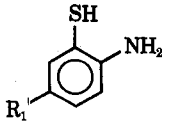
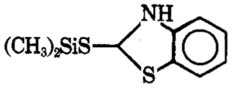
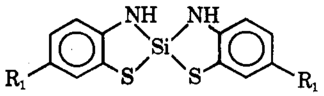


as suggested by Haberditzl.[9]

χ_{Si} in



is 19.38 and in



is 17.39–17.52. $\chi_{Si} = 19.38$ is comparable with $\chi_{Si} = 19.40$ for the series R_3–Si–N– and $\chi_{Si} = 17.39$–17.52 is comparable with $\chi_{Si} = 17.40$ for the compounds containing the linkage $R_2\text{–Si}{<}^{N}_{N}$. These studies show that the replacement of a C–Si bond by a S–Si bond does not have any effect on χ_{Si}.

[9] W. Haberditzl, *Sitzungsber. Deut. Akad. Wiss. Berlin, Kl. Chem., Geol. Biol.*, No. 2 (1964).

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Synthesis and Chemistry of μ-Silyl and μ-Germyl Carboranes[1a]

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The bridged carborane derivatives μ-$MR_3C_2B_4H_7$ (M = Si, Ge; R = H, CH_3) have been prepared in high yield (except for the germyl compound) from reactions of the 2,3-$C_2B_4H_7^-$ ion with silyl or germyl halides and structurally characterized from their ^{11}B and ^1H nmr, infrared, and mass spectra. In each compound the MR_3 bridging group replaces one of the bridge protons in 2,3-dicarba-*nido*-hexaborane(8), $C_2B_4H_8$, and is presumably bound to the adjacent boron atoms by a two-electron, three-center bond. The silyl, trimethylsilyl, and trimethylgermyl species are stable at 25° but at higher temperatures isomerize quantitatively and irreversibly to the respective 4-substituted species; the μ-germyl compound probably undergoes a similar rearrangement. Pyrolysis of μ- or 4-$(CH_3)_3SiC_2B_4H_7$ at 220–230° for 1 hr yields the 1- and 2-substituted isomers, but prolonged heating produces *closo*-carborane derivatives. Pyrolysis of μ- or 4-$SiH_3C_2B_4H_7$ at 230° yields 1- and 2-$SiH_3C_2B_4H_7$, 2,3-$C_2B_4H_8$, silyl *closo*-carboranes, and *closo*-$C_3B_5H_7$. Reaction of 2-$(CH_3)_3SiC_2B_4H_7$ with NaH in THF followed by addition of trimethylsilyl chloride yields μ,2-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$.

Although the family of known heterocarborane cage systems is steadily growing and now includes species containing heteroatoms of groups II, III, IV, and V, and a number of transition metals,[2] a rather conspicuous exception occurs in the case of silicon. Efforts to extend the known icosahedral $MC_2B_9H_{11}$ series[3] (M = Ge, Sn, or Pb) to silicon have been unsuccessful, at least at this writing, and extensive studies[4] of gas-phase silane–borane and silane–carborane reactions have not produced identifiable silacarboranes (terminally substituted silyl carborane derivatives were obtained instead). These results are contrasted with the interesting fact that every element surrounding silicon in the periodic table has been incorporated into characterizable borane or carborane cage species.

A potential route to silacarboranes and germacarboranes which appeared worthy of exploration is the insertion of silyl or germyl groups into bridging positions in the 2,3-$C_2B_4H_8$ (dicarba-*nido*-hexaborane) cage, utilizing reactions of the corresponding $C_2B_4H_7^-$ ion.[5] This approach represents an extension to the carborane field of earlier work by Gaines and Iorns,[6] who prepared pentaborane(9) derivatives containing silicon or heavier group IV bridging atoms.

Results and Discussion

Synthesis and Structures of Bridged Carboranes.— The general preparative scheme utilizes the reaction of silyl chloride, trimethylsilyl chloride, or their germanium analogs with the sodium salt[7] of $C_2B_4H_7^-$, which in turn is prepared from 2,3-$C_2B_4H_8$ and sodium hydride. The pure trimethylsilyl and trimethylgermyl compounds are obtained in yields of >60%, but substantially less of the silyl and germyl derivatives have been isolated by this method. However, an alternative route which utilizes the lithium salt has given

$$C_2B_4H_8 + NaH \xrightarrow[-H_2]{THF} Na^+C_2B_4H_7^- \xrightarrow[-NaCl]{MR_3Cl,\ 0°} \mu\text{-}MR_3C_2B_4H_7$$

$$M = Si, Ge;\ R = H, CH_3$$

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[1] (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; Abstract INOR-6. Portions of the work were also presented at the International Meeting on Boron Compounds, Prague, Czechoslovakia, June 1971; Abstract No. 19. (b) On sabbatical leave from the Department of Chemistry, Lake Forest College, Lake Forest, Ill., 1970–1971 academic year.

[2] For recent reviews see R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, Chapter 9; L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970); and M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[3] R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351 (1970).

[4] W. A. Ledoux and R. N. Grimes, *J. Organometal. Chem.*, **28**, 37 (1971).

[5] Related studies involving the *C,C'*-$(CH_3)_2C_2B_4H_5^-$ ion have been recently reported by C. G. Savory and M. G. H. Wallbridge, International Meeting on Boron Compounds, Prague, Czechoslovakia, June 1971, Abstract No. 17; see also C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc. A*, 622 (1971). The bridged trimethylsilyl and trimethylgermyl μ-$(CH_3)_3M$-*C,C'*-$(CH_3)_2C_2B_4H_5$ species reported by these workers were not observed to isomerize at 25°; behavior at higher temperatures was evidently not studied.

[6] (a) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, **90**, 6617 (1968); (b) D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 4249 (1967).

