Group IV Derivatives of Pentaborane(9)

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Abstract: Compounds having the general formula μ-$R_3M_{IV}B_5H_8$ (where M_{IV} = Si, Ge, Sn, or Pb, and R = H, CH_3, and C_2H_5) are formed in the low-temperature reaction of LiB_5H_8 with halo derivatives of appropriate group IV moieties. Several of these bridge-substituted pentaborane(9) derivatives isomerize to terminal- (2-) substituted derivatives in the presence of weak Lewis bases. Spectral evidence suggests that, in the bridge-substituted derivatives, the group IV moiety is bonded to the two adjacent boron atoms by a three-center, two-electron bond.

There have been only a few previous reports of compounds containing boron–group IV bonds (for the purposes of this paper group IV refers to all the group IV elements *except* carbon). The compounds that have been reported all contain boron–group IV σ bonds such as in B,B′,B′′-tris(triphenylsilyl)borazine,[1] $(R_3Si)_{3-n}B(NR'_2)_n$ (R = CH_3, C_6H_5; R′ = CH_3, C_2H_5),[2] X_3SiBX_2 (X = Cl, F),[3,4] $Li[(C_6H_5)MB(C_6H_5)_3]$ (M = Si, Ge),[5] and $K(H_3GeBH_3)$.[6]

We report here the preparation of a number of group IV derivatives of pentaborane(9) in which the boron–group IV bonding appears to be different from that in the compounds mentioned above.

Synthesis and Properties

The lithium salt of the octahydropentaborate(−1) anion, $B_5H_8^-$,[7,8] reacts readily with a number of group IV compounds to produce pentaborane(9) derivatives according to the general equation

$$LiB_5H_8 + XM_{IV}R_3 \longrightarrow \mu\text{-}R_3M_{IV}B_5H_8 + LiX \qquad (1)$$

$$X = Cl, Br, \text{ or } I$$

$$M_{IV} = Si \text{ or } Ge;\ R = C_2H_5, CH_3, H$$

$$M_{IV} = Sn \text{ or } Pb;\ R = CH_3$$

The reactions depicted in eq 1 were carried out in ethereal solvents at low temperatures, usually in the vicinity of −30°, because of the somewhat low thermal stability of LiB_5H_8, and because facile isomerization of the products has been observed in several cases when the reaction mixture was allowed to warm to room temperature. In most preparations yields in excess of 60% were obtained.

The ^{11}B and ^1H nmr spectra (*vide infra*) of the compounds μ-$R_3M_{IV}B_5H_8$ suggest that the group IV substituent is located in a bridging position between two of the boron atoms in the base of the pentaborane(9) pyramid. This suggested molecular configuration has been further verified by a single-crystal X-ray investigation of 1-Br-μ-$(CH_3)_3SiB_5H_7$ in the laboratory of Professor L. F. Dahl.[9] In this X-ray study the silicon atom was found in a position analogous to that of a bridge hydrogen in pentaborane(9). In addition the methyl groups were found to be arranged around the silicon atom at tetrahedral angles. Thus the silicon atom can be considered to be sp^3 hybridized and bound to the pentaborane(9) framework by a boron–silicon–boron three-center two-electron bond.

Electron-deficient bonding of this type probably occurs in the carbon bridge of trimethylaluminum dimer.[10] Trimethylboron, however, is monomeric, as are alkylgallium, -indium, and -thallium compounds.[10] In addition there are no known organo derivatives of boron in which carbon is bonded to two adjacent boron atoms by a three-center two-electron bond. (The carboranes involve carbon bound to three, four, or five adjacent framework atoms and to a single external group. The bonding in these compounds is thus more complex and is best described on the basis of a more comprehensive molecular orbital model.[11])

Three-center two-electron bonding has also been proposed for tin compounds having a coordination number greater than four.[12,13] For example, in $Me_2Sn(C_9H_6NO)_2$ the bonding could involve sp^3 orbitals on the tin participating in normal covalent bonds to the methyl groups and three-center bonds directed between the oxygen and nitrogen atoms of the oxinate groups.[14] This possibility is supported by the Me–Sn–Me bond angle of 110.7°, which is very close to the tetrahedral angle.

The bridged silicon and germanium derivatives of pentaborane(9) isomerize essentially quantitatively to the corresponding 2-substituted derivatives at room temperature when in the presence of weak Lewis bases such as dimethyl or diethyl ether. The 2-substituted isomers prepared were all more volatile than the corresponding bridged isomers. The μ-$(CH_3)_3SnB_5H_8$ did not isomerize under the above conditions, though some degradation was noted. The low thermal stability of μ-$(CH_3)_3PbB_5H_8$ rendered isomerization experiments impractical.

