

The Chemistry of Pentaborane(9)

Donald F. Gaines

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received March 5, 1973

Pentaborane(9), B_5H_9 , has been known for 50 years¹ and its structure was determined over 20 years ago,² but its unusual and interesting chemical properties have been extensively studied only during the last half-dozen years. This Account will summarize the more important reactions of B_5H_9 and its conjugate base, the octahydropentaborate(1-) anion, $B_5H_8^-$.

In the laboratory B_5H_9 has been handled almost exclusively in high vacuum apparatus³ because of its toxicity, its unpredictable combustibility, and its propensity to detonate unexpectedly in air.⁴⁻⁶ Pentaborane(9) has been commercially prepared by pyrolysis of diborane(6),⁵ while laboratory quantities are conveniently obtained *via* pyrolysis of $[(C_4H_9)_4N^+][B_3H_7Br^-]$.⁶ The physical properties of B_5H_9 are: mp -47° ; bp 60° ; and vapor pressure = 65 Torr at 0° and 209 Torr at 25° .^{3,5}

Pentaborane(9) is the most thermally stable of the lower boranes. The structure of the boron framework is not that of an icosahedral fragment, as are most other boranes, but rather has the form of a square-based pyramid and is thus a fragment of an octahedron, as shown in Figure 1. The molecular symmetry of B_5H_9 is C_{4v} as determined by single-crystal X-ray,² electron diffraction,⁷ and microwave studies.⁸ X-Ray studies of 2,3-(CH_3)₂ B_5H_7 ⁹ and 1-Br- μ -[(CH_3)₃Si] B_5H_7 ¹⁰ have shown that the basic B_5 framework is essentially unchanged by substitution of hydrogen atoms by other atoms or groups.

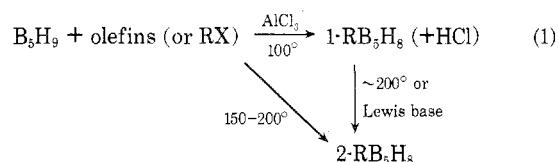
The bonding in B_5H_9 can be conveniently described as a series of resonance structures (Figure 2) in terms of the three-center bond formalism developed by Lipscomb and coworkers for describing "semitopological" valence structures of boranes.¹¹

Detailed molecular orbital calculations of B_5H_9 using self-consistent-field wave functions have been performed.¹²

The structures of B_5H_9 derivatives can usually be deduced unambiguously from their ¹¹B nmr spectra. Several collections of ¹¹B and ¹H nmr data for B_5H_9 derivatives are available elsewhere.¹³⁻¹⁵

Alkyl Derivatives of Pentaborane(9)

Alkylations of B_5H_9 at 25 – 100° by olefins or alkyl halides in the presence of aluminum halides produce 1-alkylpentaborane(9) derivatives in good yields (eq 1).¹⁶⁻¹⁸ If these alkylation reactions are carried out



at *ca.* 200° , or if a 1-alkylpentaborane is heated to *ca.* 200° , the major product is the 2-alkylpentaborane(9) derivative.¹⁶ Yields are often less than 50%, and the product usually contains appreciable 1-alkylpentaborane(9) impurity. On the other hand, rearrangement of 1-alkylpentaborane(9) to the corresponding 2 isomer is essentially quantitative in the presence of Lewis base catalysts such as 2,6-dimethylpyridine or hexamethylenetetramine.^{14,19} The reaction of B_5H_9 with olefins at *ca.* 150° in the absence of Friedel-Crafts catalysts also produces 2-alkylpentaborane derivatives in up to 80% yields, but only 5–10% of the B_5H_9 is generally consumed under these conditions.²⁰

A number of di- and trimethyl and mixed methyl-halo derivatives of B_5H_9 have been prepared by successive Friedel-Crafts catalyzed alkylations (or halogenations) and Lewis base-catalyzed isomerizations.¹⁴ Of particular interest is the $AlCl_3$ -catalyzed reaction of 2- $CH_3B_5H_8$ with CH_3Cl , which produces, along with the expected 1,2-(CH_3)₂ B_5H_7 , small but significant yields of 2-Cl-3- $CH_3B_5H_7$, 2-Cl-1,3-

(1) A. Stock and E. Kuss, *Ber.*, 56, 789 (1923).

(2) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, 5, 260 (1952).

(3) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(4) "Pentaborane." Technical Bulletin LF-202. Olin Mathieson Chemical Corp., New Haven, Conn., 1960; "Pentaborane," Technical Bulletin CT-1300, Callery Chemical Co., Callery, Pa., 1961.

(5) R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," Academic Press, New York, N. Y., 1967.

(6) V. H. Miller and G. E. Ryschkewitsch, *Inorg. Syn.*, 15, in press.

(7) K. Hedberg, M. E. Jones, and V. Schomaker, *Proc. Nat. Acad. Sci. U. S.*, 38, 679 (1952).

(8) H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, 22, 262 (1954).

(9) L. B. Friedman and W. N. Lipscomb, *Inorg. Chem.*, 5, 1752 (1966).

(10) J. C. Calabrese and L. F. Dahl, *J. Amer. Chem. Soc.*, 93, 6042 (1971).