[7] T. Onak and G. B. Dunks, *Inorg. Chem.*, **5**, 439 (1966).

much higher yields of the silyl carborane. This method unfortunately has not generated significant amounts

$$C_2B_4H_8 + CH_3Li \xrightarrow[-31°]{(CH_3)_2O} Li^+C_2B_4H_7^- \xrightarrow[-31°]{SiH_3Cl} \mu\text{-}SiH_3C_2B_4H_7$$

of the bridged germyl species, and the latter compound has been prepared only *via* the sodium hydride route described above.

All four bridged carboranes have been obtained in pure form and structurally characterized from ^{11}B and ^1H nmr, mass, and infrared spectra. In the proposed structures (Figure 1) the bridging MR_3 group replaces a bridge hydrogen atom in 2,3-$C_2B_4H_8$ and thus is assumed to be linked to the adjacent (4 and 5) boron atoms *via* a two-electron, three-center bond. Each compound exhibits the expected mass spectroscopic parent peak and a profile in the parent region close to that calculated for four boron atoms, taking into account the presence of silicon or germanium. The ^{11}B nmr spectra of μ-$SiH_3C_2B_4H_7$ and μ-$(CH_3)_3SiC_2B_4H_7$, shown in Figures 2a and 2e, respectively, establish that the silyl groups are in bridging positions. All of the boron resonances are assignable to doublets, indicative of terminal B–H groups; in contrast, the spectra of the terminally substituted isomers (discussed below) contain a singlet boron resonance arising from replacement of a terminal B–H proton by a silyl or germyl group (the C-substituted isomers have been independently characterized in earlier work[4]). The structures are also supported by the proton nmr data, an example of which is the spectrum of μ-$SiH_3C_2B_4H_7$ in Figure 3. The nmr spectra of μ-$GeH_3C_2B_4H_7$ and μ-$(CH_3)_3GeC_2B_4H_7$ (not shown) closely resemble those of their silicon analogs.

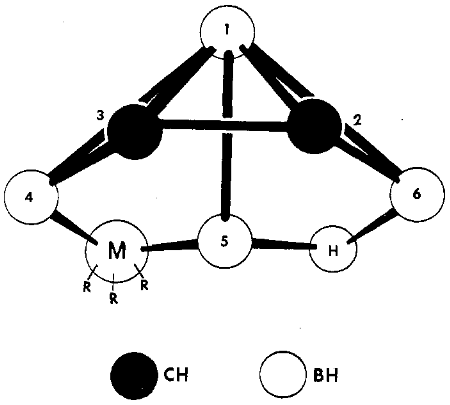

Figure 1.—Proposed structure of the μ-MR_3-2,3-$C_2B_4H_7$ species (M = Si, Ge; R = CH_3, H).

The nmr data for all the silyl and germyl derivatives obtained in this study are summarized in Tables I and II.

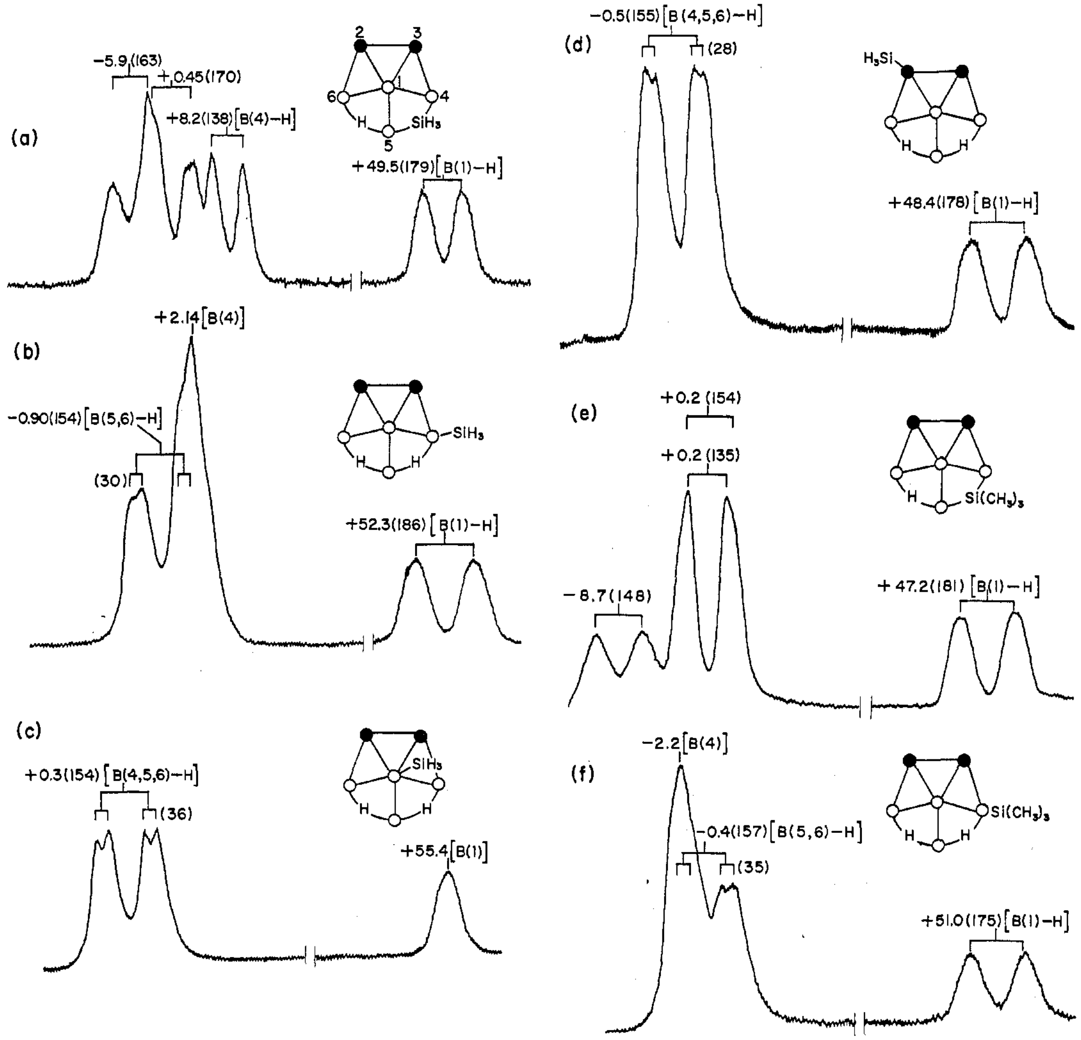

Figure 2.—^{11}B nmr spectra (32.1 MHz) of silyl and trimethylsilyl derivatives of 2,3-$C_2B_4H_8$ (neat liquids).

