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Tin- and Lead-Bridged Carboranes. Further Studies on Silicon- and Germanium-Bridged $C_2B_4H_8$ Derivatives[1]

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The compounds μ-$(CH_3)_3SnC_2B_4H_7$ and μ-$(CH_3)_3PbC_2B_4H_7$ have been prepared and structurally characterized. In contrast to the analogous silicon and germanium species, the tin and lead derivatives fail to undergo thermal rearrangement to terminally substituted isomers, but react with HCl to generate $C_2B_4H_8$ quantitatively. Reaction with DCl generates μ-$DC_2B_4H_7$ with no evidence of terminal B–D bonds. The reaction of μ-$(CH_3)_3GeC_2B_4H_7$ and μ-$(CH_3)_3SiC_2B_4H_7$ with HCl to liberate $C_2B_4H_8$ is considerably slower. The reaction of μ-$(CH_3)_3SiC_2B_4H_7$ with NaH involves both bridge deprotonation and bridge-to-terminal silicon migration, giving the 4-$(CH_3)_3SiC_2B_4H_6^-$ anion; treatment of this ion with DCl gives μ-D-4-$(CH_3)_3SiC_2B_4H_6$ and with $(CH_3)_3SiCl$ yields μ,4-$[(CH_3)_3Si]_2C_2B_4H_6$. The reaction of μ-$(CH_3)_3GeC_2B_4H_7$ with NaH followed by $(CH_3)_3SiCl$ gives a bis(carboranyl) species of apparent composition $(C_2B_4H_6)_2GeSi_2(CH_3)_8$. In contrast, μ-$(CH_3)_3$Sn- and μ-$(CH_3)_3PbC_2B_4H_7$ are nearly inert toward NaH at room temperature. The reaction of $C_2B_4H_7^-$ ion with SiH_2Cl_2 yields μ,μ'-$SiH_2(C_2B_4H_7)_2$, which at 100° converts to 4,4'-$SiH_2(C_2B_4H_7)_2$, but reaction of $C_2B_4H_7^-$ with other $RR'SiCl_2$ reagents fails to give bis(carboranyl)silanes. Thus, methyldichlorosilane and cyclotetramethylenedichlorosilane yield μ-$(CH_3SiH_2)C_2B_4H_7$ and μ-$[(CH_2)_4SiCl]C_2B_4H_7$, respectively; the latter species rearranges to the 4 isomer at 220°. The $C_2B_4H_7^-$ ion is nearly inert toward $(CH_3)_2SiCl_2$ and reacts with GeH_2Cl_2 to give only polymer.

Introduction

An earlier paper[2] from our laboratory described the synthesis and rearrangement of carboranes of the type μ-$MR_3C_2B_4H_7$ (M = Si, Ge; R = H, CH_3), which are derivatives of parent *nido*-$C_2B_4H_8$ containing ligands attached to the cage *via* B–M–B three-center bonds. In related work,[3] Wallbridge and Savory have prepared trimethylsilyl- and trimethylgermyl-bridged analogs containing methyl groups on the cage carbon atoms, the properties of which are remarkably different in some respects from the derivatives lacking C-bonded ligands (discussed below). We wish to report here the extension of our earlier work to the heavier group IV elements, as well as the synthesis of new silicon- and germanium-bridged species and some new chemistry of compounds of this type.

Results and Discussion

Preparation of μ-$(CH_3)_3SnC_2B_4H_7$ and μ-$(CH_3)_3PbC_2B_4H_7$. The reaction of sodium dicarbahexaborate(1–) with trimethylbromostannane or trimethylchloroplumbane in tetrahydrofuran (THF) solution forms the respective μ-trimethylmetaldicarbahexaborane(8) derivative in 65–70% yield. The carborane products are colorless liquids of low volatility (<0.1 Torr at 25°) but readily distillable *in vacuo*. The mass spectra of both compounds exhibit strong P – 15 peaks, corresponding to the loss of one methyl group, and profiles in good agreement with the calculated intensities based on normal isotope distributions. The ^{11}B nmr spectra (Table I) contain only doublets arising from B-H terminal groups, indicating that terminal B-Sn or B-Pb bonding is absent and the substituent groups are in bridging positions as shown in Figure 1. The proton nmr data (Table II) are similar to those of the silicon and germanium analogs presented earlier.[2] See Table III for ir data.

