Structural Characterization of 1-Bromo-μ-trimethylsilylpentaborane(9), Containing a Localized Three-Center, Two-Electron Silyl-Bridged Boron–Boron Bond

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Abstract: An X-ray crystallographic investigation of the Gaines–Iorns molecular complex, 1-Br-μ-(CH$_3$)$_3$SiB$_5$H$_7$, has unambiguously substantiated the unprecedented structural feature of a bridging R$_3$Si group whose coordination can be described in terms of a three-center two-electron bond. Its molecular configuration, which consists of a square-pyramidal framework of boron atoms, is found to be closely similar to that of the parent B$_5$H$_9$ molecule, from which it formally can be derived by the replacement of one of the four bridging hydrogen atoms linking the four basal boron atoms with the bridging trimethylsilyl ligand and by the replacement of the terminal hydrogen atom bonded to the apical boron atom with a bromine atom. Concrete evidence that the linkage of this pentacoordinated silicon atom to the two basal boron atoms may be attributed to a localized three-center electron-pair bond involving the interaction of a quasitetrahedral silicon orbital with an appropriate orbital from each boron atom is provided by the molecular dimensions, which reveal an approximate tetrahedral disposition of the three methyl groups about the silicon atom with its fourth tetrahedral bond directed toward the midpoint of the two basal boron atoms. This interpretation is also consistent with the symmetrical bridging position of the silicon atom being 2.32 (2) Å from each of the two crystallographically equivalent boron atoms and with a B–Si–B angle of only 42.6 (8)°. Four 1-Br-μ-(CH$_3$)$_3$SiB$_5$H$_7$ molecules crystallize in an orthorhombic unit cell of lattice parameters a = 10.613 (7), b = 9.364 (9), c = 10.385 (10) Å and of space group symmetry *Pmcn*, with each molecule possessing crystallographic site symmetry C_s-*m*. All hydrogen atoms, located from successive Fourier difference maps, were included as fixed-atom contributions in an anisotropic–isotropic least-squares refinement which produced discrepancy factors of R_1 = 3.6 and R_2 = 3.8% for the 200 independent nonzero diffracted beams collected with a diffractometer.

Although the existence of multicenter two-electron bonds is now well documented for carbon in bridging alkyl (and phenyl) systems,[2–6] prior to the important work of Gaines and Iorns[7–9] there were no reported analogs containing the group IVa congeners (*i.e.*, Si, Ge, Sn, and Pb) which exhibited similar delocalized bonding. Furthermore, covalent compounds with bridging alkyl (or phenyl) ligands linked to either two or three atoms have been definitely substantiated for only a few main-group elements—*viz.*, lithium,[3,10–13] beryllium,[14–16] magnesium,[15,17,18] and aluminum.[5,12,15,19–23]

We wish to report the characterization by single-crystal X-ray diffraction of 1-Br-μ-(CH$_3$)$_3$SiB$_5$H$_7$ which provides unambiguous evidence that a methyl-sub-

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[1] This paper is based in part on a dissertation submitted by J. C. C. to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, 1971.

[2] (a) R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957); (b) R. E. Rundle, *Rec. Chem. Progr.*, **23**, 195 (1962); (c) R. E. Rundle, *Surv. Progr. Chem.*, 81 (1963).

[3] (a) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965); (b) *Accounts Chem. Res.*, **1**, 23 (1968).

[4] It should be recognized that the bonding description given by Vranka and Amma[5a] in MO language for both bridge bonds in Al$_2$(CH$_3$)$_6$ is mathematically equivalent to the localized three-center electron-pair concept commonly employed for each bridge bond. The MO picture involves the placement of four electrons in the two bonding four-center (*i.e.*, extending over four atomic nuclei) orbital combinations, formed from an sp^3-like orbital on each carbon atom and two orbitals on each Al atom, of representations a$_g$ and b$_{3u}$ under assumed D_{2h}-2/*m*2/*m*2/*m* symmetry.

[5] (a) R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **89**, 3121 (1967); (b) P. H Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

[6] K. H. Levison and P. G. Perkins, *Theor. Chim. Acta*, **17**, 15 (1970); K. H. Levinson and P. G. Perkins, *Discuss. Faraday Soc.*, No. 47, 183 (1969).

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

[8] D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 4249 (1967).

[9] D. F. Gaines and T. V. Iorns, *ibid.*, **90**, 6617 (1968).

[10] E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964); E. Weiss and G. Hencken, *ibid.*, **21**, 265 (1970).

[11] H. Dietrich, *Acta Crystallogr.*, **16**, 681 (1963).

[12] R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).

[13] Since the submission of this manuscript, an X-ray diffractometric investigation of the novel LiB(CH$_3$)$_4$ compound [D. Groves, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, **93**, 1553 (1971)] has revealed that the solid-state structure contains both "bent" Li–CH$_3$–B and "linear" Li–CH$_3$–B groupings. The latter methyl-bridged carbon atom approximately conforms to an unprecedented trigonal-bipyramidal-like configuration.

[14] A. I. Snow and R. E. Rundle, *Acta Crystallogr.*, **4**, 348 (1951).

[15] J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 2538 (1969).

[16] A recent X-ray diffraction examination (J. Howatson and B. Morosin, Abstracts of Papers, National Meeting of the American Crystallographic Association, University of South Carolina, Columbia, S. C., Jan 21–Feb 4, 1971) has shown the existence of dimeric methyl-(propynyl)beryllium–trimethylamine, [CH$_3$C$_2$Be(CH$_3$)N(CH$_3$)$_3$]$_2$, containing two Be atoms symmetrically linked by two propynyl ligands such that the sp-like orbitals of the bridging triple-bonded carbon atoms interact with the appropriate Be orbitals *via* localized three-center electron-pair bonds.