The mechanism of isomerization from a bridging position to a terminal position in the base of the penta-

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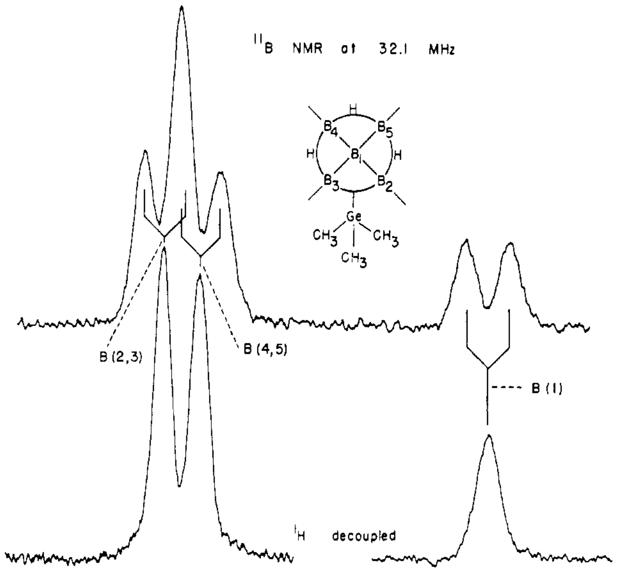
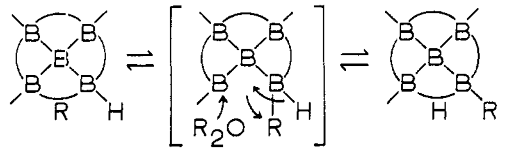


Figure 1. The 32.1-MHz ^{11}B nmr spectrum of μ-$(CH_3)_3GeB_5H_8$: upper, normal spectrum; lower, decoupled at 100 MHz.

borane(9) framework is not known. Isomerization has been observed only in the presence of weak Lewis bases, and, though strong Lewis bases would also presumably effect rearrangement, prior investigations[15] suggest that substantial undesirable side reactions would occur. The nearly quantitative conversion of the μ-SiR_3 and μ-GeR_3 derivatives to the corresponding 2 derivatives reinforces earlier indications that 2-substituted derivatives of pentaborane(9) are generally the most thermodynamically stable when the substituent is more bulky than hydrogen.[15] The data available suggest that the isomerization might occur *via* an unstable ether complex in which the substituent is displaced to a terminal position by the ether, followed by removal of the ether and movement of a less bulky hydrogen atom into a bridging position. This sort of a mechanism is consistent with the observation that μ-DB_5H_8 isomerizes reversibly in tetrahydrofuran to 2-DB_5H_8 with an equilibrium constant value close to 1.[7]



Several mechanisms have been suggested for the Lewis base catalyzed isomerization of 1-alkyl- to 2-alkylpentaborane(9)[16,17] and of 1,2-dimethyl- to 2,3-dimethylpentaborane(9).[18] At this time, however, there is not sufficient evidence to verify any particular mechanism, but it appears highly probable that the mechanism of a 1 to 2 rearrangement is considerably different from the mechanism of a μ to 2 rearrangement.

Chemical studies of μ-$(CH_3)_3SiB_5H_8$ suggest that many of the reactions of bridged group IV derivatives of pentaborane(9) are similar to the corresponding reactions of pentaborane(9) and its alkyl derivatives.[15] For example, μ-$(CH_3)_3SiB_5H_8$ decomposes in air and is slowly hydrolyzed by water. Reaction with bromine is rapid, forming 1-Br-μ-$(CH_3)_3SiB_5H_7$ along with traces of $(CH_3)_3SiBr$ and 2-BrB_5H_8. The reaction time of 3–5 min is in sharp contrast to the bromination of pentaborane(9), which under similar conditions requires several hours.[19]

Nmr Studies

The ^{11}B nmr spectra (32.1 MHz) of μ-$(CH_3)_3GeB_5H_8$ and μ-$(CH_3)_3SiB_5H_8$ are nearly identical. The low-field triplet-like group of intensity 4 consists of two overlapping doublets of equal intensity, as shown by ^1H spin decoupling at 100 MHz in the case of the Ge compound (Figure 1) and by comparison of the 9.2- and 32.1-MHz spectra in the case of the Si compound.[20] The high-field doublet of intensity 1 in these spectra is in the chemical shift region typical of the apex boron atom, B(1), in pentaborane(9) and its derivatives.[15] These data also indicate that each boron atom in these compounds has a terminal hydrogen atom attached to it, and further that the base of the pentaborane(9) pyramid (perhaps distorted) contains two sets of two magnetically equivalent boron atoms. These data suggest that the group IV substituent most probably resides in a bridging position between two equivalent basal boron atoms. The assignment of the B(4,5) resonance in μ-$(CH_3)_3SiB_5H_8$ and μ-$(CH_3)_3GeB_5H_8$ to the high-field doublet in the triplet-like group (Table I) is based on the fact that the chemical shift of this doublet is very similar to that of the basal doublet, B(2–5), of pentaborane(9) and on the assumption that the boron atoms B(2,3), to which the group IV substituent is bonded, are most likely to be shifted.

