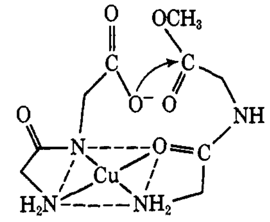
result from coordination of the ester group to the Cu(II). This may be due to electron withdrawal from the ester *via* the two coordinating atoms.

Unlike the hydrolysis of GGOMe in the other Cu(II) complexes, a fairly large fraction of its hydrolysis in Cu(H$_{-1}$GG)(GGOMe) proceeds *via* a OH$^-$ independent pathway ($k_1$, see Results). This could be ascribed to $H_2O$ rather than OH$^-$ attack in the mechanism described earlier. By dividing $k_1$ by 55 $M$ for water and comparing this constant with $k_{OH}$, one finds that the ratio of rates for OH$^-$ to $H_2O$ attack is approximately $5 \times 10^6$. This is significantly lower than is usually observed ($10^9$–$10^{11}$) for these two nucleophiles in the hydrolysis of carboxylic acid esters.[13] Hence the unusually high value of $k_1$ implies that another hydroxide-independent mechanism may be occurring. One speculative possibility is an intramolecular attack of the H$_{-1}$GG carboxylate group on the ester group as shown in structure V. If Cu(H$_{-1}$GG)(GGOMe) has the cis geometry as shown in V, the $-CO_2^-$ and $-CO_2CH_3$ groups are in an ideal position for such an attack to occur as shown by molecular models. The anhydride intermediate formed as a result of the intramolecular attack would then rapidly hydrolyze to give the observed product, Cu(H$_{-1}$GG)(GG)$^-$.



V

**Acknowledgment.** We would like to thank Dr. Pio Rechani for his valuable assistance in the preparation of glycylsarcosine methyl ester and the U. S. Public Health Service for support of this research through Grant No. GM-12626 of the National Institute of General Medical Sciences.

# Chemical and Structural Studies of the $B_{10}C_2H_{12}^{2-}$ Ions Produced from Icosahedral $B_{10}C_2H_{12}$ Carboranes

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**Abstract:** The isomeric 1,2-, 1,7-, and 1,12-$B_{10}C_2H_{12}$ carboranes and some of their derivatives can be reduced with sodium to form $B_{10}C_2H_{12}^{2-}$ ions which can be subsequently protonated to yield (13)-9,11-$B_{10}C_2H_{13}^-$ ion, (13)-7,10-$B_{10}C_2H_{13}^-$ ion, and derivatives of the (13)-7,10-$B_{10}C_2H_{13}^-$ ion. The (13)-9,11-$B_{10}C_2H_{13}^-$ ion can be thermally rearranged to the (13)-7,10-$B_{10}C_2H_{13}^-$ ion. Pyrolysis of $(CH_3)_4N^+$(13)-7,10-$B_{10}C_2H_{13}^-$ produced $(CH_3)_3N\cdot BH_2$-1,2-$B_{10}C_2H_{11}$ and $(CH_3)_4N^+$(12)-7,9-$B_9C_2H_{12}^-$.

The reduction of the icosahedral $B_{10}C_2H_{12}$ carboranes with sodium to produce $B_{10}C_2H_{12}^{2-}$ ions has been reported by several workers.[1-4] Even though the $B_{10}C_2H_{12}^{2-}$ ions have not been isolated in pure form they have been shown to undergo, *in situ*, three general types of reactions. First, in accord with the prediction of Hoffmann and Lipscomb[5] that anionic *m*- and *p*-carborane species should be comparable in stability to the ortho ion and a reversal in the ortho → meta transformation may become possible, it is known that such rearrangements occur in the $B_{10}C_2H_{12}^{2-}$ series. For example, the resultant $B_{10}C_2H_{12}^{2-}$ ion from the reduction of 1,12-$B_{10}C_2H_{12}$ can be oxidized to produce 1,7-$B_{10}C_2H_{12}$.[3,4]

$$1,12\text{-}B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{[O]} 1,7\text{-}B_{10}C_2H_{12}$$

Similarly the oxidation of the $B_{10}C_2H_{12}^{2-}$ ion produced from 1,7-$B_{10}C_2H_{12}$ yields 1,2-$B_{10}C_2H_{12}$.[2]

$$1,7\text{-}B_{10}C_2H_{12} \xrightarrow{+2e^-} B_{10}C_2H_{12}^{2-} \xrightarrow{[O]} 1,2\text{-}B_{10}C_2H_{12}$$

Finally the oxidation of the $B_{10}C_2H_{12}^{2-}$ ion produced from 1,2-$B_{10}C_2H_{12}$ yields 1,2-$B_{10}C_2H_{12}$.[2]

$$1,2\text{-}B_{10}C_2H_{12} \underset{[O]}{\overset{+2e^-}{\rightleftharpoons}} B_{10}C_2H_{12}^{2-}$$

$$4B_{10}C_2H_{12}^{2-} + 3Co^{2+} \longrightarrow 2[(B_{10}C_2H_{12})_2Co^{III}]^- + Co^0$$

Thus the 1,2 → 1,7 → 1,12 order of thermal rearrangement[1] observed for the neutral $B_{10}C_2H_{12}$ carboranes is reversed in order, 1,12 → 1,7 → 1,2, in the dianion series.[2-4] A second general reaction of the $B_{10}C_2H_{12}^{2-}$ ions involves their complexation by transition metal ions to form a series of unique 13-vertex polyhedral metallocarboranes[6,7] in which the transition metal atom occupies a vertex position. A third general

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[1] D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

[2] L. Zakharkin, V. Kalinin, and L. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2310 (1967).

[3] L. Zakharkin and V. Kalinin, *ibid.*, 194 (1969).

[4] V. Stanko, Yu. V. Gol'tyapin, and V. Brattsev, *Zh. Obsch. Khim.*, **39**, 1175 (1969).

[5] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); *Inorg. Chem.*, 2, 231 (1963).

[6] G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 2541 (1971).

