (3)-1-phenyl-1,2-dicarbadodecahydroundecaborate(−1) ion to the corresponding (3)-1,7- ion was previously described[4] and occurs at 350°.

$$\begin{tikzcd}
\text{(3)-1,2-}B_9C_2H_{11}C_6H_5^- \arrow[r, shift left, "H^+"] \arrow[dd, "350^\circ"] & \text{(3)-1,2-}B_9C_2H_{12}C_6H_5 \arrow[l, shift left, "-H^+"] \arrow[dr, "100^\circ"] & \\
 & & B_9C_2H_{10}C_6H_5 + H_2 \quad (1) \\
\text{(3)-1,7-}B_9C_2H_{11}C_6H_5^- \arrow[r, shift left, "H^+"] & \text{(3)-1,7-}B_9C_2H_{12}C_6H_5 \arrow[l, shift left, "-H^+"] \arrow[ur, "75^\circ"'] &
\end{tikzcd}$$

In addition to the results described above, degradation of the C-phenyl and C,C′-dimethyl derivatives of $B_9C_2H_{11}$ with palladium and propionic acid produced toluene and ethane, respectively. These degradation

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(1) M. F. Hawthorne, *Endeavour*, **25**, 146 (1966).

(2) W. N. Lipscomb, *Science*, **153**, 373 (1966).

(3) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(4) P. M. Garrett, F. N. Tebbe, and M. F. Hawthorne, *ibid.*, **86**, 5016 (1964).

(5) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Letters*, 715 (1965).

(6) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).

(7) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

(8) C. D. Tsai and W. E. Streib, *ibid.*, **88**, 4513 (1966).

(9) D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **6**, 113 (1967).

(10) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

(11) The fact that the two isomeric $B_9C_2H_{12}^-$ ions and the two isomeric $B_9C_2H_{13}$ species discussed in this paper are undoubtedly 11-particle icosahedral fragments capped with hydrogen atoms presents an enigma in the area of boron hydride and carborane nomenclature. This is especially true since no generally sanctioned system has been firmly adopted on an international scope. We have therefore adopted a system of nomenclature based upon the "closo" (or "clovo") nomenclature system suggested by R. M. Adams, *Inorg. Chem.*, 2, 1087 (1963). In order to clearly distinguish the position of the carbon atoms with respect to the "hole" or missing vertex in the icosahedral surface, we have assigned the missing vertex to the 3 position of the isocahedron and placed the "hole position" in parentheses preceding the name of the system in question. The carbon atoms thus become 1,2- or 1,7- in the two isomeric systems under discussion, *i.e.*, (3)-1,2-dicarbadodecahydroundecaborate(−1) for (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-dicarbadodecahydroundecaborate(−1) for (3)-1,7-$B_9C_2H_{12}^-$, respectively.

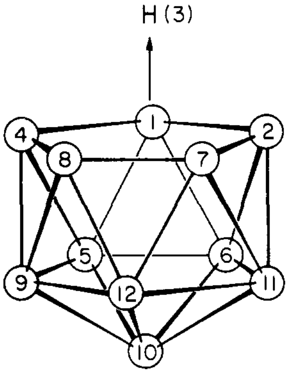


Figure 1. Simplified drawing of the $B_9C_2H_{12}^-$ ion showing the stereochemical relationship of boron and carbon atoms in (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$.

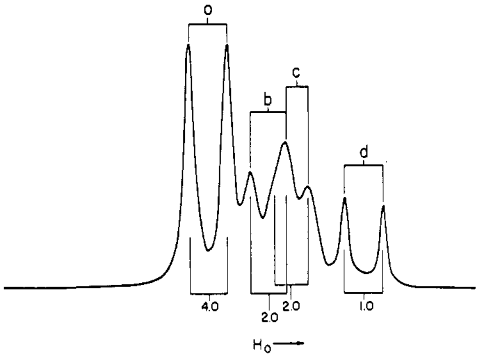


Figure 2. The ^{11}B nmr spectrum of $B_9C_2H_{11}$ in carbon disulfide solution at 60 Mc/sec. Chemical shifts, ppm ($BF_3O(CH_2CH_3)_2$ = 0), and coupling constants (cps) computed on the basis of values obtained at 19.3 Mc/sec for the doublet are (a) +1.2 (164), (b) +7.3, (c) +10.0, and (d) +17.3 (169). Relative integrated areas are indicated beneath the peaks.

products also suggested that the carbon atoms present in the $B_9C_2H_{11}$ carborane are not nearest neighbors.

Table I presents the yield and characterization data which pertain to a series of C-substituted $B_9C_2H_{11}$ carboranes. These materials were prepared by the pyrolysis of the corresponding (3)-1,2-$B_9C_2H_{13}$ produced *in situ* from the appropriate (3)-1,2-$B_9C_2H_{12}^-$ ion and polyphosphoric acid. In a single instance, a higher yield of $B_9C_2H_{11}$ was obtained from the (3)-1,7-$B_9C_2H_{12}^-$ salt.

The mass spectra of each of the derivatives presented in Table I were characterized by a parent ion peak. Infrared data are presented in Table VI (Experimental Section) and consist of strong B–H stretching absorptions at 2600 cm^{-1} and bands associated with the substituents at carbon. The unsubstituted, the 1-methyl, and the 1-phenyl derivatives displayed carborane C–H stretching bands at 3060 cm^{-1}.

The ^1H nmr spectrum of the unsubstituted $B_9C_2H_{11}$ consisted of a single singlet carborane C–H resonance at −5.8 ppm (relative to tetramethylsilane) superimposed upon broad B–H resonances. The single C–H resonance suggested that the two carbon atoms of the polyhedral structure were placed across a plane of molecular symmetry and were therefore equivalent.

The ^{11}B nmr spectrum of unsubstituted $B_9C_2H_{11}$ (60 Mc/sec) is shown in Figure 2. The doublet at highest field suggested that the over-all structure contained a unique boron atom which was probably of higher than normal coordination number. The gross 4:2:2:1 integration analysis was clearly seen. These data coupled with the ^1H nmr data led us to suggest[5] the structure of the $B_9C_2H_{11}$ carborane system shown in Figure 3 with carbon atoms in positions 1 and 8. This structure was recently confirmed[8] by single crystal X-ray diffraction studies carried out with the 1,8-dimethyl derivative.[12]

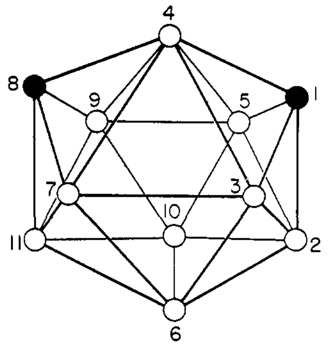


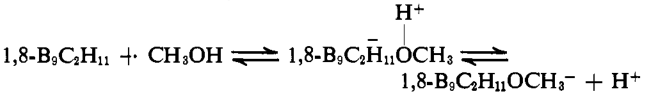
Figure 3. The structure $B_9C_2H_{11}$ where ● = C–H and ○ = B–H.

Although the chemistry of the 1,8-$B_9C_2H_{11}$ carborane system has not been extensively explored, one set of characteristic reactions has been uncovered which appears to be novel in the area of carborane chemistry. These reactions involved the reversible formation of

$$1,8\text{-}B_9C_2H_{11} + :L \rightleftarrows 1,8\text{-}B_9C_2\overset{-}{H}_{11}L^+$$

Lewis acid–base adducts with a variety of electron donors ranging from such weakly bound bases as ethyl isocyanide to strong bases such as hydroxide ion. Table II presents data pertinent to the characterization of representative ligand adducts. The reversibility of adduct formation was demonstrated by the recovery of 1-C_6H_5-1,8-$B_9C_2H_{10}$ from its hydroxide ion adduct upon acidification with polyphosphoric acid.

The reaction of the 1,8-$B_9C_2H_{11}$ carboranes with methoxide ion allowed the determination of their equivalent weights by direct potentiometric titration in anhydrous methanol solution. The 1,8-dimethyl and 1-phenyl derivatives were employed in these reactions, and the following equation illustrates the observed stoichiometry.



$$1,8\text{-}B_9C_2H_{11} + CH_3OH \rightleftharpoons 1,8\text{-}B_9C_2\overset{-}{H}_{11}\overset{\overset{H^+}{|}}{O}CH_3 \rightleftharpoons 1,8\text{-}B_9C_2H_{11}OCH_3^- + H^+$$

The structures of the ligand adducts probably resemble that of the (3)-1,7-$B_9C_2H_{12}^-$ ion with which they are isoelectronic. Such a scheme would require that the closed 1,8-$B_9C_2H_{11}$ polyhedron be opened upon attack by the ligand. Due to the electropositive nature of polyhedral carbon atoms in general, one might expect this attack to occur at the seven-coordinate boron atom in position 4 which is simultaneously bonded to the two carbon atoms.

The $B_7C_2H_{13}$ Species

Having obtained the 1,8-$B_9C_2H_{11}$ carborane, attempts were made to further degrade this carborane to a lower

[12] Note the change in position numbering which differs from that of ref 5 and 8 and which places one carbon atom at the 1 position. This system is in agreement with the polyhedral numbering system set forth by Adams.[11]

Table I. Yield and Characterization Data for $B_9C_2H_9RR'$ Species Substituted at Carbon

			Yield,	Calcd, %			Found, %		
R	R′	Mp, °C[a]	%[b]	C	H	B	C	H	B
H	H	212–213	22[c]	18.13	8.37	73.50	18.40	8.64	73.44
CH_3	H	84–84.5	60	24.59	8.94	66.46	24.66	8.90	66.63
CH_3	CH_3	57–58	75	29.93	9.42	60.66	30.17	9.61	60.38
C_6H_5	H	37–37.8	57	46.07	7.25	46.69	46.87	7.57	46.14
p-C_6H_4Br	H	100.5–101.5	72	33.41	4.87	33.89	33.49	5.08	33.61

[a] In sealed capillary and uncorrected. [b] Using corresponding (3)-1,2-$B_9C_2H_{12}^-$ isomer as starting material. [c] A 36% yield was obtained using (3)-1,7-$B_9C_2H_{12}$ isomer.

