Preparation of 4-Substituted (3)-1,7-Dicarba-*nido*-dodecahydroundecaborate(−1) Ions and 3-Substituted 1,8-Dicarba-*closo*-undecaborane(11)

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Abstract: Treatment of 1,8-dicarba-*closo*-undecaborane(11) and its C,C′-dimethyl derivative with carbanions leads to the formation of 4-substituted (3)-1,7-dicarba-*nido*-dodecahydroundecaborate(−1) ions in good yield. Certain of these ions can be subsequently converted to 3-substituted 1,8-dicarba-*closo*-undecaborane(11) derivatives which include the first examples of neutral two-cage carboranes having different numbers of boron atoms in each cage. The 4-substituted (3)-1,7-dicarba-*nido*-dodecahydroundecaborate(−1) ions and 3-substituted 1,8-dicarba-*closo*-undecaborane(11) derivatives include the first reported examples of two-cage carborane systems joined by a B–C bond.

During the past few years much work describing the preparation, characterization, and structural determination of polyhedral carboranes and borane ions has been presented and reviewed.[1,2] Especially prominent is the large amount of work concerned with (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$ ions[3–7] and the $B_8C_2H_{10}$, $B_9C_2H_{11}$, and $B_{10}C_2H_{12}$ carboranes.[8–24]

The previously described (3)-1,7-$B_9C_2H_{12}^-$ ion has been prepared by base degradation of the 1,7-$B_{10}C_2H_{12}$ carborane,[4] and this ion can be converted to the 1,8-$B_9C_2H_{11}$ carborane in good yield by treatment with polyphosphoric acid in the presence of refluxing toluene–methylcyclohexane.[10,11] Previous work has also shown that the 1,8-$B_9C_2H_{11}$ carborane and its C-substituted derivatives reacted with Lewis bases to form 1:1 adducts.[11] These adducts were suggested to be zwitterionic, boron-substituted (3)-1,7-$B_9C_2H_{11}$ derivatives.[11] We have prepared a corresponding series of ions from the reaction of selected carbanions and the 1,8-$B_9C_2H_{11}$ carborane and its C,C-dimethyl derivative.[25] In this paper we describe the synthesis and characterization of 4-substituted (3)-1,7-$B_9C_2H_{11}^-$ ions[11,25] and the synthesis and characterization of two-cage polyhedral carborane derivatives incorporating this ion and those neutral carborane systems mentioned above.

4-Substituted (3)-1,7-Dicarbadodecahydroundecaborate(−1). Reaction of the 1,8-$B_9C_2H_{11}$ carborane and its C-substituted derivatives with 1 mole equiv of $NaBH_4$ in 1,2-dimethoxyethane produced diborane and high yields of the corresponding (3)-1,7-$B_9C_2H_{12}^-$ ions which were identified by their nmr and infrared spectra.

$$\text{1,8-}B_9C_2H_{11} + BH_4^- \xrightarrow[25°]{(CH_3OCH_2)_2} \text{(3)-1,7-}B_9C_2H_{12}^- + {}^1/_2B_2H_6$$

Diborane was measured by trapping as trimethylamine–borane. In order to form the (3)-1,7-$B_9C_2H_{12}^-$ from 1,8-$B_9C_2H_{11}$ and borohydride ion, hydride ion attack must take place at boron atoms which would be incorporated into the open face of the product ion. Nucleophilic attack must therefore occur at the unique boron atom 4 or one of the equivalent boron atoms 3, 5, 7, or 9 (Figure 1). Although boron atom 4 should be more electropositive than boron atoms 3, 5, 7, and 9, because of its immediate proximity to two carbons atoms, its high coordination number might make it less susceptible to nucleophilic attack than atoms 3, 5, 7, and 9. Since attack at any of these equivalent boron atoms will yield the (3)-1,7-$B_9C_2H_{12}^-$ ion, attack at the equivalent 3, 5, 7, and 9 atoms is also favored statistically. Nucleophilic attack by groups other than hydride ion at atoms 3, 5, 7, and 9 would give rise to a substituted ion with no symmetry plane and which contains nonequivalent atoms. Ions which incorporated various organic groups into the (3)-1,7-$B_9C_2H_{11}^-$ moiety were prepared. Melting points, yields, analyses, and molecular weight data for these compounds are presented in Table I.

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Table I. Yield, Melting Point, Molecular Weight, and Analytical Data for 4-Substituted (3)-1,7-$B_9C_2H_{11}^-$ Ions

			Calcd, %					Found, %				
Compound	Mp,[c] °C[c]	Yield, %	C	H	B	N	Mol wt	C	H	B	N	Mol wt
$[(CH_3)_4N][B_9C_2H_{11}CH_3]$	354–355 dec	62	37.93	11.82	43.92	6.32	221.6	35.89	11.29	44.04	6.57	210[a]
$[(CH_3)_4N][B_9C_2H_{11}C_4H_9]$	282–285	80	45.54	12.23	36.91	5.31	263.7	48.48	11.96	37.05	...	264[a]
$[(CH_3)_4N][B_9C_2H_{11}C_5H_7O_4]$	239–240	58	39.12	8.95	28.83	4.15	337.7	38.95	8.80	28.87	4.09	335[a]
$[(CH_3)_4N][B_9C_2H_{11}CH(CN)_2]$	159–161	62	39.79	8.90	35.24	15.47	271.7	38.96	9.28	34.79	15.96	280[a]
$[(CH_3)_4N][B_9C_2H_{11}B_{10}C_2H_{10}CH_3]$	>360	72	29.70	9.97	56.47	3.85	363.9	30.09	10.09	56.23	3.96	363[b]
$CsB_9C_2H_{11}B_{10}C_2H_{11}$	>360	42	11.76	5.43	50.29		408.6	10.99	5.31	49.28		390[a]
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{11}$	244–246	59	16.50	6.00	47.06		436.7	16.43	5.86	47.04		473[b]
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3$	229–231	61	18.65	6.26	45.60		450.7	19.01	6.26	46.08		447[a]
$CsB_9C_2H_{11}B_8C_2H_9$	233–236	38	12.48	5.24	47.76		385.0	12.65	4.96	46.55		360[b]
$[(CH_3)_4N][B_9C_2H_{11}B_8C_2H_8C_2H_5]$	342–346	52	41.79	9.02	45.70	3.48	402.4	39.88	8.94	45.63	3.42	414[b]

[a] Osmometric in acetonitrile. [b] Cryoscopic in ethyl alcohol. [c] Uncorrected.

Table II. Ir Spectra of Nujol Mull of 4-Substituted (3)-1,7-$B_9C_2H_{11}^-$ Ions

Compound	Absorbance
$[(CH_3)_4N][B_9C_2H_{11}CH_3]$	2495 (s), 1295 (w), 1101 (m), 1012 (w), 978 (m), 944 (s), 828 (w), 726 (s)
$[(CH_3)_4N][B_9C_2H_{11}(n\text{-}C_4H_9)]$	2500 (s), 1402 (sh), 1295 (w), 1276 (w), 1180 (m), 1105 (m), 1035 (w), 1012 (m), 984 (m), 950 (s), 870 (w), 825 (m), 758 (w), 726 (s)
$[(CH_3)_4N][B_9C_2H_{11}(C_5H_7O_4)]$	2530 (s), 1755 (s), 1725 (sh), 1448 (sh), 1250 (s), 1199 (w), 1131 (s), 1032 (w), 1010 (w), 985 (m), 950 (m), 937 (w), 920 (w), 727 (m)
$[(CH_3)_4N][B_9C_2H_{11}CH(CN)_2]$	2530 (s), 2225 (s), 1405 (sh), 1275 (w), 1182 (m), 1132 (s), 1095 (s), 1032 (m), 985 (m), 945 (s), 902 (sh), 870 (w), 850 (w), 825 (w), 728 (s)
$[(CH_3)_4N][B_9C_2H_{11}B_{10}C_2H_{10}CH_3]$	2530 (s), 1405 (m), 1285 (w), 1195 (m), 1135 (w), 1102 (m), 1032 (sh), 1012 (m), 986 (m), 948 (s), 870 (w), 802 (w), 727 (s)
$CsB_9C_2H_{11}B_{10}C_2H_{11}$	2535 (s), 1164 (w), 1111 (sh), 1096 (m), 1014 (m), 982 (w), 923 (w), 899 (w), 721 (s)
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{11}$	2530 (s), 1293 (sh), 1152 (w), 1098 (m), 1062 (sh), 1012 (s), 990 (sh), 951 (w), 923 (m), 850 (w), 832 (w), 815 (w), 799 (w), 728 (s)
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3$	2520 (s), 1198 (w), 1137 (m), 1015 (s), 942 (m), 840 (m), 811 (w), 726 (s)
$CsB_9C_2H_{11}B_8C_2H_9$	2500 (s), 1245 (m), 1160 (w), 1100 (s), 1032 (m), 985 (m), 940 (m), 890 (w), 872 (sh), 824 (m), 752 (w), 714 (w), 678 (w)
$[(CH_3)_4N][B_9C_2H_{11}B_8C_2H_8C_6H_5]$	2500 (s), 1585 (w), 1305 (w), 1250 (w), 1175 (w), 1100 (m), 1032 (m), 983 (m), 950 (s), 920 (sh), 870 (w), 834 (m), 778 (s), 738 (w), 700 (s)