[7] D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 1109 (1973).

reaction of the $B_{10}C_2H_{12}^{2-}$ ions is their protonation to yield a series of monoanions.[2-4,8] These monoanions have been formulated as $B_{10}C_2H_{13}^-$.[2-4,8] We

$$B_{10}C_2H_{12}^{2-} + H^+ \longrightarrow B_{10}C_2H_{13}^-$$

now wish to report in some detail an investigation of the $B_{10}C_2H_{12}^{2-}$ and $B_{10}C_2H_{13}^-$ ions.

## Results and Discussion

Treatment of $Na_2B_{10}C_2H_{12}$, prepared from 1,2-$B_{10}C_2H_{12}$, with $BF_3 \cdot O(C_2H_5)_2$ followed by the addition of degassed water produced a solution which contained $Na^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-$.[9] The addition of excess tetramethylammonium cation ($TMA^+$) to the aqueous solution precipitated $TMA^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-$ (I). The crude material was recrystallized at room temperature from acetone–water solutions. The $^{11}B$ nmr spectrum of I[10] consisted of doublets of relative areas 1:2:1:2:1:3 at −12.7 (132), −3.6 (132), +3.3 (145), +6.3 (127), +15.6 (162), and +19.3 (136) ppm *vs.* $BF_3 \cdot (C_2H_5)_2O$ ($J_{BH}$) which when coupled with the chemical analysis and equivalent weight data clearly established a ten boron atom system. Moreover, the $^{11}B$ nmr spectrum can be interpreted as a 1:2:1:2:1:2:1 pattern which is consistent with a geometry which contains four unique boron atoms and three unique pairs of boron atoms. The $^1H$ nmr spectrum[10] consisted of a sharp singlet of relative area 12 at $\tau$ 6.55 and a broad peak of area 2 at $\tau$ 5.60 which were assigned to the cation resonance and to two equivalent polyhedral CH resonances, respectively. One structure which is compatible with the data is presented in Figure 1. Originally we had proposed[8] a slightly different structure for the 9,11-$B_{10}C_2H_{13}^-$ ion which involved a more compact arrangement of atoms in the open face. However, the X-ray crystal structure of the $Co^{III}(B_{10}C_2H_{12})_2^-$ ion has shown that an expanded geometry is present. The major difference between these two structures is a bonding interaction between carbons in 7,8-$B_{10}C_2H_{13}^-$ *vs.* no bonding interaction to yield 9,11-$B_{10}C_2H_{13}^-$. Either structure is compatible with the data.

Treatment of the same $Na_2B_{10}C_2H_{12}$ with 0.1 *N* aqueous NaOH produced a solution of $Na^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-$ which on addition of $TMA^+$ precipitated $TMA^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-$ (II). The $^{11}B$ nmr spectrum of II[10] consisted of six doublets of relative areas 2:1:1:2:2:2 at −16.4 (160), −12.1 (135), −0.8 (145), +8.2 (150), +16.0 (130), and +22.2 (130) ppm, which corresponds to a molecule with two unique boron atoms and four unique pairs of boron atoms. Based upon the proposed geometry, this requires the polyhedral carbon atoms to be nonequivalent and located on the mirror plane which passes through positions 1, 2, 7, and 10 and bisects the lines between equivalent positions 3,6; 4,5; 8,12; and 9,11. The $^1H$ nmr spectrum[10] measured at ambient temperature contained a sharp peak of relative area 12 at $\tau$ 6.58 which was assigned to the resonance of the cation protons and a broad peak of area 1 at $\tau$ 7.48 which was assigned to the resonance of a polyhedral CH unit. Two broad peaks of area 1 at $\tau$ 6.79 and 7.19 were also observed which were resolved into doublets ($J$ = 7 Hz) when the spectrum was measured at −50°. These peaks were assigned to the resonances of two nonequivalent protons bound to a polyhedral carbon atom.

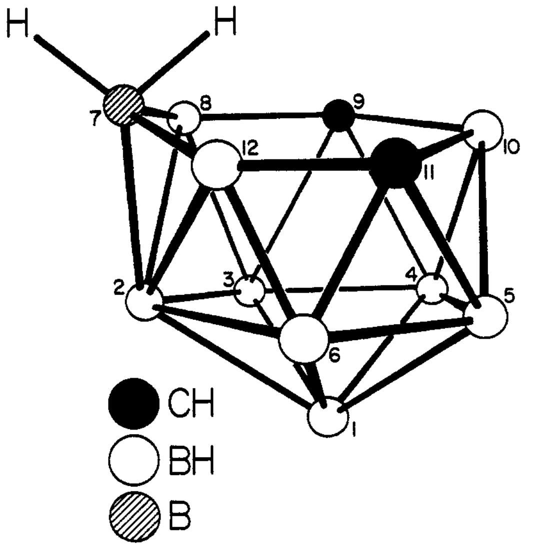

Figure 1. The proposed structure of the (13)-9,11-$B_{10}C_2H_{13}^-$ ion (I).

The carbon atoms in the (13)-7,10-$B_{10}C_2H_{13}^-$ ion and its substituted analogs (*vide infra*) were shown to be nonadjacent by decomposing $TMA^+[7,10\text{-}(CH_3)_2\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{11}]^-$ with $PdCl_2$ and propionic acid. The recovery of ethane from the degradation reaction indicated that each polyhedral carbon atom and its attached methyl group were nonadjacent. A proposed structure of II is shown in Figure 2.

Cyclic voltammetry of I and II measured in acetonitrile solution indicated that each undergoes an irreversible electrochemical oxidation at +1.10 and +1.40 V *vs.* sce, respectively. However, the oxidation mechanisms for the two compounds differ markedly. I exhibits a proton reduction wave at about 0 V *vs.* sce following oxidation, which is not observed in the cyclic voltammogram of II. The presence of the $H^+$ reduction wave qualitatively indicates that I undergoes "oxidative ligand substitution" and that II does not.[11,12] It was subsequently shown that the reaction of I with excess ferric chloride and pyridine in benzene solution produced 9-$NC_5H_5$-(12)-7,8-$B_9C_2H_{11}$ which was identical with that previously reported,[11] possibly by the solvolytic removal by pyridine of the boron atom located at position 7 followed by the formal substitution of a pyridine molecule for a hydride ion at one of the two equivalent boron atoms in positions 8 or 12 in the open face of the resulting 11-particle fragment. This result lends considerable support to

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(8) G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 899 (1972).