The spectra of μ-$H_3SiB_5H_8$ and μ-$H_3GeB_5H_8$ were also very similar to one another, consisting of a slightly asymmetric but well-resolved low-field doublet of intensity 4 and a high-field doublet of intensity 1. In these cases the structures are as indicated above except that there is only a small unmeasurable substituent effect on the chemical shifts of the basal boron atoms.

The spectra of the other bridge-substituted compounds listed in Table I are very similar to one another, consisting of a poorly resolved low-field doublet of intensity 4 and a high-field doublet of intensity 1. In these cases there is indicated a significant though unresolved magnetic nonequivalence between the basal boron atoms adjacent to the bridging group IV substituent and the boron atoms across from the substituent.

The ^{11}B nmr spectra of the 2-substituted derivatives (Table I) show overlap of the resonances due to the different basal borons, but by decoupling hydrogen the spectra can be interpreted in terms of a singlet of intensity 1, B(2), a doublet of intensity 2, B(3,5), and a doublet of intensity 1, B(4). These assignments are shown for the ^{11}B nmr spectrum of 2-$H_3SiB_5H_8$ in Figure 2.

The ^1H nmr spectra (60 and 100 MHz) of the bridge-substituted derivatives are somewhat similar to those

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Table I. ^{11}Nmr Spectral Results

Compound	Chemical shifts^a B(2,3)	B(2–5)	B(4,5)	B(1) (*J*)	Area ratio, base:apex
μ-$H_3SiB_5H_8$		12.9		50.6 (175)	4.02
μ-$(CH_3)_3SiB_5H_8$	8.7		13.2	48.0 (179)	4.01
μ-$(C_2H_5)_3SiB_5H_8$		11.7		48.8 (166)	3.91
μ-$H_3GeB_5H_8$		12.1		51.2 (176)	3.90
μ-$(CH_3)_3GeB_5H_8$	8.7		12.9	48.4 (169)	3.96
μ-$(C_2H_5)_3GeB_5H_8$		11.6		49.7 (180)	4.04
μ-$(CH_3)_3SnB_5H_8$	12.0		13.7	50.6 (175)	4.02
μ-$(CH_3)_3PbB_5H_8$		13.3		52.4 (183)	3.99
1-Br-μ-$(CH_3)_3SiB_5H_7$	7.8		12.6	33.8	4.02
1-Br-μ-$(CH_3)_3GeB_5H_7$	7.8		12.2	33.9	4.10
	B(2)	B(3,5)	B(4)		
2-$H_3SiB_5H_8$	15.0	11.2	7.1	50.0 (177)	4.01
2-$(CH_3)_3SiB_5H_8$	9.8	11.1	8.2	50.9 (176)	4.00
2-$(C_2H_5)_3SiB_5H_8$	12.5	11.9	7.4	51.0 (173)	4.03
2-$H_3GeB_5H_8$	13.6	11.0	7.9	50.1 (176)	3.88
2-$(CH_3)_3GeB_5H_8$	9.7	10.7	8.4	51.0 (176)	4.02
2-$(C_2H_5)_3GeB_5H_8$	Featureless hump at 11.5			51.9 (175)	3.99

[a] The chemical shifts are reported in ppm from $BF_3 \cdot O(C_2H_5)_2$. They are arrived at by using the *J* values from the 60-Mc ^{1}H nmr spectrum to locate the actual center of doublets when overlapping occurs. The apparent δ's and *J*'s measured from the 32.1-Mc ^{11}B nmr will differ unless hydrogen decoupling equipment is used.

of other pentaborane(9) derivatives.[15] Integrations of the ^{1}H spectra (by parts) in regions where terminal and bridge boron–hydrogen resonances are reasonably well defined agree well with the areas calculated for μ-$R_3M_{IV}B_5H_8$, which has five terminal and three bridge hydrogen atoms attached to boron.[21] The ^{1}H nmr spectra of the 2-substituted compounds are basically similar to those of the μ-substituted compounds, but the area ratios of bridge to terminal hydrogens bound to boron clearly indicate 2 substitution (Table II).