Table II. Yield and Characterization Data for $B_9C_2H_9RR'$ Ligand Adducts

				Yield,	Calcd, %			Found, %		
R	R′	Ligand	Mp, °C[a]	%	C	H	B	C	H	B
H	C_6H_5	Triphenylphosphine	252 dec	92	66.32	6.42	20.68	65.78	6.79	22.62
H	C_6H_5	Triethylamine	156–159 dec	57	54.28	9.77	31.44	52.57	9.89	32.24
CH_3	CH_3	Hydroxide ion		87[b]	38.18	11.14	38.74	38.47	11.24	38.68
CH_3	CH_3	Triethylamine	143–144 dec	49	45.89	11.55	37.21	44.60	11.88	38.68
CH_3	CH_3	Ethyl isocyanide	105–106	53	38.99	9.38	45.13	38.59	9.37	42.80

[a] In sealed capillary and uncorrected. [b] Characterized as the tetramethylammonium salt.

Table III. Yield and Characterization Data for the $B_7C_2H_{11}RR'$ Species Substituted at Carbon

			Yield,	Calcd, %			Found, %		
R	R′	Mp, °C[a]	%	C	H	B	C	H	B
H	H	60.5–61.0	76	21.30	11.62	67.09	21.36	11.61	67.09
CH_3	H	23.5–24	62	28.41	11.92	59.67	28.40	11.71	59.58
CH_3	CH_3	50.5–51.8	65	34.11	12.17	53.73	34.34	12.43	53.65
C_8H_5	H	78.5	59	50.87	9.07	40.06	51.15	9.22	39.73

[a] In sealed capillary and uncorrected.

member of the carborane family. Accordingly, aqueous ferric ion and chromic acid were examined as reagents for selective degradation. Although ferric ion and chromic acid yielded the same degradation product, the chromic acid procedure appeared to be the more practical of the two methods. The degradation product of the unsubstituted 1,8-$B_9C_2H_{11}$ carborane had the empirical formula $B_7C_2H_{13}$.[6] Assuming that each carbon and boron atom must be bonded to at least one hydrogen atom, the empirical formula requires the presence of four "extra" hydrogen atoms. Table III provides the yield and characterization data associated with the preparation of a series of C-substituted members of this carborane family. The parent member of the series gave a parent ion peak at 16 eV of 114 which corresponds to $^{11}B_7{}^{12}C_2{}^1H_{13}$. The oxidation of 1,8-$B_9C_2H_{11}$ to $B_7C_2H_{13}$ might proceed as shown in eq 2 and involve a four-electron redox reaction.

$$B_9C_2H_{11} + 6H_2O \longrightarrow B_7C_2H_{13} + 2B(OH)_3 + 4H^+ + 4e^- \quad (2)$$

Figure 4 presents the ^{11}B nmr spectrum of the C,C′-dimethyl derivative of $B_7C_2H_{13}$ at 32 Mc/sec. Five types of boron atoms are clearly seen with the relative areas 1:2:2:1:1, reading upfield. Similar ^{11}B nmr spectra were obtained for the other derivatives presented in Table III.

The infrared spectrum of each $B_7C_2H_{13}$ derivative contained absorption bands characteristic of B–H–B bridge hydrogen atoms at 2020 cm^{-1}. Sharp absorption bands were seen near 3000 cm^{-1} which were attributed to C–H stretching vibrations (Figure 7).

Table IV presents the ^1H nmr spectra of the species described in Table III. The methyl proton resonances in the spectra of the C-methyl and C,C′-dimethyl derivatives appeared as a doublet (J = 4.8 cps). In addition, the spectra of the C-methyl and the unsubstituted species contained two broad singlets of relative areas 1:2 and 2:2, respectively which represent two distinct types of carborane protons at −0.1 and +0.7 ppm relative to tetramethylsilane. These results must be interpreted in terms of two CH_2 groups separated by a plane of symmetry in the parent compound. The two remaining "extra" hydrogen atoms must therefore represent the B–H–B bridge hydrogen atoms seen in the infrared spectra. The not improbable presence of a BH_2 group was eliminated by the absence of a true triplet in the ^{11}B nmr spectrum. On the basis of this information and with the further assumption that $B_7C_2H_{13}$ had the geometry of an icosahedral fragment, we proposed[6] the topological structure shown in Figure 5 for $B_7C_2H_{13}$. The geometrical arrangement about the two equivalent carbon atoms was deduced from the steric requirements

Table IV. ^1H Nmr Spectra of $B_7C_2H_{13}$ Derivatives

		Chemical shifts, δ, ppm[a,b]		
Compound	Solvent	CH_3	CH	CH′
$B_7C_2H_{13}$	$CDCl_3$		−0.10 (2.0)	0.77 (2.0)
$B_7C_2H_{12}(CH_3)$	$C_3H_5CH_3$	−1.34 (3.0)	−0.18 (1.0)	0.69 (2.0)
$B_7C_2H_{11}(CH_3)_2$	CCl_4	−1.30 (6.0)		0.73 (2.0)
$B_7C_2H_{12}(C_6H_5)$	$CDCl_3$	. . .[c]	−0.47 (1.0)	0.74 (2.0)

[a] Relative areas in parentheses. [b] Chemical shifts relative to TMS. [c] Phenyl resonance observed at −7.38 ppm relative to TMS.

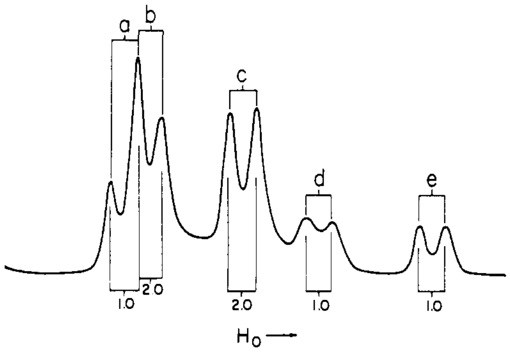


Figure 4. The ^{11}B nmr spectrum of $B_7C_2H_{11}(CH_3)_2$ in toluene solution at 32 Mc/sec. Chemical shifts, ppm ($BF_3O(CH_2CH_3)_2$ = 0, computed from values obtained at 19.3 Mc/sec for the doublet e: J = 148 cps and δ +51.0 ppm) and coupling constants (cps) are (a) −7.7, (b) −2.9, (c) +14.9 (161), (d) +29.0 (148), and (e) +51.0 (148). Relative integrated areas are indicated beneath the peaks.

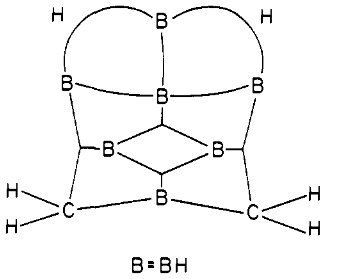


Figure 5. One topological representation of the $B_7C_2H_{13}$ structure containing sp^3-hybridized skeletal carbon atoms.

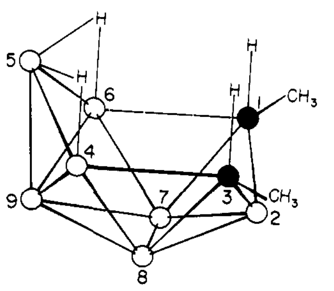


Figure 6. The structure of $B_7C_2H_{11}(CH_3)_2$ where ● = carbon, and ○ = B-H.

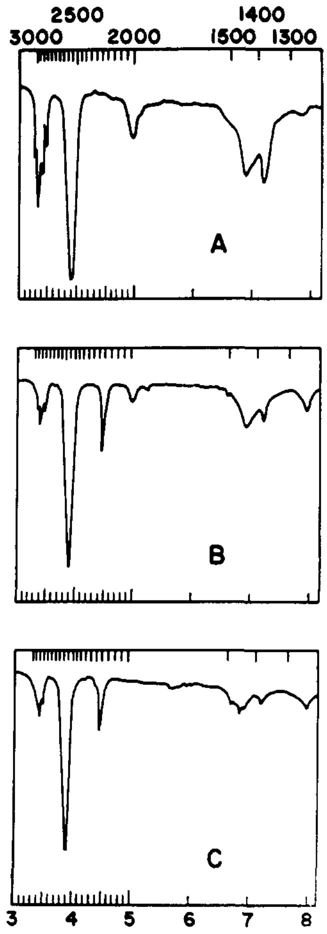


Figure 7. Liquid film infrared spectra of $B_7C_2H_{12}(CH_3)$: (A) isotopically normal, (B) acidified deuterium oxide exchanged, and (C) base-catalyzed deuterium oxide exchanged.

of methyl substituents at carbon. Thus, all C-substituted derivatives would be expected to carry equatorial substituents as opposed to axial substituents. Confirmation of this structure was recently achieved, and Figure 6 presents a representation of the equatorial 1,3-dimethyl derivative[13] employed in the single-crystal, X-ray diffraction study.[9] Axial–equatorial ^1H nmr assignments are now obvious from the data of Table IV and the known structure. The +0.7-ppm resonance must represent axial methylene hydrogen atoms while the −0.1-ppm resonance must be assigned to equatorial hydrogen atoms. Spin–spin coupling of axial and equatorial hydrogen atoms is not clearly observed due to their close proximity to neighboring boron nuclei which have appreciable quadrupole moments.