(9) The numbering system used in this paper is identical with that used previously.[7] The system is based on a *nido*-carborane ligand derived from a hypothetical 13-atom *closo* polyhedron. In transition metal complexes the metal atom presumably occupies the 13-vertex position.

(10) The $^1H$ and $^{11}B$ spectra, infrared spectra, and reproductions of the pertinent spectra discussed in this paper will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-3174. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(11) D. C. Young, D. V. Howe, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 91, 859 (1969).

(12) R. C. Nelson and R. N. Adams, *J. Electroanal. Chem.*, 16, 439 (1968).

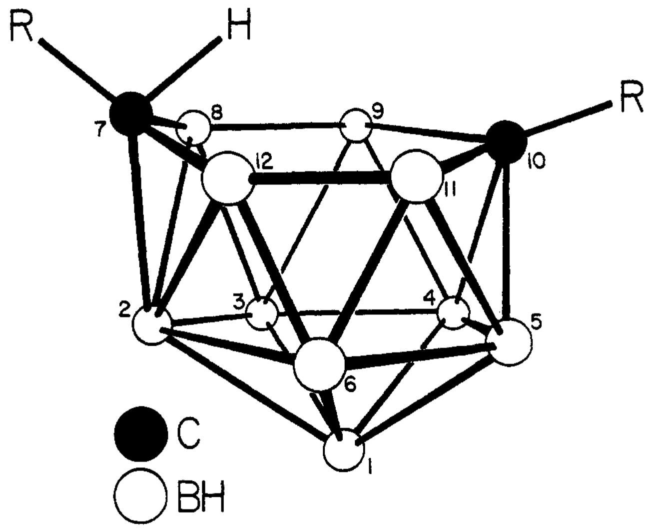


Figure 2. The proposed structure of the 7,10-$R_2$-(13)-7,10-$B_{10}C_2H_{11}^-$ ion, where R = -H (II) or -$CH_3$ (V).

the proposed structure for I. Unlike I, no reaction of II with ferric chloride and pyridine was observed. This may be due to the difficulty of removing the carbon atom at position 7.

Proton abstraction from TMA$^+$[(13)-7,10-$B_{10}C_2H_{13}$]$^-$ (II) using sodium hydride or butyllithium did not proceed under conditions similar to those employed for the deprotonation of [(12)-7,8-$B_9C_2H_{12}$]$^-$ ion.[13]

Heating *in vacuo* at 100° rearranged I to II in high yield. Further heating of II at 200° produced a mixture of products

$$\mathrm{TMA^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-} \xrightarrow{100^\circ} \mathrm{TMA^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-}$$

$$\mathrm{TMA^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-} \xrightarrow{200^\circ} \mathrm{TMA^+[(12)\text{-}7,9\text{-}B_9C_2H_{12}]^-} + \mathrm{(CH_3)_3N\cdot BH_2(1,2\text{-}B_{10}C_2H_{11})} + \mathrm{(CH_3)_3N} + \mathrm{CH_4}$$

including TMA$^+$[(12)-7,9-$B_9C_2H_{12}$]$^-$, identified by its infrared and $^{11}$B nmr spectra,[14] trimethylamine and methane, both identified by their infrared spectra, and a white sublimable solid formulated as $B_{11}C_2H_{13}\cdot N(CH_3)_3$ (III). The $^{11}$B nmr spectrum of III,[10] which exhibited a series of apparently overlapped doublets of relative areas 3:8 centered at +2.2 and +10.4 ppm, respectively, offered little help in deducing its structure. The $^1$H nmr spectrum of III contained a broad peak of relative area 1 at $\tau$ 6.25 and a peak of area 9 at $\tau$ 7.27 which were assigned to the resonances of a polyhedral CH unit and to a trimethylamine ligand, respectively. The mass spectrum of III exhibited a cutoff at $m/e$ 217 which corresponds to the $^{11}B_{11}{}^{12}C_5{}^1H_{22}{}^{14}N^+$ ion, and the chemical analysis established the proposed formula. It was found that the product from the reaction of Li$^+$1,2-$B_{10}C_2H_{11}^-$ and $(CH_3)_3N\cdot BH_2I$[15] was identical with III. The proposed structure of III is shown in Figure 3.

$$\mathrm{1,2\text{-}B_{10}C_2H_{12}} + \mathrm{Li^+C_4H_9^-} \xrightarrow{\text{benzene}} \mathrm{Li^+1,2\text{-}B_{10}C_2H_{11}^-} + \mathrm{C_4H_{10}}$$

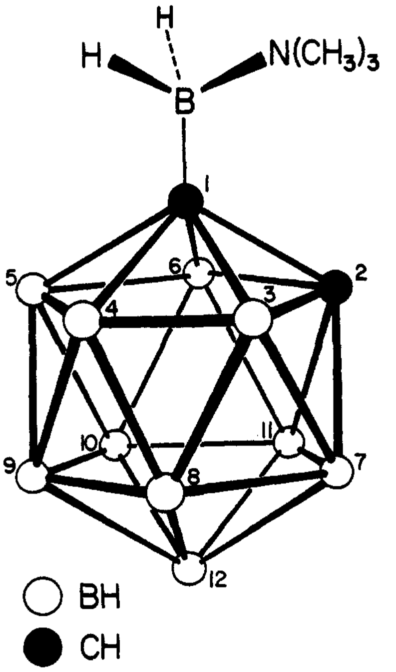
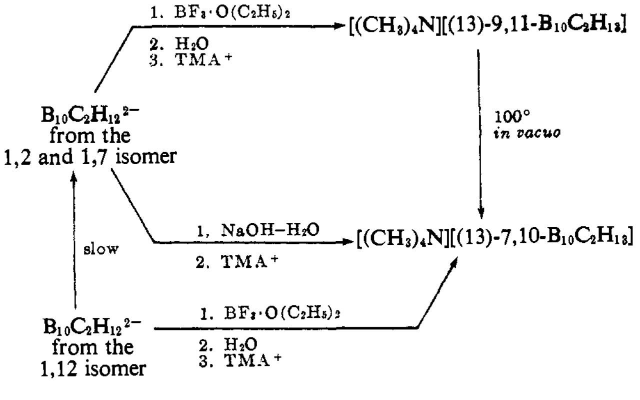