(11) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, 92, 3847 (1970).

(12) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 92, 3837 (1970).

(13) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(14) P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 9, 1430 (1970).

(15) A. B. Burg, *J. Amer. Chem. Soc.*, 90, 1407 (1968), and references therein.

(16) N. J. Blay, I. Dunstan, and R. J. Williams, *J. Chem. Soc.*, 430 (1960).

(17) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, 1, 742 (1962).

(18) G. E. Ryschkewitsch, S. W. Harris, E. J. Mezey, H. H. Sisler, E. A. Weilmuenster, and A. B. Garrett, *Inorg. Chem.*, 2, 890 (1963).

(19) G. E. Ryschkewitsch, E. J. Mezey, E. R. Altwickler, H. H. Sisler, and A. B. Garrett, *Inorg. Chem.*, 2, 893 (1963).

(20) T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, 6, 1476 (1967).

Donald F. Gaines was born in Caldwell, Idaho, and received his undergraduate training there, at the College of Idaho. In 1963 he received his Ph.D. from Indiana University, and spent the following 2 years as a Research Associate in a joint program sponsored by Indiana University and the University of Manchester. He then joined the staff at the University of Wisconsin, where he is presently an Associate Professor. His research has dealt largely with the chemistry of boron hydrides, with special emphasis on their organo group III and group IV derivatives.

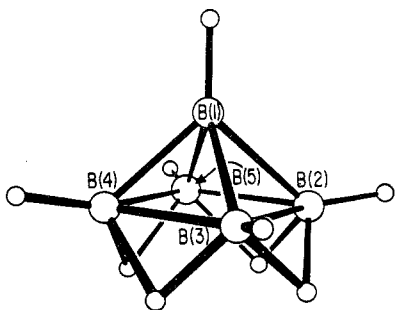


Figure 1. The structure and numbering of pentaborane(9). The interatomic connections do not correspond to bonds.

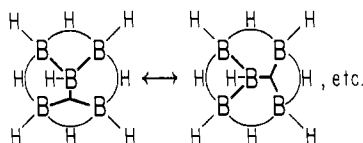


Figure 2. Favorable resonance structures for B_5H_9 .

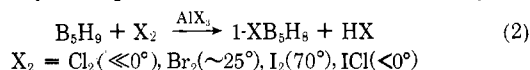
$(CH_3)_2B_5H_6$, and 2-Cl-1,4- $(CH_3)_2B_5H_6$.²⁰ Aluminum chloride catalyzed reaction of B_5H_9 with CH_2Cl_2 produces small amounts of bis(1-pentaboryl)methane, $(1-B_5H_8)_2CH_2$, and 1-pentaboryl(dichloroboryl)methane, $(1-B_5H_8)CH_2BCl_2$. These compounds were also obtained from reactions of B_5H_9 with other halocarbon compounds.²¹ Reaction of ethylene and diborane at *ca.* 100° has been shown to produce di- through pentaethylpentaborane(9)s.²²

Pentaborane(9) Rearrangements

Isomerizations between apex and basal positions on B_5H_9 derivatives are thought to occur *via* intramolecular polyhedral rearrangements¹⁹ in which the intermediate has the approximate form of a trigonal bipyramid.⁹ The rearrangement scheme proposed in Figure 3 is a slight variation of that proposed by Lipscomb and coworkers⁹ and shows the possible role of a Lewis base catalyst in the isomerization.¹⁹ Many isomerizations may also be thermally induced, and these undoubtedly involve a somewhat similar trigonal bipyramidal intermediate. Detailed mechanistic studies of these rearrangements will be possible when methods become available for preparing B_5H_9 derivatives in which the apex (or basal) boron atoms are isotopically labeled.

Halo Derivatives of Pentaborane(9)

Pentaborane(9) is readily halogenated, exclusively at the apex position, by elemental chlorine,²³ bromine,²⁴ or iodine¹⁵ in the presence of an aluminum halide catalyst (eq 2). Iodine monochloride may be



substituted for iodine, the reaction then occurring at a much lower temperature²⁵ (eq 2). In the case of

(21) E. R. Altwickler, G. E. Ryschkewitsch, A. B. Garrett, and H. H. Sisler, *Inorg. Chem.*, **3**, 454 (1964).

(22) N. J. Blay, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 424 (1960).

(23) D. F. Gaines and J. A. Martens, *Inorg. Chem.*, **7**, 704 (1968), and references therein.

(24) A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, **87**, 3787 (1965), and references therein.

(25) D. F. Gaines and L. Ardini, unpublished results.