During the course of this investigation, a series of deuterium exchange experiments were carried out under acidic, neutral, and basic conditions. Exchange was monitored by infrared and ^1H nmr spectra. The 1-methyl derivative was employed as the substrate throughout these studies.

Treatment of the 1-methyl derivative with deuterated phosphoric acid in D_2O–tetrahydrofuran solution afforded deuterated product which retained strong B–H–B bridge absorption in its infrared spectrum and a C–D stretching band at 2230 cm^{-1} (Figure 7). The ^1H nmr spectrum of this deuterated product contained no resonance associated with the axial C–H hydrogen atoms. The methyl hydrogen atom resonance was a sharp singlet and the equatorial C–H hydrogen atom appeared as the characteristic broad singlet at −0.1 ppm (Figure 8). Identical results were obtained using D_2O–tetrahydrofuran as the exchange medium.

Base-catalyzed exchange reactions employed a K_2CO_3–D_2O–tetrahydrofuran medium, and the product recovered under these conditions was identical with that obtained under acid-catalyzed exchange conditions except for the absence of B–H–B bridge absorption in the infrared spectrum (Figures 7 and 8). It is therefore evident that basic conditions lead to bridge hydrogen atom exchange as well as exchange of the two axial C–H hydrogen atoms. The product obtained by the direct oxidation of 1-methyl-1,8-dicarbaclovoundecaborane(11) in D_2O was identical with that of the base-catalyzed exchange reaction.

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(13) The numbering system employed here differs from that of ref 9 and places the two carbon atoms at positions 1 and 3.

Table V. Pyrolysis Products from 1,3-Dimethyl-1,3-dicarbanonaborane(13)

Compound	Mp, °C	Bp, °C (mm)	Yield,[b] %	Yield,[c] %	Calcd, % C	H	B	Found, % C	H	B
$B_6C_2H_6(CH_3)_2$	(−40.4)-(39.4)[a]	62 (134)	30	0	38.43	9.68	51.89	37.42	9.82	52.10
$B_7C_2H_7(CH_3)_2$	(−22)-(−21.3)[a]		7	0	35.11	9.58	55.31	35.14	9.74	55.76
1,6-$B_8C_2H_8(CH_3)_2$	1.0-1.6[a]	73 (32)	28	41	32.32	9.49	58.18	31.97	9.69	57.84
1,10-$B_8C_2H_8(CH_3)_2$	26.5-27.5[a]		95[d]	..	32.32	9.49	58.18	33.35	9.67	57.63
1,7-$B_{10}C_2H_{10}(CH_3)_2$[e]	170		0	8	27.89	9.36	62.75	27.80	9.21	62.61

[a] In sealed capillary. [b] When prepared in the absence of diborane. [c] When prepared in the presence of diborane. [d] Prepared from 1,6-$B_8C_2H_8(CH_3)_2$. [e] Although several C-substituted derivatives of 1,7-$B_{10}C_2H_{12}$ have been reported [D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963)], the 1,7-dimethyl derivative has not been previously characterized. We thank F. P. Olsen for a sample of the authentic material.

Treatment of diequatorial 1,3-dimethyl-1,3-dicarbanonaborane(13) with sodium hydride in diethyl ether rapidly liberated 1 mole of hydrogen. Acidification of the resulting monoanion regenerated starting material. When the resulting monoanion was acidified with DCl, the regenerated diequatorial 1,3-dimethyl-1,3-dicarbanonaborane(13) contained deuterium in one axial position of the methylene group as indicated by infrared and ^1H nmr spectra. The monoanions derived from 1-phenyl- and 1,3-dimethyl-1,3-dicarbanonaborane(13) were also isolated as their cesium and tetramethylammonium salts when the correspondingly substituted 1,3-$B_7C_2H_{13}$ was treated with aqueous hydroxide ion.

$$1,3\text{-}(CH_3)_2B_7C_2H_{11} + NaH \longrightarrow Na^+ + 1,3\text{-}(CH_3)_2B_7C_2H_{10}^- + H_2$$

The enhanced acidity of the axial hydrogen atom of the methylene group in 1,3-$B_7C_2H_{13}$ has no precedent in carborane chemistry. Voet and Lipscomb[9] have carried out a calculation of charge densities at all atoms in $B_7C_2H_{13}$ using their nonempirical molecular orbital method.[14,15] The relative positive charge densities observed are: axial-CH > bridge B–H–B > equatorial-CH, in agreement with the observations described above.

The $B_6C_2H_8$, $B_7C_2H_9$, and $B_8C_2H_{10}$ Carboranes

The 1,3-$B_7C_2H_{13}$ system described above appeared to be a logical precursor to the unknown $B_7C_2H_9$ carborane since pyrolysis of thermally unstable $B_7C_2H_{13}$ derivatives might lead to the expulsion of hydrogen. Consequently, the thermal decomposition of 1,3-dimethyl-1,3-dicarbanonaborane(13) was investigated[7] at 200–225°. Much to our surprise, this initial attempt led to the formation of three products which were subsequently identified as the C,C′-dimethyl derivatives of the $B_6C_2H_8$, $B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ carboranes (see Figures 9–11). Later work employed diphenyl ether as a reaction solvent at 215°, and the products obtained under these conditions are presented in Table V. It will be noted that the normal pyrolysis procedure produced nearly equivalent amounts of $B_6C_2H_8$ and 1,6-$B_8C_2H_{10}$ derivatives and low yields of the $B_7C_2H_9$ derivative. These results suggested that the pyrolysis reaction proceeds with predominant disproportionation of the 1,3-$B_7C_2H_{13}$ derivative. In order to increase the yields of the 1,6-$B_8C_2H_{10}$ derivative by preventing disproportionation, pyrolyses were carried out as before, but in the presence of a continuous supply of B_2H_6. Table V presents the results of these reactions, and it is seen that the $B_6C_2H_8$ and $B_7C_2H_9$ derivatives are not produced under these conditions. The dominant products were the 1,6-$B_8C_2H_{10}$ derivative and a low yield of the 1,7-$B_{10}C_2H_{12}$ derivative. The latter product probably arises from the reaction of the 1,6-$B_8C_2H_{10}$ derivative with excess diborane, and this point was experimentally substantiated, in part, by carrying out the reaction of the C,C′-dimethyl derivative of 1,6-$B_8C_2H_{10}$ with excess diborane under the conditions employed in the pyrolysis reactions. The C,C′-dimethyl derivative of 1,7-$B_{10}C_2H_{12}$ was obtained in 27% yield and 37% of the starting material was recovered.

$$1,3\text{-}B_7C_2H_{13} \longrightarrow 2H_2 + B_7C_2H_9$$

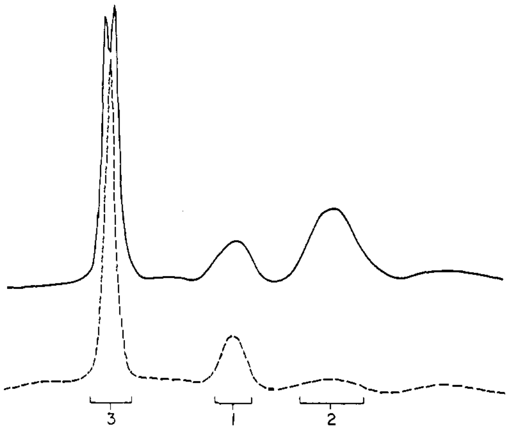

Figure 8. ^1H nmr spectra of $B_7C_2H_{12}(CH_3)$ at 60 Mc/sec. Isotopically normal (——) and exchanged in acidic or basic deuterium oxide solution (----). Integrated areas are indicated beneath the peaks.

C,C′-Dimethyl Derivative of $B_6C_2H_8$. Williams and Gerhart[16] obtained the C,C′-dimethyl derivative of $B_6C_2H_8$ in low yield by another route, and some discrepancies were noted with respect to their reported ^{11}B nmr spectrum (12.8 Mc/sec) and melting point.[17] Figure 9 presents the ^{11}B nmr spectrum of the C,C′-

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(14) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

(15) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *ibid.*, **88**, 2361 (1966).

(16) R. E. Williams and F. J. Gerhart, *ibid.*, **87**, 3513 (1965).

(17) The previously reported chemical shifts in the ^{11}B nmr spectrum of $B_6C_2H_6(CH_3)_2$ appear to be offset to low field by about 6 ppm. Comparison of the product obtained in this study with a sample kindly supplied by Dr. R. E. Williams confirms this situation. The melting point of highly purified $B_6C_2H_6(CH_3)_2$ prepared in this laboratory was −40.4 to −39.4°, which may be compared with the previously reported melting point of −58 to −63°. Retention times were identical with both samples using an Aerograph Model A350-B gas chromatograph employing a 0.25 in. × 10 ft 20% Carbowax on 45/60 HMDS Chromosorb P column operating at 143°. The retention time of $B_6C_2H_6(CH_3)_2$ under these conditions is 1.62 with respect to benzene.

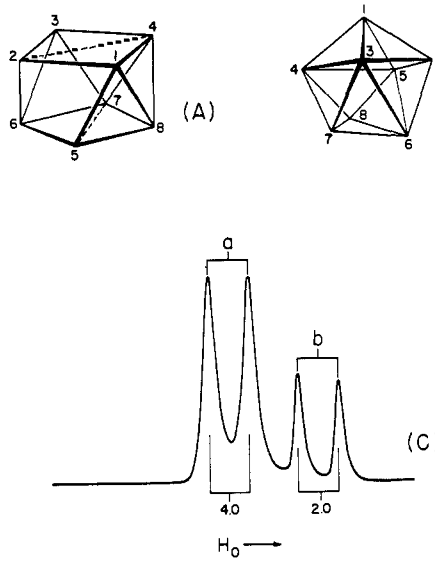

Figure 9. (A) Archimedean antiprism geometry for the $B_6C_2H_8$ carborane system. (B) The dodecahedral structure for $B_6C_2H_8$. (C) The 32-Mc/sec ^{11}B nmr spectrum of $B_6C_2H_6(CH_3)_2$ in toluene solution. Chemical shifts, ppm ($BF_3O(CH_2CH_3)_2$ = 0), and coupling constants (cps) are (a) −7.18 (167) and (b) +4.26 (171). Relative integrated areas are indicated beneath the peaks.