TABLE I

32.1-MHz BORON-11 NMR DATA[a]

Compound	B(1)	B(4,5,6)[b]		
μ-$SiH_3C_2B_4H_7$	+49.5 (179)	+8.2 (138)	−5.9 (163)	+0.4 (170)
4-$SiH_3C_2B_4H_7$	+52.3 (186)	+2.1 [B(4)]	−0.9 (154)	
2-$SiH_3C_2B_4H_7$	+48.4 (178)	−0.5 (155)		
1-$SiH_3C_2B_4H_7$	+55.4	+0.3 (154)		
μ-$(CH_3)_3SiC_2B_4H_7$	+47.2 (181)	+0.2 (135)	+0.2 (154)	−8.7 (148)
4-$(CH_3)_3SiC_2B_4H_7$	+51.0 (175)	−2.2 [B(4)]	−0.4 (157)	
2-$(CH_3)_3SiC_2B_4H_7$	+57.0 (185)[c]	*c, d*		
μ-$(CH_3)_3GeC_2B_4H_7$	+46.4 (179)	+0.2 (150)	−8.4 (155)	+0.3 (140)
4-$(CH_3)_3GeC_2B_4H_7$	+49.8 (168)	−3.0 [B(4)]	−0.6 (153)	
μ-$GeH_3C_2B_4H_7$	+48.9 (177)	+7.3 (148)	−6.2 (177)	+0.7 (183)
2,3-$C_2B_4H_8$	+50.5 (181)[e]	+3.3 (154)[e]	+0.6 (160)[e]	

[a] Neat liquid samples; chemical shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$; coupling constants in parentheses. [b] Boron–bridge hydrogen coupling constants, occasionally observed, are given in Figure 2. [c] From ref 4. [d] Basal B–H groups exhibit an envelope of overlapping doublets centered at δ +3.0 ppm. [e] From ref 7.

TABLE II

100-MHz PROTON NMR DATA[a]

Compound	H–Si	CH_3	H–B(1)	H–B(4,5,6)	H_{bridge}	$H–C_{cage}$
μ-$SiH_3C_2B_4H_7$	−3.51		+0.9 (181)	−3.2 (137) −3.5 (160) −3.9 (150)	+2.2	−6.76 −6.26
4-$SiH_3C_2B_4H_7$	−3.14		+1.15 (178)	−3.34 (154)	+2.4	−6.20
2-$SiH_3C_2B_4H_7$	−3.72		+1.50 (182)	−3.24 (155)	+2.5	−6.20
1-$SiH_3C_2B_4H_7$	−2.14			−2.84 (159)	+3.0	−5.69
μ-$(CH_3)_3SiC_2B_4H_7$		+0.39	+1.53 (180)	−2.89 (135) −2.94 (154) −3.19 (148)	+3.2	−5.95
4-$(CH_3)_3SiC_2B_4H_7$		+0.10	+1.49 (175)	−3.28 (157)	+2.5	−6.19
2-$(CH_3)_3SiC_2B_4H_7$		+0.50[b]	*b, c*	*b, c*	*b, c*	−6.1[b]
μ-$(CH_3)_3GeC_2B_4H_7$		−0.44	+0.92 (178)	−3.65 (155) −3.67 (148) −3.37 (139)	+2.6	−6.5

[a] Neat liquid samples; chemical shifts in ppm relative to tetramethylsilane; coupling constants in parentheses. [b] From ref 4. [c] Not observed.

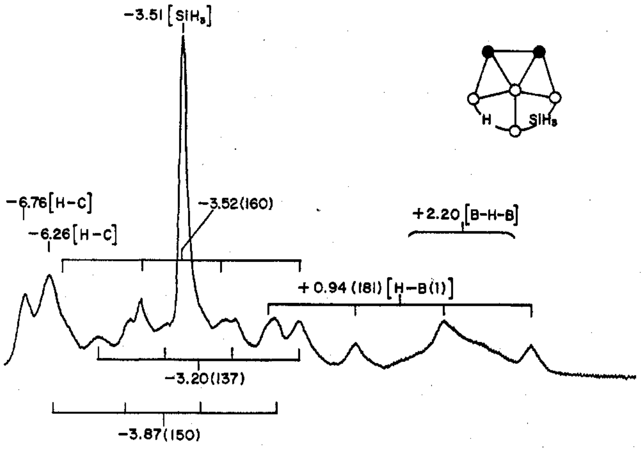

Figure 3.—Proton nmr spectrum (100 MHz) of μ-SiH_3-2,3-$C_2B_4H_7$ (neat liquid).

The infrared spectra of the silicon and germanium compounds (Table III) all contain the expected cage C–H (~3050 cm^{-1}), B–H (2500–2600), and B–H–B (1900–2000) stretching bands. A characteristic feature in the spectra of all of the bridged compounds is a split (doublet or triplet) B–H absorption. In contrast, the B–H stretch appears as a sharp singlet in the spectra of each terminally substituted isomer.

Carboranes Containing Two Substituent Groups.—The sodium hydride–THF method, described above, has also been employed in the preparation of bridge, terminal-disubstituted species such as μ,2-bis(trimethylsilyl)-2,3-dicarbahexaborane(8).

$$2\text{-}(CH_3)_3SiC_2B_4H_7 \xrightarrow[THF]{NaH} Na^+(CH_3)_3SiC_2B_4H_6^- \xrightarrow{(CH_3)_3SiCl} \mu,2\text{-}[(CH_3)_3Si]_2C_2B_4H_6 + NaCl$$

On the other hand, attempts to synthesize bridge-disubstituted compounds have been unsuccessful.[8] Thus, the reaction of μ-$SiH_3C_2B_4H_7$ with excess NaH in THF evolves 1 mol equiv of H_2, but subsequent treatment with SiH_3Cl does not produce detectable amounts of the expected μ,μ′-$(SiH_3)_2C_2B_4H_6$. The principal carborane product is μ-$SiH_3C_2B_4H_7$, identical with the starting material.