[17] E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964).

[18] E. Weiss, *ibid.*, **4**, 101 (1965).

[19] V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc*, **91**, 2544 (1969); **90**, 3269 (1968).

[20] J. F. Malone and W. S. McDonald, *Chem. Commun.*, 444 (1967).

[21] J. F. Malone and W. S. McDonald, *ibid.*, 280 (1970).

[22] J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick, and J. P. Oliver, *J. Amer. Chem. Soc.*, **93**, 1035 (1971).

[23] A recent proposal was made [S. K. Byram, J. K. Fawcett, S. C. Nyburg, and R. J. O'Brien, *Chem. Commun.*, 16, (1970)] that one of the three hydrogen atoms of each bridging methyl group in Al$_2$(CH$_3$)$_6$ is directly involved in bonding to an aluminum atom. This claim, based on further efforts to refine the hydrogen positions (of large uncertainties) from the X-ray photographic data recollected by Vranka and Amma,[5a] has been rejected [F. A. Cotton, *Inorg. Chem.*, **9**, 2804 (1970)] as not being a viable structural alternative to the originally determined geometry[5] of Al$_2$(CH$_3$)$_6$, by which each of the two methyl carbon atoms is bonded equally to the two aluminum atoms by means of a localized three-center two-electron bond involving a quasitetrahedral orbital on the carbon atoms. It is noteworthy that the reported ^{27}Al nqr spectrum

stituted silyl group is linked (in place of a bridging hydrogen atom) to two basal boron atoms of a pentaborane(9) framework by means of a three-center electron-pair bond involving a quasitetrahedral orbital on the silicon atom. In 1967 Gaines and Iorns[7] found that pentaborane(9) would react with alkyllithium reagents in ethereal solvents at low temperatures to form the solvated lithium salt of the $B_5H_8^-$ anion. Upon treatment with deuterium chloride they obtained exclusively μ-DB_5H_8 in which the deuterium was established from a ^1H nmr spectrum to be in a basal bridging position of the pentaborane(9) square pyramid. Further reactions by Gaines and Iorns[8,9] of the lithium salt of the octahydropentaborate(-1) anion with a number of group IVa compounds yielded the unique pentaborane(9) derivatives μ-$R_3M_{IV}B_5H_8$ (M_{IV} = Si or Ge with R = H, CH_3, C_2H_5; M_{IV} = Sn or Pb with R = CH_3). On the basis of ^{11}B and ^1H nmr spectra, Gaines and Iorns[8,9] proposed that the group IVa substituent is likewise located in a bridging position between two of the basal boron atoms.[24]

These Gaines–Iorns complexes are novel in at least two aspects. In addition to being unprecedented with regard to the coordination of any main group IVa element M_{IV} (other than carbon) as a bridging R_3M_{IV} ligand *via* a localized three-center two-electron bond,[25–28] there are no previously known examples[13,29] of boron complexes containing any bridging R_3M_{IV} ligands (where M_{IV} here includes carbon as well as its congener elements).[30] An added incentive for a structural investigation of a representative member of this series of complexes was the opportunity not only to determine the geometry about the silicon atom and thereby to provide direct evidence for the three-center electron-pair B–$Si(CH_3)_3$–B bonding, but also to allow a detailed examination of the effect of the substitution of a bridging $(CH_3)_3M_{IV}$ ligand in place of a hydrogen atom on the pentaborane(9) architecture. Since at room temperature μ-$H_3SiB_5H_8$ is a liquid[9] and μ-$(CH_3)_3SiB_5H_8$ a low-melting solid (mp 16–17°),[9] the crystallographic determination of the molecular configuration of these μ-$R_3M_{IV}B_5H_8$ complexes was most conveniently accomplished by an X-ray diffraction analysis of the relatively nonvolatile bromo-substituted pentaborane(9) analog 1-Br-μ-$(CH_3)_3SiB_5H_7$, prepared by the direct bromination of μ-$(CH_3)_3SiB_5H_8$.[31]

Experimental Section

X-Ray Data Collection. Suitable single crystals of the highly moisture-sensitive 1-Br-μ-$(CH_3)_3SiB_5H_7$ compound were obtained by slow sublimation (*i.e.*, over a week's time for the transfer and growth of a crystal within a given glass capillary) under vacuum conditions in thin-walled Lindemann glass capillaries (of diameter 0.5 mm) which were maintained at ice-bath temperatures. This technique was performed by the attachment of a given glass capillary to a vacuum line (containing a sample of the compound) *via* a soft-glass joint. Upon the obtaining of a suitable crystal, each capillary was filled with argon and then hermetically sealed. Zero and higher layer Weissenberg photographs displayed orthorhombic Laue symmetry D_{2h}-$2/m2/m2/m$.