A butyl derivative, 4-(n-C_4H_9)-(3)-1,7-$B_9C_2H_{11}^-$, was prepared in high yield by reaction of 1,8-$B_9C_2H_{11}$ with 1 mole equiv of butyllithium in hexane. The 32.1-Mc/sec ^{11}B nmr spectrum of the 4-(n-C_4H_9)-(3)-1,7-$B_9C_2H_{11}^-$ ion exhibited a singlet of area 1 at δ +15.9, indicating a carbon-substituted boron atom. The remainder of the spectrum was very reminiscent of that of (3)-1,7-$B_9C_2H_{12}^-$ (Figure 2).

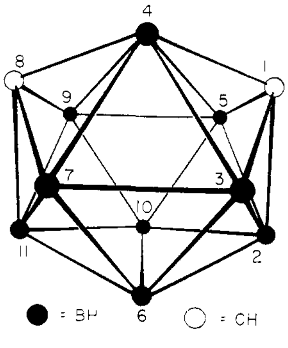

Figure 1. Skeletal framework and numbering system of 1,8-dicarba-*closo*-undecaborane.

An ion incorporating the malononitrile grouping, 4-(–$CH(CN)_2$)-(3)-1,7-$B_9C_2H_{11}^-$, was prepared by treatment of $CH_2(CN)_2$ in ether with 1 mole equiv of butyllithium in hexane, followed by 1 mole equiv of 1,8-$B_9C_2H_{11}$ in benzene. The infrared spectrum of 4-(–$CH(CN)_2$)-(3)-1,7-$B_9C_2H_{11}^-$ (Table II) exhibited a single sharp absorption at 2225 cm^{-1}, indicative of the C≡N

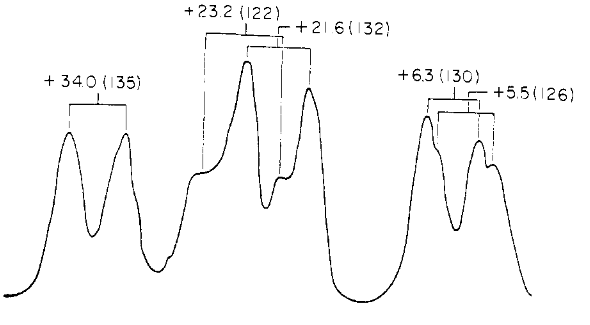

Figure 2. A 32.1-Mc/sec ^{11}B nmr spectrum of (3)-17-$B_9C_2H_{12}^-$ prepared from $NaBH_4$ and $B_9C_2H_{11}$ in dimethoxyethane. Chemical shifts (coupling constants) are relative to external $BF_3 \cdot O(C_2H_5)_2$.

Table III. 32.1-Mc/sec ^{11}B Nmr of 4-Substituted (3)-1,7-$B_9C_2H_{11}^-$ Ions[a]

Compound	Feature	δ (*J*, cps)	Rel. peak area
$[(CH_3)_4N][B_9C_2H_{11}CH_3]$	Doublet	+37.4 (122)	2.0
	2 doublets	+26.9 (120)	3.0
		+24.8 (116)	
	Singlet	+16.9	1.1
	Doublet	+9.5 (129)	3.0
	Doublet	+6.9 (122)	
$[(CH_3)_4N][B_9C_2H_{11}(n\text{-}C_4H_9)]$	Doublet	+37.3 (122)	2.0
	Doublet	+27.5 (116)	3.1
	Doublet	+25.4 (114)	
	Singlet	+15.9	1.1
	Doublet	+11.5 (114)	1.0
	Doublet	+9.4 (134)	2.0
$[(CH_3)_4N][B_9C_2H_{11}(C_5H_7O_4)]$	Doublet	+38.0 (135)	2.0
	Doublet	+26.1 (125)	3.0
	Singlet	+16.2	0.9
	Doublet	+8.4 (116)	3.0
	Doublet	+6.6 (120)	
$[(CH_3)_4N][B_9C_2H_{11}CH(CN)_2]$	Doublet	+134.4 (131)	2.0
	Doublet	+23.9 (113)	
	Doublet	+20.0 (132)	4.1
	Singlet	+16.6	
	Doublet	+5.6 (136)	3.0
	Doublet	+5.1 (138)	3.0
$[(CH_3)_4N][B_9C_2H_{11}B_{10}C_2H_{10}CH_3]$	Doublet	+37.4 (136)	2.0
	Doublet	+23.7 (136)	
	Singlet	+17.3	4.1
	Doublet	+9.3 (149)	13.2
$CsB_9C_2H_{11}B_{10}C_2H_{11}$	Doublet	+35.4 (126)	2.0
		+24.0 (120)	
	Overlapping doublets	+20.3 (144)	16.6
		+9.9 (133)	
		+3.1 (114)	
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{11}$	Overlapping doublets	+35.2 (133)	2.0
		+33.0 (123)	
	Doublet	+22.7 (126)	17.1
	Doublet	+9.8 (140)	
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3$	Overlapping doublets	+37.0 (138)	2.0
		+34.9 (134)	
	Doublet	+19.2 (121)	
	Doublet	+10.5 (151)	17.3
	Doublet	+1.4 (130)	
$CsB_9C_2H_{11}B_8C_2H_9$	Doublet	+34.7 (121)	2.0
	Doublet	+25.9 (124)	2.9
	Doublet	+23.0 (124)	
	Doublet	+12.3 (150)	11.8
	Doublet	+10.7 (150)	
	Doublet	+5.7 (136)	
$[(CH_3)_4N][B_9C_2H_{11}B_8C_2H_8C_6H_5]$	Doublet	+36.7 (120)	2.0
	Doublet	+26.2 (143)	
	Doublet	+23.4 (150)	3.1
	Overlapping doublets	+11.9 (165)	11.7

[a] Chemical shifts are in parts per million relative to external $BF_3 \cdot O(C_2H_5)_2$.

stretch of the cyano groups. The 32.1-Mc/sec ^{11}B nmr of this ion (Figure 3, Table III) exhibited both the high-field doublet seen in the spectrum of (3)-1,7-$B_9C_2H_{12}^-$ and the singlet (δ +16.6) exhibited in the spectrum of 4-(n-C_4H_9)-(3).1,7-$B_9C_2H_{11}^-$. The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt in pyridine (Table IV) contained a broad singlet of intensity 1.0 at δ −4.01, in addition to the carborane resonance (intensity 2) and cation resonance (intensity 12). This broad resonance was assigned to the proton of the malononitrile substituent.