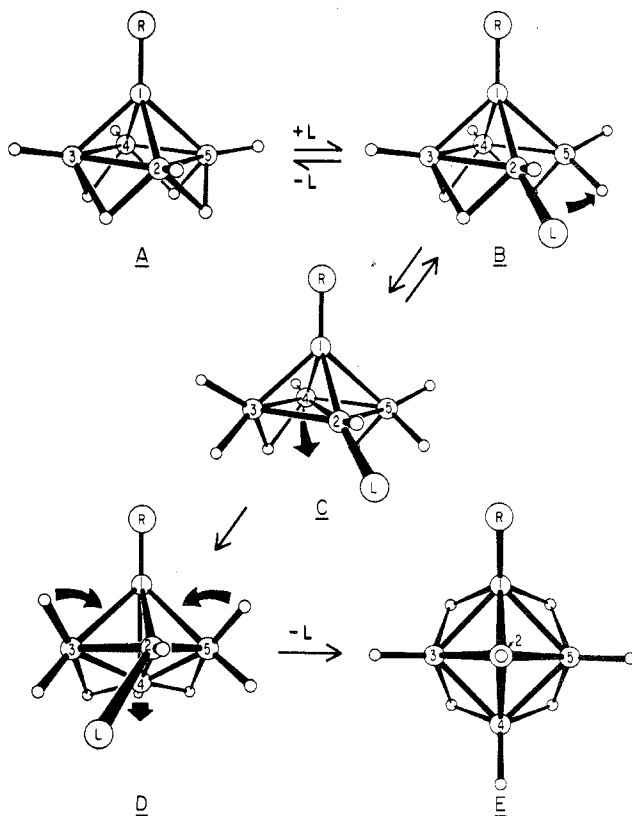
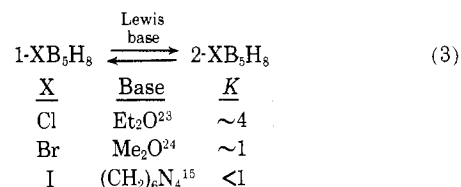


Figure 3. A proposed rearrangement scheme for the base-catalyzed isomerization of B_5H_9 derivatives. The B_5 frameworks are the same in A and E, but in E the view is from above the pyramid. In C and D the B_5 framework is in an approximately trigonal-bipyramidal configuration.

chlorination, a solvent such as BCl_3 is employed to moderate the reaction.²³

Isomerization of 1-halopentaborane(9) to the corresponding 2-halopentaborane usually occurs in the presence of rather weaker Lewis bases than are required for alkylpentaborane(9) isomerizations. Furthermore, the isomerization of a halopentaborane(9) is usually reversible. While quantitative equilibrium studies have not been successful, qualitative observations indicate that the thermodynamic stability of the 2 isomer (with respect to the 1 isomer) decreases from 2-Cl B_5H_8 to 2-IB B_5H_8 (eq 3). Chlorination and



bromination of B_5H_9 in the absence of strong Lewis acid catalysts produce small amounts of 2-Cl B_5H_8 and 2-Br B_5H_8 , respectively, along with the corresponding 1 isomers. The overall yields, however, are significantly lower than those obtained from catalyzed reactions.^{23,24} These uncatalyzed reactions apparently occur *via* free-radical mechanisms.²⁶

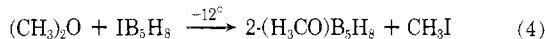
The only known fluoropentaborane(9), 2-F B_5H_8 , has been prepared most efficiently from 2-IB B_5H_8 by

(26) Uncatalyzed chlorination of B_5H_9 can be very hazardous. Liquid B_5H_9 has been observed to enflame in a chlorine atmosphere (D. F. Gaines, unpublished results) and mixtures of solid B_5H_9 in liquid Cl_2 may explode unexpectedly.¹⁵

halogen exchange with SbF_3 .¹⁵ Halogen exchange reactions have also been used to prepare low yields of 1- ClB_5H_8 from 1- IB_5H_8 and HgCl_2 ,¹⁵ and 2- ClB_5H_8 from 1- BrB_5H_8 and AlCl_3 .²⁷

Di- and trichloropentaborane(9)s have been prepared by successive isomerizations and aluminum chloride catalyzed chlorinations.^{23,28} A number of other basal-substituted pentaborane derivatives have been halogenated at the apex position under Friedel-Crafts or heterolytic cleavage conditions,¹⁴ indicating that substitution on basal boron atoms in B_5H_9 often does not have a significant effect on the reactivity of the apex B-H.

Isomerization of halopentaboranes using dimethyl ether as a catalyst is often complicated by competing reactions. For example, when isomerization of either 1- or 2- IB_5H_8 was attempted in dimethyl ether solutions, the major process observed was cleavage of the ether and formation of 2-(H_3CO) B_5H_8 in moderate yield according to the idealized reaction shown in eq 4.²⁹ While 1- BrB_5H_8 isomerizes in $(\text{CH}_3)_2\text{O}$ to 2-



BrB_5H_8 in 50% yield at 0° , competing side reactions become more noticeable at higher temperatures. At 38° all the BrB_5H_8 is consumed in the production of a moderate yield of 1- $\text{H}_3\text{CB}_5\text{H}_8$.²⁴

Lewis Base Adducts of Pentaborane(9)

Several types of Lewis base adducts of B_5H_9 have been identified, but structural characterization has been difficult owing to the obtuse spectroscopic and chemical properties of most of the adducts.