For the collection of intensity data, a crystal which had approximately cubic dimensions of edge 0.19 × 0.16 × 0.17 mm was placed on a General Electric full-circle Datex-controlled diffractometer. After a preliminary alignment by optical and X-ray techniques[32] and attempted data collection, it became obvious that the crystal was not stationed in the capillary sufficiently well enough over the necessary period of time to allow completely automatic collection of the data. Hence, each of the 200 nonzero diffracted beams from one independent octant of the orthorhombic reciprocal lattice of intensities was manually optimized in χ, ϕ, 2θ before utilization of the θ–2θ scan technique. Miller indices of the diffracted beams were verified by use of the Weissenberg photographs. New angle settings were calculated[32] six times during the course of the entire data collection, with the results yielding the cell parameters and estimated standard deviations given below. Intensities were measured with zirconium-filtered Mo Kα radiation at a takeoff angle of 2.0°. A symmetric 2θ range of 2.0° was scanned for each reflection at a rate of 2.0°/min with stationary-counter–stationary-crystal background counts for 20 sec being recorded on each side of the scan. The pulse-height analyzer was adjusted to accept

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of $Al_2(CH_3)_6$ has been cited [M. J. S. Dewar and D. B. Patterson, *Chem. Commun.*, 544 (1970); M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Amer. Chem. Soc.*, **93**, 1030 (1971)] as evidence for ruling out any Al–H bonded structure. Direct crystallographic evidence that the geometry of a bridging methyl group between two aluminum atoms conforms to the original Lewis–Rundle model (without any metal–hydrogen interaction) is provided by the X-ray diffractometric study of Magnuson and Stucky[19] on $Al_2(CH_3)_5N(C_6H_5)_2$, which is formally derived from $Al_2(CH_3)_6$ by the substitution of a bridging diphenylamino group in place of one of the two bridging CH_3 groups. In this well-performed structural analysis the least-squares-refined hydrogen atoms of the one bridging methyl group were unequivocally shown to be not only nonbonding to the aluminum atoms but also oriented such that the localized threefold axis of the methyl group (which defines the direction of the fourth sp^3-like carbon orbital) expectedly bisects (within experimental error) the Al–Al bond. The structural studies of the tricyclopropylaluminum dimer[22] and 1-Br-μ-$(CH_3)_3SiB_5H_7$ (reported here) furnish additional strong support for the Lewis–Rundle structure for $Al_2(CH_3)_6$.

(24) The constitution of μ-$(CH_3)_3SiB_5H_8$ was established by Gaines and Iorns[6,9] not only from their interpretation of the ^{11}B and ^1H nmr spectra but also from mass spectral data, from an analysis of the B_5H_8 portion of the molecule based on hydrolysis followed by measurement of the hydrolytic hydrogen and titration of the generated boric acid, and from the reaction of μ-$(CH_3)_3SiB_5H_8$ with $LiAlH_4$ to give $(CH_3)_3SiH$ (in 90% yield), which shows that the $(CH_3)_3Si$ fragment remains intact. Their same structural assignment for other analogs was made primarily from the close similarities of the ^{11}B and ^1H nmr spectra.

(25) Recent crystallographic studies[26,27] have shown the existence of pentacoordinated silicon complexes in which the geometry of coordination about the central silicon atom was found in each case to be trigonal bipyramidal or a distortion thereof. It should be noted that such a ligand arrangement about the pentacoordinated silicon atom (as well as the mode of bonding of the silicon to the five ligands) is entirely different from that shown from our crystallographic study to exist for the pentacoordinated silicon atom in μ-$R_3SiB_5H_8$ complexes.

(26) (a) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 90, 4026 (1968); (b) F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, 90, 5102 (1968); (c) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, 90, 6973 (1968).

(27) R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *ibid.*, 89, 5157 (1967).

(28) Multicenter bonding involving sp^3 hybridized orbitals (and thereby excluding the use of valence d orbitals) on the central M_{IV} atom may be invoked as a possible qualitative bonding scheme to rationalize the geometries of six-coordinated M_{IV} complexes. This type of valence-bond model was suggested [E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967)] for the six-coordinated tin atom in dimethyltin bis(8-hydroxyquinolinate), $Sn(C_9H_6NO)_2(CH_3)_2$, where the H_3C–Sn–CH_3 bond angle is 110.7 (8)°. In the molecular complex two of the sp^3 hybrid orbitals on the tin atom are presumed to participate in normal covalent bonding with the two methyl groups, while each of the other two sp^3-like tin orbitals is then involved in the formation of three-center two-electron bonds with the oxygen and nitrogen atoms of a chelating oxinate ligand.

(29) The synthesis of a trimethylsilyldecaborane(14) derivative, $(CH_3)_3SiB_{10}H_{13}$, has been recently reported [E. Amberger and P. Leidl, *J. Organometal. Chem.*, 18, 345 (1969)] from the reactions of $(CH_3)_3SiCl$ with alkali metal salts of the tridecahydrodecaborate(-1) anion, $MB_{10}H_{13}$ (where M = Li, Na, K), but the resulting position of the $(CH_3)_3Si$ group has not as yet been determined.

(30) Attempts by Gaines and Iorns[9] to replace a basal bridging hydrogen atom in the pentaborane(9) molecule with R_3C ligands (including the one with R = CH_3) by analogous reactions of $Li^+B_5H_8^-$ with various alkyl halide reagents have been unsuccessful to date.

(31) The position of substitution of the bromine atom in this complex and in the analogously produced 1-Br-μ-$(CH_3)_3GeB_5H_7$ molecule was correctly demonstrated by Gaines and Iorns[8,9] from their observation that the upfield doublet in the ^{11}B nmr spectra collapses to a singlet, indicating that the bromine has replaced the terminal hydrogen atom attached to B(1), while the triplet-like grouping at low field remains unchanged indicating that the remaining part of the molecule is left intact.