$$Na^+C_2B_4H_7^- + (CH_3)_3MX \xrightarrow[\text{1 hr}]{\text{23°, THF}} \mu\text{-}(CH_3)_3MC_2B_4H_7 + NaX$$

$$M = Sn,\ X = Br;\ M = Pb,\ X = Cl$$

The μ-trimethyltin and -lead carboranes complete the series of group IV bridged $C_2B_4H_8$ derivatives, except for the analogous carbon-bridged species which remains unknown.

Attempted Isomerization of μ-$(CH_3)_3SnC_2B_4H_7$ and μ-$(CH_3)_3PbC_2B_4H_7$. In contrast to the μ-trimethylsilyl and μ-trimethylgermyl derivatives, which rearrange quantitatively to terminally B-substituted species at elevated temperatures,[2] this work has yielded no evidence of isomerization of the tin- and lead-bridged species as monitored by ^{11}B nmr spectroscopy. The tin compound is stable indefinitely at 120° but decomposes rapidly at 220°, yielding trimethylstannane and parent $C_2B_4H_8$; at intermediate temperatures the same compounds are formed more slowly. The lead derivative is less stable, decomposing completely to analogous products in 48 hr at room temperature and more rapidly at 120°. In no experiments with either compound has an intermediate species been detected.

$$\mu\text{-}(CH_3)_3MC_2B_4H_7 \xrightarrow{\Delta} 4\text{-}(CH_3)_3MC_2B_4H_7 \quad (M = Si, Ge)$$

$$\mu\text{-}(CH_3)_3MC_2B_4H_7 \xrightarrow{\Delta} (CH_3)_3MH + C_2B_4H_8 + \text{solids} \quad (M = Sn, Pb)$$

A possible rationale for the failure of the tin and lead compounds to isomerize is that the bulky MR_3 groups preclude formation of a suitable transition state. For example, if the transition state for rearrangement to the 4-$(CH_3)_3MC_2B_4H_7$ species involves simultaneous bonding of a terminal hydrogen and a terminal MR_3 group to B(4), prior to migration of the terminal hydrogen to the vacant bridging position, models suggest that it would be sterically more difficult for a trimethylstannyl or -plumbyl moiety to achieve such a configuration than would be the case with the smaller trimethylsilyl and -germyl groups in which the M-CH_3 bonds are expected to be ~0.2 Å shorter. The probability that kinetic rather than thermodynamic factors are primarily responsible for the failure of the tin- and lead-bridged compounds to rearrange is supported by the fact that μ-$(CH_3)_3SnC_2B_4H_7$ remains largely unchanged over long periods at 180°, a temperature sufficient to cause rapid isomerization of the analogous silicon and germanium carboranes.[2]

Reaction of Group IV Bridged Carboranes with HCl. The tin- and lead-bridged derivatives react easily with anhydrous HCl to generate parent $C_2B_4H_8$ in nearly quantitative yield. The corresponding reaction with DCl produces μ-$DC_2B_4H_7$

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 1972.

[2] M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, 11, 1925 (1972).

[3] (a) C. G. Savory and M. G. H. Wallbridge, *Chem. Commun.*, 622 (1971); (b) C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 8/9, 918 (1972).

Table I. 32.1-MHz Boron-11 Nmr Data[a]