Figure 3. The proposed structure of $(CH_3)_3N\cdot BH_2$-1,2-$B_{10}C_2H_{11}$.

$$\mathrm{Li^+1,2\text{-}B_{10}C_2H_{11}^-} + \mathrm{(CH_3)_3N\cdot BH_2I} \xrightarrow{\text{benzene}} \mathrm{(CH_3)_3N\cdot BH_2\text{-}1,2\text{-}B_{10}C_2H_{11}} + \mathrm{Li^+I^-}$$

The $Na_2B_{10}C_2H_{12}$ prepared from 1,7-$B_{10}C_2H_{12}$ in liquid ammonia with 2 equiv of sodium followed by protonation was found to yield products identical with those obtained from the $Na_2B_{10}C_2H_{12}$ prepared from 1,2-$B_{10}C_2H_{12}$. Moreover the $Na_2B_{10}C_2H_{12}$ prepared from 1,12-$B_{10}C_2H_{12}$ in a similar manner produced II after protonation and precipitation with TMA$^+$. These reactions are summarized in Scheme I.

**Scheme 1.** Reaction Sequence Leading to the (13)-9,11-$B_{10}C_2H_{13}^-$ and (13)-7,10-$B_{10}C_2H_{13}^-$ Ions



The $^{11}$B nmr spectra of the $B_{10}C_2H_{12}^{2-}$ ions produced from 1,2- and 1,7-$B_{10}C_2H_{12}$ are virtually identical[10] and consist of three broad resonances centered at −3, +5, and +25 ppm and which exhibit no well defined B–H doublets. The $^{11}$B nmr spectrum of the $B_{10}C_2H_{12}^{2-}$ ion from 1,12-$B_{10}C_2H_{12}$ is clearly different and exhibits broad resonances centered at +5 and +35 ppm; however, it slowly rearranged to a $B_{10}C_2H_{12}^{2-}$ ion identical with that prepared from 1,2- and 1,7-$B_{10}C_2H_{12}$. Little structural information can be obtained from the spectra due to the broadness of the peaks, which reflects possible fluxional behavior.

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[14] D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.*, **10**, 2516 (1971).

[15] G. E. Ryschkewitsch and J. M. Garrett, *J. Amer. Chem. Soc.*, **90**, 7234 (1968).

Line broadening caused by paramagnetic impurities can be ruled out owing to the sharp doublet observed in the spectra of the $B_{10}C_2H_{12}^{2-}$ ions (from 1,12-$B_{10}C_2H_{12}$) due to unreacted starting material.

Methyl and phenyl derivatives of the 1,2-$B_{10}C_2H_{12}$ carborane were found to undergo reduction and subsequent protonation reactions which differed from the unsubstituted compound only in that the substituted analogs of the [(13)-9,11-$B_{10}C_2H_{13}$]$^-$ were not observed. The $^{11}B$ nmr spectra[10] of TMA$^+$[7-R-(13)-7,10-$B_{10}C_2H_{12}$]$^-$ where R = $CH_3$ (IV), $C_6H_5$ (VI), *p*-$FC_6H_4$ (VIII), and *m*-$FC_6H_4$ (IX) and of TMA$^+$[7,10-$R_2$-(13)-7,10-$B_{10}C_2H_{11}$]$^-$ where R = $CH_3$ (V) and $C_6H_5$ (VII) were found to consist of doublets of relative areas 2:1:1:2:2:2 and were interpreted as in the case of II above.

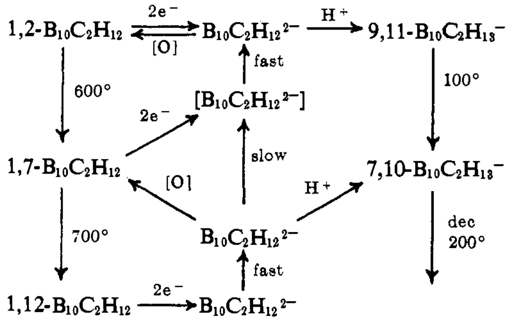
In the (13)-$B_{10}C_2H_{13}^-$ ions there appear to be three possible locations of the extra hydrogen atom: a bridging position which in the (13)-9,11-$B_{10}C_2H_{13}^-$ ion would probably be a tautomeric bridge hydrogen between $B_7$–$B_{12}$ and $B_7$–$B_8$, a position over the open face of the ion in which the extra hydrogen atom was equally bound to three or more polyhedral boron and carbon atoms, and finally the extra hydrogen atom could be localized on one polyhedral boron or carbon atom. The $^1H$ nmr spectrum measured at room temperature of $(C_6H_5)_4As^+$[7,10-$(CH_3)_2$-(13)-7,10-$B_{10}C_2H_{11}$]$^-$ [10] consisted of a broad peak of relative area 1 at $\tau$ 6.45, a very broad peak of area 3 at $\tau$ 8.67, and a broad peak of area 3 at $\tau$ 8.32. Under the influence of $^{11}B$ decoupling or thermal decoupling,[16] the peaks at $\tau$ 6.45 and 8.67 were resolved into a quartet and a doublet, respectively ($J$ = 6 Hz). Solubility at $-60°$ required the use of $(CH_3)_4N^+$ cation which overlapped the quartet. The peak at $\tau$ 8.32 was significantly sharpened in both cases. The coupling of a proton and the methyl group protons observed in the $^{11}B$ decoupled spectrum measured at room temperature indicates that both were bound to the same atom. Therefore the presence of a tautomeric hydrogen atom over the open face is unlikely. Thus, it would appear that of the possible locations of the "extra" hydrogen atom in the (13)-$B_{10}C_2H_{13}^-$ ions, the data support the view that the extra hydrogen atom is localized on the atom in the 7 position in the open face. A proposed structure of V is shown in Figure 3.