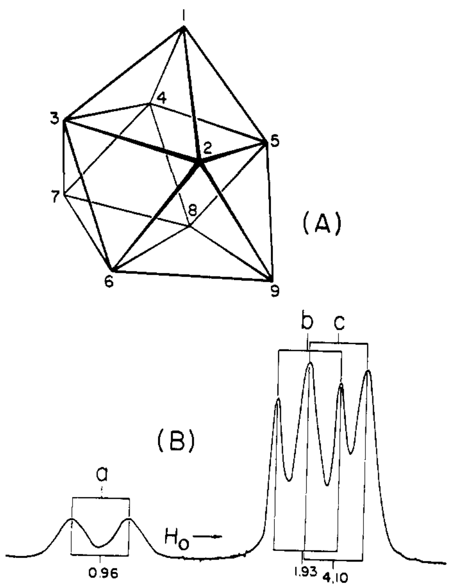

Figure 10. (A) The tricapped trigonal prism geometry. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of $B_7C_2H_7(CH_3)_2$. Chemical shifts, ppm ($BF_3O(CH_2CH_3)_2$ = 0), and coupling constants (cps) are (a) −25.5 (160), (b) +4.50 (173), and (c) +8.90 (163). Relative integrated areas are indicated beneath the peaks.

dimethyl derivative of $B_6C_2H_8$ at 32 Mc/sec, and it is seen to consist of two doublets of relative areas 4:2. The ^1H nmr spectrum contained singlet methyl resonances at −2.16 ppm relative to tetramethylsilane, a result which proves the equivalence of the methyl groups and their attached carborane carbon atoms. These data are in agreement with a square antiprism structure which would contain equivalent carbon atoms at positions 1 and 3 (Figure 9A). A more likely structure, which was suggested by Williams and Gerhart,[16] contains only trigonal faces and constitutes a dodecahedron (Figure 9B) which could be formed by compression of the

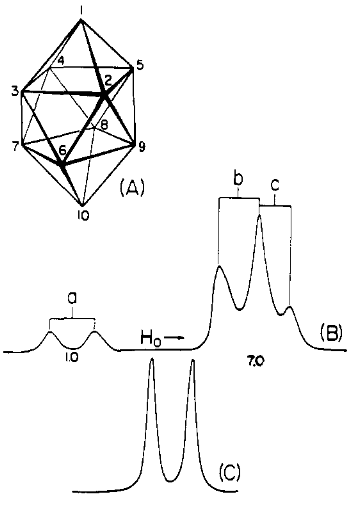

Figure 11. (A) The bicapped Archimedean antiprism geometry. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,6 isomer of $B_8C_2H_8(CH_3)_2$. Chemical shifts, ppm ($BF_3O(CH_2CH_3)_2$ = 0) and coupling constants (cps) are (a) −19.8 (178), (b) +15.3 (apparent 167), and (c) +22.9 (apparent 128). Relative integrated areas are beneath the peaks. (C) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,10 isomer of $B_8C_2H_8(CH_3)_2$. The chemical shift ($BF_3O(CH_2CH_3)_2$ = 0) and coupling constant are +103 ppm and 162 cps, respectively.

gross antiprism structure along the dotted lines. The dodecahedral structure would not be expected to contain adjacent carbon atoms due to their mutual coulombic repulsion, and the two doublets found in the ^{11}B nmr spectrum would require the coincidental congruency of two of the three types of ^{11}B nmr resonances expected to arise from the dodecahedral structure. The actual structure of this compound was recently determined by single-crystal X-ray diffraction studies[18] and consists of a distorted dodecahedron which resembles B_8Cl_8. This distortion is toward a square antiprism structure, and the carbon atoms appear at positions 1 and 6 (Figure 9B).

C,C′-Dimethyl Derivative of $B_7C_2H_9$. The 19.3-Mc/sec ^{11}B nmr spectrum of the C,C′-dimethyl derivative $B_7C_2H_9$ is presented in Figure 10. Three doublets of relative areas 1:2:4 are evident. The ^1H nmr spectrum contained one singlet methyl group resonance at −2.5 ppm relative to tetramethylsilane which requires that the carborane carbon atoms be equivalent. The low-field doublet found in the ^{11}B nmr spectrum suggests the presence of a single boron atom of coordination number 5 which resembles the apical boron atoms of the $B_{10}H_{10}^{-2}$ ion.[19,20] The remaining 2:4 sequence falls into place if a tricapped trigonal prism structure is adopted with carbon atoms at the equivalent apical positions 1 and 7. This structure was recently confirmed[18] by X-ray diffraction studies.

The C,C′-Dimethyl Derivatives of 1,6-$B_8C_2H_{10}$. The C,C′-dimethyl derivative of the 1,6-$B_8C_2H_{10}$ carborane which was directly obtained from the pyrolysis of the corresponding 1,3-$B_7C_2H_{13}$ species exhibited two singlet methyl group ^1H nmr resonances at −2.81 and −1.31 ppm relative to tetramethylsilane. The carborane car-

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(18) H. V. Hart and W. N. Lipscomb, *J. Am. Chem. Soc.*, 89, 4220 1967.

(19) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, 81, 5833 (1959).

(20) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, 37, 1779 (1962).

Table VI. Infrared Spectra (cm^{-1})

$B_9C_2H_{11}$[a]	3060 (w), 2880 (s), 2585 (s), 1455 (s), 1372 (m), 1145 (m), 1090 (m), 828 (m), 792 (w), 761 (w), 702 (w)
$B_9C_2H_{10}(CH_3)$[a]	3060 (w), 2890 (s), 2570 (s), 1447 (s), 1370 (m), 1253 (w), 1132 (s), 995 (s), 978 (s), 886 (w), 832 (s), 792 (m), 759 (m), 702 (m), 692 (m)
$B_9C_2H_9(CH_3)_2$[a]	2885 (s), 2550 (s), 1448 (s), 1375 (m), 1280 (w), 1250 (w), 993 (s), 948 (m), 921 (m), 884 (w), 841 (m), 797 (m), 763 (m), 712 (s)
$B_9C_2H_{10}(C_6H_5)$[a]	3060 (w), 2910 (s), 2580 (s), 1444 (s), 1370 (m), 1133 (s), 1104 (w), 1073 (m), 996 (w), 923 (m), 833 (s), 807 (w), 792 (w), 749 (s), 689 (s)
$B_7C_2H_{13}$[a]	3055 (w), 2910 (s), 2555 (s), 2015 (w), 1455 (s), 1378 (m), 1082 (s), 1048 (s), 1033 (s), 986 (m), 925 (m), 887 (s), 816 (m), 742 (m), 734 (m), 708 (m), 665 (s)
$B_7C_2H_{12}(CH_3)$[b]	3050 (w), 2980 (m), 2565 (s), 2015 (w), 1453 (m), 1385 (m), 1132 (m), 1072 (s), 1053 (m), 1020 (w), 988 (s), 922 (m), 888 (s), 808 (w), 773 (w), 734 (m), 708 (m), 667 (s)
$B_7C_2H_{11}(CH_3)_2$[a]	2925 (s), 2575 (s), 2020 (w), 1460 (s), 1382 (m), 1142 (m), 1119 (m), 1092 (w), 993 (s), 818 (w), 739 (s), 697 (m), 667 (s)
$B_7C_2H_{12}(C_6H_5)$[a]	2880 (s), 2562 (s), 2015 (w), 1595 (w), 1460 (s), 1379 (m), 1258 (w), 1077 (w), 1032 (m), 1020 (m), 997 (m), 942 (w), 912 (w), 882 (w), 829 (w), 763 (s), 696 (s), 665 (m)
$B_6C_2H_6(CH_3)_2$[b]	2930 (m), 2565 (s), 1447 (m), 1155 (w), 1004 (w), 972 (m), 911 (m), 822 (m), 789 (m), 767 (w), 742 (m), 718 (m)
$B_7C_2H_7(CH_3)_2$[b]	2935 (m), 2595 (s), 1457 (m), 1310 (m), 1112 (w), 1000 (w), 961 (m), 918 (w), 858 (m), 817 (m), 795 (m), 768 (w), 698 (w)
1,6-$B_8C_2H_8(CH_3)_2$[b]	3005 (w), 2960 (m), 2575 (s), 1455 (s), 1390 (w), 1316 (m), 1197 (m), 1128 (w), 1105 (w), 967 (s), 920 (m), 871 (s), 823 (w), 797 (m), 767 (m), 697 (s)
1,10-$B_8C_2H_8(CH_3)_2$[b]	2970 (m), 2580 (s), 1445 (m), 1380 (w), 1285 (w), 995 (s), 925 (m), 855 (m), 812 (m), 694 (s)

[a] Nujol mull. [b] Neat liquid film.

bon atoms are therefore nonequivalent. The 19.3-Mc/sec ^{11}B nmr spectrum of the compound is presented in Figure 11 and consists of a low-field doublet of relative area 1 and an unresolved array of relative area 7 at higher field. If one adopts the known $B_{10}H_{10}^{-2}$ structure[19] as a model for the framework of the $B_8C_2H_{10}$ carborane, it is attractive to assign the low-field doublet to a boron atom in an apical position such as position 10 (Figure 11). This assumption requires that position 1 be occupied by a carbon atom. Since it is quite unlikely that the two carbon atoms are nearest neighbors, it follows that the second carbon atoms should occupy position 6. On this basis we have assigned the 1,6 configuration to this C,C′-dimethyl derivative of $B_8C_2H_{10}$.