(32) ANGSET, a local modification of "Orientation and Angles Setting Generation Program," Program B-101, Argonne National Laboratory, 1965.

approximately 90% of the diffracted intensity. A standard reflection sampled at intervals of every 20 reflections revealed no indications of either crystal decay or electronic instability. The room temperature during the course of the entire data collection was maintained close to 68°F in order to minimize crystal movement in the glass capillary.

The data were reduced[33] in the usual manner, with the standard deviation of each corrected intensity estimated from the formula $\sigma(I) = [S + Bt^2 + EI^2]^{1/2}$, where S is the total integrated scan count, B is the mean background count, and t is the ratio of the scan to background count times. The integrated intensity, I, was taken as $S - Bt$, while the constant E was assigned a value of 0.001. The intensities were corrected for Lorentz and polarization effects and then converted to structure factor amplitudes $|F_o| = (I/Lp)^{1/2}$, with $\sigma(F_o)$ taken as $\sigma(I)/(2F_oLp)$. No absorption corrections of the intensities were made, since with the linear absorption coefficient having a value of μ = 28.8 cm^{-1} for Mo Kα radiation, the calculated transmission coefficients[34] for the crystal ranged from only 0.60 to 0.66. Effects of extinction were also ignored.

Crystal Data. The orthorhombic lattice parameters and their estimated errors are a = 10.613 (7), b = 9.364 (9), and c = 10.385 (10) Å. The cell volume is 1032.06 Å^3, and the total number of electrons in the unit cell, $F(000)$, is 432. Systematic absences of $\{hk0\}$ for $h + k$ odd and of $\{h0l\}$ for l odd define the probable space group as either $P2_1cn$ [nonstandard setting of $Pna2_1$ (C_{2v}^9, no. 33)] or $Pmcn$ [nonstandard setting of $Pnma$ (D_{2h}^{16}, no. 62)]. The subsequent structural analysis showed that the latter centrosymmetric space group, in which each molecule lies on a mirror plane, is the correct choice. The assumption of four molecules per cell yields a calculated density of 1.26 g/cm^3; this value is in reasonable accord with the calculated value of 0.83 g/cm^3 obtained by Friedman and Lipscomb[35] in their structural determination of 2,3-dimethylpentaborane(9), 2,3-$(CH_3)_2B_5H_7$, after allowance is made for an expected increase in density due to the presence of a bromine atom substituted in place of a hydrogen atom.

Determination and Refinement of the Structure. Initial coordinates for one bromine and one silicon atom were obtained from an interpretation of a computed three-dimensional Patterson function.[36] Since for $Pmcn$ the positional parameters of these two atoms lie on a mirror plane, this centrosymmetric space group was then utilized during the entire structural determination; its use was verified by the successful least-squares refinement of the crystal structure. Since each of the four molecules of 1-Br-μ-$(CH_3)_3SiB_5H_7$ per cell is crystallographically required to lie on a mirror plane, the independent unit is comprised of one Br atom, one B atom, one Si atom, one C atom, one bridging boron-attached H atom, and one carbon-attached H atom, each occupying a fourfold set of special positions (4c) of crystallographic site symmetry C_s-m, and two B atoms, one bridging and two terminal boron-attached H atoms, one C atom, and four carbon-attached H atoms each occupying an eightfold set of general positions (8d). These positions are as follows: 8d, $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 + y, {}^1/_2 - z;\ {}^1/_2 - x, y, z;\ x, {}^1/_2 - y, {}^1/_2 + z)$; 4c, $\pm(x, y, z;\ {}^1/_4, {}^1/_2 - y, {}^1/_2 + z)$.

The five remaining independent nonhydrogen atoms (*viz.*, the two carbon and three boron atoms) were located from successive Fourier maps, the initial one being phased on the bromine and silicon atoms. However, after the resulting positional parameters were subjected to an isotropic least-squares refinement[37] which converged at R_1 = 11.3%,[38a] the calculated boron cage distances were inconsistent with the expected values. Hence, an anisotropic least-squares refinement of only the bromine and silicon atoms was carried out, after which new initial coordinates for the carbon and boron atoms were obtained from a calculated Fourier difference synthesis. Several cycles of least squares with anisotropic thermal parameters utilized for the bromine and silicon atoms and isotropic ones for the carbon and boron atoms converged at R_1 = 6.5 and R_2 = 7.5%,[38b] to give positional parameters which conformed to much more reasonable distances within the molecule. A Fourier difference map yielded peaks corresponding to the expected positions of all the hydrogen atoms along with definite evidence that the hydrogen atoms of the methyl group located on the mirror plane were twofold disordered about its Si–C axis. At this stage, it was decided to refine further the nonhydrogen atoms in the presence of the hydrogen atoms whose positions were idealized by by the use of the program MIRAGE[39] in the following manner. The calculated coordinates for each terminal boron-attached hydrogen atom were based on an assumed B–H bond length of 1.0 Å together with an assumed B(apical)–B(basal)–H angle of 130°, with the hydrogen atom restricted to the particular plane defined by the apical boron atom, its coordinated basal boron atom, and the

Table I. Atomic Parameters for 1-Br-μ-$(CH_3)_3SiB_5H_7$[a] with Hydrogen Atoms Based on Positions from Final Fourier Difference Map