An ion incorporating the enolic malonate ester functional group, the 4-($OC(OCH_3){=}CHCOOCH_3$)-(3)-1,-7-$B_9C_2H_{11}^-$ ion, was prepared in good yield in analogous fashion by addition of butyllithium in hexane to 1 mole equiv of dimethyl malonate in ether, followed by 1 mole equiv of 1,8-$B_9C_2H_{11}$ in benzene. The infrared spectrum of the tetramethylammonium salt (Table IV) exhibited a strong sharp absorption at 1725 cm^{-1}, which was assigned to the C=O stretch of the ester carbonyl group. The 32.1-Mc/sec ^{11}B spectrum (Table III) showed both the aforementioned high-yield doublet seen in the spectrum of (3)-1,7-$B_9C_2H_{12}^-$ and a singlet of intensity 1 at δ +16.2. The 60-Mc/sec ^1H nmr spectrum of $[(CH_3)_4N]$[4-($OC(OCH_3){=}CHCOOCH_3$)-(3)-1,-7-$B_9C_2H_{11}$] (Table IV) exhibited, in addition to cation methyl and carborane C–H resonances, a broad singlet of observed intensity 0.9 at δ −3.24, which was assigned to

Table IV. ^{1}H Nmr of 4-Substituted (3)-1,7-$B_9C_2H_{11}^-$ Ions[a]

Compound	Feature	δ, ppm	Rel peak area	Assignment[b]
$[(CH_3)_4N][B_9C_2H_{11}CH_3]$	Broad singlet	−0.35	3.0	(a) (CH_3)
($(CH_3)_2CO$)	Broad singlet	−1.45	2.0	(c)
	Sharp singlet	−3.36	12.0	(b)
$[(CH_3)_4N][B_9C_2H_{11}(n\text{-}C_4H_9)]$	Broad singlet	−1.51	2.1	(c)
($(CD_3)_2CO$)	Overlapping broad multiplets	−0.9 −1.2	8.7	(a) (butyl)
	Sharp singlet	−3.35	12.0	(b)
$[(CH_3)_4N][B_9C_2H_{11}(C_5H_7O_4)]$ ($(CD_3)_2CO$)	2 sharp singlets	−3.67, 3.59	3.0, 3.0	(a) (malonate) $-CH_3$
	Broad singlet	−1.23	2.1	(c)
	Broad singlet	−3.24	0.9	(a) (malonate) -C–H
	Sharp singlet	−3.46	12.0	(b)
$[(CH_3)_4N][B_9C_2H_{11}CH(CN)_2]$	Broad singlet	−1.82	2.0	(c)
(C_5H_5N)	Broad singlet	−4.01	0.94	(a) (malononitrile)
	Sharp singlet	−3.10	12.0	(b)
$[(CH_3)_4N][B_9C_2H_{11}B_{10}C_2H_{10}CH_3]$	Sharp singlet	−2.11	3.0	(e)
(C_5H_5N)	Broad singlet	−1.68	2.0	(c)
	Sharp singlet	−3.09	12.0	(b)
$CsB_9C_2H_{11}B_{10}C_2H_{11}$	Broad singlet	−1.29	2.0	(c)
($(CD_3)_2CO$)	Broad singlet	−3.79	1.0	(f)
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{11}$	Broad singlet	−3.17	1.0	(g)
($(CD_3)_2CO$)	Broad singlet	−1.68	6.0	(d)
$CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3$	Sharp singlet	−2.19	3.0	(e)
($(CD_3)_2CO$)	Sharp singlet	−1.49	3.0	(d)
	Sharp singlet	−1.64	3.0	(d)
$CsB_9C_2H_{11}B_8C_2H_9$	Broad singlet	−6.90	1.0	(h)
($(CO_3)_2CO$)	Broad singlet	−1.34	1.0	(c)
	Broad singlet	−1.70	1.0	(c)
$[(CH_3)_4N][B_9C_2H_{11}B_8C_2H_8C_6H_5]$	Broad singlet	−1.30	2.0	(a)
($(CD_3)_2CO$)	Multiplets	−7.55	4.9	(i)
	Sharp singlet	−3.36	12.0	(b)

[a] Chemical shifts are in ppm relative to $(CH_3)_4Si$. [b] (a) 4-Substituent C–H protons; (b) $(CH_3)_4N^+$ cation protons; (c) (3)-1,7-$B_9C_2H_{11}$ carborane protons; (d) (3)-1,7-$B_9C_2H_9(CH_3)_2CH_3$ protons; (e) 2′,-CH_3 methyl protons of (1′-2′-CH_3-1′,2-$B_{10}C_2H_{10}$); (f) 2′-carborane proton of (1′-1′,2′-$B_{10}C_2H_{11}$); (g) 7′-carborane proton of (1′-1′,7′-$B_{10}C_2H_{11}$); (h) 10′-carborane proton of (1′-1′,10′-$B_8C_2H_9$); (i) 10′-C_6H_5 protons of (1′-10′-C_6H_5-1,10′-$B_8C_2H_8$).

the malonate C–H group. In addition, two malonate methyl resonances of equal intensity 3 were observed. These two nonequivalent malonate methyl groups suggested that the enol form of the dimethyl malonate group was bound to the cage through a $=C(OCH_3)$–O–B linkage. This would be the product arising from reaction of 1,8-$B_9C_2H_{11}$ with the enol form of the dimethyl malonate anion.

$$-CH(COOCH_3)_2 \rightleftarrows {}^-O{-}C(OCH_3){=}CH(COOCH_3)$$

The methyl derivative, 4-CH_3-(3)-1,7-$B_9C_2H_{11}^-$ ion, was obtained by addition of methyllithium in ether to 1 mole equiv of 1,8-$B_9C_2H_{11}$ in hexane. The 32.1-Mc/sec nmr spectrum of $[(CH_3)_4N][4\text{-}CH_3\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ (Figure 4, Table III) exhibited both the characteristic high-field doublet and a singlet at δ +16.9. The 60-Mc/sec ^{1}H nmr spectrum (Table IV) contained, in addition to cation methyl and carborane C–H signals, a broad singlet of intensity 3.0 at δ −0.35, which was assigned to the 4-CH_3 group. When 2 mole equiv of methyllithium in ether was allowed to react with 1 mole equiv of 1,8-$B_9C_2H_{11}$, 1.02 mole equiv of methane was evolved, and $[(CH_3)_4N][4\text{-}CH_3\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ was obtained in 55% yield after treatment with aqueous $(CH_3)_4N^+Cl^-$. This mole of methane was presumed formed by reaction of methyllithium with the initially formed 4-CH_3-(3)-1,7-$B_9C_2H_{11}^-$, to produce the corresponding 4-CH_3-(3)-1,7-$B_9C_2H_{10}^{2-}$

$$CH_3Li + 1,8\text{-}B_9C_2H_{11} \longrightarrow 4\text{-}CH_3\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}^- + Li^+$$

$$CH_3Li + 4\text{-}CH_3\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}^-Li^+ \longrightarrow CH_4 + 4\text{-}CH_3\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{10}^{2-}Li^+_2$$

which was reconverted to the monoanion upon addition of aqueous $(CH_3)_4N^+Cl^-$. This proposed 4-CH_3-(3)-1,7-$B_9C_2H_{10}^{2-}$ ion was assumed to be isostructural and isoelectronic with (3)-1,7-$B_9C_2H_{11}^{2-}$,[26] which can be

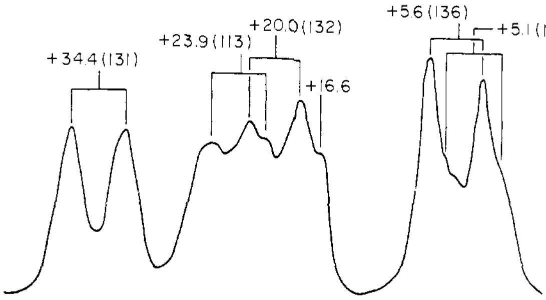

Figure 3. A 32.1-Mc/sec ^{11}B nmr spectrum of $[(CH_3)_4N][B_9C_2H_{11}\text{-}CH(CN)_2]$ prepared from $LiCH(CN)_2$ and $B_9C_2H_{11}$. Chemical shifts (coupling constants) are relative to external $BF_3\cdot O(C_2H_5)_2$.