Experimental Section

Ether was distilled from lithium aluminum hydride immediately prior to use. Trimethylchlorosilane was obtained from Dow Corning Corp. and purified using standard high-vacuum techniques.[22] All other chemicals were used as received. Pentaborane(9) was obtained from Callery Chemical Co. Silane was obtained from Research Organic Chemical Co. Trimethylchlorogermane, triethyliodogermane, trimethylbromostannane, germanium tetrachloride, and tetramethyllead were obtained from Alpha Inorganics, Inc. Triethylchlorosilane was obtained from Peninsular Chemresearch, Inc. Chlorosilane,[23] germane,[24] chlorogermane,[25] and trimethylchloroplumbane[26] were prepared using previously reported procedures. *n*-Butyllithium in hexane or pentane solution was obtained from Foote Mineral Co.

All reactions were carried out in a 100-ml round-bottomed flask containing a Teflon-coated magnetic stirring bar and having a right-angle Delmar O-ring stopcock.[27] Standard high-vacuum techniques were used for manipulation and purification of volatile materials.[22]

The ^{11}B nmr spectra were recorded at 32.1 MHz using a Varian HA-100 spectrometer and are presented in Table I. In some cases ^{1}H decoupling was effected by simultaneous irradiation at 100 MHz,[28] as shown in Figures 1 and 2. The ^{1}H nmr spectra were recorded at 60 MHz on a Varian A-60A spectrometer and at 100 MHz on a Varian HA-100 spectrometer. Integrations of the 100-MHz spectra were measured with a planimeter. Comparison of the ratios of bridge to terminal boron hydrogens with calculated ratios were made on the bases of assignments that are analogous to those shown in ref 21. The abundances of ^{11}B and ^{10}B used in the calculations were 80 and 20%, respectively. The results are presented in Table II. The measurements were somewhat complicated by overlap of the resonances from the R_3M_{IV} moiety. Thus it was necessary to use different though analogous regions of the spectra for different compounds.

Infrared spectra were recorded on a Beckman IR-10 instrument and are presented in Table III. The infrared spectra were of little use in quantitative structural characterization of the compounds. In most cases the B–H absorption at about 2600 cm^{-1} had a shoulder at about 2580 cm^{-1} for the μ-substituted compounds.

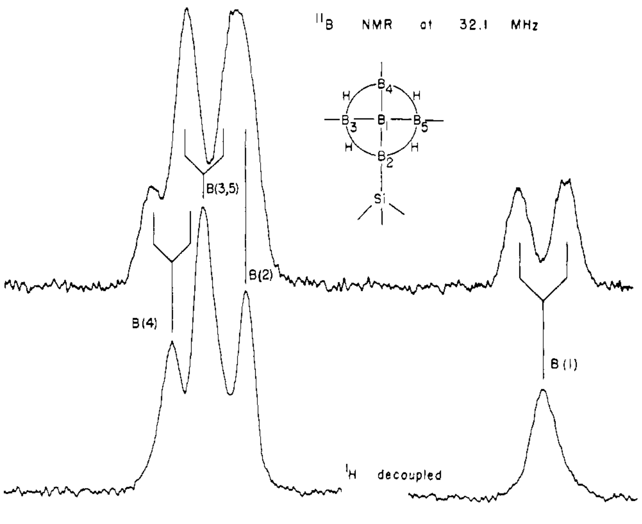

Figure 2. The 32.1-MHz ^{11}B nmr spectrum of 2-$H_3SiB_5H_8$. The upper trace is normal; the lower is decoupled at 100 MHz.

Mass Spectra. These were recorded on a Consolidated Electrodynamics Corp. Type 21-103C mass spectrometer using the standard gas inlet system. The mass spectra of these compounds were characteristic of boron hydride derivatives. They all showed peaks in the fragmentation pattern which represented the complex loss of individual hydrogens. In all cases, a sharp cut-off was observed at the value of *m*/*e* which corresponded to the parent ion, as shown in Table IV. It was often the case, however, that the most intense peaks were not in the region of the parent ion but in the region of the parent ion with one or two of the alkyl groups missing. This phenomenon is also characteristic of alkyl derivatives of group

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(28) The details of the experimental setup used for decoupling experiments will be published elsewhere.