Rearrangement of μ-Silyl and μ-Germyl Carboranes.—All four of the bridge-monosubstituted compounds are stable at room temperature but are hydrolyzed by traces of moisture, forming parent $C_2B_4H_8$. The bridged silyl, trimethylsilyl, and trimethylgermyl species undergo rapid, essentially quantitative conversion to the respective 4-substituted derivatives at temperatures ranging from 80 to 175° (Table IV). These isomerizations have been monitored by ^{11}B nmr spectroscopy[9] of neat liquid samples (see Figures 2a,b,e,f) and subsequently confirmed by glpc analysis. A similar rearrangement apparently occurs at 120° in the germyl compound, μ-$GeH_3C_2B_4H_7$. Since this material is the least thermally stable and most difficult to

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[8] Since the submission of this paper, compounds believed to be μ,μ′-$[(CH_3)_3Si]_2C_2B_4H_6$ and μ,μ′-$(CH_3)_3Si(CH_3)_3GeC_2B_4H_6$ have been prepared in this laboratory: A. Tabereaux and R. N. Grimes, unpublished results.

[9] (a) The assignment of 4(6)- rather than 5-substitution is not strictly unambiguous since the nmr spectra could be reconciled with either. However, the fact that the MR_3 groups migrate to the carbon atoms on heating (see below) points strongly to substitution at B(4), adjacent to carbon. (b) The experimental conditions indicated in Table IV and in the text do not necessarily represent the minimum temperature required to induce isomerization.

TABLE III

GAS-PHASE INFRARED ABSORPTIONS (cm^{-1})[a]

μ-$SiH_3C_2B_4H_7$	3050 (s), 2610 (vs), 2540 (s), 2170 (vs), 1940 (m, b), 1565 (sh), 1550 (s), 1530 (sh), 1330 (s), 1120 (m), 1070 (s), 1025 (m), 850–980 (b, vvs), 750 (s), 680 (m), 645 (m), 610 (s)
1-$SiH_3C_2B_4H_7$	3040 (m), 2603 (vs), 2180 (sh), 2145 (vs), 2110 (sh), 1915 (m), 1515 (s), 1350 (m), 1070 (m), 970 (sh), 905 (vs), 870 (sh), 770 (m), 710 (s), 640 (m)
2-$SiH_3C_2B_4H_7$	3010 (m), 2603 (vs), 2220 (m), 2170 (vs), 1940 (m), 1890 (w, b), 1525 (s), 1345 (m), 1245 (m), 1110 (s), 980 (m), 930 (vs), 875 (m), 840 (m), 760 (sh), 730 (sh), 710 (s), 640 (s)
4-$SiH_3C_2B_4H_7$	3042 (s), 2600 (vs), 2140 (vs), 1920 (s), 1570 (m), 1470 (vs, b), 1350 (m–s), 1320 (m–s), 1065 (vs), 1035 (s), 880–970 (b, vvs), 850 (m), 800 (s), 758 (s), 720 (vs), 670 (m), 600 (vs)
SiH_3-*closo*-$C_2B_3H_4$[b]	2610 (vs), 2160 (vs), 1500 (w, b), 1400 (w), 1330 (vs), 1290 (sh), 1220 (m), 1060 (vs), 990 (sh), 933 (vs), 915 (sh), 870 (vs), 800 (s), 675 (s)
$(CH_3)_3Si$-*closo*-$C_2B_3H_4$[b]	2965 (vs), 2905 (m), 2602 (vs), 1410 (m), 1330 (vs), 1255 (vs), 1065 (vs), 902 (s), 865 (vs), 840 (vs), 805 (sh), 755 (s), 695 (m), 630 (s)
μ-$(CH_3)_3SiC_2B_4H_7$	3045 (m), 2960 (s), 2900 (m), 2615 (vs), 2592 (vs), 2532 (m), 1560 (m, b), 1315 (m), 1260 (s), 1070 (s), 965 (m), 845 (vs), 765 (m), 695 (m), 640 (s)
1-$(CH_3)_3SiC_2B_4H_7$	3042 (m), 2960 (vs), 2900 (m), 2600 (vs), 1910 (m), 1515 (s), 1255 (vs), 1067 (m), 920 (s), 880 (m), 838 (vs), 770 (m), 745 (m), 690 (m)
2-$(CH_3)_3SiC_2B_4H_7$	3020 (m), 2960 (vs), 2900 (m), 2600 (vs), 1935 (m), 1520 (s), 1490 (sh), 1420 (w), 1340 (s), 1260 (vs), 1103 (vs), 1055 (w), 980 (m), 915 (s), 840 (vs), 750 (m), 700 (m), 650 (w), 630 (m)
4-$(CH_3)_3SiC_2B_4H_7$	3040 (m), 2960 (vs), 2900 (m), 2600 (vs), 1925 (m, b), 1480 (m, b), 1315 (m, b), 1255 (s), 1065 (m), 1030 (w), 960 (m), 840 (vs), 800 (m), 760 (m), 695 (m), 615 (s)
μ-$GeH_3C_2B_4H_7$	3045 (m), 2620 (sh), 2600 (vs), 2572 (s), 2085 (vs), 1555 (s, b), 1328 (m), 1065 (s), 1023 (w), 965 (s), 865 (s), 815 (vs), 775 (s), 750 (m), 680 (w, b), 660 (sh)
μ-$(CH_3)_3GeC_2B_4H_7$	3045 (m), 2985 (m), 2915 (m), 2617 (s), 2592 (s), 2540 (m), 1550 (w, b), 1410 (w), 1315 (w), 1240 (m), 1065 (m), 960 (m), 832 (s), 760 (m)

[a] Derivatives of 2,3-dicarba-*nido*-hexaborane(8), except where otherwise indicated. [b] Isomer not identified.

prepare of the bridged carboranes reported here, its isomerization has not been studied in detail.