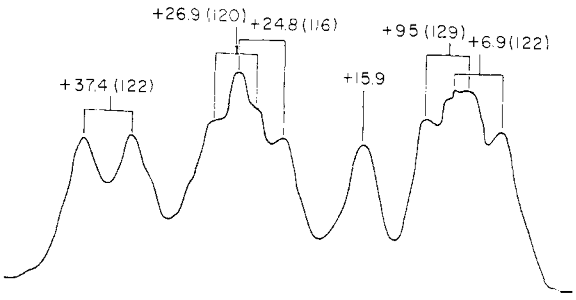

Figure 4. A 32.1-Mc/sec ^{11}B nmr spectrum of $[(CH_3)_4N][B_9C_2H_{11}CH_3]$ prepared from $LiCH_3$ and $B_9C_2H_{11}$. Chemical shifts (coupling constants) are relative to external $BF_3 \cdot O(C_2H_5)_2$.

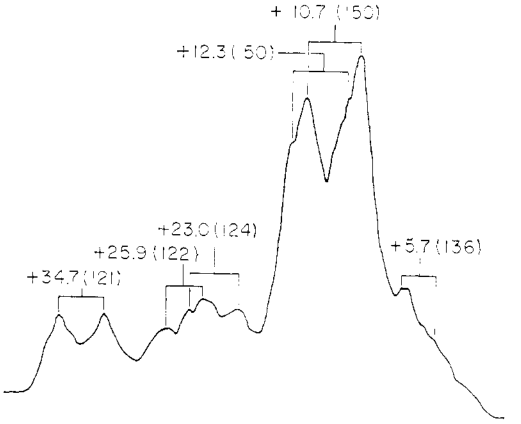

Figure 5. A 32.1-Mc/sec ^{11}B nmr spectrum of $CsB_9C_2H_{11}B_8C_2H_9$ in acetone solution. Chemical shifts (coupling constants) are relative to external $BF_3 \cdot O(C_2H_5)_2$.

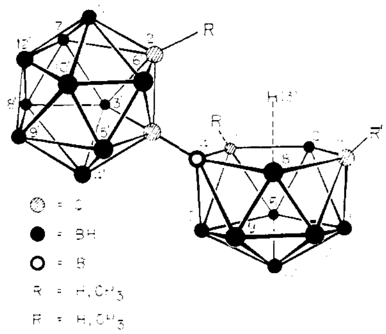

Figure 6. Proposed skeletal framework and numbering system for the $B_9C_2H_9R'_2B_{10}C_2H_{10}R^-$ ion.

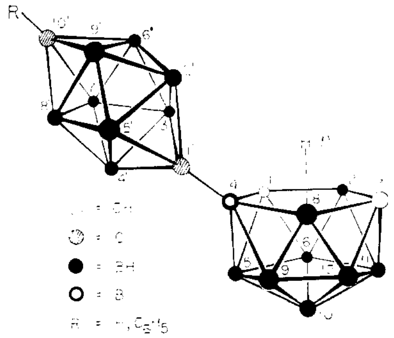

Figure 7. Proposed skeletal framework and numbering system for the $B_9C_2H_{11}B_8C_2H_8R^-$ ion.

generated from CH_3Li and (3)-1,7-$B_9C_2H_{12}^-$ with simultaneous evolution of 1 mole of methane.

Attempts were made to introduce other organic functional groups by reaction of their carbanions with the 1,8-$B_9C_2H_{11}$ carborane: these included phenyl, phenylacetylenyl, acetylacetonato, and cyclopentadienyl; in each case reaction did occur with 1,8-$B_9C_2H_{11}$, but the ions formed were not sufficiently stable to allow characterization.

Carbanions formed from 1,2-$B_{10}C_2H_{12}$, 1,7-$B_{10}C_2H_{12}$, and 1,10-$B_8C_2H_{10}$ and their C-substituted derivatives were also allowed to react with 1,8-$B_9C_2H_{11}$ and its C,C′-dimethyl derivative and gave rise to similar 4-substituted (3)-1,7-$B_9C_2H_{11}^-$ ions. Reaction of 1-Li-2-CH_3-1,2-$B_{10}C_2H_{10}$[14,27] with 1,8-$(CH_3)_2$-1,8-$B_9C_2H_9$[11] in diethyl ether afforded the $B_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3^-$ ion in good yield. The 60-Mc/sec ^1H nmr of this ion consisted of three equal-intensity singlets (Table IV) at δ -2.11, -1.68, and -1.49. The resonance at δ -2.11 was assigned to a 1,2-$B_{10}C_2H_{10}CH_3$ group with confidence, from comparison with 1-CH_3-1,2-$B_{10}C_2H_{11}$ (δ -1.98) and 1,2-$(CH_3)_2$-1,2-$B_{10}C_2H_{10}$ (τ -2.02),[27] while the resonances at δ -1.68 and -1.49 were assigned to the (3)-1,7-$B_9C_2H_9(CH_3)_2^-$ moiety, by comparison with (3)-1,7-$B_9C_2H_{10}(CH_3)_2^-$ (δ -1.42).[4] Reaction of similarly prepared 1-Li-1,10-$B_8C_2H_9$ with 1 mole equiv of 1,8-$B_9C_2H_{11}$ in ether gave the analogous $B_9C_2H_{11}B_8C_2H_9^-$ ion in moderate yield. The 60-Mc/sec ^1H nmr (Table IV) of $CsB_9C_2H_{11}B_8C_2H_9$ consisted of three equal-intensity singlets at δ -1.34, -1.70, and -6.90. The resonance at δ -6.90 was assigned to the C–H group of the 1,10-$B_8C_2H_9$ group by comparison with 1,10-$B_8C_2H_{10}$ (δ -6.9).[28] The resonances at δ -1.34 and -1.70 were assigned to the (3)-1,7-$B_9C_2H_{11}^-$ moiety by comparison with (3)-1,7-$B_9C_2H_{12}^-$ (δ -1.08) and 1-C_6H_5-(3)-1,7-$B_9C_2H_{11}^-$ (δ -1.30).[4] The 32.1-Mc/sec ^{11}B nmr of this species (Figure 5, Table III) exhibits the high-field doublet seen in (3)-1,7-$B_9C_2H_{12}^-$ and also the large doublet very reminiscent of the spectrum of 1,10-$B_8C_2H_{10}$ and its C-substituted derivatives.[4,11,28]

From the asymmetry of the ions, the similarity of their nmr spectra to that of the (3)-1,7-$B_9C_2H_{12}^-$ ion and its C-substituted derivatives, and the assumption that the boron atom undergoing attack becomes a part of the open face of the substituted (3)-1,7-$B_9C_2H_{11}^-$ ion formed, the 4 position was assigned with some certainty as the position of substitution of the 1,2-$B_{10}C_2H_{11}$ and 1,10-$B_8C_2H_9$ moieties (Figures 6 and 7). This position, as stated previously, would result from nucleophilic attack by the carbanion at boron atoms 3, 5, 7, and 9. The ^1H nmr of these substituted ions exhibited only C–H resonances from (3)-1,7-$B_9C_2H_{11}$ C–H groups, and

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(26) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

(27) M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren, P. A. Wegner, and D. C. Young, *Inorg. Syn.*, **10**, 91 (1967).

(28) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **91**, 4707 (1969).

Table V. Yields, Melting Points, and Analytical Data for the 3-Substituted 1,8-$B_9C_2H_{10}$ Carboranes

Compound	Mp, °C[a]	Yield, %	Calcd, % C	Calcd, % H	Calcd, % B	Calcd mass spectral parent peak	Found, % C	Found, % H	Found, % B	Mass spectral parent peak cutoff
$B_9C_2H_{10}B_{10}C_2H_{10}CH_3$	116–118	75	20.80	8.03	71.17	292	20.40	8.02	70.66	292
$B_9C_2H_{10}B_{10}C_2H_{11}$	156–158	85	17.49	7.70	74.81	278	17.85	7.72	74.82	278
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{11}$	82–83	72	23.80	8.32	67.88	306	24.21	8.65	66.80	306
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$	101–102	71	26.54	8.59	64.87	320	26.55	8.41	64.97	320
$B_8C_2H_9B_9C_2H_{10}$	116–118	78	19.13	7.63	73.22	254	20.17	7.85	72.66	254

[a] Uncorrected.