Reaction of B_5H_9 and many of its derivatives with strong unhindered Lewis bases at low temperatures produces adducts having the general formula $\text{B}_5\text{H}_9 \cdot 2\text{L}$.^{19,30,31} When the bases are alkylamines, the adducts decompose slowly at ambient temperature and above to a number of different boron nitrogen compounds. The mode of decomposition depends primarily on the type of amine but is influenced in some cases by the thermal conditions.³⁰⁻³² Reaction of *N,N,N',N'*-tetramethylethylenediamine (TMED) with B_5H_9 produces $\text{B}_5\text{H}_9 \cdot \text{TMED}$. Although this adduct is air stable at ambient temperature,³³ it undergoes solvolysis in methanol to produce $\text{B}_4\text{H}_8 \cdot \text{TMED}$.

Reaction of $(\text{CH}_3)_3\text{P}$ with B_5H_9 produces air-stable $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$,³⁴ the structure of which is shown in Figure 4.³⁵ This very unusual structure may be present in the amine adducts of B_5H_9 , but the data presently available are inconclusive.

When B_5H_9 reacts with ammonia at -78° the pentaborane(9) framework is cleaved in the formation of $[\text{H}_2\text{B}(\text{NH}_3)_2]^+[\text{B}_4\text{H}_7]^-$, which is unfortunately very

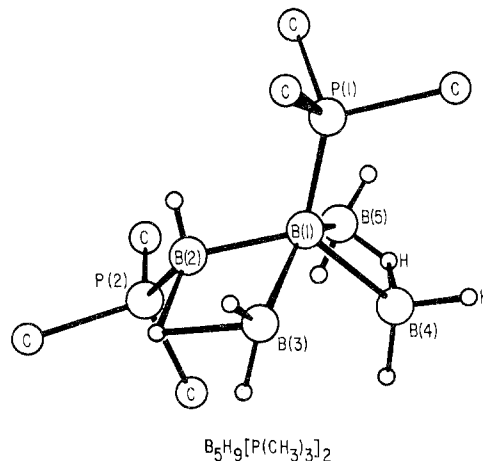
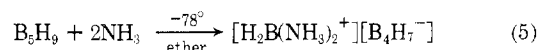


Figure 4. The X-ray determined molecular structure of $\text{B}_5\text{H}_9 \cdot 2\text{P}(\text{CH}_3)_3$.

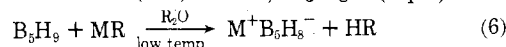
unstable at ambient temperature (eq 5). This salt of



the previously unknown B_4H_7^- anion has been chemically characterized by its nearly quantitative reactions to form the known $[\text{H}_2\text{B}(\text{NH}_3)_2]^+\text{Cl}^-$ and $(\text{CH}_3)_2\text{NPF}_2\text{B}_4\text{H}_8$.³⁶

Deprotonation of Pentaborane(9)

One of the more important developments in the systematic study of the chemistry of B_5H_9 was the discovery that it reacts at low temperatures (-30° to -80°) with alkali metal hydrides and alkyllithium reagents to produce nearly quantitative yields of the octahydropentaborate(1-) anion, B_5H_8^- (eq 6).^{37,38}



MR = lithium alkyls, NaH, KH

Chemical and spectral studies of the B_5H_8^- anion strongly suggest that it is derived from the parent B_5H_9 by removal of a proton from a bridging position.³⁸ This structure was first suggested by the observation that B_5H_8^- reacts with DCl to produce exclusively $\mu\text{-DB}_5\text{H}_8$.³⁷ Subsequent ^{11}B and ^1H nmr studies are consistent with this structural assignment. Low-temperature nmr studies suggest that the three bridge hydrogens in B_5H_8^- are involved in rapid intramolecular tautomerism. The proposed structure and exchange process can be visualized as shown in Figure 5.³⁹

Numerous derivatives of B_5H_9 may also be deprotonated under conditions similar to those required for B_5H_9 . Representative examples of the anions obtained include 1- Cl -, 1- Br -, 1- CH_3 -, and 1- $[(\text{CH}_3)_3\text{Si}]\text{B}_5\text{H}_7^-$ and 2- CH_3 -⁴⁰ and 2- $[(\text{CH}_3)_3\text{Si}]\text{B}_5\text{H}_7^-$, but not $\mu\text{-}[(\text{CH}_3)_3\text{Si}]\text{B}_5\text{H}_7^-$.²⁸ Bridge hydrogen tautomerism appears to be a general feature of B_5 anions, as illustrated by the observation of bridge hydrogen equivalence in the ^1H nmr spectra of B_5 anions and by the partial quenching of

(27) T. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(28) D. F. Gaines, unpublished results.

(29) D. F. Gaines, *J. Amer. Chem. Soc.*, **91**, 1230 (1969).

(30) A. B. Burg, *J. Amer. Chem. Soc.*, **79**, 2129 (1957).

(31) A. F. Zhigach, F. B. Kazakova, and I. S. Antonov, *J. Gen. Chem. USSR*, **27**, 1725 (1957).

(32) A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, **89**, 1626 (1967).

(33) N. E. Miller, H. C. Miller, and E. L. Muettterties, *Inorg. Chem.*, **3**, 866 (1964).

(34) M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

(35) A. Fratini, M. Denniston, G. Sullivan, and S. G. Shore, private communication.

(36) G. Kodama, *J. Amer. Chem. Soc.*, **92**, 3482 (1970).

(37) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 3375 (1967).