Position	Atom	x	y	z	B, Å^2
4c	Br	$^1/_4$	0.0142 (3)	0.2047 (2)	*b*
4c	Si	$^1/_4$	0.5609 (5)	0.3114 (6)	*b*
4c	B(1)	$^1/_4$	0.1771 (21)	0.3123 (22)	2.8 (6)
8d	B(3)	0.1705 (15)	0.3296 (15)	0.3091 (15)	4.5 (4)
8d	B(4)	0.1657 (18)	0.2109 (17)	0.4297 (17)	5.9 (5)
4c	C(1)	$^1/_4$	0.6106 (24)	0.1494 (20)	7.2 (7)
8d	C(3)	0.1102 (14)	0.6372 (14)	0.3868 (13)	5.5 (4)
8d	H(3)	0.085[d]	0.350	0.267	4.0[d]
8d	H(4)	0.116	0.154	0.463	4.0
8d	H(3–4)	0.129	0.354	0.411	4.0
4c	H(4–5)	$^1/_4$	0.255	0.477	4.0
4c	CH(1–1)[c]	$^1/_4$	0.690	0.138	4.0
4c	CH(1–1′)[c]	$^1/_4$	0.547	0.108	4.0
8d	CH(1–2)[c]	0.194	0.583	0.116	4.0
8d	CH(1–2′)[c]	0.306	0.654	0.131	4.0
8d	CH(3–1)	0.090	0.670	0.340	4.0
8d	CH(3–2)	0.110	0.611	0.444	4.0
8d	CH(3–3)	0.040	0.612	0.360	4.0

[a] Standard deviations of last significant figures are given in parentheses. [b] Anisotropic temperature factors of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used for the bromine and silicon atoms. For these atoms in special positions (4c) on mirror planes, the thermal coefficients B_{12} and B_{13} are required by symmetry to be zero. The resulting thermal coefficients (×10^4), with esd's of the last significant figure given in parentheses, are as follows.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	189 (4)	90 (4)	99 (3)	0	0	−31 (4)
Si	104 (9)	97 (10)	72 (7)	0	0	2 (7)

[c] The crystal-disorder model utilized for the three hydrogen atoms CH(1–1), CH(1–2), and CH(1–3) (with CH(1–3) related to CH(1–2) by the mirror plane located at $a/4$ along [100]) assumes a statistical distribution as two sets of triangular arrays of half-weighted atoms with the two orientations related to each other by a localized twofold rotation axis along the Si–C direction. The coordinates of the CH(n) and CH(n') atoms are related to each other by the twofold rotation. Of the resulting hexagon of half-weighted atoms, the two peaks on the mirror plane corresponding to CH(1–1) and CH(1–1′) were resolved on the Fourier difference map, whereas the two peaks on a given side of the mirror plane were amalgamated into one elongated peak. Hence, the program MIRAGE[39] was utilized to obtain idealized coordinates for CH(1–2) and CH(1–2′) by a sixfold rotation of the known coordinates first of CH(1–1) and then of CH(1–1′). The closeness of the corresponding positional parameters within the third decimal place to each other confirmed our assumed crystal-disorder model; the listed parameters are the average values. [d] The positional and thermal parameters of the hydrogen atoms were not varied in the course of refinement. A value of 4.0 Å^2 was arbitrarily assumed for each isotropic temperature factor.

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(33) E. F. Epstein, Ph.D. Thesis, University of Wisconsin, Madison, Jan 1969.

(34) J. F. Blount, DEAR, an absorption correction program based on the methods of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957).

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

(36) All Patterson and Fourier syntheses were carried out with the Blount program: J. F. Blount, Ph.D. Thesis, University of Wisconsin, Madison, 1965.

(37) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(38) (a) $R_1 = [\Sigma||F_o| - |F_c|/\Sigma|F_o|]100$; (b) $R_2 = [\Sigma w_i||F_o| - |F_o||^2/\Sigma w_i|F_o|^2]^{1/2}100$; (c) the standard deviation of an observation of unit weight, defined as $[\Sigma w_i||F_o| - |F_c||^2/(m - n)]^{1/2}$, where m is the number of observations and n the number of parameters fitted to the data set.

(39) J. C. Calabrese, "MIRAGE," Ph.D. Thesis, University of Wisconsin, Madison, 1971.