Using the chemical shift differences of the $^{19}F$ resonance of VIII and IX *vs.* fluorobenzene, $\sigma_I$ and $\sigma_R$ were found to be $-0.209$ and $-0.103$, respectively. These values differ slightly from those reported previously.[17] Thus the [7,10-$B_{10}C_2H_{12}$]$^-$ moiety "donates" electron density both by inductive and resonance mechanisms as observed for $[7,8\text{-}B_9C_2H_{11}]^{2-}$.[18]

## Conclusion

The chemistry of the $B_{10}C_2H_{12}^{2-}$ ions prepared from 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes appears to be identical even at $-45°$. The oxidation of the $B_{10}C_2H_{12}^{2-}$ ion from 1,2-$B_{10}C_2H_{12}$ and the $B_{10}C_2H_{12}^{2-}$ ion from 1,7-$B_{10}C_2H_{12}$ both produced exclusively 1,2-$B_{10}C_2H_{12}$.[2] Thus it appears that the $B_{10}C_2H_{12}^{2-}$ ion from 1,7-$B_{10}C_2H_{12}$ rearranges very easily to a thermally more stable $B_{10}C_2H_{12}^{2-}$ ion which is identical with that prepared from 1,2-$B_{10}C_2H_{12}$. The oxidation of the $B_{10}C_2H_{12}^{2-}$ ion from 1,12-$B_{10}C_2H_{12}$ produced exclusively 1,7-$B_{10}C_2H_{12}$[3,4] while protonation produced the [(13)-7,10-$B_{10}C_2H_{13}$]$^-$ ion. Therefore, the $B_{10}C_2H_{12}^{2-}$ ion from 1,12-$B_{10}C_2H_{12}$ also rearranges very easily ($-50°$) to a "meta" $B_{10}C_2H_{12}^{2-}$ different from the unstable "meta" $B_{10}C_2H_{12}^{2-}$ produced directly from 1,7-$B_{10}C_2H_{12}$. Finally the $^{11}B$ nmr spectra of the dianions show that the $B_{10}C_2H_{12}^{2-}$ ion from 1,12-$B_{10}C_2H_{12}$ (rearranged?) is slowly converted at room temperature to the $B_{10}C_2H_{12}^{2-}$ ion produced directly from 1,2-$B_{10}C_2H_{12}$. The known interconversions of the "$B_{10}C_2H_{12}$" system are summarized in Scheme II.

**Scheme II.** Summary of Rearrangements of the $B_{10}C_2H_{12}$ System



## Experimental Section

**Apparatus, Materials, and Procedures.** Proton nmr spectra were measured using a Varian HA-100. Heteronuclear decoupling measurements were made using an NMR Specialties HD60 decoupler with a Hewlett-Packard 200 CD audio oscillator. The $^{11}B$ nmr spectra were measured using a research instrument operating at 80.5 MHz which was designed and built by Professor F. A. L. Anet and his coworkers. Fluorine-19 nmr spectra were measured using a Varian HR-60 spectrometer operating at 56.4 MHz. Infrared spectra were measured using a Perkin-Elmer 137 sodium chloride spectrophotometer. An electrochemical device based upon a design of Lawless and Hawley[19] was used for cyclic voltammetry experiments. Measurements were taken in acetonitrile solution 0.1 *F* in tetraethylammonium perchlorate using a Pt button electrode. A Leeds and Northrup 7401 pH meter was used in the equivalent weight determinations. Acetone, benzene, hexane, anhydrous magnesium sulfate, and pyridine were reagent quality obtained from Mallinckrodt Chemical Works and were used without further purification. Tetrahydrofuran was obtained from Mallinckrodt Chemical Works and was distilled under a nitrogen atmosphere from $LiAlH_4$ prior to use. Boron trifluoride diethyl etherate (98%), anhydrous ferric chloride, 1,2-dimethoxyethane, fluorobenzene, heptane, and palladium chloride were obtained from Matheson Coleman and Bell and were used without further purification. Propionic acid was obtained from Eastman Organics. Anhydrous ammonia was obtained from Liquid Carbonic Corp. Silica gel (60–200 mesh) was obtained from J. T. Baker Chemical Co. Dowex 50W-X8 was used in the equivalent weight determinations. Tetraphenylarsonium chloride was obtained from Aldrich Chemical Co. Sodium metal was obtained from Allied Chemical. Acetone-$d_6$ (99.5% isotopic purity) was obtained from Stohler Isotope Chemicals. The 1,2-$B_{10}C_2H_{12}$ and its methyl and dimethyl derivatives were prepared[20] and the 1,2-$B_{10}C_2H_{12}$ rearranged[21] by literature methods. The 1-$C_6H_5$-1,2-$B_{10}C_2H_{11}$,[22] 1,2-$(C_6H_5)_2$-1,2-$B_{10}C_2H_{10}$,[23] 1-*m*-$FC_6H_4$-1,2-$B_{10}C_2H_{11}$,[24]

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and $1\text{-}p\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$[24] were also prepared by known methods.

Chemical analyses and the osmometric molecular weight were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

**$Na_2B_{10}C_2H_{12}$.** To a dry 500-ml, three-neck flask fitted with a mechanical stirrer and a nitrogen inlet were added 1.0 g (43.5 mg-atoms) of sodium metal in small pieces, 2.9 g (20.1 mmol) of freshly sublimed $1,2\text{-}B_{10}C_2H_{12}$, and 100 ml of dry THF. The mixture was stirred under nitrogen at room temperature for 15 hr. The solution of $Na_2B_{10}C_2H_{12}$ was then ready for use.