Table II. ^{1}H Nmr Spectral Results

	Chemical shifts[a]						Area ratios, H_b/H_t		
	Base		Apex		Bridge	Substituent			
Compound	δ	(J)	δ	(J)	δ	δ	Obsd	Calcd (μ)	Calcd (2-)
μ-$SiH_3B_5H_8$	−2.24	(163)	−0.40	(174)	2.23	−3.72	0.95	0.95	1.58
μ-$(CH_3)_3SiB_5H_8$	−2.30	(157)	−0.62	(174)	2.55	−0.37	1.11	1.10	1.86
μ-$(C_2H_5)_3SiB_5H_8$	−2.14	(150)	−0.27	(172)	2.86	−0.57	1.10	1.10	1.86
μ-$H_3GeB_5H_8$	−2.60	(166)	−0.73	(174)	2.07	−4.07	0.99	0.95	1.58
μ-$(CH_3)_3GeB_5H_8$	−2.28	(163)	−0.58	(171)	2.47	−0.57	1.06	1.10	1.86
μ-$(C_2H_5)_3GeB_5H_8$	−2.38	(152)	−0.68	(170)	2.60	−1.07	1.51	1.44	2.44
μ-$(CH_3)_3SnB_5H_8$	−2.37	(150)	−0.55	(174)	2.87	−0.48	1.18	1.10	1.86
1-Br-μ-$(CH_3)_3SiB_5H_8$	−2.73	(158)			1.60	−0.54	1.02	1.03	0.58
1-Br-μ-$(CH_3)_3GeB_5H_8$	−2.77	(161)			1.67	−0.78	1.07	1.03	0.58
2-$H_3SiB_5H_8$	−2.38	(165)	−0.42	(171)	2.50	−3.00	1.54	0.95	1.58
2-$(CH_3)_3SiB_5H_8$	−2.44	(162)	−0.42	(174)	2.44	+0.10	2.31	1.44	2.44
2-$(C_2H_5)_3SiB_5H_8$	−2.44	(165)	−0.58	(171)	2.33	−0.90	1.61	1.10	1.86
2-$H_3GeB_5H_8$	−2.67	(164)	−0.73	(174)	2.17	−3.04	1.48	0.95	1.58
2-$(CH_3)_3GeB_5H_8$	−2.28	(160)	−0.25	(175)	2.34	+0.05	2.32	1.44	2.44
2-$(C_2H_5)_3GeB_5H_8$	−2.16	(164)	−0.23	(174)	2.44	−0.12	2.19	1.44	2.44

[a] Chemical shifts are positive when upfield from the standard, tetramethylsilane, and are ±0.1 ppm. Coupling constants are ±5 Hz.

Table III. Infrared Spectra (cm^{-1})[a]