C,C′-Dimethyl Derivative of 1,10-$B_8C_2H_{10}$. During the past few years, the thermal isomerization of polyhedral carboranes and substituted polyhedral ions have become well known.[1,2] Perhaps the isomerization of the 1,2- to the 1,7-dicarbaclovododecaborane(12) stands as the most generally known example.[21] Accordingly, it was found that the C,C′-dimethyl derivative of the 1,6-$B_8C_2H_{10}$ carborane discussed above could be thermally rearranged at 350° in nearly quantitative yield to an isomeric compound.

The ^1H nmr spectrum of the rearranged species exhibited a single methyl group resonance which appeared as a singlet at -2.78 ppm relative to tetramethylsilane. This observation was taken as evidence for the equivalence of the carborane carbon atoms. Figure 11 presents the ^{11}B nmr spectrum of this compound determined at 19.3 Mc/sec. The simple doublet observed proves the equivalence of the eight boron atoms, and this evidence coupled with the ^1H nmr data leads to the unique assignment of the two carbon atoms to positions 1 and 10. This isomer could be expected to be the most stable of the known isomer pair since the carbon and boron atoms have quite favorable coordination numbers and the mutually repulsive carbon atoms are at opposite vertices of the polyhedron.

Experimental Section

Methods and Materials. (3)-1,2-Dicarbadodecahydroundecaborate(−1) and its 1-phenyl, 1-*p*-bromophenyl, 1-methyl, and 1,2-dimethyl derivatives were prepared by literature methods.[10,22] Diglyme was distilled from sodium, and boron trifluoride etherate was vacuum distilled just prior to use. Diphenyl ether was distilled under vacuum from calcium hydride, and tetrahydrofuran was distilled from lithium aluminum hydride. Polyphosphoric acid was obtained from the Victor Chemical Co. All other solvents and reagents were reagent grade and were used without further purification.

Infrared spectra were obtained on a Beckman IR-5 spectrophotometer and are presented in Table VI. Mass spectra were measured on a Consolidated Engineering Corp. Model 620-A mass spectrometer. Proton nmr spectra were recorded on a Varian Associates A-60 spectrometer, and the 19.3-Mc/sec boron nmr spectra

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(21) D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

(22) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).

were recorded on a Varian Associates HR-60 spectrometer; the 60-Mc/sec boron nmr spectrum was recorded on a Varian Associates experimental nmr spectrometer which is described elsewhere.[23]

All melting points were measured in sealed capillaries. Analyses were conducted by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Vapor phase chromatography (vpc) was performed with an Aerograph vapor phase chromatograph, Model A-350-B, using 10 ft, $^3/_8$ in. o.d. preparative or 0.25 in. o.d. analytical columns packed with 20% Apiezon L on 60–80 HMDS Chromosorb P and 20% Carbowax 20M on 45–60 HMDS Chromosorb P. Spinning-band distillations were carried out with a 3-ft Nester–Faust column.

All reactions were conducted under an atmosphere of nitrogen, and subsequent product work-ups required either a nitrogen atmosphere or minimum exposure to air.

Preparation of 1,8-Dicarbaclovoundecaborane(11). The potassium or cesium salt of (3)-1,2-$B_9C_2H_{12}^-$ must be well dried before conversion to 1,8-$B_9C_2H_{11}$. The hygroscopic potassium salt may be isolated and dried by a previously described procedure[22,24] or, alternatively, may be converted to the nonhygroscopic cesium salt. Into a 1-l magnetically stirred autoclave were placed 49.9 g (0.187 mole) of (3)-1,2-$CsB_9C_2H_{12}$, 150 g of polyphosphoric acid, and 350 ml of *n*-pentane. The vessel was thoroughly flushed with dry nitrogen, sealed, and heated at 125 ± 5° for 2 hr with stirring. After cooling, the hydrogen was vented, and the pentane solution containing the 1,8-$B_9C_2H_{11}$ was removed with minimum exposure of the solution to air. The polyphosphoric acid residue was washed once by the addition of 350 ml of fresh pentane, closing the vessel and stirring at 120° for 30 min. Solvent was removed from the combined pentane fractions in a conventional high-vacuum system. The product was sublimed under high vacuum by slowly raising the temperature to 80° using a cold finger maintained at −45°. The yield was 5.5 g or 22% (mp 204–208°). In addition to the 1,8-$B_9C_2H_{11}$, an unidentified solid was isolated in 5% yield when the sublimation temperature was increased to 100°. Purification of the crude 1,8-$B_9C_2H_{11}$ was accomplished by recrystallization under vacuum from *n*-pentane. After three recrystallizations, followed by sublimation under vacuum, the colorless carborane melted at 212–213°. Using the (3)-1,7-$CsB_9C_2H_{12}$ isomer[22] in the above procedure, the yield of 1,8-$B_9C_2H_{11}$ was increased to 36%.

Preparation of 1,8-Dimethyl-, 1-Methyl-, and 1-Phenyl-1,8-dicarbaclovoundecaborane(11). The procedure for preparing these three derivatives is illustrated using the 1,8-dimethyl derivative as an example, although each derivative requires a unique isolation and purification procedure. The apparatus consisted of a 5-l. round-bottom, three-necked flask fitted with a mechanical paddle stirrer and a 4-ft packed distillation column. The third neck of the flask was fitted with a glass stopper to permit the introduction of polyphosphoric acid. The distillation head assembly consisted of a Dean–Stark azeotropic distillation apparatus with a nitrogen inlet. Powdered cesium (3)-1,2-dimethyl-1,2-dicarbadodecahydroundecaborate(−1) (239 g, 0.812 mole) was placed in the flask with 2.3 l. of toluene. After flushing the system with nitrogen, toluene was distilled with stirring until the head temperature reached 110°. The hygroscopic potassium salt was particularly suited for this procedure since the water present may be easily removed by azeotropic distillation.[24] The reaction vessel was then cooled to about 60° and, under a rapid stream of nitrogen, about 1000 g of warm polyphosphoric acid was added with rapid stirring and without removing the distillation assembly. The reaction was slowly and cautiously brought to the toluene reflux temperature and maintained with vigorous stirring until hydrogen evolution had ceased (1.5 hr). After cooling, the toluene–carborane solution was decanted from the polyphosphoric acid residue with minimum exposure to air. The residue was washed once with 500 ml of toluene with heating and stirring. Solvent was removed from the combined toluene fractions by distillation under nitrogen at atmospheric pressure until the Claisen head temperature reached 115°, and the remaining toluene was removed on a high-vacuum sublimation apparatus.

Isolation and Purification of 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11). The carborane was sublimed at 50° to a collection surface chilled to −5° with a salt–ice bath. The yield was 97.8 g or 57% (mp 55.0–56.5°). Further purification was accomplished by recrystallization from *n*-pentane followed by vacuum sublimation. Recrystallization was carried out without special precaution, but prolonged exposure to air was avoided. After three cycles of the purification procedure, the white material melted at 57.1–58.0°.

Isolation and Purification of 1-Methyl-1,8-dicarbaclovoundecaborane(11). The product was sublimed under high vacuum to a surface chilled to −30°. The yield was 23 g (60%) based on 0.254 mole of the cesium salt. The sublimation temperature was then raised to about 100° and an unidentified material was isolated in low yield. The product was further purified by recrystallization from *n*-pentane (avoid prolonged exposure to air) and resublimation under vacuum through a trap cooled to −8° to a trap cooled to −31° (mp 84.0–84.5°).

Isolation and Purification of 1-Phenyl-1,8-dicarbaclovoundecaborane(11). The flask containing the product was transferred to an alembic still[24] attached to a high-vacuum line, and the residual toluene was removed under vacuum. The still reflux jacket was then cooled with tap water, and the temperature of the distillation flask was raised slowly by means of a heated silicone oil bath to 145° while continuous evacuation was maintained. The yield of the pale yellow product (mp 36.5–38.0°) was 112 g (57%) based on 0.938 mole of potassium salt. Two recrystallizations from *n*-pentane with minimum exposure to air followed by double sublimation under vacuum from a container at room temperature to a cold finger maintained at 0° gave analytically pure (mp 37.0–37.8°) product.

Reaction of (3)-1-Phenyl-1,7-dicarbadodecahydroundecaborate(−1) with Polyphosphoric Acid. Into a 500-ml, round-bottom flask was placed 7.6 g (0.022 mole) of dry and well-powdered (3)-1,7-$CsB_9C_2H_{11}(C_6H_5)$ and 55 g of polyphosphoric acid. After mixing the reactants, the flask was connected to an alembic still[24] attached to a high-vacuum line. The flask was initially evacuated and then heated by means of a silicone oil bath at 130 ± 5° for 2 hr under 0.75 atm of dry nitrogen. After cooling, the contents of the flask were slowly heated to 150° with continuous evacuation using tap water in the still jacket. The product weighed 2.5 g (54%) and was identical with the 1-phenyl-1,8-dicarbaclovoundecaborane(11) prepared from the isomeric (3)-1-phenyl-1,2 anion.