From all observations, the bridge-to-terminal rearrangements are irreversible and in this respect parallel the behavior of the silyl- and germyl-bridged B_5H_9 derivatives.[6] However, the μ-$MR_3B_5H_8$ species are reportedly stable in ether solvents only at low temperature and rearrange quantitatively in these media to terminally substituted isomers at room temperature;[6b] in contrast, the μ-$MR_3C_2B_4H_7$ derivatives are stable in ether or THF at 25°, at least over a few hours (some evidence of very slow isomerization of μ-$(CH_3)_3SiC_2B_4H_7$ in THF at 25° over a 5-day period was observed).

TABLE IV

THERMAL REARRANGEMENTS OF SILYL AND GERMYL CARBORANES

Starting material (mmol)	Temp, °C	Reaction time	Volatile products (% yield)
μ-$(CH_3)_3SiC_2B_4H_7$ (0.20)	175	0.5 hr	4-$(CH_3)_3SiC_2B_4H_7$ (99)
μ-$(CH_3)_3SiC_2B_4H_7$ (0.50)	170	19 hr	4-$(CH_3)_3SiC_2B_4H_7$ (95) 2-$(CH_3)_3SiC_2B_4H_7$ (tr) 1-$(CH_3)_3SiC_2B_4H_7$ (tr)
μ-$(CH_3)_3SiC_2B_4H_7$ (0.30)[a]	230[a]	1.0 hr	2-$(CH_3)_3SiC_2B_4H_7$ (90) 4-$(CH_3)_3SiC_2B_4H_7$[b] 1-$(CH_3)_3SiC_2B_4H_7$[b] $C_2B_4H_8$[b]
μ-$(CH_3)_3SiC_2B_4H_7$ (0.50)[a]	220[a]	4 days	2-$(CH_3)_3SiC_2B_4H_7$ (85) 2-$(CH_3)_3Si$-*closo*-2,4-$C_2B_5H_6$ (3) 2-$(CH_3)_3Si$-*closo*-$C_2B_3H_4$ (4) *closo*-1,2-$C_2B_4H_6$ (2)
2-$(CH_3)_3SiC_2B_4H_7$ (0.43)[d]	240	4 days	2-$(CH_3)_3Si$-*closo*-2,4-$C_2B_5H_6$ (16) 2-$(CH_3)_3Si$-*closo*-$C_2B_3H_4$ (16) $(CH_3)_3SiH$ (4) *closo*-1,2-$C_2B_4H_6$ (2) H_2, CH_4[c]
μ-$SiH_3C_2B_4H_7$ (0.29)	120	1.5 hr	4-$SiH_3C_2B_4H_7$ (99)
μ-$SiH_3C_2B_4H_7$ (1.09)	230	16.5 hr	*closo*-$C_3B_5H_7$ (23) 1-$SiH_3C_2B_4H_7$ (5) 4-$SiH_3C_2B_4H_7$ (3) 2-$SiH_3C_2B_4H_7$ (12) $C_2B_4H_8$ (14) *closo*-2,4-$C_2B_5H_7$ (tr) SiH_3-*closo*-$C_2B_3H_4$ (1) SiH_4, H_2[b]
4-$SiH_3C_2B_4H_7$ (0.29)[e]	220	65 hr	*closo*-$C_3B_5H_7$ (26) 1-$SiH_3C_2B_4H_7$ (5) 2-$SiH_3C_2B_4H_7$ (5) $C_2B_4H_8$ (12) *closo*-2,4-$C_2B_5H_7$ (2) SiH_3-*closo*-$C_2B_3H_4$ (1) SiH_4 (11) H_2[b]
μ-$(CH_3)_3GeC_2B_4H_7$ (0.5)[f]	80	3.0 hr	4-$(CH_3)_3GeC_2B_4H_7$ (99)

[a] At 220–230°, pyrolysis of 4-$Si(CH_3)_3C_2B_4H_7$ yields the same products. [b] Yields not determined. [c] Combined yield of H_2 and CH_4 was 0.106 mmol. [d] 70% of the starting material was recovered. [e] 4% of the starting material was recovered. [f] Pyrolysis of liquid sample in sealed nmr tube.

At higher temperatures the terminally B-substituted carboranes undergo further isomerization as well as more complex cage rearrangements. These reactions have been studied in detail for the silyl and trimethylsilyl derivatives, and data from some of the more illustrative experiments are presented in Table IV.

Rearrangement of Terminally Substituted $(CH_3)_3SiC_2B_4H_7$ Isomers.—The 4-trimethylsilyl derivative is converted in high yield to 2-$(CH_3)_3SiC_2B_4H_7$ at 220–240° (the same product is also formed directly from μ-$(CH_3)_3SiC_2B_4H_7$). On prolonged heating, the 2-substituted compound is converted to trimethylsilyl derivatives of the *closo*-carboranes $C_2B_3H_5$ and $C_2B_5H_7$, presumably by disproportionation of the C_2B_4 cage (Table IV). This latter process appears to parallel the synthesis of *closo*-carboranes from parent $C_2B_4H_8$ at high temperatures.[10,11] (See Scheme I.)

These results tend to confirm the higher thermodynamic stability of the *C*-trimethylsilyl carborane species as compared to their B-substituted isomers, which

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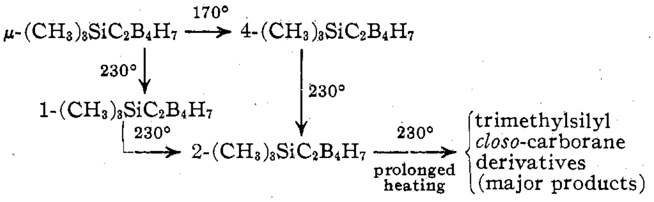
(10) (a) J. F. Ditter, *Inorg. Chem.*, **7**, 1748 (1968); (b) T. P. Onak, R. P. Drake, and G. B. Dunks, *ibid.*, **3**, 1686 (1964).