μ-$H_3SiB_5H_8$	2600 (s), 2580 (sh), 2190 (s), 2150 (s), 1820 (m, b), 1450 (sh), 1410 (s), 1105 (m), 955 (s), 900 (s), 805 (m), 750 (w), 645 (sh), 600 (m), 530 (m)
2-$H_3SiB_5H_8$	2600 (s), 2190 (sh), 2150 (s), 2110 (sh), 1825 (w, b), 1450 (sh), 1405 (m), 1300 (sh), 1110 (w), 990 (sh), 930 (m), 900 (s), 855 (sh), 780 (w), 740 (vw), 670 (m), 600 (m), 530 (w)
μ-$H_3GeB_5H_8$	2600 (s), 2100 (sh), 2060 (s), 1820 (b, w), 1440 (sh), 1395 (m), 1100 (vw), 1010 (w), 925 (m), 880 (s), 815 (s), 790 (sh), 650 (m), 610 (m), 545 (m), 475 (w)
2-$H_3GeB_5H_8$	2600 (s), 2110 (sh), 2070 (s), 2030 (sh), 1820 (b, w), 1450 (m), 1400 (s), 1110 (vw), 1020 (w), 925 (m), 885 (m), 810 (s), 770 (w), 660 (m), 600 (w), 550 (m), 480 (w)
μ-$(CH_3)_3SiB_5H_8$	2960 (w), 2905 (vw), 2600 (s), 2570 (sh), 1820 (b, w), 1410 (b), 1255 (m), 930 (sh), 855 (sh), 840 (s), 760 (w), 680 (w), 610 (w)
1-Br-μ-$(CH_3)_3SiB_5H_7$	2970 (m), 2950 (m), 2900 (m), 2800 (w), 2595 (s), 2580 (sh), 1830 (m, b), 1330 (w), 1250 (s), 1140 (m), 1030 (w), 940 (m), 900 (m), 840 (s), 780 (m), 760 (m), 690 (m), 640 (sh), 620 (m)
2-$(CH_3)_3SiB_5H_8$	2965 (m), 2906 (w), 2600 (s), 1830 (b, m), 1450 (sh), 1402 (m), 1252 (m), 1100 (vw), 1070 (vw), 930 (m), 867 (s), 836 (s), 745 (w), 695 (m), 665 (m), 619 (w)
μ-$(CH_3)_3GeB_5H_8$	2980 (s), 2910 (s), 2800 (w), 2590 (s), 2570 (sh), 1920 (sh), 1820 (m, b), 1770 (sh), 1410 (s), 1340 (sh), 1240 (s), 1100 (w), 1025 (w), 1020 (sh), 980 (w), 940 (s), 890 (s), 830 (s, b), 760 (s), 690 (m), 660 (m), 600 (s), 560 (m)
1-Br-μ-$(CH_3)_3GeB_5H_7$	2980 (m), 2900 (m), 2800 (m), 2600 (s), 2580 (sh), 1820 (m, b), 1530 (w), 1240 (m), 1140 (m), 1030 (w), 935 (m), 870 (sh), 830 (s), 770 (m), 685 (m), 650 (w), 610 (sh), 595 (m)
2-$(CH_3)_3GeB_5H_8$	2980 (m), 2905 (m), 2600 (s), 1830 (m, b), 1490 (w), 1390 (m), 1370 (sh), 1240 (m), 1100 (w), 1010 (w), 925 (m), 875 (w), 820 (s), 745 (w), 655 (w), 590 (w)
μ-$(C_2H_5)_3Si$-B_5H_8	2950 (s), 2900 (s), 2880 (s), 2800 (w), 2590 (s), 1820 (m, b), 1530 (w), 1235 (m), 1065 (w), 1010 (sh), 1000 (s), 940 (m), 880 (m), 850 (w), 800 (w), 720 (s), 690 (w), 650 (w), 610 (w), 565 (w)
2-$(C_2H_5)_3SiB_5H_8$	2950 (s), 2905 (s), 2880 (s), 2800 (w), 2595 (s), 1830 (m, b), 1400 (s), 1235 (m), 1100 (w), 1070 (w), 1010 (m), 955 (m), 925 (m), 880 (m), 845 (m), 770 (w), 720 (w), 700 (sh), 660 (s), 605 (w)
μ-$(C_2H_5)_3GeB_5H_8$	2950 (s), 2880 (s), 2830 (m), 2740 (w), 2590 (s), 1920 (sh), 1820 (m, b), 1380 (m), 1350 (sh), 1220 (m), 1100 (vw), 1020 (sh), 1010 (s), 970 (m), 940 (s), 900 (sh), 885 (s), 840 (vw), 810 (w), 780 (vw), 750 (w), 700 (s), 655 (m), 610 (s), 570 (s), 525 (m)
2-$(C_2H_5)_3GeB_5H_8$	2920 (s, b), 2870 (s), 2810 (w), 2595 (s), 1810 (w, b), 1380 (m, b), 1220 (w), 1100 (w), 1015 (m), 960 (sh), 950 (m), 920 (m), 880 (m), 840 (m), 700 (m), 660 (m), 600 (w), 565 (w)
μ-$(CH_3)_3SnB_5H_8$	2980 (s), 2905 (s), 2780 (vw), 2580 (s, b), 1910 (w), 1810 (m, b), 1740 (w), 1630 (w), 1385 (m), 1300 (sh), 1195 (sh), 1190 (m), 1095 (w), 1020 (w), 940 (s), 900 (sh), 880 (s), 770 (s, b), 720 (sh), 680 (m), 640 (m), 605 (s)

[a] Obtained in CS_2 solution and/or in the gas phase (10-cm cell).

IV metals.[29] A portion of the mass spectrum of μ-$H_3SiB_5H_8$ obtained with an ionizing voltage of 12.5 V is tabulated in Table V.

Octahydropentaborate(−1) Anion, $B_5H_8^-$. In a typical preparation, 4.8 mmoles of *n*-butyllithium in hexane solution was placed in a nitrogen-filled reaction flask using a hypodermic syringe. The flask was evacuated and the hexane was evaporated. About 20 ml of diethyl ether was distilled in to dissolve the viscous *n*-butyllithium. About 5 mmoles of pentaborane(9) was distilled into the flask at −196°. The contents of the flask was warmed to −78° and then, with continuous stirring, from −78 to −30° over a 1-hr period. In most cases the next reactant was added at this point, without fractionating the volatile materials from the initial reaction.