(38) R. A. Geanangel and S. G. Shore, *J. Amer. Chem. Soc.*, **89**, 6771 (1967).

(39) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).

(40) V. T. Brice and S. G. Shore, *Inorg. Chem.*, **12**, 309 (1973).

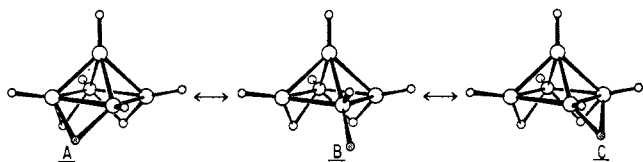


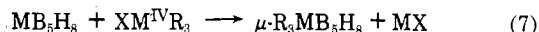
Figure 5. A proposed mechanism for tautomerism of bridge hydrogens in the $B_5H_8^-$ anion and its derivatives.

this tautomerism observed in low temperature 1H spectra of the $2-CH_3B_5H_7^-$ anion.⁴⁰

The chemistry of the $B_5H_8^-$ anion and its derivatives is unusual on several counts. First, reactions with numerous reagents produce unprecedented bridge-substituted derivatives of B_5H_9 . Second, reactions with boranes and borane anions provide new selective routes to other borane anions.

Group IV Derivatives of Pentaborane(9)

Salts of the $B_5H_8^-$ anion react with a number of group IV compounds (at low temperatures in etheral solvents) to produce good yields of bridge-substituted B_5H_9 derivatives (eq 7).^{41,42} The ^{11}B and 1H



M^{IV}	$X = Cl, Br, I$	R
Si		$CH_3, C_2H_5, H, \text{mixed } H \text{ and } CH_3$
Ge		CH_3, C_2H_5, H
Sn, Pb		CH_3

nmr spectra of these compounds indicated that the group IV substituent is in a bridging position between two boron atoms in the base of the pentaborane pyramids. A subsequent single-crystal X-ray study of $1-Br-\mu-[(CH_3)_3Si]B_5H_7$ has verified this general structural feature.¹⁰ In this structure, the methyl groups on the silicon atom are at nearly tetrahedral angles. The assumed fourth tetrahedral orbital on silicon is then directed toward the midpoint between the two adjacent boron atoms (Figure 6). The bonding between the silicon (for any group IV atom except carbon) and the borane framework can thus be described as a three-center two-electron interaction involving the quasitetrahedral silicon orbital and an appropriate orbital from each of the two adjacent boron atoms.¹⁰

The placement of group IV moieties in a bridging position in pentaborane(9) derivatives appears to be kinetically controlled. The bridged derivatives are not thermodynamically stable, however, with respect to rearrangement to the corresponding 2- and 1-substituted isomers. The bridged silicon and germanium derivatives isomerize irreversibly and essentially quantitatively to the corresponding 2-substituted derivatives at room temperature in the presence of weak Lewis bases such as dimethyl or diethyl ether. These rearrangements are undoubtedly intramolecular, and though no mechanistic studies have been undertaken, it is reasonable to assume that the Lewis base can compete effectively with the group IV substituent for one of the adjacent boron orbitals to produce a short-lived activated complex, such as that shown in eq 8, which can rearrange to the far

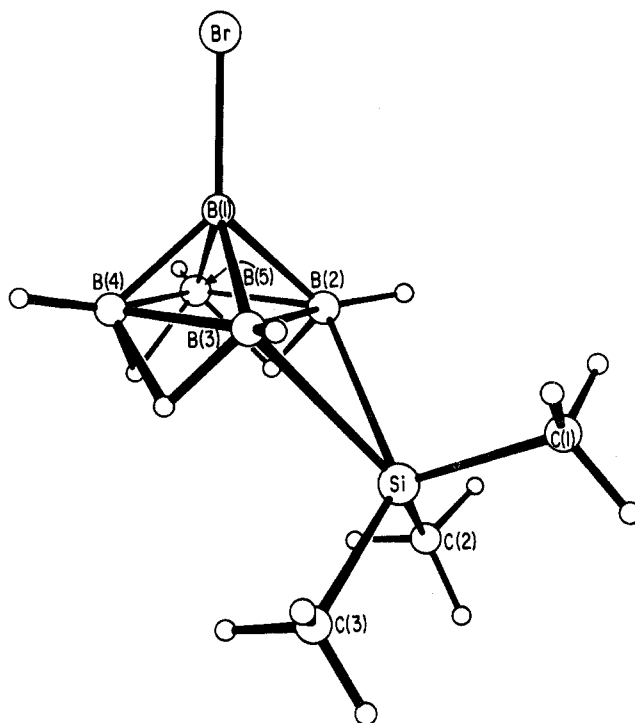
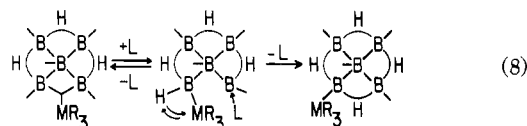


Figure 6. The molecular structure of $1-Br-\mu-[(CH_3)_3Si]B_5H_7$.