**$(CH_3)_4N^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-$ (I).** The flask which contained the $Na_2B_{10}C_2H_{12}$ from above was cooled to 0° in an ice bath and 3 g (20.7 mmol) of 98% $BF_3 \cdot O(C_2H_5)_2$ was added dropwise; the solution was stirred for 10 min. Water (20 ml) (degassed by bubbling $N_2$ for 10 min) was added and the solution stirred 10 min. The contents of the flask could be handled in air at this point and was poured into a 1000-ml separatory funnel to which 200 ml of $H_2O$ and 200 ml of hexane had been added. The aqueous layer was separated and washed three times with 200-ml portions of hexane. The hexane fractions were combined and dried over $MgSO_4$, filtered, and stripped to dryness on a rotary evaporator using a water aspirator. The solids were sublimed *in vacuo* to a 0° cold finger and found to be $1,2\text{-}B_{10}C_2H_{12}$ from the infrared spectrum. Excess saturated $(CH_3)_4N^+Cl^-$ solution was added to the aqueous layer and a white precipitate formed which was allowed to stand at room temperature for 15 min and filtered using a medium porosity frit. The solids were taken up in approximately 200 ml of acetone, and 50 ml of water was added. The solution was slowly stripped at ambient temperature using a rotary evaporator and a water aspirator. The white crystals formed were filtered and dried *in vacuo* at room temperature to yield 2.3 g (14.6 mmol, 73%) of $(CH_3)_4N^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-$ (I).

**$(CH_3)_4N^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-$ (II).** To a $Na_2B_{10}C_2H_{12}$ solution prepared as above and cooled to 0° was added dropwise 60 ml of aqueous 0.1 *N* NaOH (degassed) solution, and the solution was stirred 20 min. The resulting solution was then treated exactly as in the preparation of I above. The yield of $(CH_3)_4N^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-$ (II) was 0.89 g (4.1 mmol, 20%).

**$(CH_3)_4N^+[7\text{-}CH_3\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (IV).** The $B_{10}C_2H_{11}CH_3^{2-}$ ion was prepared by stirring at room temperature for 24 hr 1.0 g (43.5 mg-atoms) of sodium and 3.2 g (20.2 mmol) of freshly sublimed $1\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{11}$ in 100 ml of THF under conditions similar to those used for the unsubstituted derivative above. To the THF solution of $Na_2B_{10}C_2H_{11}CH_3$ at 0° was added dropwise 3 g (20.7 mmol) of 98% $BF_3 \cdot O(C_2H_5)_2$, and the solution was stirred 10 min, followed by the addition of 20 ml of (degassed) water, and stirring was continued 10 additional min. The mixture was poured into a 1000-ml separatory funnel which contained 200 ml of $H_2O$ and 200 ml of hexane. The layers were separated and the aqueous fraction was extracted with three additional 200-ml portions of hexane. The hexane fraction was dried over $MgSO_4$, filtered, and stripped to dryness. The trace of solid which remained was identified as $1\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{11}$ from the $^{11}B$ nmr. Excess saturated $(CH_3)_4N^+Cl^-$ solution was added to the aqueous fraction and a white precipitate formed which was allowed to stand 15 min. The precipitate was filtered, and the solids were taken up in approximately 70 ml of acetone. Water was added to hot acetone solution until the solution was cloudy, and the solution was then placed on a 40° warming bench overnight. The white crystals formed were filtered and dried *in vacuo* at room temperature to yield 4.4 g (18.9 mmol, 94%) of $(CH_3)_4N^+[7\text{-}CH_3\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (IV).

**$(CH_3)_4N^+[7,10\text{-}(CH_3)_2\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{11}]^-$ (V).** The $B_{10}C_2H_{10}(CH_3)_2^{2-}$ ion was prepared from 1.0 g (43.5 mg-atoms) of sodium and 3.4 g (19.8 mmol) of $1,2\text{-}(CH_3)_2\text{-}1,2\text{-}B_{10}C_2H_{10}$ in 100 ml of THF, and the resulting $Na_2B_{10}C_2H_{10}(CH_3)_2$ solution was treated exactly as in the preparation of IV above. The yield was 2.6 g (10.6 mmol, 53%) of $(CH_3)_4N^+[7,10\text{-}(CH_3)_2\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{11}]^-$ (V).

**$(CH_3)_4N^+[7\text{-}C_6H_5\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (VI).** The $B_{10}C_2H_{11}C_6H_5^{2-}$ ion was prepared from 1.0 g (43.5 mg-atoms) of sodium and 4.4 g (20.0 mmol) of $1\text{-}C_6H_5\text{-}1,2\text{-}B_{10}C_2H_{11}$ in 100 ml of THF, and the resulting $Na_2B_{10}C_2H_{11}C_6H_5$ solution was treated exactly as in the preparation of IV above. The yield of $(CH_3)_4N^+[7\text{-}C_6H_5\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (VI) was 5.4 g (18.3 mmol, 91%).

**$(CH_3)_4N^+[7,10\text{-}(C_6H_5)_2\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{11}]^-$ (VII).** The $B_{10}C_2H_{10}(C_6H_5)_2^{2-}$ ion was prepared from 0.5 g (21.7 mg-atoms) of sodium and 3.0 g (10.1 mmol) of $1,2\text{-}(C_6H_5)_2B_{10}C_2H_{10}$ in 100 ml of THF, and the resulting $Na_2B_{10}C_2H_{10}(C_6H_5)_2$ solution was treated exactly as in the preparation of IV above. In the recrystallization step an oil formed which crystallized on standing. The yield of $(CH_3)_4N^+[7,10\text{-}(C_6H_4)_2\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{11}]^-$ (VII) was 3.0 g (8.1 mmol, 80%).