μ-Silyl-pentaborane(9), μ-$H_3SiB_5H_8$. Chlorosilane (8.1 mmoles) was condensed at −196° into a reaction flask containing LiB_5H_8 (6.6 mmoles) in diethyl ether. The contents of the flask was warmed to −78° and then, with continuous stirring, from −78 to −40° over a period of 1.5 hr. The product was isolated by distillation through a U-tube trap at −45° and by condensation in a −63° trap. The product was a liquid having a vapor pressure of 7 mm at 0° and 19 mm at 24°, yield 0.495 g (5.3 mmoles), 80%.

The other bridge-substituted compounds were prepared in the same manner as was μ-$H_3SiB_5H_8$ using similar quantities of reagents and similar warming times. The highest temperatures to which the reaction mixtures were warmed varied from −45° for the μ-$H_3GeB_5H_8$ preparation to −22° for the μ-$(C_2H_5)_3SiB_5H_8$ preparation.

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[29] B. G. Hobrock and R. W. Koser, *J. Phys. Chem.*, **66**, 155 (1962); V. H. Dibeler, *J. Res. Natl. Bur. Std.*, **49**, 235 (1952), and references therein.

Table IV. Mass Spectral Molecular Weights

Compound	m/e, cut-off	Parent ion[a]
$\mu\text{-}H_3SiB_5H_8$	95	$H_3{}^{29}Si^{11}B_5H_8^+$
$\mu\text{-}H_3GeB_5H_8$	142	$H_3{}^{76}Ge^{11}B_5H_8^+$
$\mu\text{-}(CH_3)_3SiB_5H_8$	138	${}^{12}C_2{}^{13}CH_9{}^{29}Si^{11}B_5H_8^+$
$\mu\text{-}(CH_3)_3GeB_5H_8$	184	${}^{12}C_3H_9{}^{76}Ge^{11}B_5H_8^+$
$\mu\text{-}(CH_3)_3SnB_5H_8$	232	${}^{12}C_3H_9{}^{124}Sn^{11}B_5H_8^+$
$2\text{-}(CH_3)_3SiB_5H_8$	138	${}^{12}C_2{}^{13}CH_9{}^{29}Si^{11}B_5H_8^+$
$2\text{-}(CH_3)GeB_5H_8$	184	${}^{12}C_3H_9{}^{76}Ge^{11}B_5H_8^+$

[a] Probable parent ions but not necessarily unique assignments.

Table V. Partial Mass Spectrum of $\mu\text{-}H_3SiB_5H_8$ at 12.5 V

m/e	Rel intensity	m/e	Rel intensity
95	1	80	3
94	8	79	3
93	17	78	5
92	86	77	3
91	100	76	51
90	57	64	3
89	26	63	4
88	10	62	7
87	3	61	6
86	1	60	4
85	1	59	3
		58	1

$\mu\text{-}H_3GeB_5H_8$ was purified by distillation through a trap at −30° and condensation in a trap at −63° and was obtained in 74% yield. The product had vapor pressures of 2 mm at 0° and about 7 mm at 26°, though it was unstable at the higher temperature.

$\mu\text{-}(CH_3)_3SiB_5H_8$ was purified by distillation through a trap at −22° and by condensation in a trap at −45° and was obtained in 90% yield. The melting range was 16–17° and the room temperature vapor pressure was about 1 mm.

$\mu\text{-}(CH_3)_3GeB_5H_8$ was purified by distillation through a trap at −8° and by condensation in a trap at −22° and was obtained in 88% yield. This compound melted sharply at 11.5° and had no measurable vapor pressure at room temperature.

$\mu\text{-}(CH_3)_3SnB_5H_8$ was purified by condensation at −22° and was obtained in about 60% yield. It had no measurable vapor pressure at room temperature.

$\mu\text{-}(CH_3)_3PbB_5H_8$ was purified by sublimation directly from the reaction vessel. It melted with decomposition at about −5°.

$\mu\text{-}(C_2H_5)_3SiB_5H_8$ was purified by condensation in a −22° trap and was obtained in 10% yield. The major reaction product was $(C_2H_5)_3SiH$. It exhibited no measurable vapor pressure at room temperature.

$\mu\text{-}(C_2H_5)_3GeB_5H_8$ was purified by distillation through a trap at −8° and by condensation in a trap at −22° and was obtained in 88% yield. It exhibited no measurable vapor pressure at room temperature.