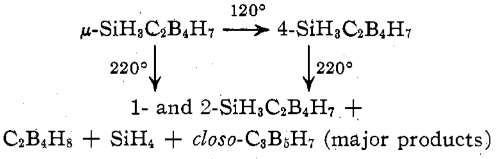
(11) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Amer. Chem. Soc.*, **85**, 3378 (1963).

SCHEME I



was previously suspected from studies[4] of alkylsilane-carborane reactions which gave only C-substituted silyl carboranes.

Rearrangement of Terminally Substituted SiH_3-$C_2B_4H_7$ Isomers.—The chemistry of the silyl carboranes at high temperature differs substantially from that of the trimethylsilyl species. At 220–230° 4-$SiH_3C_2B_4H_7$ produces modest yields of both the 1- and 2-$SiH_3C_2B_4H_7$ isomers (Figures 2c and 2d), but the major product is a novel material which has been characterized[12] as *closo*-$C_3B_5H_7$, a carborane system containing a hydrogen-free carbon atom. Pyrolysis of μ-$SiH_3C_2B_4H_7$ (a precursor of the 4-SiH_3 isomer) at 220° generates essentially the same product distribution (Table IV). These products imply that three different processes are important in the thermolysis of μ-$SiH_3C_2B_4H_7$ at progressively higher temperatures: (1) isomerization to the 4-SiH_3 derivative, which in turn is converted to roughly equal amounts of 1- and 2-$SiH_3C_2B_4H_7$ (higher temperatures favor the 1 isomer); (2) disproportionation to produce *closo*-carboranes, during which the $C_3B_5H_7$ probably forms; and (3) decomposition to the parent $C_2B_4H_8$, silane, hydrogen, and solids. Since neither significant decomposition nor $C_3B_5H_7$ formation is observed when μ-$(CH_3)_3SiC_2B_4H_7$ is pyrolyzed under similar conditions, one assumes that the high reactivity of the Si–H bond is primarily responsible for the difference and that radicals containing Si–C bonds may be important in the mechanism.



The existence of an equilibrium between the 1-, 2-, and 4-silyl derivatives at 220° is suggested by one experiment in which the pyrolysis of 1-$SiH_3C_2B_4H_7$ at that temperature generated small amounts of the 2 and 4 isomers. Since the reaction also produced $C_2B_4H_8$, *closo*-carboranes, and H_2 (see Experimental Section), it appeared too complex for detailed investigation and was not studied further.

Experimental Section

General Procedures.—Standard high-vacuum techniques were used throughout. Gas–liquid chromatography was conducted on columns constructed of 0.25 in. × 12 ft copper tubing and sealed into a vacuum system. The liquid phases employed were Apiezon L and Kel-F greases, each 30% by weight on Chromosorb W, with nitrogen carrier gas.

Known silanes, germanes, boranes, and carboranes were identified from their infrared and/or mass spectra by comparison with literature spectra. Vapor pressure and glpc data for the new compounds are given in Table V.

Instrumentation.—The equipment included a Beckman IR-8 grating spectrophotometer, a Perkin-Elmer Hitachi RMU-6D mass spectrometer, and a Varian HA-100 nmr spectrometer (for ^1H and ^{11}B resonances). Gas infrared spectra were obtained in 9-cm Pyrex cells fitted with NaCl windows.

TABLE V

VAPOR PRESSURES AND CHROMATOGRAPHIC RETENTION VOLUMES

Compound	Vapor pressure, Torr 0°	Vapor pressure, Torr 23°	Relative R_v[a] (°C)
μ-$SiH_3C_2B_4H_7$	6.5	16	*b*
4-$SiH_3C_2B_4H_7$	6.8	24.0	3.6 ± 0.3 (73°)[c]
1-$SiH_3C_2B_4H_7$	10.5	34.0	2.6 ± 0.1 (73°)[c]
2-$SiH_3C_2B_4H_7$		(36)[d]	2.0 ± 0.1 (73°)[c,e]
closo-$C_3B_5H_7$	7.8	26.8	2.0 ± 0.1 (73°)[c,e]
μ-$(CH_3)_3SiC_2B_4H_7$		1.4 (24°)	*b*
4-$(CH_3)_3SiC_2B_4H_7$		3.3	1.3 ± 0.1 (110°)[f]
2-$(CH_3)_3SiC_2B_4H_7$		4.0	1.00 (110°)
1-$(CH_3)_3SiC_2B_4H_7$		~4	0.85 ± 0.03 (110°)[f]
2-$(CH_3)_3$Si-*closo*-2,4-$C_2B_5H_6$			0.59 ± 0.03 (110°)[f]
$(CH_3)_3$Si-*closo*-$C_2B_3H_4$			0.18 ± 0.02 (110°)[f]
μ-$GeH_3C_2B_4H_7$		7.5 ± 0.5	*b*

[a] Apiezon L on Chromosorb W (see Experimental Section). [b] Very long R_v; chromatographic separation not practicable. [c] R_v relative to 2,3-$C_2B_4H_8$ = 1.0. [d] Estimated value. [e] 2-$SiH_3C_2B_4H_7$ and $C_3B_5H_7$ are separated on a Kel-F column (see Experimental Section) at 41°, with $R_v(SiH_3C_2B_4H_7)/R_v(C_3B_5H_7) = 0.62$. [f] R_v relative to 2-$(CH_3)_3SiC_2B_4H_7$ = 1.0.