**$(CH_3)_4N^+[7\text{-}(p\text{-}FC_6H_4)\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (VIII).** The $B_{10}C_2H_{11}(p\text{-}FC_6H_4)^{2-}$ ion was prepared from 1.0 g (43.5 mg-atoms) of sodium and 4.8 g (20.2 mmol) of $1\text{-}p\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$ in 100 ml of THF, and the resulting $Na_2B_{10}C_2H_{11}(p\text{-}FC_6H_4)$ solution was treated exactly as in the preparation of IV above. The yield of $(CH_3)_4N^+[7\text{-}(p\text{-}FC_6H_4)\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (VIII) was 5.5 g (17.6 mmol, 87%).

**$(CH_3)_4N^+[7\text{-}(m\text{-}FC_6H_4)\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (IX).** The $B_{10}C_2H_{11}(m\text{-}FC_6H_4)^{2-}$ ion was prepared from 1.0 g (43.5 mg-atoms) of sodium and 4.8 g (20.2 mmol) of $1\text{-}m\text{-}FC_6H_4\text{-}1,2\text{-}B_{10}C_2H_{11}$ in 100 ml of THF, and the resulting $Na_2B_{10}C_2H_{11}(m\text{-}FC_6H_4)$ solution was treated exactly as in the preparation of IV above. The yield of $(CH_3)_4N^+[7\text{-}(m\text{-}FC_6H_4)\text{-}(13)\text{-}7,10\text{-}B_{10}C_2H_{12}]^-$ (IX) was 5.5 g (17.6 mmol, 87%).

**Thermal Isomerization of I.** Into a 20-ml Pyrex tube which could be attached to a standard high-vacuum system was placed 1.0 g (4.6 mmol) of $(CH_3)_4N^+[(13)\text{-}9,11\text{-}B_{10}C_2H_{13}]^-$ and the tube was evacuated. A 100° mineral oil bath was placed about the tube for 6 hr. The tube and contents were cooled and removed from the vacuum system. The solids were taken up in acetone, and water was added until cloudiness appeared. The solution was stripped at room temperature on a rotary evaporator using a water aspirator. The white crystals which formed were dried *in vacuo* at room temperature to yield 0.9 g (4.1 mmol, 89%) of II which was identified by its infrared and $^{11}B$ nmr spectra.

**Pyrolysis of II.** Into a 100-ml flask was placed 1.5145 g (6.9 mmol) of $TMA^+[(13)\text{-}7,10\text{-}B_{10}C_2H_{13}]^-$ (II). The flask was attached through a small sublimer to a standard high-vacuum system and evacuated. The sublimer cold finger was maintained with running water at 8°. The flask was slowly heated to 200° and maintained there for 4 hr. The volatile gases were pumped past the cold finger and through traps maintained at 0 and −196°. After the reaction was complete a residue remained in the flask. The residue was extracted with acetone and filtered and the solution condensed to approximately 25 ml. Water was added to the hot solution until cloudiness appeared. After standing, crystals formed which were filtered and dried. The crystals (0.36 g, 1.9 mmol, 27.5%) were identified as $TMA^+[(12)\text{-}7.9\text{-}B_9C_2H_{12}]^-$ by their infrared and $^{11}B$ nmr spectra. The material which condensed on the cold finger was dissolved in ethyl ether and hexane was added. After standing, crystals formed which were filtered and dried at room temperature *in vacuo*. The yield of $(CH_3)_3N \cdot BH_2\text{-}1,2\text{-}B_{10}C_2H_{11}$ was 0.40 g (1.9 mmol, 27.5%). The 0° trap contained a trace of $1,2\text{-}B_{10}C_2H_{12}$. The −196° trap contained 1.3 mmol of trimethylamine which was identified by its infrared spectrum.

In a separate experiment, 0.2170 g (0.99 mmol) of II was sealed in an evacuated tube which was heated at 200° for 4 hr. The tube was attached to the vacuum system and cooled to −196°. The tube was opened and the noncondensable gas was collected with a Sprengel pump, 0.238 mmol (24%). The gas was allowed to equilibrate into an infrared cell. The infrared spectrum indicated that the gas was methane.

**Reaction of $1,2\text{-}B_{10}C_2H_{12}$ with Sodium in Liquid Ammonia.** Approximately 70 ml of anhydrous ammonia was condensed at −50° into a 200-ml flask fitted with a side nitrogen inlet and a Pyrex-covered magnetic stirring bar. Under a blanket of nitrogen, with stirring, 2.9 g (20.1 mmol) of $1,2\text{-}B_{10}C_2H_{12}$ was added and allowed to dissolve followed by the slow addition of 1.0 g (43.5 mg-atoms) of sodium metal in small pieces over 20 min. THF (40 ml) was added and the flask was allowed to warm slowly while a stream of nitrogen was allowed to pass rapidly over the solution. With the flask at room temperature, a small aliquot of the THF solution was syringed rapidly into a dry. nitrogen filled nmr tube which was immediately evacuated and sealed for nmr examination. The flask with the remainder of the THF solution was cooled to 0° and treated exactly as in the preparation of I above. The yield of I was 2.6 g (11.9 mmol, 60%).

**Reaction of $1,7\text{-}B_{20}C_2H_{12}$ with Sodium in Liquid Ammonia.** With the reaction conditions identical with those in the reaction of $1,2\text{-}B_{10}C_2H_{12}$ above, 2.9 g (20.1 mmol) of $1,7\text{-}B_{10}C_2H_{12}$ and 1.0 g (43.5 mg-atoms) of sodium reacted in 40 min. The solution was

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treated exactly as in the reaction of 1,2-$B_{10}C_2H_{12}$ above. The yield of I was 0.9 g (4.1 mmol, 20%).