Reaction of (3)-*d*-1-Phenyl-1,7-dicarbadodecahydroundecaborate(−1) with Polyphosphoric Acid. Partially resolved[22] cesium (3)-*d*-1-phenyl-1,7-dicarbadodecahydroundecaborate(−1) ($[\alpha]^{24}_{385}$ +14.6°) was employed in this experiment. In a 250-ml, round-bottom flask was placed 97 g of polyphosphoric acid and 4.24 g of dried and powdered cesium salt. The flask was connected to an alembic column[24] and evacuated on a high-vacuum line. The contents of the flask were heated at 135 ± 5° for 40 min under 0.75 atm of nitrogen. After cooling, the product was distilled at 140° under high vacuum. The yield of 1-phenyl-1,8-dicarbaclovoundecaborane(11) isolated was 2.42 g or 93% (mp 37.0–38.0°) and exhibited no optical activity.

Preparation of 1-(*p*-Bromophenyl)-1,8-dicarbaclovoundecaborane(11). In a 1-l., three-necked, round-bottom flask equipped with a mechanical stirrer and reflux condenser were placed 10.6 g (0.0251 mole) of dry cesium (3)-1-(*p*-bromophenyl)-1,2-dicarbadodecahydroundecaborate(−1), 100 g of polyphosphoric acid, and 200 ml of toluene. After flushing the system with nitrogen, the contents of the flask were maintained at the toluene reflux temperature with vigorous stirring for 3 hr. After cooling, the solvent was decanted and distilled under a nitrogen atmosphere to a small volume. The flask was transferred to a high-vacuum sublimation apparatus, and the remaining toluene was removed under vacuum. The solid product was sublimed at 90° to a cold finger maintained at 0°. The yield was 5.2 g or 72% (mp 98.0–100.0°). An analytical sample was obtained by two sublimations followed by recrystallization from *n*-pentane in a drybox and two additional sublimations (mp 100.5–101.5°).

Reaction of 1-Phenyl-1,8-dicarbaclovoundecaborane(11) with Triphenylphosphine. Into a 250-ml erlenmeyer flask were placed 3.0 g (0.014 mole) of 1-phenyl-1,8-dicarbaclovoundecaborane(11) and 100 ml of dry diethyl ether. To the solution was added 4.4 g (0.017 mole) of triphenylphosphine. The flask was stoppered and gently heated on a steam bath for 5 min, cooled, and filtered giving 6.2 g (92%) of adduct. The product was purified by recrystallization from methylene chloride followed by recrystallization from acetonitrile–benzene (mp 252° dec).

Reaction of 1-Phenyl-1,8-dicarbaclovoundecaborane(11) with Triethylamine. 1-Phenyl-1,8-dicarbaclovoundecaborane(11) (9.7 g, 0.047 mole) was dissolved in 150 ml of benzene to which 5 g of triethylamine was slowly added. After allowing the solution to

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(23) See R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc.*, 402 (1964), for further examples of 60-Mc/sec ^{11}B nmr spectra.

(24) M. F. Hawthorne, *et al.*, *Inorg. Syn.*, **10**, 103 (1967).

stand for a few minutes, the benzene and excess triethylamine were evaporated at low pressure and the resulting solid was crystallized from acetonitrile (mp 156–159° dec) giving 8.2 g (57%) of adduct. Further purification was accomplished by two recrystallizations from acetonitrile in a dry nitrogen atmosphere (mp 157.0–159.0° dec).

Reaction of 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11) with Triethylamine. The same procedure was followed as in the case of the 1-phenyl derivative described above. In 30 ml of benzene was dissolved 4.3 g (0.016 mole) of 1,8-dimethyl-1,8-dicarbaclovoundecaborane(11) to which an excess of triethylamine diluted in benzene was slowly added. The solution was cooled in an ice bath and the product was filtered and recrystallized from cold acetonitrile. The yield of adduct was 2.1 g (49%). An analytically pure sample was obtained by two recrystallizations from acetonitrile in a dry nitrogen atmosphere (mp 143.0–144.0° dec).

Reaction of 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11) with Ethyl Isocyanide. Into a 250-ml, round-bottom flask were placed 6.3 g (0.039 mole) of 1,8-dimethyl-1,8-dicarbaclovoundecaborane(11) and 190 ml of toluene. The system was flushed with nitrogen and chilled to −10° with a salt–ice bath. From a dropping funnel, 3.6 ml (0.044 mole) of freshly distilled ethyl isocyanide was added over a 30-min period with stirring. After complete addition, the solution was stirred for an additional 1.5 hr at −10°. The excess ethyl isocyanide and the solvent were removed at room temperature with a water aspirator. The resulting oil was dissolved in 30 ml of benzene to which 70 ml of *n*-heptane was added. This solution was rotary evaporated giving a yield of 4.4 g (53%) of the off-white crystalline adduct. The product was purified by three recrystallizations from benzene–heptane (mp 105.0–106.0°).

Reaction of 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11) with Hydroxide Ion. In 25 ml of diethyl ether was dissolved 4.8 g (0.030 mole) of freshly sublimed 1,8-dimethyl-1,8-dicarbaclovoundecaborane(11). To this solution was added 100 ml of 1 *M* potassium hydroxide solution and the solution was stirred for 15 min. The solution was stripped free of the ether solvent, and the hydroxide adduct was isolated by precipitation as its tetramethylammonium salt. The white crystalline product was dried under vacuum giving 5.9 g (83%). Purification was accomplished by four recrystallizations from acetonitrile–water.

Preparation and Acidolysis of the Hydroxide Ion Adduct of 1-Phenyl-1,8-dicarbaclovoundecaborane(11). The hydroxide ion adduct of 1-phenyl-1,8-dicarbaclovoundecaborane(11) was prepared as described immediately above and isolated as the cesium salt. In a 500-ml flask 4.0 g (0.011 mole) of this cesium salt and 50 g of polyphosphoric acid were mixed. The flask was attached to an alembic still[24] on a high-vacuum line and the flask evacuated. The reactants were then heated at 140° for 1 hr under about 0.75 atm of nitrogen. After cooling, the product was distilled by slowly raising the temperature to 150° using tap water in the alembic still jacket. The yield of the pale yellow product was 0.95 g (41%) and was identified as authentic 1-phenyl-1,8-dicarbaclovoundecaborane(11) by its infrared spectrum.

Equivalent Weight Determination of 1-Phenyl- and 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11) in Methanol. A standard potentiometric titration procedure was used employing a Leeds and Northrup pH meter with a mercury electrode *vs.* sce. The concentration of the standard sodium hydroxide in anhydrous methanol was 0.970 *N*. In 30 ml of anhydrous methanol was dissolved 98.8 mg of freshly sublimed 1-phenyl derivative which was then covered, with the electrodes and a nitrogen bubbler immersed in the solution. The titration was carried out without delay: calculated equivalent weight for $B_9C_2H_{10}(C_6H_5)$, 208.6; found, 207. The same procedure was employed for the 1,8-dimethyl derivative, using 129.4 mg of freshly sublimed carborane: calculated equivalent weight for $B_9C_2H_9(CH_3)_2$, 160.5; found, 163.

Palladium-Catalyzed Degradation of 1-Phenyl- and 1,8-Dimethyl-1,8-dicarbaclovoundecaborane(11) in Propionic Acid. In 150 ml of propionic acid was dissolved 12.5 g (0.060 mole) of freshly distilled 1-phenyl-1,8-dicarbaclovoundecaborane(11). To this solution was added 0.84 g of palladium chloride, and the resulting mixture was stirred at 0° for 5 hr. The solution was then heated to the reflux temperature until hydrogen evolution ceased which required 25 hr. After cooling, 250 ml of water was added and the solution was extracted five times with 250-ml portions of *n*-pentane. The combined *n*-pentane fractions were washed with dilute base followed by water. After drying over magnesium sulfate, the *n*-pentane was distilled off leaving a clear brown solution. This solution was refluxed for 7 hr with 13 g of potassium hydroxide and 80 ml of absolute ethanol. Water was added to the cool solution followed by extraction with *n*-pentane. The pentane fractions was washed with dilute hydrochloric acid and dried over magnesium sulfate and activated charcoal. Distillation followed by vpc analyses of the cuts gave 0.395 g (7% yield) of toluene.

In a 500-ml, round-bottom flask fitted with a break-off seal was placed 0.8345 g (0.0052 mole) of freshly sublimed 1,8-dimethyl-1,8-dicarbaclovoundecaborane(11), 0.3676 g of palladium chloride, and 60 ml of propionic acid. The flask was evacuated, sealed off, and heated at 135° for 31 hr. After the heating period, the flask was opened into a vacuum line, and the product was collected after passing through a −160° trap and a −78° trap. Ethane, as identified by its mass spectrum, was obtained in 67% yield employing CO_2 as a calibration standard and using corrected atmospheric pressure and temperature.

Preparation of 1,3-Dicarbanonaborane(13) and 1-Phenyl-1,3-dicarbanonaborane(13). The procedure for the preparation of 1,3-dicarbanonaborane(13) and 1-phenyl-1,3-dicarbanonaborane(13) is the same although each has a unique isolation and purification procedure. The preparation of the 1-phenyl derivative is given as the general procedure. Into a 1-l. three-necked flask equipped with mechanical stirrer, dropping funnel, and nitrogen inlet was dissolved 21.3 g (0.102 mole) of 1-phenyl-1,8-dicarbaclovoundecaborane(11) in 200 ml of 2 *N* H_2SO_4 with rapid stirring under a nitrogen atmosphere. The dissolution of solid required 20 min. To this solution was then added 200 ml of toluene and the resulting mixture chilled to 0°. A sodium dichromate solution, 31 g (0.102 mole) of $Na_2Cr_2O_7\cdot 2H_2O$ dissolved in about 250 ml of 2 *N* H_2SO_4, was added dropwise over a period of 1 hr while rapidly stirring the solution at 0°. After the complete addition of the dichromate solution, the reaction mixture was stirred an additional 5 min. The work-up is best carried out without delay. The contents of the reaction vessel were transferred to a separatory funnel with an additional 500 ml of water. The water layer was washed three times with 150-ml portions of toluene, and the combined toluene extracts were dried over anhydrous magnesium sulfate.