Mass Spectra.—At 70 eV ionizing voltage, the mass spectra of all of the silicon and germanium carborane derivatives exhibit considerable hydrogen loss. When low (~15–20 eV) ionizing voltages are employed, this effect is minimized and the calculated polyisotopic spectrum is approximated. In all cases a sharp cutoff is observed at the value of *m/e* corresponding to the parent ion. In the spectra of the trimethylsilyl and trimethylgermyl derivatives, the most intense peaks are found near P − 15 (corresponding to loss of a methyl group), a phenomenon typically encountered among group IV alkyl derivatives.[13]

Materials.—Pentaborane(9) and silane (both from Matheson), trimethylchlorogermane, methyllithium (1.66 *M* solution in diethyl ether), tetrachlorogermane (all from Alfa), trimethylchlorosilane (Matheson Coleman and Bell), and sodium hydride (61% dispersion in mineral oil, Metal Hydrides, Inc.) were used as received. Tetrahydrofuran (Eastman) was dried over lithium aluminum hydride and distilled *in vacuo* immediately prior to use. Dimethyl ether (Matheson) was allowed to stand overnight over lithium aluminum hydride at −78°. Acetylene (Matheson) was fractionated through a −128° trap before use. Di-*n*-butyl ether (Baker) was distilled from lithium aluminum hydride. Hydrogen chloride was generated from reagent grade sodium chloride and sulfuric acid and passed through a −128° trap. 2,3-Dicarbahexaborane(8) was prepared from pentaborane(9) and acetylene by the method of Onak, *et al.*[10b] Chlorosilane was prepared from the gas-phase reaction of silane and hydrogen chloride in the presence of aluminum chloride[14] and was purified by fractionation through traps at −112, −135, and −196°. Chlorosilane was collected at −135° and its purity checked by vapor pressure measurements (49 Torr at −78°). Germane was prepared by reducing tetrachlorogermane with lithium aluminum hydride in di-*n*-butyl ether.[15] Chlorogermane was obtained from the gas-phase reaction of germane and hydrogen chloride at room temperature in the presence of aluminum chloride,[16] and was purified by passage through a −78° trap and condensation in a −112° trap (vapor pressure at −30.6° = 45 Torr).

2,3-Heptahydrodicarbahexaborate(1−) Anion, $C_2B_4H_7^-$.—Ethereal solutions of this anion were prepared by two routes, the method chosen depending upon the bridged carborane to be prepared (see below).

Method 1.[7]—Typically, a mixture of 0.212 g of sodium hydride–mineral oil dispersion (61 wt % NaH, 5.40 mmol of active hydride) and 2.0 ml of dry tetrahydrofuran was placed in an

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(12) M. L. Thompson and R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 6677 (1971).

(13) (a) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962); (b) V. H. Dibeler, *J. Res. Nat. Bur. Stand.*, **49**, 235 (1952), and references therein.

(14) (a) A Stock and C. Somieski, *Ber.*, **52**, 695 (1919); (b) H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).

(15) A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 2692 (1947).

(16) L. M. Dennis and P. R. Judy, *ibid.*, **51**, 2321 (1929).

evacuated apparatus containing a medium-porosity glass filter. To this material at −196° was added 2.00 mmol of 2,3-dicarbahexaborane(8) by vacuum distillation. Evolution of hydrogen began shortly after removal of the liquid nitrogen bath and continued until the reactor had been at room temperature for several minutes. The hydrogen was removed by pumping and the contents then filtered, giving a filtrate consisting of a solution of $Na^+C_2B_4H_7^-$ in tetrahydrofuran; excess sodium hydride was retained on the filter. The solution of $Na^+C_2B_4H_7^-$ was removed from the filtration assembly under vacuum prior to further work.

Method 2.—This procedure affords solutions of the lithium salt in dimethyl ether. Typically, 3.0 ml of a 1.66 *M* solution of methyllithium in diethyl ether (5.0 mmol of active methyllithium) was transferred to a reaction tube which had previously been evacuated, degassed, and filled with nitrogen. After attachment to the vacuum line the diethyl ether was distilled away, and approximately 4 ml of dimethyl ether was condensed into the bulb at −196° followed by 5.04 mmol of 2,3-$C_2B_4H_8$. Following the reaction, the mixture was cooled to −196° and the evolved methane was pumped off.

μ-Trimethylsilyl-2,3-dicarbahexaborane(8).—Trimethylchlorosilane (2.58 mmol) was condensed at −196° into a reaction flask containing 1.86 mmol of $Na^+C_2B_4H_7^-$ in tetrahydrofuran. The contents of the flask was warmed to 0° over 0.5 hr and then maintained at 0° for 1 hr while stirring magnetically. The product was isolated by distillation through a trap at −23° and condensation at −45°. Several passes through the −45° trap were necessary to remove all of the solvent and excess trimethylchlorosilane. Small amounts of 2,3-dicarbahexaborane(8) and bis(trimethylsilyl) ether were also obtained in the −45° distillate. The product, a colorless liquid with a vapor pressure of ~1 Torr at 23°, was obtained in 60% yield (166 mg).

μ-Silyl-2,3-dicarbahexaborane(8).—The preferred synthesis utilized dimethyl ether solutions of $Li^+C_2B_4H_7^-$ (method 2 above) in order to minimize difficulties of separating the product and solvent. Typically, chlorosilane (5.26 mmol) was condensed into a flask containing 5.04 mmol of $Li^+C_2B_4H_7^-$ in dimethyl ether. The flask was warmed slowly to −31°, and that temperature was maintained for 2 hr in a bromobenzene slush bath while stirring. The product, a colorless liquid (3.0 mmol, 60% yield), was purified by condensation in a −63° trap; several passes were necessary to remove all traces of diethyl ether, $C_2B_4H_8$, and disilyl ether, which passed through. The μ-SiH_3-$C_2B_4H_7$ appears stable at room temperature but is very susceptible to hydrolysis, as evidenced by the detection of $C_2B_4H_8$ and $(SiH_3)_2O$ in samples which were transferred to freshly evacuated Pyrex bulbs containing traces of moisture.