**Reaction of 1,12-$B_{10}C_2H_{12}$ with Sodium in Liquid Ammonia.** With the reaction conditions identical with those in the reaction of 1,2-$B_{10}C_2H_{12}$ above, 2.5 g (17.4 mmol) of 1,12-$B_{10}C_2H_{12}$ (sparingly soluble in ammonia at −50°) and 0.8 g (34.7 mg-atoms) of sodium reacted in 2 hr. The resultant solution was treated exactly as in the reaction of 1,2-$B_{10}C_2H_{12}$ above. The yield of II was 1.9 g (8.7 mmol, 50%).

**Preparation of [(13)-7,10-$B_{10}C_2H_{13}]^-$ in Liquid Ammonia at −50°.** To a 200-ml flask fitted with a nitrogen inlet and a Pyrex-covered magnetic stirring bar was condensed (−50°) approximately 100 ml of ammonia. Under a stream of nitrogen, 2.9 g (20 mmol) of 1,12-$B_{10}C_2H_{12}$ was added followed by the addition of 1.0 g (43.5 mg-atoms) of sodium metal in small pieces over a 2-hr period. The mixture was allowed to warm to room temperature under a stream of nitrogen, then transferred in air to a 1000-ml separatory funnel which contained 200 ml of hexane and 200 ml of water. The layers were separated and the aqueous fraction was extracted with three 200-ml portions of hexane. The hexane fractions were combined and dried over $MgSO_4$, filtered, and stripped to dryness using a rotary evaporator and a water aspirator. The remaining solid was sublimed *in vacuo* to a −80° cold finger. The solid was identified as 1,12-$B_{10}C_2H_{12}$ by its infrared spectrum (1.25 g, 8.7 mmol). The aqueous fraction was divided into equal portions to which excess $(CH_3)_4N^+Cl^-$ and $(C_2H_5)_4N^+Br^-$ were added, respectively. Each precipitate was filtered and taken up in approximately 50 ml of acetone. Water was added to the solutions at ambient temperature until slight cloudiness appeared followed by slow evaporation on the rotary evaporator. The yield was 1.4 g (6.4 mmol, 56% based on carborane consumed) of II and 0.65 g (2.4 mmol, 20% based on carborane consumed) of $[(C_2H_5)_4N]^+[7,10\text{-}B_{10}C_2H_{13}]^-$, respectively.

**Reaction of I with Pyridine and $FeCl_3$.** To a 500-ml three-neck flask fitted with a reflux condenser (topped with a nitrogen inlet) and a magnetic stirring bar was added 4.0 g (18.6 mmol) of I, 200 ml of dry benzene, and 4.0 g (50.5 mmol) of pyridine. The flask was heated to reflux under nitrogen with stirring and a solution (prepared in a nitrogen filled drybox) of 6.5 g (37.2 mmol) of anhydrous $FeCl_3$ in 80 ml of benzene and 10 ml of pyridine was added dropwise. Heating was continued at reflux for 1 hr. The solution was cooled and filtered in air using a medium porosity frit. The benzene solution was extracted with ten 200-ml portions of water. The aqueous fractions were discarded. The benzene fraction was dried over $MgSO_4$ and filtered. Silica gel (50 g) was added and the solution was stripped to dryness using a rotary evaporator and water aspirator. The dry silica gel was added to a 4 × 30-cm silica gel column and eluted with benzene. A yellow band was eluted. On cooling the benzene solution, to which heptane had been added, pale yellow crystals formed which were filtered and dried *in vacuo*, mp 156–157°. This material was identified as 9-$NC_5H_5$-(12)-7,8-$B_9C_2H_{11}$ from the infrared and nmr spectra.[11]

**$^{19}F$ Nmr Studies.** The samples for $^{19}F$ nmr were approximately 1 *M* solutions in dimethoxyethane which contained 10% fluorobenzene. The methods used for determining the chemical shift *vs.* internal fluorobenzene and the calculations of the $\sigma_1$ and $\sigma_R$ have been described previously.[18] The observed chemical shifts for the *p*-fluorophenyl (VIII) and *m*-fluorophenyl (IX) derivatives were +5.13 and +2.08 ppm. respectively. These chemical shifts indicate the values $\sigma_R = -0.103$ and $\sigma_1 = -0.209$.

**$PdCl_2$ Decomposition of V.** Into a 500-ml flask fitted with a breakseal was placed 1.1657 g (4.7 mmol) of V and 0.3325 g of $PdCl_2$. The flask was evacuated, filled with nitrogen, and cooled to −196°. Under a blanket of nitrogen, propionic acid, 50 ml, was added and the flask was evacuated and sealed. The flask and its contents were heated at 130° for 18 hr and cooled, and the flask was attached to the vacuum system. The volatiles were passed through −80 and −196° traps while the flask was cooled to 0°. The −80° trap contained propionic acid. The −196° trap contained 2.65 mmol (28%) of ethane which was identified by its infrared spectrum.[25]

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(25) NOTE ADDED IN PROOF. Recent crystallographic studies of the $B_{10}C_2H_{11}(CH_3)_2^-$ (M. R. Churchill, private communication) and the $B_{10}C_2H_{11}(C_6H_5)_2^-$ ions (W. N. Lipscomb, private communication) have confirmed the gross overall geometry of these ions. However, differences in the bonding interactions of the polyhedral framework have been observed. The structure of the $B_{10}C_2H_{11}(CH_3)_2^-$ ion has been shown to possess a bridging $CH_3CH$ moiety between two boron atoms in a pentagonal face similar to the bridging $(CH_3)_2Al$ moiety in $B_9C_2H_{12}Al(CH_3)_2$.[26] These bonding interactions can be generated from the proposed geometry (Figure 2, where R = $CH_3$) by breaking the 2–7 interaction and making an 8–12 interaction. These changes result in the movement of the $CH_3CH$ moiety toward the center of the resultant pentagonal face. Both structures are compatible with our nmr data. The correct numbering of the $B_{10}C_2H_{11}(CH_3)_2^-$ ion is 7-$CH_3$-*exo*-12-$CH_3$-(13)-7,12-$B_{10}C_2H_{11}^-$.

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