more thermodynamically stable 2 derivative with a minimum of atom motion.⁴²

Gas phase thermolysis of $\mu-(CH_3)_3SiB_5H_8$ at 80° also produces $2-(CH_3)_3SiB_5H_8$ irreversibly at a moderate rate, suggesting that unstable intermediates such as those in eq 8 are also thermally accessible. At higher temperatures ($120-150^\circ$) μ or 2 isomers of $H_3SiB_5H_8$, $(CH_3)_3SiB_5H_8$, and $(CH_3)_3GeB_5H_8$ rearrange to a mixture of the corresponding 1- and 2-substituted isomers.⁴³ These isomerizations can also be effected using moderately strong Lewis bases such as 2,6-dimethylpyridine or hexamethylenetetramine. The formation of 1-substituted derivatives is reversible, the 1 isomer predominating by a factor of 3-4 in the case of $(CH_3)_3SiB_5H_8$. Thus the apparent thermodynamic stability of the isomers of silyl and germyl derivatives of pentaborane(9) increases in the order $\mu- \ll 2- < 1-R_3MB_5H_8$. This order of stability is the opposite of that observed for $CH_3B_5H_8$, where the apparent thermodynamic stability increases in the order $1- \ll 2-CH_3B_5H_8$ and the isomerization process is not detectably reversible.¹⁴

The silicon-boron bond in silyl derivatives of B_5H_9 is susceptible to cleavage by strong hydridic reducing agents. An illustration is the reaction of $2-(CH_3)_3SiB_5H_8$ with $LiAlH_4$, which produces nearly quantitative yields of the corresponding silane, $(CH_3)_3SiH$.⁴²

Reactions at the group IV atom in B_5H_9 derivatives have not been extensively studied, but may be of considerable interest. For example, reaction of boron trichloride with μ -, 2-, and 1- $H_3SiB_5H_8$ pro-

(41) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **89**, 4249 (1967).

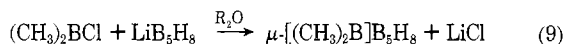
(42) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **90**, 6617 (1968).

(43) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, **10**, 1094 (1971).

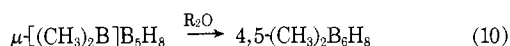
duces the corresponding μ -, 2-, and 1-(ClH₂Si)B₅H₈.^{44,45}

Group III Derivatives of Pentaborane(9)

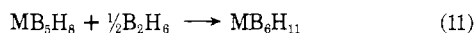
Reactions of LiB₅H₈ with (CH₃)₂BCl produce μ -dimethylborylpentaborane(9), μ -[(CH₃)₂B]B₅H₈, in good yield (eq 9).⁴⁶ The nmr data indicate that the



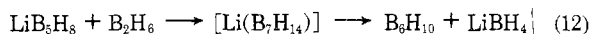
(CH₃)₂B moiety in this compound is in a bridging position. Thus the (CH₃)₂B boron may be considered to be sp² hybridized and attached to the B₅ framework *via* a three-center two-electron bond to the two adjacent basal boron atoms, as shown in Figure 7. Free rotation of the (CH₃)₂B moiety is indicated, at ambient temperature, by a single methyl resonance in the ¹H nmr spectrum. At low temperatures, however, the appearance of two equally intense methyl resonances suggests a static structure in which the (CH₃)₂B group is in a plane perpendicular to the plane of the basal boron atoms, as shown in Figure 7. In the presence of ether, μ -[(CH₃)₂B]B₅H₈ isomerizes in good yield to 4,5-(CH₃)₂B₆H₈, which is thought to have a pentagonal-pyramidal B₆H₁₀ structure (eq 10).



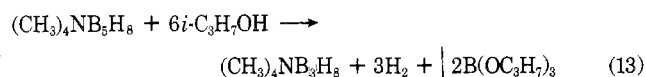
Diborane(6) adds rapidly and irreversibly to etheral solutions of LiB₅H₈ at -78° up to a mole ratio of 0.5 (eq 11).⁴⁷



Reaction of the B₆H₁₁⁻ anion with anhydrous HCl appears to be the best route to B₆H₁₂. On a much slower time scale, dimethyl ether solutions of LiB₅H₈ will absorb up to an equimolar quantity of B₂H₆ at -78°. Upon slow warming of this product mixture to room temperature, with continuous evacuation through a -196° trap, up to 30% yields of B₆H₁₀ and significant quantities of B₁₀H₁₄ are obtained. The reaction sequence is complex but the B₆H₁₀ formation can be expressed by the idealized reaction in eq 12.⁴⁸



Degradation of B₅H₈⁻ salts by isopropyl alcohol produces the corresponding B₃H₈⁻ salt in 75% yield (eq 13).³⁸ Ether solutions of alkali metal salts of the



B₅H₈⁻ anion decompose at ambient temperature in a complex fashion to produce BH₄⁻, B₃H₈⁻, B₉H₁₄⁻, and other unidentified materials.⁴⁹ Salts of the B₉H₁₄⁻ anion are also produced, in 30% yield, by the reaction of B₅H₉ with NaBH₄ or LiBH₄.⁵⁰

(44) T. C. Geisler and A. D. Norman, *Inorg. Chem.*, **9**, 2167 (1970).

(45) T. C. Geisler and A. D. Norman, *Inorg. Chem.*, **11**, 2549 (1972).