Isolation and Purification of 1-Phenyl-1,3-dicarbanonaborane(13). The solution was filtered and the toluene removed under mechanical vacuum with gentle heating. The resulting solid weighed 11.4 g (59%). Purification was accomplished by recrystallization from *n*-pentane in a nitrogen atmosphere followed by sublimation at 50° to a 0° cold finger (mp 77.0–78.3°), followed by two recrystallizations from *n*-pentane under nitrogen and a final sublimation (mp 78.5°).

Isolation and Purification of 1,3-Dicarbanonaborane(13). After filtering the solution, the toluene was reduced at room temperature to a low volume on a mechanical vacuum pump. The flask was then transferred to a sublimation apparatus attached to a high-vacuum line where the remaining toluene was removed. The solid product was sublimed at room temperature to a −40° collection surface. The yield of the crude solid was 5.3 g (76%) based on 0.0607 mole of 1,8-dicarbaclovoundecaborane(13). An analytical sample was obtained by three recrystallizations at 0° from *n*-pentane under vacuum followed by sublimation (mp 60.5–61.0°).

Preparation of 1-Methyl- and 1,3-Dimethyl-1,3-dicarbanonaborane(13). The preparation of 1,3-dimethyl-1,3-dicarbanonaborane(13) is given as the general preparative procedure although each derivative requires a unique isolation and purification procedure. In a 2-l., three-necked flask equipped with a mechanical stirrer, addition funnel, and nitrogen inlet was dissolved 30.2 g (0.188 mole) of 1,8-dimethyl-1,8-dicarbaclovoundecaborane(11) in 175 ml of glacial acetic acid with rapid stirring under a nitrogen atmosphere. After dissolution, 400 ml of water and 300 ml of toluene were added and the resulting mixture was chilled to 0°. A sodium dichromate solution consisting of 56 g (0.188 mole) of $Na_2Cr_2O_7\cdot 2H_2O$ and 300 ml of 2 *N* H_2SO_4 was added dropwise over about a 1-hr period. After complete addition of dichromate, the mixture was stirred an additional 5 min at 0°. The contents of the flask were transferred without delay to a separatory funnel with an additional 500 ml of chilled 2 *N* H_2SO_4. The layers were separated and the aqueous layer was washed four times with 100-ml portions of toluene. The combined toluene fractions were dried over magnesium sulfate. The bulk of the toluene was stripped using a mechanical vacuum pump.

Isolation and Purification of 1,3-Dimethyl-1,3-dicarbanonaborane(13). The flask was transferred to a high-vacuum sublimation apparatus and the remaining toluene was removed. The product was then sublimed at 50° to a collection surface at −80°. The yield of the crystalline solid was 17.1 g (65%). The crude product was purified under a nitrogen atmosphere by five recrystallizations in *n*-pentane followed by sublimation at room temperature to a 0° cold finger (mp 50.5–51.8°).

Isolation and Purification of 1-Methyl-1,3-dicarbanonaborane(13). The flask was attached to an alembic still[24] and a high-vacuum line and the remaining toluene was removed. The product was distilled with continuous pumping at 60° with the alembic still jacket maintained at 0°. The yield of the colorless liquid product was 9.1 g (62%) based on 0.116 mole of 1-methyl-1,8-dicarbaclovononaborane(13). Purification of the product was accomplished by preparative vpc employing an Apiezon L preparative column at 165°. The pure product was collected in a U tube fitted with a stopcock at 0°. The product was then transferred under high vacuum from the vpc U tube collection assembly to another U tube maintained at −10° (mp 23.5–24.0°).

Reaction of 1-Phenyl- and 1,3-Dimethyl-1,3-dicarbanonaborane(13) with Hydroxide Ion. The general procedure is illustrated with the reaction of the 1-phenyl-1,3-dicarbanonaborane(13) with aqueous hydroxide ion. In a 250-ml flask was dissolved 3.6 g (0.191 mole) of 1-phenyl-1,3-dicarbanonaborane(13) in 75 ml of 5% sodium hydroxide solution. The resulting monoanion was immediately isolated by precipitation of its cesium salt. After drying under vacuum, the yield of cesium salt was 5.8 g (94%). The first crystallization was carried out in dilute ammonium hydroxide (mp 183° dec). An analytical sample was obtained by further recrystallizations from acetonitrile–methylene chloride in a dry nitrogen atmosphere (mp 178° dec). *Anal.* Calcd for $CsB_7C_2H_{11}(C_6H_5)$: C, 29.95; H, 5.03; B, 23.59; Cs, 41.43. Found: C, 29.85; H, 5.04; B, 24.10; Cs, 41.08.

The 1,3-dimethyl monoanion was also isolated as its cesium salt as described above. The yield of cesium dimethyl salt, after one crystallization from dilute ammonium hydroxide, was 6.6 g (91%) based on 0.0265 mole of starting material. Further purification was accomplished by three recrystallizations from acetonitrile–methylene chloride in a dry nitrogen atmosphere (mp 185° dec). *Anal.* Calcd for $CsB_7C_2H_{10}(CH_3)_2$: C, 17.62; H, 5.91; B, 27.75. Found: C, 18.16; H, 6.32; B, 27.95.

Oxidation of 1-Methyl-1,8-dicarbaclovoundecaborane(11) in D_2O–D_3PO_4. The D_3PO_4 required for the reaction was prepared by dissolving 20.5 g of P_2O_5 in 75 ml of D_2O followed by heating this solution for 3 hr under a nitrogen atmosphere. Into a 300-ml, three-necked, round-bottom flask was dissolved 2.13 g (0.0146 mole) of freshly sublimed 1-methyl-1,3-dicarbaclovoundecaborane(11) in 4 ml of tetrahydrofuran. The system was flushed with nitrogen and chilled to 0°. To this solution was added 25 ml of the D_3PO_4 solution, and the resulting solution was stirred at 0° for 10 min. From a dropping funnel, a dichromate solution consisting of 8.1 g (0.027 mole) of $K_2Cr_2O_7$ dissolved in 30 ml of the D_3PO_4 solution was added dropwise over an 8-min period at 0° with rapid stirring. After complete addition of the dichromate solution, the contents of the flask were stirred an additional 10 min at 0°. To the solution was then added 150 ml of toluene, and stirring was continued for an additional 20 min. The toluene solution was dried over anhydrous magnesium sulfate and filtered, and the bulk of the toluene was removed under high vacuum. The remaining solvent was removed on an alembic still[24] under high vacuum, and the product was then distilled at 60° to a still jacket maintained at 0°. The yield of the product, $B_7C_2H_8D_4(CH_3)$, which was identified by its infrared, ^{1}H nmr, and ^{11}B nmr spectra, was 0.26 g (14%). All transfers required for identification of the product were made under vacuum or in a nitrogen atmosphere.

Exchange of 1-Methyl-1,3-dicarbanonaborane(13) with D_3PO_4 in D_2O–Tetrahydrofuran. In a 300-ml, round-bottom flask maintained under a nitrogen atmosphere was placed 0.6 6g (5.2 mmoles) of freshly sublimed 1-methyl-1,3-dicarbanonaborane(13) and 3 ml of tetrahydrofuran. To this solution was added 4 ml of a D_3PO_4 solution prepared as described above, and the resulting solution was stirred for 1 hr at 0°. About 60 ml of toluene was added and the solution was stirred an additional 30 min at 0°. The toluene and aqueous phases were separated and the toluene phase was dried over anhydrous magnesium sulfate. The toluene solution was filtered and evaporated to a low volume under high vacuum. The remaining solution was transferred to an alembic still[24] attached to a high-vacuum line and the residual toluene was removed. The product was distilled at 45° to a still jacket maintained at −5°. The recovery was 0.54 g (82%). The product, $B_7C_2H_{10}D_2(CH_3)$, was identified by its infrared, ^{1}H nmr, and ^{11}B nmr spectra. All transfers required in identification were carried out under vacuum or in a nitrogen atmosphere.

Exchange of 1-Methyl-1,3-dicarbanonaborane(13) with K_2CO_3 in D_2O. In a 300-ml, round-bottom flask maintained under a nitrogen atmosphere was dissolved 1.67 g (0.0165 mole) of freshly sublimed 1-methyl-1,3-dicarbanonaborane(13) in 30 ml of tetrahydrofuran. To this solution was added 0.058 g of K_2CO_3 in 45 ml of D_2O, and the resulting solution was stirred for 30 min at room temperature. The product was recovered using the procedure described above. The yield of $B_7C_2H_8D_4(CH_3)$ was 1.1 g (62%), and the product was identical with the $B_7C_2H_8D_4(CH_3)$ prepared by oxidization of 1-methyl-1,8-dicarbaclovoundecaborane(11) with potassium dichromate in D_2O solution.

Reaction of 1-Methyl-1,3-dicarbanonaborane(13) with Sodium Hydride. Into a 100-ml flask equipped with a break-off seal, a seal-off standard taper joint, and a side arm with a seal-off standard taper joint was placed 2.0721 g (0.01469 mole) of pure 1,3-dimethyl-1,3-dicarbanonaborane(13). In the side arm was placed 2.40 g of 56.1% sodium hydride dispersion in mineral oil. The flask was chilled to 0° and evacuated. About 10 ml of diethyl ether was then condensed into the flask from lithium aluminum hydride on a vacuum line. The two taper joints were then sealed off. During the condensation of the ether and while the seal-offs were made, the contents of the flask were maintained at −196°. All weighings and transfers were made under a nitrogen atmosphere. The contents of the flask were then warmed to 0°, and the ether solution was mixed with the sodium hydride. The reaction vessel was maintained at 0° for a total of 5 min. The contents of the flask were then immediately frozen to −196°, the break-seal was broken, and the evolved H_2 was expanded into a calibrated Toepler system. The yield was 0.0147 mole of H_2 using the corrected atmospheric pressure and temperature.