Table VI. Ir Spectra of Nujol Mulls of 3-Substituted 1,8-$B_9C_2H_{10}$ Carboranes

Compound	
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{11}$	2540 (s), 1190 (s), 1162 (w), 1142 (w), 1132 (w), 1005 (m), 983 (w), 950 (w), 920 (w), 836 (s), 768 (m), 714 (s)
$B_9C_2H_{10}B_{10}C_2H_{11}$	2540 (s), 1213 (m), 1110 (s), 1060 (s), 1010 (w), 920 (w), 828 (m), 760 (m), 714 (s)
$B_9C_2H_{10}C_2H_{10}CH_3$	2550 (s), 1205 (m), 1132 (m), 1076 (m), 1032 (w), 980 (w), 935 (w), 834 (s), 770 (m), 723 (s)
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$	2550 (s), 1190 (m), 1092 (w), 1040 (m), 1010 (m), 990 (m), 962 (m), 933 (m), 865 (w), 841 (s), 800 (m), 780 (m), 716 (s)
$B_9C_2H_{10}B_8C_2H_9$	2550 (s), 1295 (m), 1140 (s), 1105 (s), 1090 (s), 935 (w), 890 (w), 875 (w), 780 (w), 761 (w), 680 (m)

one carbon atom of the substituent; hence the point of substitution on the $B_{10}C_2H_{11}$ and $B_8C_2H_9$ cages is C-1 in each case. The properties of several other ions of this family, including the 4-(1′-1′,7′-$B_{10}C_2H_{11}$)-1,7-$(CH_3)_2$-(3)-1,7-$B_9C_2H_9^-$ ion,[29] which incorporated the 1,7-$B_{10}C_2H_{11}$ moiety,[22] are presented in Tables I–IV.

3-Substituted 1,8-Dicarba-*closo*-undecaborane(11). It has been previously shown that the (3)-1,7-$B_9C_2H_{12}^-$ ion and its C-substituted derivatives could be converted to hydrogen and 1,8-$B_9C_2H_{11}$ and its C-substituted derivatives by acidification with polyphosphoric acid in refluxing toluene or toluene–methylcyclohexane.[11]

$$\text{(3)-1,7-}B_9C_2H_{12}^- + H^+ \xrightarrow[CH_3C_6H_5]{(HPO_3)_n} \text{1,8-}B_9C_2H_{11} + H_2$$

Using this general reaction, it was possible to convert 4-substituted (3)-1,7-$B_9C_2H_{11}^-$ ions to the correspondingly substituted 1,8-$B_9C_2H_{10}$ species in high yield. Melting points, yields, analyses, and mass spectral parent peaks for these substituted 1,8-$B_9C_2H_{10}$ species are presented in Table V. Infrared spectra of these compounds, all of which contain an absorbance at around 830 cm^{-1}, characteristic of 1,8-$B_9C_2H_9R_2$ systems, are presented in Table VI. When Cs-4-(1′-2′-CH_3-1′,2′-$B_{10}C_2H_{10}$)-(3)-1,-7-$B_9C_2H_{11}$ was refluxed in toluene for 90 min with a large excess of polyphosphoric acid, 0.94 mole equiv of H_2 was evolved, and a neutral, air-sensitive solid was isolated in good yield by sublimation at 135°. This compound gave a mass-spectral cutoff at *m/e* 292, corresponding to $^{11}B_{19}{}^{12}C_5{}^1H_{23}$, or $B_9C_2H_{10}B_{10}C_2H_{10}CH_3$. The 60-Mc/sec ^1H nmr in chloroform (Table VII) exhibited a sharp singlet of intensity 3.0 at δ −2.08 and a very broad singlet of intensity 1.9 at δ −6.09. The sharp singlet was assigned to a 1,2-$B_{10}C_2H_{10}CH_3$ methyl group, by comparison with 1-CH_3-1,2-$B_{10}C_2H_{11}$ (δ −1.98) and 1,2-$(CH_3)_2$-1,2-$B_{10}C_2H_{10}$ (δ −2.02), while the broad singlet centered at δ −6.09 was assigned to the carborane C–H protons, by comparison with 1,8-$B_9C_2H_{11}$ (δ −5.8). The 32.1-Mc/sec ^{11}B nmr spectrum (Table VIII) was marked by a doublet of approximate intensity 1 at δ +17.9, reminiscent of the doublet in $B_9C_2H_{11}$ at δ +17.3. A large doublet at δ +9.2 was very reminiscent of a similar feature in 1,2-$B_{10}C_2H_{10}R_2$ systems.[30] It was assumed that no 1,2-$B_{10}C_2H_{10}CH_3$ cage rearrangement occurred, and the product was proposed to be a 1,8-$B_9C_2H_{10}$ moiety substituted at boron by 1,2-$B_{10}C_2H_{10}CH_3$. Similar reaction of Cs-4-(1′-2′-CH_3-1′,2′-$B_{10}C_2H_{10}$)-1,7-$(CH_3)_2$-(3)-1,7-$B_9C_2H_9$ with polyphosphoric acid in toluene followed by distillation of the product afforded the analogous $B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$ in high yield. The mass spectrum exhibited a cutoff at *m/e* 320, corresponding to $^{11}B_{19}{}^{12}C_7{}^1H_{27}$ or $B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$. The 60-Mc/sec ^1H nmr spectrum in $CHCl_3$ (Figure 8, Table VII) consisted of three equal-area sharp singlets at δ −2.08, −2.54, and −2.71

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(29) We have chosen to tentatively adopt the following as a nomenclature system. If the 4-substituent on boron in the 4-substituted (3)-1,7-$B_9C_2H_{11}^-$ ion or the 3-substituent on boron in the 3-substituted 1,8-$B_9C_2H_{10}$ carborane is a carborane group, the carbon atom connected to this 4- or 3-boron is C-1′, and the other polyhedron atoms are numbered 2′, 3′, etc., as in the parent carborane of the substituent. Hence, the $B_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3^-$ ion would be formally expressed as

$$\text{4-(1}'\text{-2}'\text{-}CH_3\text{-1}',2'\text{-}B_{10}C_2H_{10}\text{)-1,7-}(CH_3)_2\text{-(3)-1,7-}B_9C_2H_9(-1)$$

and named 4-(1′-2′-methyl-1′,2′-dicarba-*closo*-dodecaborano(12)) 1,7-dimethyl-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate(−1).

(30) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. G. Pier, *Proc. Chem. Soc.*, 402 (1964).

Table VII. 60-Mc/sec ^{1}H Nmr Spectra of 3-Substituted 1,8-$B_9C_2H_{10}$ Carboranes

Compound	Feature	δ, ppm	Rel peak area	Assignment[a]
$B_9C_2H_{10}B_{10}C_2H_{10}CH_3$	Sharp singlet	−2.08	3.0	(a)
($CHCl_3$)	Broad singlet	−6.09	1.9	(f)
$B_9C_2H_{10}B_{10}C_2H_{11}$	Broad singlet	−3.50	0.9	(b)
($CHCl_3$)	Broad singlet	−6.14	2.0	(f)
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{11}$	Sharp singlet	−2.51	2.83	(e)
($CHCl_3$)	Sharp singlet	−2.63	3.00	(e)
	Broad singlet	−2.95	1.0	(c)
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$	Sharp singlet	−2.08	1.0	(a)
($CHCl_3$)	Sharp singlet	−2.54	1.0	(e)
	Sharp singlet	−2.71	1.0	(e)
$B_9C_2H_{10}B_8C_2H_9$	Broad singlet	−6.03	1.9	(f)
($CHCl_3$)	Broad singlet	−6.87	1.0	(d)

[a] (a) 2′-CH_3 methyl protons of (1′-2′-CH_3-1′,2′-$B_{10}C_2H_{10}$); (b) 2′-H carborane proton of (1′-2′-$B_{10}C_2H_{11}$); (c) 7′-H carborane proton of (1′-1′,7-$B_{10}C_2H_{11}$); (d) 10′-H carborane proton of (1′-1′,10′-$B_8C_2H_9$); (e) 1,8 $(CH_3)_2$ methyl proton of 1,8-$B_9C_2H_8(CH_3)_2^-$; (f) 1,8 carborane protons of 1,8-$B_9C_2H_{10}^-$.