(46) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **92**, 4571 (1970).

(47) H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, **93**, 3798 (1971).

(48) R. A. Geanangel, H. D. Johnson, II, and S. G. Shore, *Inorg. Chem.*, **10**, 2363 (1971).

(49) V. T. Brice, H. D. Johnson, II, D. L. Denton, and S. G. Shore, *Inorg. Chem.*, **11**, 1135 (1972).

(50) C. G. Savory and M. G. H. Wallbridge, *Inorg. Chem.*, **10**, 419 (1971).

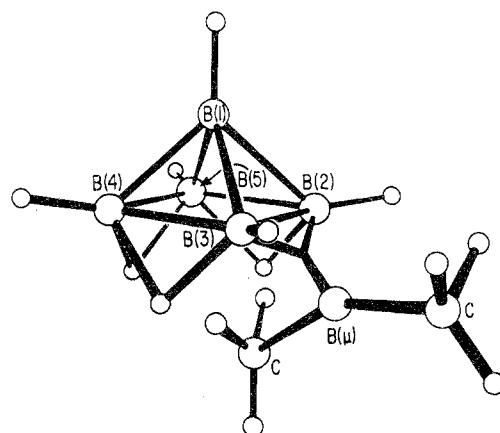


Figure 7. The proposed low temperature structure of μ -[(CH₃)₂B]B₅H₈ showing the proposed three-center two-electron bond between the (CH₃)₂B moiety and the two adjacent boron atoms.

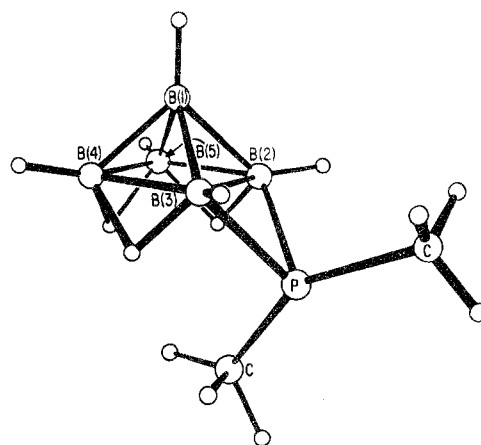


Figure 8. The proposed molecular structure of μ -[(CH₃)₂P]B₅H₈.

Group V Derivatives of Pentaborane(9)

Reaction of the B₅H₈⁻ anion with several types of phosphines at low temperatures produces another group of pentaborane(9) derivatives in which the phosphine often occupies a bridging position in the B₅ framework. With phosphines of the type R₂PCL, the derivatives μ -[(CH₃)₂P]B₅H₈, 1-[(CF₃)₂P]B₅H₈, μ -[(C₆H₅)₂P]B₅H₈, and μ -[CH₃(CF₃)P]B₅H₈-A have been prepared.^{51,52} Also, μ -[Cl(CH₃)P]B₅H₈ was prepared from CH₃PCl₂ and 2-[CF₃S(CF₃)P]B₅H₈ was prepared from (CF₃S)₂PCF₃.⁵²

In contrast to the bonding in the group III and group IV bridged derivatives, the bonding between phosphorus and the two adjacent boron atoms in the phosphine-bridged derivatives does not appear to be electron deficient. The proposed structure of μ -[(CH₃)₂P]B₅H₈, shown in Figure 8, is similar to that recently found for 5,6- μ -[(C₆H₅)₂P]B₁₀H₁₃,⁵³ in which the P-B bond distances are in good agreement with those found in H₃PBH₃ and (CH₃)₃PBH₃.

Though the μ -[CH₃(CF₃)P]B₅H₈-A isomer is preferentially formed in the low-temperature synthesis, it is unstable at ambient temperature, isomerizing irreversibly to μ -[CH₃(CF₃)P]B₅H₈-B. Spectroscopic data indicate that these two isomers are essentially identical, and it appears that they differ only in that the CH₃ and CF₃ groups are interchanged. The ab-

(51) A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).

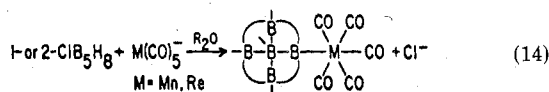
(52) I. B. Mishra and A. B. Burg, *Inorg. Chem.*, **11**, 664 (1972).

(53) L. B. Friedman and S. L. Perry, *Inorg. Chem.*, **12**, 288 (1973).

solute identities of the isomers are not yet known, nor is the driving force for the preferential formation of the less stable A isomer or the origin of the apparently large stability difference between the isomers.⁵⁴ The 2-[CF₃S(CF₃)P]B₅H₈ is also unstable at ambient temperature, isomerizing in 1 day to 1-[CF₃S(CF₃)P]B₅H₈.⁵²

Metallopentaborane(9)s

Two types of metallopentaborane(9) compounds have been prepared. The first examples were prepared by reaction of 1- or 2-ClB₅H₈ with alkali metal salts of Mn(CO)₅⁻ and Re(CO)₅⁻, producing the corresponding 2-[M(CO)₅]B₅H₈ (eq 14).⁵⁴ In these



compounds the bonding between the B₅H₈ moiety and the metal carbonyl appears to be similar to that observed in the alkyl metal carbonyls. The second type of metallopentaborane(9) was prepared by reaction of the B₅H₈⁻ anion with [(C₆H₅)₃P]₃CuCl to produce [(C₆H₅)₃P]₂CuB₅H₈. Nmr spectral studies suggest that in this compound the copper may be in a bridging position.⁵⁵