Table II

A. Bond Lengths, Å[a]			
B(1)–Br	1.96 (2)	B(3)–H(3)	1.04
B(3)–Si	2.32 (2)	B(4)–H(4)	0.84
B(2)–B(3)	1.69 (3)	B(3)–H(3–4)	1.26
B(3)–B(4)	1.77 (2)	B(4)–H(3–4)	1.41
B(4)–B(5)	1.78 (4)	B(4)–H(4–5)	1.12
B(1)–B(3)	1.66 (2)	C(1)–CH(1–1)	0.75
B(1)–B(4)	1.64 (2)	C(1)–CH(1–2)	0.79
Si–C(1)	1.90 (2)	C(1)–CH(1–1′)	0.75
Si–C(3)	1.86 (1)	C(1)–CH(1–2′)	0.79
		C(3)–CH(3–1)	0.65
		C(3)–CH(3–2)	0.70
		C(3)–CH(3–3)	0.84
B. Bond Angles, Deg[a]			
B(2)–Si–B(3)	42.6 (8)	B(5)–B(4)–H(4)	129
B(2)–B(3)–B(4)	91.6 (8)	B(3)–B(4)–H(4)	140
B(3)–B(4)–B(5)	88.4 (8)	B(3)–H(3–4)–B(4)	83
B(2)–B(1)–B(3)	61.1 (12)	B(4)–H(4–5)–B(5)	106
B(4)–B(1)–B(5)	66.0 (16)	B(2)–B(3)–H(3–4)	110
B(3)–B(1)–B(4)	64.8 (10)	B(5)–B(4)–H(3–4)	106
B(3)–B(1)–B(5)	97.3 (13)	B(3)–B(4)–H(4–5)	97
B(1)–B(3)–B(2)	59.5 (6)	B(1)–B(3)–H(3–4)	108
B(1)–B(3)–B(4)	57.0 (9)	B(1)–B(4)–H(3–4)	102
B(1)–B(4)–B(3)	58.2 (10)	B(1)–B(4)–H(4–5)	91
B(1)–B(4)–B(5)	57.0 (8)	B(3)–B(4)–H(3–4)	45
Br–B(1)–B(3)	131.0 (13)	B(4)–B(3)–H(3–4)	52
Br–B(1)–B(4)	131.5 (12)	B(4)–B(5)–H(4–5)	37
B(1)–B(3)–Si	128.1 (9)	H(3)–B(3)–H(3–4)	95
B(4)–B(3)–Si	125.9 (10)	H(4)–B(4)–H(3–4)	120
B(2)–B(3)–Si	68.7 (4)	H(4)–B(4)–H(4–5)	122
B(3)–Si–C(1)	102.4 (8)	Si–C(1)–CH(1–1)	114
B(3)–Si–C(3)	94.2 (6)	Si–C(1)–CH(1–2)	114
M(B2–B3)–Si–C(1)	101.9	Si–C(3)–CH(3–1)	94
M(B2–B3)–Si–C(3)	111.6	Si–C(3)–CH(3–2)	107
C(1)–Si–C(3)	110.6 (6)	Si–C(3)–CH(3–3)	116
C(2)–Si–C(3)	106.1 (9)	CH(1–1)–C(1)–CH(1–2)	105
B(1)–B(3)–H(3)	128	CH(1–2)–C(1)–CH(1–3)	105
B(1)–B(4)–H(4)	126	CH(3–1)–C(3)–CH(3–2)	159
B(2)–B(3)–H(3)	150	CH(3–1)–C(3)–CH(3–3)	63
B(4)–B(3)–H(3)	117	CH(3–2)–C(3)–CH(3–3)	104
C. External Dihedral Angles[b]			
B(1)B(2)B(3)–B(3)B(2)Si	182.2 (15)		
B(1)B(3)B(4)–B(4)B(3)H(3–4)	194		
B(1)B(4)B(5)–B(5)B(4)H(4–5)	204		

[a] Standard deviations of last significant figures are given in parentheses. [b] See ref 51.

diagonal basal boron atom of the boron square pyramid. Each bridging hydrogen atom was positioned at a distance of 1.3 Å from its two coordinated boron atoms such that the external dihedral angle between the plane containing the hydrogen and its two basal boron atoms and the plane containing the apical boron and two basal boron atoms was 200°. These arbitrarily assumed conditions for the calculation of the idealized hydrogen positions were chosen from considerations of the corresponding distances and angles obtained from the X-ray diffraction investigation[35] of $(CH_3)_2B_5H_7$ and from the X-ray diffraction[40] and microwave[41] studies of B_5H_9. The methyl hydrogen atoms were placed in idealized positions which conformed to a regular tetrahedral geometry about the carbon atoms, with the C–H distances set at 1.0 Å. The disordered model utilized for three hydrogen atoms linked to the methyl carbon atom lying on the mirror plane assumed that the triangular-arranged hydrogen atoms are randomly oriented about the Si–C bond axis in one of two positions (with one hydrogen atom in each position lying on the mirror plane) such as to produce a localized twofold axis along the Si–C direction for the average structure. The second independent CH_3 group was oriented about its Si–C bond direction to give the closest agreement to the hydrogen coordinates obtained from the Fourier difference map. After one cycle of least-squares refinement in which the nine hydrogen atoms of the asymmetric unit were included as fixed-atom contributions, new idealized hydrogen coordinates were calculated[39] from the shifted positions of the nonhydrogen atoms; computation of a second least-squares cycle resulted in convergence with R_1 = 4.0 and R_2 = 4.2%. It is noteworthy that the estimated standard deviations of the determined atomic positions (as well as those of the calculated distances and bond angles) for this refinement model decreased by nearly a factor of 2 from the corresponding values obtained from the previous refinement of only the nonhydrogen atoms, even with insignificant changes in atomic positions for the two refinements. New coordinates for the hydrogen atoms obtained from another Fourier difference map were then included as fixed-atom contributions to a final requirement of the nonhydrogen atoms. This refinement, which contained the twofold disordered model[42] for the one CH_3 group, converged in two cycles to give R_1 = 3.6 and R_2 = 3.8% with a goodness-of-fit parameter[38c] of 1.46. Comparison of the nonhydrogen atomic coordinates from this last refinement with those from the previous refinement showed statistically nonsignificant changes with ten differences in corresponding coordinates less than 1σ, two less than 2σ, and the largest 2.5σ. Agreement of the corresponding positional parameters of the hydrogen atoms obtained from the last three Fourier difference maps was also remarkably good. It is presumed that the much sharper peaks found on these maps for the hydrogen atoms attached to the boron cage compared with those for the methyl hydrogen atoms are partly a

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

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

(42) The validity of this model in better representing the disposition of electron density of the one methyl group (as also indicated from the final Fourier difference map) is suggested by the fact that an analogous refinement without the assumed twofold disorder of the methyl hydrogen atoms yielded higher R_1 and R_2 values of 3.9 and 4.0%, respectively.