relative to internal $(CH_3)_4Si$. The singlet at δ −2.08 was assigned as before to a 1,2-$B_{10}C_2H_{10}CH_3$ methyl group,[27] and the chemical shifts of the remaining two singlets compared favorably with that for 1,8-$(CH_3)_2$-1,8-$B_9C_2H_9$ (δ −2.51).[11] These two nonequivalent methyl groups indicated that the $B_9C_2H_8(CH_3)_2$ moiety was asymmetrical. It was assumed that no rearrangement of the 1,2-$B_{10}C_2H_{10}CH_3$ group had occurred and that this moiety remained attached to the same boron atom that it was bound to in the 4-(1′-2′-CH_3-1′,2′-$B_{10}C_2H_{10}$)-1,7-$(CH_3)_2$-(3)-1,7-$B_9C_2H_9^-$ ion. Upon formation of the $B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$ molecule the asymmetric 4-(1′-2′-CH_3-1′,2′-$B_{10}C_2H_{10}$) group would then become an asymmetric 3-(1′,2′-CH_3′-1′,2-$B_{10}C_2H_{10}$) group. We tentatively propose the structure shown in Figure 9 for the parent species, 3-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,8-$B_9C_2H_{10}$, which is prepared in identical fashion in high yield from Cs^+4-(1′-1′,2′-$B_{10}C_2H_{11}$)-(3)-1,7-$B_9C_2H_{11}^-$. Its properties are given in Tables V–VIII.

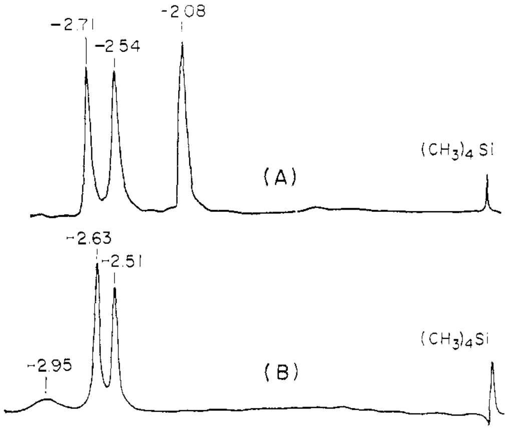

Figure 8. (a) A 60-Mc/sec ^{1}H nmr spectrum of $B_9C_2H_8(CH_3)_2$-$B_{10}C_2H_{10}CH_3$ in chloroform. Chemical shifts are relative to internal $(CH_3)_4Si$. (b) A 60-Mc/sec ^{1}H nmr spectrum of $B_9C_2H_8(CH_3)_2B_{10}$-C_2H_{11} in chloroform. Chemical shifts are relative to internal $(CH_3)_4Si$.

Treatment of Cs^+4-(1′-1′,7′-$B_{10}C_2H_{11}$)-1,7-$(CH_3)_2$-(3)-1,7-$B_9C_2H_9^-$ in analogous manner produced a neutral solid in high yield. The mass spectrum exhibited a cutoff at *m/e* 306, which corresponded to $^{11}B_{19}{}^{12}C_6{}^1H_{25}$. The 60-Mc/sec ^{1}H nmr spectrum (Figure 8, Table VII) showed a broad C–H resonance of intensity 1.0 at δ −2.95, which was assigned to a 1,7-$B_{10}C_2H_{11}$ C–H group,[22] and two intensity 3 sharp singlets at δ −2.51 and −2.63, which were assigned, as before, to nonequivalent C–CH_3 groups in the 1,8-$B_9C_2H_8(CH_3)_2$ moiety.[11] Using the same assumptions made above, we propose the structure 3-(1′-1′,7′-$B_{10}C_2H_{11}$)-1,8-$(CH_3)_2$-1,8-$B_9C_2H_8$[29] for this species.

Table VIII. 32.1-Mc/sec ^{11}B Nmr Spectra of 3-Substituted 1,8-$B_9C_2H_{10}$ Carboranes

Compound	Feature	δ (*J*, cps)[a]	Rel peak area
$B_9C_2H_{10}B_{10}C_2H_{11}$	Overlapping doublets	+17.9 (156)	
		+9.6 (168)	
		+4.0 (170)	
$B_9C_2H_{10}B_{10}C_2H_{10}CH_3$	Overlapping doublets	+17.9 (130)	1.0
		+9.2 (124)	18.3
		+5.2 (118)	
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{11}$	Overlapping doublets	+14.3 (141)	
		+9.3 (165)	
$B_9C_2H_8(CH_3)_2B_{10}C_2H_{10}CH_3$	Overlapping multiplet	+12.8	
		+3.3 (117)	
$B_9C_2H_{10}B_8C_2H_9$	Doublet	+10.7 (153)	
	Doublet	+5.6 (156)	

[a] Relative to external $BF_3 \cdot O(C_2H_5)_2$.

Similar treatment of Cs^+4-(1′-1′,10′-$B_8C_2H_9$)-(3)-1,7-$B_9C_2H_{11}^-$ with polyphosphoric acid in refluxing toluene afforded a white, easily sublimable solid, the mass spectrum of which exhibited a cutoff at *m/e* 254, which corresponded to $^{11}B_{17}{}^{12}C_2{}^1H_{19}$, or $B_9C_2H_{10}B_8C_2H_9$. The 32.1-Mc/sec ^{11}B nmr spectrum of $B_9C_2H_{10}B_8C_2H_9$ exhibited a large doublet at δ +10.7, relative to $BF_3 \cdot O(C_2H_5)_2$, which was very reminiscent of the doublet in 1,10-$B_8C_2H_{10}$ systems (δ +10.3).[11] The 60-Mc/sec ^{1}H nmr spectrum (Table VII) exhibited a singlet of intensity 1 at δ −6.87 and a broad singlet of intensity 2 at

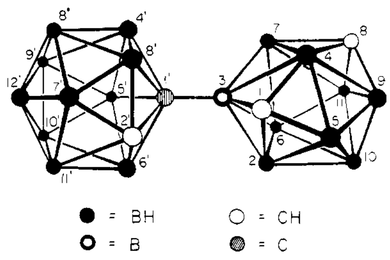

Figure 9. Proposed skeletal framework and numbering system of $B_9C_2H_{10}B_{10}C_2H_{11}$.

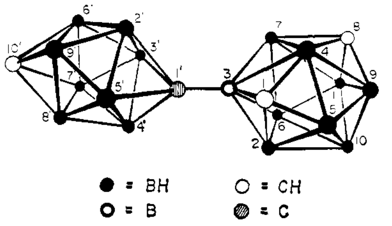

Figure 10. Proposed skeletal framework and numbering system of $B_9C_2H_{10}B_8C_2H_9$.

δ −6.03. These resonances were assigned to one 1,10-$B_8C_2H_9$ C–H group and two 1,8-$B_9C_2H_{10}$ C–H groups, respectively.[11] From these nmr and mass spectral data, we tentatively propose the structure shown in Figure 10 as 3-(1′-1′,10′-$B_8C_2H_9$)-1,8-$B_9C_2H_{10}$.[29]

These two-cage systems represent both the first reported examples of polyhedral two-cage systems containing different numbers of boron atoms, and of polyhedral two-cage systems connected by a C–B "single" bond. Studies which are determining the possibility of conversion of these neutral two-cage polyhedral systems to larger ionic and neutral species, and studies of the formation of transition metal complexes[26] incorporating the 4-substituted (3)-1,7-$B_9C_2H_{12}^-$ ions, are under way.