Compound	B(1)	B(4,5,6)
μ-$(CH_3)_3SnC_2B_4H_7$	+51.3 (182)	+2.28 (137), –5.35 (147), –2.12 (158)
μ-$(CH_3)_3PbC_2B_4H_7$	+51.0 (183)	+0.89 (138), –5.34 (148), –2.54 (157)
$\mu(5,6),4$-$[(CH_3)_3Si]_2C_2B_4H_6$	+53.5 (183)	–10.9 [B(4)], +1.56 (155) [B(5,6)][b]
μ-D-4-$(CH_3)_3SiC_2B_4H_6$	+54.0 (184)	–2.34 [B(4)], +0.25 (162) [B(5,6)][b]
μ,μ'-$SiH_2(C_2B_4H_7)_2$	+45.7 (184)	+6.95 (137) [B(4,4′)–H], –12.8 (163) [B(5,5′)–H], –1.60 (167) [B(6,6′)–H]
4,4′-$SiH_2(C_2B_4H_7)_2$	+52.4 (182)	–0.80 [B(4,4′)], –1.86 (158) [B(5,5′,6,6′)–H][b]
μ-$(CH_3SiH_2)C_2B_4H_7$	+47.7 (175)	+3.18 (138), –7.00 (160), –0.77 (159)
μ-$[(CH_2)_4SiCl]C_2B_4H_7$	+44.7 (185)	+4.66 (162), –14.9 (157), –0.30 (165)
4-$[(CH_2)_4SiCl]C_2B_4H_7$	+52.0 (183)	+0.76 [B(4)], –1.79 (157) [B(5,6)][b]

[a] CS_2 solutions; chemical shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$; coupling constants in parentheses. [b] Chemical shifts of B(5) and B(6) are not identical, as shown by slight asymmetry of the doublet assigned to these borons.

Table II. 100-MHz Proton Nmr Data[a]

Compound	H–C cage	CH_3	H–B(1)	H–B(4,5,6)	H bridge	Other
μ-$(CH_3)_3SnC_2B_4H_7$	–6.95 –6.49	–0.43	+0.87 (181)	–3.29 (138) –3.72 (149) –3.67 (157)	+3.01	
μ-$(CH_3)_3PbC_2B_4H_7$	–7.05 –6.60	–1.42	+0.74 (182)	–3.37 (137) –3.84 (147) –3.86 (153)	+2.98	
$\mu(5,6),4$-$[(CH_3)_3Si]_2C_2B_4H_6$	–6.29	–0.11	+0.94 (181)	–3.37 (153)	+1.95	
μ-D-4-$(CH_3)_3SiC_2B_4H_6$	–6.32	0.0	+1.20 (181)	–3.34 (153)	+1.81	
μ,μ'-$SiH_2(C_2B_4H_7)_2$	–7.15 –6.75		+0.55 (182)	–3.32 (135) –3.78 (165) –4.35 (159)	+1.69	–4.00 [H–Si]
4,4′-$SiH_2(C_2B_4H_7)_2$	–6.72		+0.90 (180)	–3.65 (157)	+2.10	–3.60 [H–Si]
μ-$(CH_3SiH_2)C_2B_4H_7$	–6.35 –6.60	–0.21	+0.92 (180)	–3.15 (135) –3.70 (158) –3.80 (145)	+0.98	–3.79 [H–Si]
μ-$[(CH_2)_4SiCl]C_2B_4H_7$	–7.44	–1.36[b] –1.99[b]	+0.70 (180)	–3.79 (140) –4.40 (160) –4.60 (152)	+1.68	
4-$[(CH_2)_4SiCl]C_2B_4H_7$	–8.09	–1.11[b] –1.74[b]	+0.94 (185)	–3.68 (165)	+1.75	

[a] CS_2 solutions; chemical shifts in ppm relative to tetramethylsilane; coupling constants (Hz) in parentheses. [b] Methylene resonances.

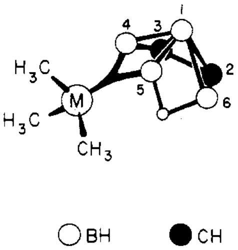

Figure 1. Proposed structure of μ-$(CH_3)_3MC_2B_4H_7$ carboranes, with M = Si, Ge, Sn, or Pb.

$$\mu\text{-}(CH_3)_3MC_2B_4H_7 + HCl \xrightarrow[1\ \text{hr}]{23°} C_2B_4H_8 + (CH_3)_3MCl$$

$$M = Sn, Pb$$

with no evidence of deuteration in terminal positions, confirming that the bridging $M(CH_3)_3$ group is replaced by the proton in the attacking HCl reagent without intramolecular hydrogen migration on the cage framework.