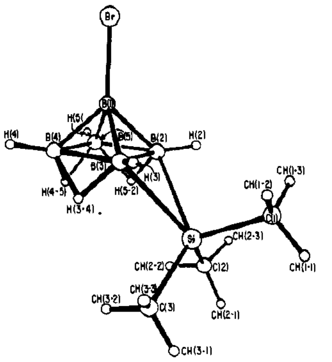

Figure 1. Geometry of the 1-Br-μ-$(CH_3)_3SiB_5H_7$ molecule of crystallographic site symmetry C_s-m.

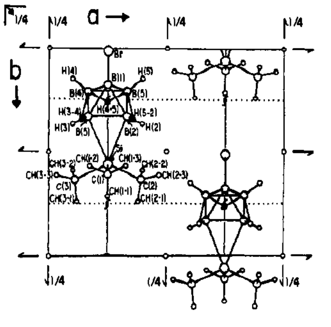

Figure 2. [001] projection from $z = 0$ to $z = {}^1/_2$ of the orthorhombic unit cell of symmetry *Pmcn* showing two of the four 1-Br-μ-$(CH_3)_3SiB_5H_7$ molecules per cell.

consequence of some torsional motion of each methyl group about its Si–C axis.

The positional and thermal parameters from the output of the last least-squares cycle are given in Table I.[43] Distances and angles, with their estimated standard deviations computed from the full variance–covariance matrix (which included the uncertainties in the lattice parameters)[44] are presented in Table II.

In all refinements the scattering factors of Hanson, *et al.*,[45] were utilized for the nonhydrogen atoms and those of Stewart, *et al.*,[46] for the hydrogen atoms, along with real and imaginary anomalous dispersion corrections[47,48] for the bromine and silicon atoms. The function minimized in the refinements was $\Sigma w_i||F_o| - |F_c||^2$, where the weights w_i were alloted according to the estimated standard deviations of the observed structure factors.

Results and Discussion

The crystal structure of 1-Br-μ-$(CH_3)_3SiB_5H_7$ is composed of individual molecules with the configuration depicted in Figure 1. In substantiation of the structure proposed by Gaines and Iorns,[8,9] its overall molecular geometry may be simply viewed as a substituted derivative of the C_{4v} pentaborane(9) structure from which the apical boron-attached hydrogen atom has been replaced by a bromine atom and one of the four bridging basal hydrogen atoms has been replaced by a trimethylsilyl group. The resulting molecule is crystallographically constrained to C_s-m site symmetry with the Br, B(apical), Si, and one CH_3 group of the $(CH_3)_3Si$ fragment lying on the mirror plane.

The crystalline arrangement of the molecules in the unit cell is shown in Figure 2. The closest approaches between molecules of 2.6, 2.8, and 2.9 Å for the H···H contacts and of 3.13, 3.26, 3.28, and 3.35 Å for the Br···H contacts are equivalent to or somewhat longer than normal van der Waals distances (*viz.*, 2.4 Å for H···H intermolecular contacts and 3.15 Å for Br···H intermolecular contacts),[49] thereby signifying that the architecture of 1-Br-μ-$(CH_3)_3SiB_5H_7$ is not appreciably affected by crystal-packing forces.

The most salient and heretofore unknown stereochemical feature is, of course, the occupation of a basal bridging site of the pentaborane(9) framework by a $(CH_3)_3Si$ ligand; furthermore, the molecular dimensions strikingly illustrate that the connection of this resulting five-coordinated silicon atom to the two basal boron atoms may be ascribed to a three-center electron-pair bond involving the interaction of a quasitetrahedral silicon orbital with an appropriate orbital from each boron atom. The symmetrical bridging position of the silicon is 2.32 (2) Å from each of the two crystallographically equivalent boron atoms [*viz.*, B(2) and B(3)] with a B(2)–Si–B(3) angle of only 42.6 (8)°; in $Al_2(CH_3)_6$ the Al–CH_3(bridging) distance is of average value 2.14 (1) Å (*vs.* a shorter Al–CH_3(terminal) distance, characteristic of a normal electron-pair bond, of average value 1.97 (1) Å), while the Al–CH_3–Al angle is 74.7 (4)°.[5a,50] Direct evidence of the sp^3-like hybridization of the silicon orbitals in the 1-Br-μ-$(CH_3)_3SiB_5H_7$ molecule is revealed from the approximate tetrahedral disposition of the three methyl groups about the silicon atom as shown by the crystallographically identical C(1)–Si–C(2) and C(1)–Si–C(3) angles of 110.8 (6)° and the C(2)–Si–C(3) angle of 106.1 (9)°. With the reasonable assumption that the direction of the fourth tetrahedral-like silicon orbital is perpendicular to the plane of the methyl carbon atoms, it is found that the normal of this plane through the silicon is nearly parallel with the line defined by the midpoint of B(2) and B(3) [*i.e.*, designated as M(B2–B3)] and the Si atom—the angle between these two lines being only 6.0°. The smallness of this angle, which suggests that the silicon sp^3-like orbital lies nearly in the Si, B(2), B(3) plane, is also reflected in the fact that the plane of the three methyl carbon atoms

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(43) Calculated and observed structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(44) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(45) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(46) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(47) The values of the dispersion corrections to the atomic scattering factors for Mo Kα radiation are $\Delta f' = -0.3$, $\Delta f'' = 2.6$ for Br and $\Delta f' = 0.1$, $\Delta f'' = 0.1$ for Si.[48]