Experimental Section

Materials. 1,8-Dicarba-*closo*-undecaborane(11), 1-phenyl-1,8-dicarba-*closo*-undecaborane(11), 1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11), 1-methyl-1,2-dicarba-*closo*-dodecaborane(12), 1,2-dicarba-*closo*-dodecaborane(12), 1,7-dicarba-*closo*-dodecaborane(12), 1,10-dicarba-*closo*-decaborane(10), and 1-phenyl-1,10-dicarba-*closo*-dodecaborane(10) were prepared by literature methods.[10,11,12,27,28] Malononitrile was Mallinckrodt technical grade and was sublimed at room temperature and high vacuum to a −70° cold finger immediately before use. Dimethyl malonate (Eastman) was distilled from molecular seives before use. Methyllithium and *n*-butyllithium were supplied by Foote Chemical Co. and used without further purification. All reactions were carried out in a nitrogen atmosphere. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 137 infrared spectrometer. Proton nmr spectra were obtained using a Varian A-60 spectrometer, while ^{11}B nmr spectra were obtained using a Varian HA-100 spectrometer. Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Osmometric molecular weights were obtained by using a Mechrolab Model 301A vapor pressure osmometer. Elemental analyses and cryoscopic molecular weights were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Tetramethylammonium 4-*n*-Butyl-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. To 4.00 g (0.0302 mole) of 1,8-dicarba-*closo*-undecaborane(11) in 100 ml of dry hexane was added 20 ml of 1.6 *N* *n*-butyllithium (0.032 mole) in hexane, dropwise over a period of 45 min. A white solid formed to which was cautiously added 50 ml of distilled water. The layers were separated, and the aqueous layer was washed with two 200-ml portions of pentane. To the aqueous solution was added 10 ml of 50% aqueous $(CH_3)_4N^+Cl^-$. The solid was collected and recrystallized from 75 ml of hot ethanol to which 50 ml of distilled water was added at boiling. The yield was 80%.

Tetramethylammonium 4-Dimethylmalonato-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. To a solution of 1.32 g of dimethyl malonate (0.01 mole) in 100 ml of anhydrous ethyl ether was added 6.7 ml of 1.6 *N* *n*-butyllithium in hexane (0.0102 mole). After stirring for 2 hr, a solution of 1.32 g of $B_9C_2H_{11}$ in 10 ml of benzene was added, and the reaction mixture was stirred for another 2 hr. The reaction mixture was rotary evaporated to near dryness, and the oil was dissolved in 50 ml of distilled water. The aqueous solution was washed with two 100-ml portions of hexane and 5 ml of 50% aqueous $(CH_3)_4N^+Cl^-$. The precipitate solid was collected and recrystallized twice from 50 ml of 1:1 hot alcohol-water, yield 2.0 g, 58%.

Tetramethylammonium 4-Malononitrilo-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. To a solution of 0.66 g of malononitrile (0.01 mole) in 100 ml of dry ether was added 6.7 ml of 1.6 *N* *n*-butyllithium in hexane (0.0102 mole). After stirring for 90 min, a solution of 1.32 g of $B_9C_2H_{11}$ in 5 ml benzene was added, and the reaction mixture was stirred for another hour. The reaction mixture was rotary evaporated to near dryness, and the oil was dissolved in 50 ml of distilled water. The aqueous solution was mixed with 5 ml of 50% aqueous $(CH_3)_4N^+Cl^-$ and precipitate was collected and recrystallized from 25 ml of hot ethyl alcohol. The yield was 1.7 g, 62%.

Tetramethylammonium 4-Methyl-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. To 4.00 g (0.0302 mole) of 1,8-dicarba-*closo*-undecaborane(11) in 100 ml of dry hexane was added 16 ml of 2 *N* methyllithium (0.032 mole) in ether. The mixture was stirred for 4 hr, and an oily solid separated. Distilled water (50 ml) was added cautiously, the layers were separated, and to the filtered aqueous solution was added 10 ml of aqueous 50% $(CH_3)_4N^+Cl^-$. The solid was collected and recrystallized from 30 ml of pure acetone–70 ml distilled H_2O under an N_2 atmosphere. The yield was 4.2 g, 62%.

Reaction of 1,8-$B_9C_2H_{11}$ with 2 Mole Equiv of Methyllithium. In a nitrogen-filled 500-ml reactor equipped with a side arm, a breakoff seal joint, and a constricted inlet joint, was placed 1.32 g of 1,8-$B_9C_2H_{11}$. In the side arm was placed 10 ml of 2 *N* methyllithium in ether; 20 ml of ether was placed with the $B_9C_2H_{11}$. The entire system was cooled to −196°, evacuated, and sealed using a torch. The system was allowed to warm to room temperature, and the reactor was tipped to mix the reactants. After 2 hr, the reactor was connected with a magnet in the breakoff joint to break the seal, and the system was again cooled to −196°. The breakoff seal was broken and the contents of the system collected by means of a Toepler pump. Methane, 0.0102 mole, was collected and identified by its gas-phase infrared spectrum. The residue in the reactor was mixed with 50 ml of water, and 5 ml of 50% aqueous $(CH_3)_4N^+Cl^-$ was added; 1.5 g of $(CH_3)_4N^+B_9C_2H_{11}CH_3^-$, identified by its infrared spectrum, was collected.

Reaction of $B_9C_2H_{11}$ with Excess NaH. In a similar 500-ml reactor were placed 1.0 g of 56.1% NaH (0.023 mole, Metal Hydrides, Inc.) and 20 ml of ether. In the side arm were placed 1.32 g of $B_9C_2H_{11}$ (0.010 mole) and 20 ml of ether. The system was allowed to warm up to room temperature and was tipped to mix the reactants. After 48 hr at room temperature, the reactor was cooled to −196° and broken on a high-vacuum line as before; 0.0092 mole of H_2 was collected by a Toepler pump. The residue in the flask was dissolved, treated with 50 ml of methanol, and rotary evaporated; the resulting oil was dissolved in 50 ml of water, to which 5 ml of 50% aqueous $(CH_3)_3NH^+Cl^-$ was added. Recrystallization of the precipitate from 60 ml of hot water yielded 1.06 g (55%) of $(CH_3)_3NH^+$(3)-1,7-$B_9C_2H_{12}$, identified by its ^{11}B nmr and ir spectra.

Reaction of 1,8-$B_9C_2H_{11}$ and $NaBH_4$ in 1,2-Dimethoxyethane. In a 500-ml three-neck flask equipped with magnetic stirrer and N_2 inlet tube was placed 0.38 g of $NaBH_4$ (Ventron) and 100 ml of dry (distilled from Na) 1,2-dimethoxyethane. To this solution by means of a pressure-equalizing dropping funnel was added 1.32 g of 1,8-$B_9C_2H_{11}$ in 10 ml of 1,2-dimethoxyethane. Gas was evolved and blown in a stream of nitrogen into 50 ml of a saturated solution of trimethylamine in heptane. After stirring at room temperature of 2 hr, the reaction mixture was rotary evaporated to a crystalline solid, which was dissolved in 50 ml of distilled water and mixed with 5 ml of 50% $(CH_3)_3NH^+Cl^-$. The solid formed was collected by filtration aqueous and recrystallized from 80 ml of hot H_2O. The yield was 1.53 g (80%) of $(CH_3)_3N^+H$-(3)-1,7-$B_9C_2H_{12}^-$, identified by its ^{11}B nmr and ir spectra.[4] The heptane solution was rotary evaporated to dryness, and the solid obtained (0.45 g) was shown by its ^{11}B nmr and infrared spectrum to be $(CH_3)_3NBH_3$ (61%).