Reaction of the Monoanion of 1,3-Dimethyl-1,3-dicarbanonaborane(13) with HCl. The excess sodium hydride was removed by filtration in a glove box from the ether solution of the anion prepared above. The filtrate was transferred to a vacuum line and evacuated. To the anion solution was added 550 ml (700 mm) of dry hydrogen chloride. The contents of the flask were warmed to room temperature and stirred for 10 min. The ether was removed under high vacuum and the product was sublimed at 50° to a 0° cold finger. The yield of the recovered 1,3-dimethyl-1,3-dicarbanonaborane(13) was 1.4 g (72%), which was identified by its characteristic infrared and ^{1}H nmr spectra and melting point.

Reaction of the Monoanion of 1,3-Dimethyl-1,3-dicarbanonaborane(13) with Deuterium Chloride. In a glove box, 2.00 g (0.0125 mole) of freshly sublimed 1,3-dimethyl-1,3-dicarbanonaborane(13) was dissolved in 45 ml of diethyl ether freshly distilled from lithium aluminum hydride. To this ether solution, 2.4 g of 56% sodium hydride dispersion in mineral oil was slowly added with stirring, and stirring was continued for an additional 3 min. The solution was filtered through a fritted disk filter and transferred to a high-vacuum sublimation apparatus. The sublimer was evacuated, and 503 ml (248 mm) of pure dry deuterium chloride was condensed into the sublimer. The ether solution of anion was stirred at 0° for 5 min and then frozen. The solution was slowly warmed to 0° with stirring and the ether was distilled off. The product was sublimed at 50° to a cold finger at 0°, transferred to a glove box, and weighed, giving 0.43 g (21%). The product was identified by its infrared, ^{1}H nmr, and ^{11}B nmr spectra as $B_7C_2H_{10}D(CH_3)_2$.

Equivalent Weight Determination of $CsB_7C_2H_{11}(C_6H_5)$. The equivalent weight determination was performed employing a Mechrolab osmometer. $(CH_3)_4NB_9C_2H_{12}$ in acetonitrile was used for the calibration curve. Into a 5-ml volumetric flask was weighed 0.0506 g (0.1578 mmole) of freshly recrystallized $CsB_7C_2H_{11}(C_6H_5)$ which was then dissolved in acetonitrile and made up to the 5-ml mark. The solution required 5 min to come to equilibrium with the pure solvent and an average of three runs gave an equivalent weight of 157 (calculated for $CsB_7C_2H_{11}(C_6H_5)$, 160.4).

Pyrolysis of 1,3-Dimethyl-1,3-dicarbanonaborane(13) in Diphenyl Ether Solution. Into a 500-ml, three-necked flask equipped with a magnetic stirrer, Dry Ice reflux condenser, and nitrogen inlet was placed 25.4 g (0.180 mole) of freshly sublimed 1,3-dimethyl-1,3-dicarbanonaborane(13) and 250 ml of diphenyl ether. The solution was heated at 210 ± 5° for 50 min with stirring under nitrogen. There was considerable hydrogen evolution and the solution slowly turned dark brown in color. After heating, the solution was cooled to room temperature and transferred to a spinning-band distillation column. The first distillate was collected at 54° (134 mm), and, upon the temperature reaching 94°, the pressure was reduced to 32 mm at which pressure the diphenyl ether began to distil at 126°. The distillation was performed in a nitrogen atmosphere. A total of seven cuts were made, two of which gave the C,C′-dimethyl derivative of $B_6C_2H_8$ and dimethyl-1,6-dicarbaclovododecaborane(10) in 95% purity. These two cuts were made at 62° (134 mm) and 72–74° (32 mm), respectively The C,C′-dimethyl derivative of $B_7C_2H_9$ was isolated in two cuts, 80–94° (134 mm) and 70–72° (32 mm). The seventh cut (126–148°, 32 mm) was essentially pure diphenyl ether. The total weight of the fractions, excluding the diphenyl ether fraction, was 16.5 g including the material collected in the pump trap. Vapor phase chromatographic analysis gave the yield data shown in Table V. In addition, trace amounts of the C,C′-dimethyl derivative of $B_6C_2H_7$ were collected. The carboranes in those cuts which were mixtures were isolated by preparative vpc employing a preparative Apiezon L column at 130° and collecting the cuts at $-80°$ in U tubes fitted with stopcocks. Analytically pure samples were obtained by preparative vpc employing a preparative Apiezon L column and then a preparative Carbowax 20M column; the pure carboranes were transferred under high vacuum from the vpc collection U tube into another U tube containing a few grams of Fisher Scientific Co. molecular sieve type 4A to remove any moisture present.

Pyrolysis of 1,3-Dimethyl-1,3-dicarbanonaborane(13) in Diphenyl Ether in the Presence of Diborane. Diborane was prepared by standard literature methods.[25] The reaction vessel for the pyrolysis was a 500-ml, three-necked, round-bottom flask fitted with a mechanical stirrer, Dry Ice reflux condenser, diborane inlet extending into the flask, and a nitrogen inlet which also served as a diborane and hydrogen outlet. Into the flask were placed 26.5 g (0.182 mole) of 1,3-dimethyl-1,3-dicarbanonaborane(13) and 300 ml of diphenyl ether. The system was thoroughly flushed with nitrogen. The contents of the reaction vessel were then rapidly heated to 215 ± 10° for a period of 50 min. During this 50-min heating period, 1.5 moles of diborane, which was generated at the time, was added as evenly as possible. The excess diborane was passed through an acetone trap. As the reaction vessel cooled to room temperature, a slow stream of nitrogen was passed through the solution to remove the residual diborane. The solution was then transferred to a spinning-band distillation column, and the products were distilled under nitrogen. The first fraction was collected at 70–73.5° (32 mm) and was identified by vpc analysis as 99% pure C,C′-dimethyl derivative of $1,6\text{-}B_8C_2H_{10}$. The yield was 11.2 g (41%). The second fraction collected was 2.4 g (8%) of 1,7-dimethyl-1,7-dicarbaclovododecaborane(12).[7]

Preparation of the C,C′-Dimethyl Derivative of $1,10\text{-}B_8C_2H_{10}$. In a thick-walled tube was placed 2.2 g of the pure C,C′-dimethyl derivative of $1,6\text{-}B_8C_2H_{10}$. The tube was sealed off under vacuum and placed in a bomb to which diphenyl ether had been added for pressure equalization. The bomb was heated at 350 ± 5° for 12 hr. After cooling, the tube was opened and its contents distilled into a weighing tube attached to a high-vacuum line. No hydrogen pressure was observed when the tube was opened. The yield of $1,10\text{-}B_8C_2H_{10}$ derivative was 2.1 g (95%). An analytically pure sample (mp 26.5–27.5°) was obtained by preparative vpc. The sample was first passed through a preparative Apiezon L column at 172° and then through a preparative Carbowax 20M column at 170°. The product was collected at $-80°$ in a U tube fitted with a stopcock and was transferred under high vacuum into another U tube containing a few grams of molecular sieve to remove moisture.

Reaction of the C,C′-Dimethyl Derivative of $1,6\text{-}B_3C_2H_{10}$ with Diborane. The apparatus employed here was the same as that described above in the reaction of 1,3-dimethyl-1,3-dicarbanonaborane(13) with diborane. Into the reaction vessel was placed 5.0 g (0.0338 mole) of the C,C′-dimethyl derivative of $1,6\text{-}B_8C_2H_{10}$ and 150 ml of diphenyl ether. The solution was heated to 225 ± 5° under a nitrogen atmosphere. With stirring, 1.5 moles of diborane was then added over 1.5 hr, maintaining the temperature at 225°. After cooling, the solution was transferred to a spinning-band distillation column and distilled under reduced pressure. The products are described in Table V.

Acknowledgment. This research was generously supported by the National Cancer Institute, U. S. Public Health Service, under Grant No. CA 06773, and the Army Research Office (Durham). The authors express their thanks for this support. We also wish to acknowledge the assistance of Messrs. James C. Smart and David A. Owen for certain experimental assistance.

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[25] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y.. 1962.

π-Dicarbollyl Derivatives of the Transition Metals. Metallocene Analogs

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Abstract: The $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ and $(3)\text{-}1,7\text{-}B_9C_2H_{12}^-$ ions are converted to the "dicarbollide" ions, $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2}$ and $(3)\text{-}1,7\text{-}B_9C_2H_{11}^{-2}$, when treated with bases. The dicarbollide ions serve as ligands in the formation of transition metal complexes which often resemble the well-known metallocenes. The preparation, characterization, reactions, and structures of these complexes are discussed.

The relatively young areas of boron hydride and carborane chemistry and the much older area of transition metal coordination chemistry have become established, in their own right, as nearly sacrosanct subdisciplines of inorganic chemistry. However, a point of separate development was reached which allowed the fusion of these two quite different fields of endeavor and the appearance of the chemistry described in this paper and, in part, in preliminary communications.[2–6] The striking similarity of this new chemistry to that of the

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[1] (a) National Science Foundation Trainee, 1965–1968; (b) National Institutes of Health Predoctoral Fellow, 1967–1968.

[2] (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, 87, 1818 (1965). (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

[3] M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, 87, 3987 (1965).

[4] M. F. Hawthorne and T. D. Andrews, *ibid.*, 87, 2496 (1965).

[5] P. A. Wegner and M. F. Hawthorne, *Chem. Commun.*, 861 (1966).

[6] L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, 89, 470 (1967).

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