(48) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(49) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(50) Although a similar comparison of the equivalent B(2)–Si and B(3)–Si distances with a distance for a "normal" electron-pair B–Si bond would be enlightening, structural data of boron–silyl linkages are to our knowledge as yet not reported. The observed B–Si (bridging) distance of 2.32 (2) Å is larger by 0.35 Å than the value of 1.97 Å based on the sum of the accepted covalent radii for boron (0.80 Å) and silicon (1.17 Å). A rough estimate of a distance for an electron-pair B–Si (terminal) bond may be obtained from the assumption that the B–Si (terminal) distance is proportional to the ratio of the B–H (terminal) distance to B–H (bridging) distance for other boron hydrides; for B_2H_6 based on an electron diffraction study [K. Hedburg and V. Schomaker, *J. Amer. Chem. Soc.*, 73, 1482 (1951)], this ratio of 1.19 Å/1.33 Å leads to a calculated value of 2.08 Å, while for B_5H_9 based on the microwave investigation[41] this ratio of 1.22 Å/1.35 Å gives 2.10 Å. The corresponding ratio from $Al_2(CH_3)_6$ of 1.97 Å/2.14 Å[5a] produces a calculated value of 2.14 Å for the B–Si(terminal) bond.

is nearly at right angles (95.5 (8)°) to the plane containing Si, B(2), and B(3). Further strong support for the premise of a tetrahedral-like silicon atom with one orbital participating in the three-center electron-pair B–Si$(CH_3)_3$–B bond is based on the M(B2–B3)–Si–C(1) angle of 103.5° and the two identical M(B2–B3)–Si–C(2) and M(B2–B3)–Si–C(3) angles of 113.0° being near the regular tetrahedral value of 109.5°. Thus, this structural study provides concrete evidence for the existence of a three-center two-electron bond for a bridging R_3M_{IV} ligand.[23]

Of interest is that there appears to be no appreciable structural influence on the pentaborane architecture due to the substitution of a trimethylsilyl group in place of a bridging hydrogen atom. Some evidence (which is not of definite statistical significance) for a possible distortion of the boron cage from the tetragonal-pyramidal geometry possessed by B_5H_9[40,41] is given by the B(2)–B(3) distance, 1.69 (3) Å, being somewhat shorter than the B(3)–B(4) and B(4)–B(5) distances of 1.77 (2) and 1.78 (4) Å, respectively. In the B_5H_9 molecule of C_{4v} geometry the B(basal)–B(basal) distance was found to be 1.805 (14) Å from a microwave study[41] and 1.77 (2) Å from an X-ray diffraction investigation,[40] while in $(CH_3)_2B_5H_7$[35] the three independent B(basal)–B(basal) distances are 1.80 (1), 1.80 (1), and 1.82 (2) Å. The two independent B(apical)–B(basal) distances of 1.64 (2) and 1.66 (2) Å in 1-Br-μ-$(CH_3)_3SiB_5H_7$ are commensurate not only with the corresponding microwave[41] and X-ray diffraction[40] values of 1.687 (5) and 1.66 (2) Å, respectively, found for B_5H_9 but also with the corresponding X-ray diffraction values[35] of 1.66 (1) and 1.67 (1) Å determined for $(CH_3)_2B_5H_7$.

The closeness of the silicon atom to being in the plane containing the apical boron and two silicon-coordinated basal boron atoms is revealed from the external dihedral angle[51] between the B(1)B(2)B(3) plane and the B(3)B(2)Si plane being 182.2°. The external dihedral angles of 194° for the B(1)B(3)B(4)–B(4)B(3)H(3–4) planes and of 204° for the B(1)B(4)B(5)–B(5)B(4)H(4–5) planes compare favorably with the corresponding X-ray diffraction values[35] of 194, 196, and 203° in $(CH_3)_2B_5H_7$ and with the microwave value[41] of 196 (2)° in B_5H_9. The two independent B(apical)–B(basal)–H(terminal) angles of 126° and 128° in 1-Br-μ-$(CH_3)_3SiB_5H_7$ are similar to the X-ray value[35] of 126 (3)° in $(CH_3)_2B_5H_7$ and to the microwave value[41] of 136.2 (5)° and the X-ray value[40] of 115 (5)° in B_5H_9.

The observed B(1)–Br bond length of 1.96 (2) Å in 1-Br-μ-$(CH_3)_3SiB_5H_7$ is in accord with the B–Br bond length of 1.930 (5) Å determined for B_2H_5Br from a microwave study[52] and with the B–Br bond length of 1.99 (2) Å found for m-$B_{10}Br_2H_8C_2H_2$ from an X-ray diffraction investigation.[53] The B(1)–Br line in the 1-Br-μ-$(CH_3)_3SiB_5H_7$ molecule expectedly makes an angle of 90° with the plane of basal boron atoms. The two independent Si–CH_3 bond lengths of 1.86 (1) and 1.90 (2) Å are also in excellent agreement with those in other complexes.[54]

The nature of bonding in the 1-Br-μ-$(CH_3)_3SiB_5H_7$ molecule is presumed to be not unlike the latest bonding representation given[55] for the parent B_5H_9 molecule.

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(51) The dihedral angles given in this manuscript and elsewhere[35] are defined as the angles directly between pairs of planes rather than as angles between normals to the planes.

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