Reaction of 1-Phenyl-1,8-dicarba-*closo*-undecaborane(11) with Sodium Borohydride in 1,2-Dimethoxyethane. To a solution of 1.52 g of $NaBH_4$ (0.04 mole) in 200 ml of dry 1,2-dimethoxyethane was added a solution of 8.36 g (0.04 mole) of 1-C_6H_5-1,8-$B_9C_2H_{10}$ in 50 ml of 1,2-dimethoxyethane. After refluxing the reaction mixture for 2 hr, the reaction mixture was filtered and rotary evaporated, and the remaining oil was dissolved in 100 ml of distilled water. To the chilled aqueous solution was added 25 ml of 50% cold $(CH_3)_4N^+Cl^-$ (0°), and the resulting solid was collected by filtration and recrystallized from 150 ml of hot ethyl alcohol. The yield was 9.4 g (84%) of $(CH_3)_4N$-(3)-1,7-$B_9C_2H_{11}C_6H_5$, identified by its ^{11}B nmr and ir spectra.[4]

Reaction of 1,8-Dimethyl-1,8-dicarba-*closo*-undecaborane(11) with Sodium Borohydride in 1,2-Dimethoxyethane. To a solution of 1.14 g of $NaBH_4$ (0.03 mole) in 150 ml of dry 1,2-dimethoxyethane was added a solution of 4.82 g of $B_9C_2H_9(CH_3)_2$ (0.030 mole). After refluxing the solution for 2 hr, it was filtered and rotary evaporated to near dryness. The resulting oily solid was dissolved in 50 ml of distilled water, and to this aqueous solution was added 10 ml of 50% aqueous $(CH_3)_3NH^+Cl^-$. The precipitate was filtered and recrystallized from 200 ml of hot water. The yield was 6.2 g (93%) of $(CH_3)_3N^+H$-(3)-1,7-$B_9C_2H_{10}(CH_3)_2^-$, identified by its ^1H nmr, ^{11}B nmr, and ir spectra.[4]

Tetramethylammonium 4-(1′-2′-Methyl-1′,2′-dicarba-*closo*-dodecaborano(12))-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. General Procedure for Synthesis of Two-Cage Ions. To a solution of 4.7 g of 1-methyl-1,2-dicarba-*closo*-dodecaborane(12) (0.030 mole) in 500 ml of dry ether was added 1.9 ml of 1.6 *N* *n*-butyllithium in hexane (0.0304 mole). The reaction mixture was stirred for 2 hr, and a solution of 4.00 g of $B_9C_2H_{11}$ (0.0302 mole) in 25 ml of benzene was added over a 10-min period. The reaction mixture was stirred for an additional 2 hr, and then rotary evaporated to near dryness; a mixture of 100 ml of distilled water and 200 ml of hexane was added to the oil. The layers were separated, the aqueous layer was rotary evaporated to 75 ml, and 10 ml of 50% $(CH_3)_4N^+Cl$ was added. The resulting solid was collected by filtration and recrystallized from 125 ml of hot 1:2 alcohol–water. Two crops yielded 7.65 g (72%). Evaporation of the hexane fraction followed by high-vacuum sublimation at 100° of the residue to a 0° cold finger gave 0.9 g of 1-methyl-1,2-dicarba-*closo*-dodecaborane(12) (19%).

Cesium 4-(1′-2′-Methyl-1′,2′-dicarba-*closo*-dodecaborano(12))-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate. The cesium salt was prepared by adding 25 ml of 50% cold (0°) aqueous CsCl to a chilled aqueous $LiB_9C_2H_{11}B_{10}C_2H_{10}CH_3$ solution as prepared above and was recrystallized from 200 ml of hot H_2O. The yield was 8.60 g (68%).

Cesium 4-(1′-1′,2′-dicarba-*closo*-dodecaborano(12))-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate was prepared using the general procedure above using 1,2-dicarba-*closo*-dodecaborane(12) in place of 1-methyl-1,2-dicarba-*closo*-dodecaborane(12), and the salt was recrystallized from 250 ml of water. The yield was 5.4 g (42%).

Cesium 4-(1′-1′,7′-dicarba-*closo*-dodecaborano(12))-(3)-1,7-dimethyl-1,7-dicarba-*nido*-dodecahydroundecaborate was prepared using the general procedure above, substituting 1,7-dicarba-*closo*-dodecaborane(12) for 1-methyl-1,2-dicarba-*closo*-dodecaborane(12) and 1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) for 1,8-dicarba-*closo*-undecaborane(11). The salt was recrystallized from 200 ml of hot water and yielded 7.72 g (59%).

Cesium 4-(1′-2′-methyl-1′,2′-dicarba-*closo*-dodecaborano(12))-(3)-1,7-dimethyl-1,7-dicarba-*nido*-dodecahydroundecaborate was prepared using the general procedure above in 0.06 *M* quantities using 1-methyl-1,2-dicarba-*closo*-dodecaborane(12) and 1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11). The salt was recrystallized from 250 ml of hot 1:9 ethyl alcohol–water and the yield was 16.5 g (61%).

Cesium 4-(1′-1′,10′-dicarba-*closo*-decaborano(10))-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate was prepared using the general procedure above in 0.01 *M* quantities substituting 1,10-dicarba-*closo*-decaborane(10) for 1-methyl-1,2-dicarba-*closo*-dodecaborane-(12). The salt was recrystallized from 50 ml of hot water. The yield was 1.46 g (38%).

Tetramethylammonium 4-(1′-10′-phenyl-1′,10′-dicarba-*closo*-decaborano(10))-(3)-1,7-dicarba-*nido*-dodecahydroundecaborate was prepared using the general procedure outlined above in 0.01 *M* quantities, substituting 1-phenyl-1,10-dicarba-*closo*-decaborane(10) for 1-methyl-1,2-dicarba-*closo*-dodecaborane(12). The salt was recrystallized from 30 ml of hot 1:2 acetone–water. Two fractions yielded 2.1 g (52%).

Preparation of 3-(1′-1′,2′-Dicarba-*closo*-dodecaborano(12))-1,8-dicarba-*closo*-undecaborane(11). General Procedure for Acidification and Pyrolysis. To a mixture of 200 ml of toluene and 75 g of polyphosphoric acid in a 500-ml three-neck flask equipped with mechanical stirrer, N_2 inlet, and water-cooled reflux condenser was placed 4.08 g of finely powdered $CsB_9C_2H_{11}B_{10}C_2H_{11}$ (0.01 mole), and the reaction mixture was refluxed for 90 min. Hydrogen evolution began, and after 90 min 0.0094 mole of H_2 was collected. The toluene layer was decanted, and the polyphosphoric acid layer was refluxed for 15 min with 100 ml of additional toluene. The combined toluene portions were rotary evaporated, and the residue was vacuum sublimed at 130° into a water-cooled West condenser. The yield of sublimate was 2.33 g (85%). The sublimate was recrystallized unchanged from 15 ml of hot $CHCl_3$.

3-(1′-1′,7′-Dicarba-*closo*-dodecaborano(12))-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) was prepared by the general procedure above, using 4.26 g of $CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{11}$ (0.01 mole) as starting material. After rotary evaporation of the combined toluene portions, the residue was alembically distilled under high vacuum at 150° using a water-cooled condenser. The colorless liquid crystallized upon cooling and was recrystallized from 20 ml of pentane at −80°. The yield was 2.18 g (72%).

3-(1′-2′-Methyl-1′,2′-dicarba-*closo*-dodecaborano(12))-1,8-dimethyl-1,8-dicarba-*closo*-undecaborane(11) was prepared by the general procedure above, using 4.51 g of $CsB_9C_2H_9(CH_3)_2B_{10}C_2H_{10}CH_3$ (0.01 mole) as starting material. After rotary evaporation of the combined toluene portions, the residue was alembically distilled under high vacuum at 160° using a water-cooled condenser. The colorless liquid crystallized upon cooling and was crystallized from 15 ml of pentane at −80°. The yield was 2.25 g (71%).

3-(1′-2′-Methyl-1′,2′-dicarba-*closo*-dodecaborano(12))-1,8-dicarba-*closo*-undecaborane(11) was prepared by the general procedure above, using 4.22 g of $CsB_9C_2H_{11}B_{10}C_2H_{10}CH_3$ (0.01 mole) as starting material. After rotary evaporation of the combined toluene portions, the residue was sublimed at 140° into a water-cooled West condenser. Recrystallization of the sublimate from 10 ml of hexane at −45° yielded 2.23 g (75%).

3-(1′-1′,2′-Dicarba-*closo*-decaborano(10))-1,8-dicarba-*closo*-undecaborane(11) was prepared by the general reaction using 1.00 g of $CsB_9C_2H_{11}B_8C_2H_9$ (0.0026 mole) as starting material. After rotary evaporation of the combined toluene portions, the residue was sublimed at 110° into a water-cooled West condenser. The yield was 0.49 g (76%).

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