Tetrahedron Letters No.12, pp. 715-720, 1965. Pergamon Press Ltd.
Printed in Great Britain.

COMMENTS REGARDING THE STRUCTURE OF $B_9C_2H_{11}$

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(Received 21 December 1964; in revised form 28 January 1965)

The recently discovered $B_9C_2H_{11}$ carborane(1) and its C-substituted derivatives present an interesting structural problem since the eleven heavy atoms are most likely arranged in a <u>clovo</u>[c] manner. We have obtained ^{11}B N.M.R. spectra and certain stereochemical results which bear upon this problem. The 60 Mc./sec. ^{11}B N.M.R. spectrum[d] of $B_9C_2H_{11}$ is presented in Fig. 1 and is seen to consist of four doublets of relative

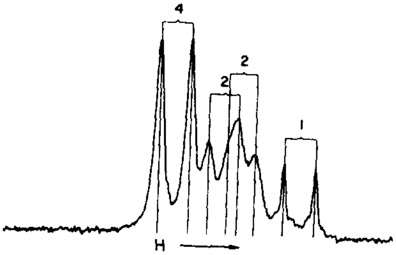

FIG. 1

The ^{11}B N.M.R. spectrum of $B_9C_2H_{11}$ at 60 Mc./sec.

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[a] National Institutes of Health Predoctoral Fellow.

[b] Alfred P. Sloan Research Fellow.

[c] Meaning "cage" as described by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

[d] Obtained through the cooperation of Mr. Eugene Pier, Varian Associates, Palo Alto, California, with an experimental cryogenic solenoid field source operating at 44 K gauss.

area 4:2:2:1 reading up-field. Previously described chemical evidence suggested that the carbon atoms in $B_9C_2H_{11}$ are not nearest neighbors.(1) The latter suggestion is strongly supported(2) by the very facile formation of the C-substituted $B_9C_2H_{10}\emptyset$ (I) from the precursor salt, $B_9C_2H_{11}\emptyset^-$ (II) obtained by degradation of C-substituted meta-$B_{10}C_2H_{11}\emptyset$.

$$\begin{tikzcd}
\underline{o}\text{-}B_{10}C_2H_{11}\emptyset \arrow[r, "410^\circ"] & \underline{m}\text{-}B_{10}C_2H_{11}\emptyset \arrow[dl, "OH^-"', "EtOH"] \\
\underline{m}\text{-}B_9C_2H_{11}^-\emptyset \arrow[r, "H^+", "-H_2"'] & B_9C_2H_{10}\emptyset
\end{tikzcd}$$

A reasonable structure for II is presented in Fig. 2, in which

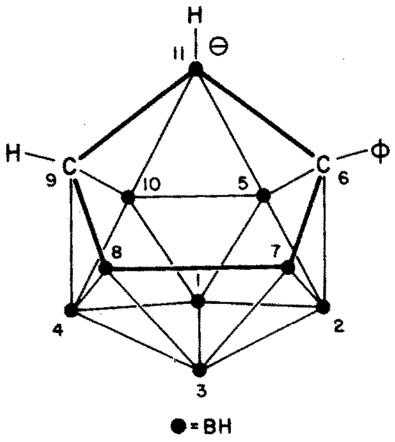

FIG. 2

A reasonable structure for C-phenyl $B_9C_2H_{11}\emptyset^-$

the "extra" hydrogen atom attached to the pentagonal face is depicted as a $BH_2^{\ominus}$ group. Equally attractive structures for II may be constructed with the two carbon atoms at positions 2 and 4 and/or a bridge hydrogen atom on the open face rather than the $BH_2^{\ominus}$ group depicted in Fig. 2. Consistent with this gross picture of II is the fact that II exists in enantiomorphic forms which have been partially separated by recrystallization of its (d-α-phenylethyl) trimethylammonium salt. The latter salt was then converted to an optically active cesium salt (III) by an ion-exchange procedure ($[\alpha] = +14.6^{\circ}$ at 365 mμ). Treatment of III with polyphosphoric acid followed by sublimation at 135° produced <u>optically inactive</u> I in 94% yield. This observation suggests, but does not conclusively prove, that the carbon atoms present in the framework of I lie upon a plane of molecular symmetry. Finally, the methyl hydrogen atoms of $B_9C_2H_9(CH_3)_2$ are equivalent in its 60 Mc./sec. ^1H N.M.R. spectrum.