μ-Trimethylgermyl-2,3-dicarbahexaborane(8).—Trimethylchlorogermane (1.30 mmol) was condensed at −196° into a flask containing 0.97 mmol of $Na^+C_2B_4H_7^-$ in 2 ml of tetrahydrofuran. The reaction appeared to proceed very slowly (as indicated by the appearance of insoluble sodium chloride) as the contents was warmed to room temperature. After stirring for 1 hr at room temperature, the volatiles were passed through a series of traps at −23, −45, and −196°. The major portion of the desired product was collected at −23° with a smaller amount in the −45° trap. The −196° condensate consisted of tetrahydrofuran and excess trimethylchlorogermane. The product, obtained in >70% yield, exhibits <0.1 Torr vapor pressure at 23° but distills readily *in vacuo*.

μ-Germyl-2,3-dicarbahexaborane(8), μ-$GeH_3C_2B_4H_7$.—Chlorogermane (1.87 mmol) was condensed at −196° into a bulb containing 1.94 mmol of $Na^+C_2B_4H_7^-$ in 2 ml of tetrahydrofuran. Yellow deposits formed immediately upon removal of the liquid nitrogen. The contents was allowed to warm to 0° and maintained at 0° for 0.5 hr. The desired product was purified by repeated condensation in a −45° trap; the distillate was identified as a mixture of tetrahydrofuran, 2,3-$C_2B_4H_8$, and chlorogermane. The pure product was obtained in 2% yield (0.039 mmol).

An attempted preparation using chlorogermane and $Li^+C_2B_4H_7^-$ in dimethyl ether was carried out on a larger scale (3.0 mmol). Yellow deposits were again immediately evident on warming from −196°. The reaction temperature was held at or below −31° for 0.5 hr. Fractional condensation of the volatiles resulted in recovery of 1.9 mmol of $C_2B_4H_8$, but no detectable amount of the bridged germyl derivative was obtained.

Preparation of μ-Trimethylsilyl-2-trimethylsilyl-2,3-dicarbahexaborane(8).—A 0.25-mmol sample of 2-$(CH_3)_3SiC_2B_4H_7$ was allowed to react with excess sodium hydride in tetrahydrofuran at 25°. Approximately 1 mmol of noncondensable gas was evolved. After filtration, an excess of trimethylchlorosilane was condensed into the filtrate at −196°. No obvious formation of a white precipitate was evident as the contents warmed to room temperature. The volatiles were passed through a 23° trap, and the resulting −23° condensate exhibited 0.1 Torr vapor pressure at room temperature. A mass spectrum of this material corresponded to $[(CH_3)_3Si]_2C_2B_4H_6$, with a series of peaks cutting off at *m/e* 222 (assigned to $^{29}Si_2{}^{12}C_8{}^{11}B_4H_{24}{}^+$) and a series at 149 (corresponding to loss of a $(CH_3)_2SiCH_2$ group).

Attempted Preparation of Di-μ-silyl-dicarbahexaborane(8).—μ-Silyl-2,3-dicarbahexaborane(8) (0.43 mmol) was treated with an excess of sodium hydride in 2 ml of tetrahydrofuran. Deprotonation of the remaining bridge hydrogen appeared to go to completion, as evidenced by the evolution of an appropriate quantity of a noncondensable gas. After filtration to remove the excess sodium hydride, the filtrate was treated with 0.70 mmol of chlorosilane. White deposits appeared in the mixture as it was stirred, and the temperature was raised from −196° to room temperature. Attempts to isolate the desired product by fractional condensation yielded only solvent, chlorosilane, and the original μ-SiH_3-2,3-$C_2B_4H_7$.

Thermolysis of Silyl-, Trimethylsilyl- and Trimethylgermyl-dicarbahexaboranes.—In the usual procedure the starting material was distilled into an evacuated degassed Pyrex bulb at −196° equipped with either a breakoff tip or a Teflon high-vacuum stopcock containing Viton O-rings (Ace Scientific Co.) (apparatus of the latter type was used only at temperatures below 165°). After sealing and warming to room temperature, the reactor was placed in an oven. Following the reaction, the bulb was cooled to −196° and opened on the vacuum line, and the volatile materials were distilled and separated by fractionation and/or gas chromatography. Data from selected experiments are presented in Table IV. The silyl and trimethylsilyl *closo*-carborane products were identified from their mass spectra, which in all cases contained strong parent peaks and profiles in agreement with calculated intensities, and from infrared spectra. The compound 2-$(CH_3)_3Si$-2,4-$C_2B_4H_6$ has been previously reported.[4,17]

In a few instances, neat liquid samples were pyrolyzed in sealed Pyrex 5-mm diameter nmr tubes so that the isomerization could be followed periodically by boron-11 nmr spectroscopy. By this method the virtually quantitative conversions of μ-$(CH_3)_3SiC_2B_4H_7$ to 4-$(CH_3)_3SiC_2B_4H_7$ in 8 hr at 175° and of μ-$(CH_3)_3GeC_2B_4H_7$ to 4-$(CH_3)_3GeC_2B_4H_7$ in 3 hr at 80° were monitired at intervals of 20–30 min. Similar treatment of μ-$GeH_3C_2B_4H_7$ was inconclusive: the 32.1-MHz ^{11}B nmr spectrum of a sample which was heated at 120° for 0.5 hr underwent substantial change which is attributed to partial isomerization, probably to the 4-GeH_3 isomer. Further pyrolysis of the same sample at 170° for 20 min resulted in complete decomposition with formation of yellow-orange solids.

Pyrolysis of a 0.06-mmol sample of 1-$SiH_3C_2B_4H_7$ at 220° for 15.5 hr produced 2-$SiH_3C_2B_4H_7$ (0.004 mmol), 4-$SiH_3C_2B_4H_7$ (0.006), traces of SiH_3-*closo*-$C_2B_3H_4$, $C_2B_4H_8$, and SiH_4, and H_2; 0.027 mmol of the 1 isomer remained unreacted.

Acknowledgments.—We thank Dr. Alton Tabereaux for assistance in obtaining some of the nmr data reported herein. This work was supported by the Office of Naval Research.

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[17] R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 5072 (1970).