1-Bromo-μ-trimethylsilyl-pentaborane(9), $1\text{-}Br\text{-}\mu\text{-}(CH_3)_3SiB_5H_7$. Liquid bromine, 0.10 ml (1.8 mmoles), was placed in a reaction flask with a hypodermic syringe. The flask was then cooled and evacuated, and 1.7 mmoles of $\mu\text{-}(CH_3)_3SiB_5H_8$ was condensed in at −196°. The flask was warmed to room temperature, whereupon the soluion of $\mu\text{-}(CH_3)_3SiB_5H_8$ in bromine bubbled and the color faded. After 3 min the reaction was complete and only a light yellow solid remained. Fractionation of the volatile materials yielded HBr (1.5 mmoles) and traces of $2\text{-}BrB_5H_8$ and $(CH_3)_3SiBr$. The product was transferred to a sublimator in a nitrogen-filled glove bag and then sublimed under vacuum onto a cold finger at −80°.

1-Bromo-μ-trimethylgermyl-pentaborane(9), $1\text{-}Br\text{-}\mu\text{-}(CH_3)_3GeB_5H_7$. The reaction was carried out as above using 0.10 ml of liquid bromine and excess $\mu\text{-}(CH_3)_3GeB_5H_8$. Fractionation gave $\mu\text{-}(CH_3)_3GeB_5H_8$, HBr (1.6 mmoles), and traces of $2\text{-}BrB_5H_8$ and $(CH_3)_3GeBr$. The product was finally purified by vacuum sublimation at 40° onto a cold finger at −78°.

Reaction of μ-Trimethylsilyl-pentaborane(9) with Lithium Aluminum Hydride. $\mu\text{-}(CH_3)_3SiB_5H_8$ (1.45 mmoles) and about 1 ml of tetrahydrofuran (THF) were condensed in on excess $LiAlH_4$ at −196°. The flask was warmed to room temperature for about 3 hr. The flask was then cooled to −196° and there was no evidence of noncondensable gases. Fractionation of the volatile materials yielded THF and trimethylsilane, $(CH_3)_3SiH$ (1.32 mmoles, 91%), which was identified by its infrared spectrum.[30] There was no evidence for a volatile boron hydride species.

Hydrolysis of μ-Trimethylsilyl-pentaborane(9). $\mu\text{-}(CH_3)_3SiB_5H_8$, 0.0815 g (0.589 mmole), was condensed into a reaction flask containing 1 ml of dilute hydrochloric acid. The flask was warmed to 110° for 7 hr. The hydrogen was moved into a standard volume with a Toepler pump and measured. The boric acid solution was titrated in the presence of mannitol using the constant pH method. *Anal.* Calcd for $2(CH_3)_3SiB_5H_8 + 31H_2O = 10B(OH)_3 + [(CH_3)_3Si]_2O + 24H_2$: B, 39.9%, H, 88.7 mmoles/g. Found: B, 40.3%; H, 88.7 mmoles/g.

2-Silyl-pentaborane(9), $2\text{-}H_3SiB_5H_8$. The isomerization was effected by warming a solution of about 3 mmoles of $\mu\text{-}H_3SiB_5H_8$ in about 1 ml of diethyl ether to room temperature for 8 hr. The product was collected in an estimated 75% yield after purification by distillation through a trap at −63° and condensation in a −78° trap. The $2\text{-}H_3SiB_5H_8$ melted sharply at −62.5° and had vapor pressures of 8.5 ± 0.5 mm at 0° and 28.0 ± 0.5 mm at 24°.

The other 2-substituted pentaborane(9) derivatives were prepared by isomerization of the corresponding bridged compounds under conditions similar to those used to prepare $2\text{-}H_3SiB_5H_8$. In several cases dimethyl ether vapor (1 atm) was used in place of liquid diethyl ether.

$2\text{-}(CH_3)_3SiB_5H_8$ was purified by distillation through a trap at −45° and by condensation in a −63° trap. The product had vapor pressures of 1.0 ± 0.2 mm at 0° and 5.0 ± 0.2 mm at 25°. The yield was 94%.

$2\text{-}(C_2H_5)_3SiB_5H_8$ was purified by condensation in a −30° trap. The product was obtained in near-quantitative yield and had no measurable vapor pressure at room temperature.

$2\text{-}H_3GeB_5H_8$ was purified by distillation through a trap at −45° and by condensation in a trap at −78° and was obtained in about 50% yield. The product melted slightly above −63° and had vapor pressures of 5.0 ± 0.5 mm at 0° and 14.0 ± 0.5 mm at 26°.

$2\text{-}(CH_3)_3GeB_5H_8$ was purified by distillation through a trap at −30° and by condensation in a trap at −45° and was obtained in about 50% yield. The pure product had a vapor pressure of about 1 mm at 26°.

$2\text{-}(C_2H_5)_3GeB_5H_8$ was purified by condensation in a −22° trap and was obtained in about 80% yield. This material had no measurable vapor pressure at room temperature.

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(30) S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953).