The evidence outlined above prompts us to make the tentative suggestion that $B_9C_2H_{11}$ has the structure shown in Fig. 3 in which positions 6 and 9 are occupied by carbon CH units and all other positions represent BH units.(3) This structure may be generated by the formation of a three-center bond between boron atoms 11, 7, and 8. The overall reaction from $B_9C_2H_{12}^-$ could possible proceed through collapse of a $B_9C_2H_{11}$ intermediate which has an open orbital on boron atom 11 and the geometry of an icosahedral fragment. Such an intermediate could be generated by the protolytic removal of a hydride ion from a $-BH_2^{\ominus}$ group at position 11 in $B_9C_2H_{12}^-$ (see Fig. 2).

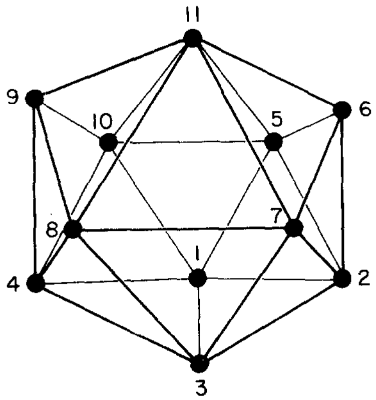

FIG. 3

A proposed structure for $B_9C_2H_{11}$

The facile reaction of $B_9C_2H_{11}$ and its C-substituted derivatives with electron donors (L) to generate $B_9C_2H_{11}L$ species$^{(1)}$ may occur by nucleophilic attack of the ligand at position 11 in $B_9C_2H_{11}$. If attack of the ligand occurred at positions 5, 7, 8, or 10, a *mono-C-substituted* $B_9C_2H_{11}$ such as I would be expected to yield two isomeric $B_9C_2H_{11}L$ racemates. No evidence which suggests the existence of more than one isomer or racemate has yet been obtained.

The unknown $B_{11}H_{11}^{-2}$ ion which provides an isoelectronic model for $B_9C_2H_{11}$ requires an 0930 topology.$^{(4)}$ The proposed $B_9C_2H_{11}$ ($B_{11}H_{11}^{-2}$) structure fulfills this topological requirement if a hypothetical $B_{10}H_{10}^{-2}$ fragment produced by the formal removal of $2H_2$ from the known $B_{10}H_{14}^{-2}$ ion$^{(4,5,6)}$ is bonded with a neutral sp^2 hybridized BH fragment as shown in Fig. 4.

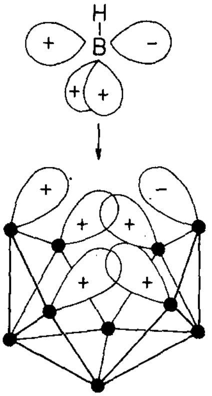

FIG. 4

The sp^2 BH group and the $B_{10}H_{10}^{-2}$ fragment prepared for bonding

In this localized model the BH group at position 11 forms a set of two central three-center bonds with orbitals associated with boron atoms 7-8 and 5-10. The *p*-orbital of the BH fragment is bonded to carbon(3) (boron) atoms 6 and 9 by an open three-center bond. Many other canonical structures may be obtained with this molecular geometry and 0930 topology.

Acknowledgements: The authors gratefully acknowledge the support of this work by the National Cancer Institute, U.S. Public Health Service, under Grant CA-06773 MCHB. In addition, this investigation was supported in part by a Public Health Service Predoctoral Fellowship 1-F1-GM-23,433-01 from the National Institute of General Medical Sciences to T.E.B.

References

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

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

(3) Prof. W. N. Lipscomb, in the capacity of a referee, has suggested the possibility that the two carbon atoms of $B_9C_2H_{11}$ reside in the 2 and 4 positions (Fig. 3). This structural possibility is in agreement with the ^{11}B N.M.R. spectrum (Fig. 1) and might arise through a more extensive thermal rearrangement of the icosahedral fragment during the pyrolysis step. Alternatively, II may actually have carbon atoms in the 2 and 4 positions.

(4) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N.Y., 1963.

(5) R. H. Toeniskoetter, Ph.D. thesis, St. Louis University, 1956.

(6) R. H. Toeniskoetter, G. W. Schaeffer, E. C. Evers, R. E. Hughes, and G. E. Bagley, Abstracts, 134th Meeting of the American Chemical Society, Chicago, Sept. 1958, pp. 23-24.