The reaction of μ-$(CH_3)_3GeC_2B_4H_7$ with HCl is comparatively sluggish, proceeding to 47% completion in 1 hr, while that with μ-$(CH_3)_3SiC_2B_4H_7$ is even slower, giving only a 13% yield of $C_2B_4H_8$ within 1 hr. These results are viewed as a consequence of the relatively polar B–Sn and B–Pb bonds which would be expected to be highly susceptible to HCl attack, in contrast to the less polar boron–metal bonds in the silicon and germanium derivatives (even the latter bridged compounds, however, are easily hydrolyzed to $C_2B_4H_8$ on exposure to water or moist air).

Preparation of Bis(ligand) Derivatives and Base-Catalyzed Bridge–Terminal Rearrangement. Treatment of μ-$(CH_3)_3SiC_2B_4H_7$ with sodium hydride in THF was expected to remove the remaining bridge proton and generate the μ-$(CH_3)_3SiC_2B_4H_6^-$ anion, following which reaction with $(CH_3)_3SiCl$ would presumably yield the bridge-disubstituted species μ,μ'-$[(CH_3)_3Si]_2C_2B_4H_6$. Such a reaction sequence does in fact yield a bis(trimethylsilyl) derivative, which contrary to our original assumption[4] is a bridge, terminal-disubstituted carborane, $\mu,4$-$[(CH_3)_3Si]_2C_2B_4H_6$. The 32.1-MHz ^{11}B nmr (Figure 2a) contains a singlet arising from terminal substitution of silicon on one basal boron, while all of the remaining

$$\mu\text{-}(CH_3)_3SiC_2B_4H_7 + NaH \xrightarrow[25°]{THF} Na^+[(CH_3)_3SiC_2B_4H_6]^- + H_2$$

$$Na^+[(CH_3)_3SiC_2B_4H_6]^- + (CH_3)_3SiCl \rightarrow \mu,4\text{-}[(CH_3)_3Si]_2C_2B_4H_6$$

resonances are doublets indicative of B–H terminal bonds. Thus, only one of the two ligand groups is located in a bridging position. Of the three possible isomers[5] $\mu(4,5),4$-, $\mu,5$-, and $\mu(5,6),4$-$[(CH_3)_3Si]_2C_2B_4H_6$, the $\mu(5,6),4$ structure seems most consistent with the nmr data and with other findings presented in this and earlier papers.[6,7]

Since the substitution at B(4) appeared likely to have come about *via* isomerization of the original μ-$(CH_3)_3SiC_2B_4H_7$ in the presence of sodium hydride, the $[(CH_3)_3SiC_2B_4H_6]^-$ ion produced in the NaH reaction was treated with excess DCl. The sole carborane product, obtained in 80% yield, has been identified as μ-D-4-$[(CH_3)_3Si]C_2B_4H_6$ (see Experimental

[4] See ref 2, footnote 8.

[5] The $\mu(4,5)$ notation indicates bridging between B(4) and B(5). The $\mu(4,5),4$ isomer is, of course, an enantiomer of $\mu(5,6),6$-$[(CH_3)_3Si]_2C_2B_4H_6$.