Bipentaboranes

All three isomers of the parent bipentaborane, or pentaboran(9)ylpentaborane(9) (Figure 9), have recently been isolated and characterized. The first to be isolated was 1-[1'-pentaboran(9)yl]pentaborane(9), 1,1'-(B₅H₈)₂, which was prepared by passing a B₅H₉-H₂ mixture through an electrical glow discharge.⁵⁶ The structural identity of 1,1'-(B₅H₈)₂ was indicated by its ¹¹B nmr spectrum and verified by a single-crystal X-ray investigation.⁵⁷ Compounds exhibiting similar spectroscopic properties have also been obtained from deutron bombardment⁵⁸ and gas phase radiolysis⁵⁹ of B₅H₉.

Small quantities of 1,2'-(B₅H₈)₂ and 2,2'-(B₅H₈)₂ have been isolated from commercially produced B₅H₉. These may have been produced in the original synthesis, or they may have formed very slowly from liquid B₅H₉ at ambient temperature.⁶⁰ The formation of the bipentaboranes in the original synthesis of B₅H₉ by pyrolysis of B₂H₆ appears to be quite possible in view of recent studies of the reaction of B₅H₉ with B₂H₆ at elevated temperatures in which 1,1'-(B₅H₈)₂ and 2,2'-(B₅H₈)₂ were isolated.⁶¹ There is

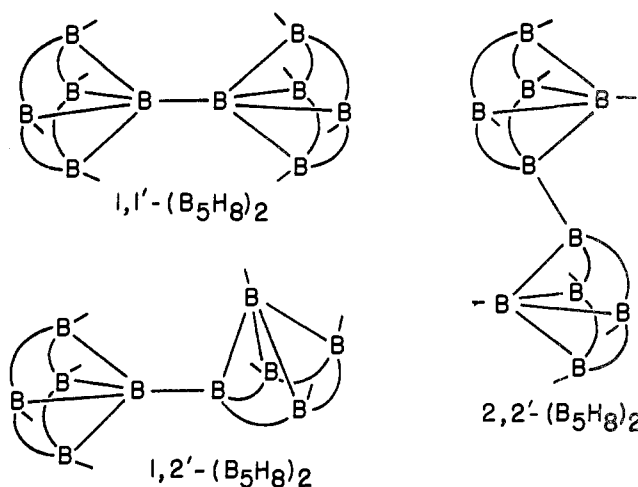


Figure 9. The three known isomers of bipentaborane(9) or pentaboran(9)ylpentaborane(9) (B₅H₈)₂.

some evidence that tri- and tetrapentaboranes may exist.²⁸

In spite of the recent rapid growth of knowledge concerning the chemistry of B₅H₉, the surface of understanding has only been scratched. Detailed studies are needed in order to predict and understand the mechanisms of pentaborane(9) reactions. For example, virtually nothing is known about the mechanism of conversion of B₅H₉ to the B₉H₁₄⁻ anion, nor are rational methods known for coupling pentaborane molecules to produce bi- and poly-pentaboranes. As yet there is no known route to selectively boron-labeled B₅H₉ derivatives, which are necessary for detailed mechanistic studies of internal rearrangements. The use of B₅H₉ to prepare stable metalloboranes is in its infancy, and attempts to prepare a closo-B₅ anion have thus far been unsuccessful.

Summary

Much of the chemistry of B₅H₉ can be summarized as follows. Alkyl and halo substitution and olefin addition occur exclusively at the apex (1-) position on B₅H₉ in the presence of strong Lewis acids under conditions similar to those used for aromatic electrophilic substitution. Nucleophilic conditions generally favor substitution at the 2 position, but in these cases side reactions often reduce yields. Strong Lewis bases form adducts, often unstable, having the general formula B₅H₉·2L. Deprotonation of B₅H₉ (and its derivatives) is effected by alkali metal hydrides and alkyl lithium reagents. The chemistry of the resulting B₅H₈⁻ anion indicates that the proton is most likely removed from a bridging hydrogen position. The B₅H₈⁻ anion reacts with various group III, IV, and V reagents to form compounds having the group III, IV, or V atom in a bridging position between two adjacent boron atoms in the base of the B₅H₉ framework.

(61) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, 9, 2161 (1970).

(54) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 7, 1041 (1968).

(55) V. T. Brice and S. G. Shore, *Chem. Commun.*, 1312 (1970).

(56) R. N. Grimes and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 48, 496 (1962).

(57) R. Grimes, E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 47, 996 (1961).

(58) L. H. Hall and W. S. Koski, *J. Amer. Chem. Soc.*, 84, 4205 (1962).

(59) J. W. Pinson and G. Lin, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR-98.

(60) D. F. Gaines, T. V. Iorns, and E. C. Clevenger, *Inorg. Chem.*, 10, 1096 (1971).