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

μ-$(CH_3)_3SnC_2B_4H_7$	3030 (m), 2985 (s), 2910 (s), 2600 (vs), 2515 (s), 1530 (m, b), 1335 (m), 1307 (s), 1200 (m), 1062 (m), 1021 (w), 961 (s), 892 (w), 780 (vs)
μ-$(CH_3)_3PbC_2B_4H_7$[b]	3020 (s), 2924 (s), 2590 (vs), 2515 (s), 1530 (m, b), 1390 (w), 1333 (m), 1300 (s), 1167 (s), 1151 (m), 1062 (s), 1055 (sh), 1020 (m), 959 (s), 920 (m), 887 (m), 845 (w), 780 (vs), 765 (sh), 745 (sh)
μ(5,6),4-$[(CH_3)_3Si]_2C_2B_4H_6$[b]	3025 (w), 2957 (s), 2930 (s), 2880 (m), 2605 (vs), 1500 (m, b), 1390 (w), 1335 (m), 1252 (s), 1100 (s), 1065 (m), 1025 (w), 960 (m), 870 (sh), 845 (vs), 755 (m, b)
μ,μ'-$SiH_2(C_2B_4H_7)_2$[c]	3030 (w), 2600 (vs), 2530 (sh), 2230 (m), 2150 (s), 1920 (m, b), 1812 (m), 1450 (sh), 1405 (sh), 1350 (vs), 1320 (sh), 1110 (sh), 1065 (vs), 960 (s), 865 (s), 840 (sh)
4,4'-$SiH_2(C_2B_4H_7)_2$[b]	3030 (w), 2600 (vs), 2110 (s), 1930 (w, b), 1485 (m), 1470 (m, b), 1350 (m), 1060 (m), 1025 (m), 970 (w), 945 (w), 925 (m), 865 (w), 840 (w), 790 (m, b), 750 (w)
μ-$CH_3SiH_2C_2B_4H_7$	3040 (m), 2982 (s), 2970 (sh), 2870 (m), 2620 (vs), 2538 (s), 2158 (vs), 1930 (w, b), 1600 (sh), 1545 (s), 1500 (w), 1450 (w), 1420 (w), 1380 (w), 1325 (m), 1260 (s), 1070 (vs), 1025 (m), 960 (vs), 905 (sh), 880 (vvs), 860 (sh), 735 (vs), 694 (m)
μ-$[(CH_2)_4SiCl]C_2B_4H_7$	3030 (m), 2940 (vs), 2870 (vs), 2600 (vs), 2520 (m), 1930 (w, b), 1550 (m, b), 1450 (m), 1400 (m), 1330 (m), 1318 (m), 1250 (w), 1152 (w), 1078 (s), 1065 (m), 1032 (m), 1020 (m), 962 (m), 890 (w), 850 (w), 795 (s), 745 (w)
4-$[(CH_2)_4SiCl]C_2B_4H_7$[c]	3030 (w), 2940 (vs), 2865 (vs), 2605 (vs), 2330 (w), 1920 (m, b), 1570 (w, b), 1455 (s), 1400 (s), 1330 (s, vb), 1255 (s), 1220 (s), 1152 (w), 1080 (s), 1020 (s), 980 (s), 682 (s), 655 (m)

[a] Gas phase except where otherwise indicated. [b] Cell heated to ~80°. [c] CCl_4 solution *vs.* CCl_4. Frequencies differ slightly from gas-phase spectrum.[7]

Section), confirming that migration of the trimethylsilyl group to the terminal position occurs during treatment with NaH; subsequent reaction of the 4-$(CH_3)_3SiC_2B_4H_7^-$ anion with $(CH_3)_3SiCl$ leads to reintroduction of silicon into a bridging location as shown in Figure 3. The bridge-terminal migration during reaction with NaH may be reasonably interpreted as a Lewis base catalyzed process similar to the rearrangement of μ-trimethylsilyl-pentaborane(9).[8] However, it is noteworthy that isomerization of the latter compound is instigated even by relatively weak bases such as ethers, whereas the bridged carborane is stable over extended periods under these conditions.[2]

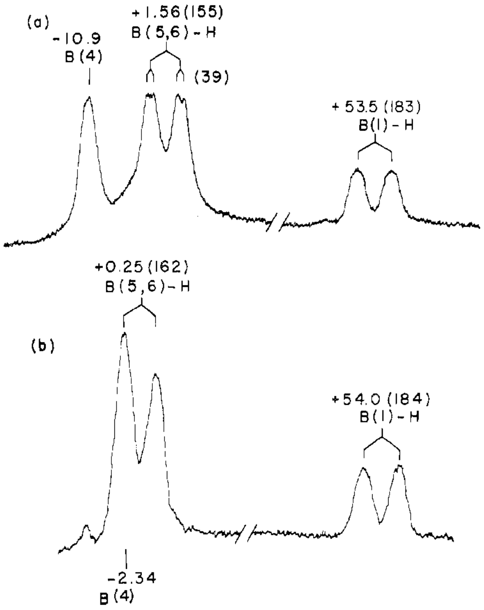

Figure 2. The 32.1-MHz ^{11}B nmr spectra of (a) μ,4-$[(CH_3)_3Si]_2$-$C_2B_4H_6$ and (b) μ,D-4-$[(CH_3)_3Si]C_2B_4H_6$ in CS_2 solutions. Chemical shifts are relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants are in parentheses.

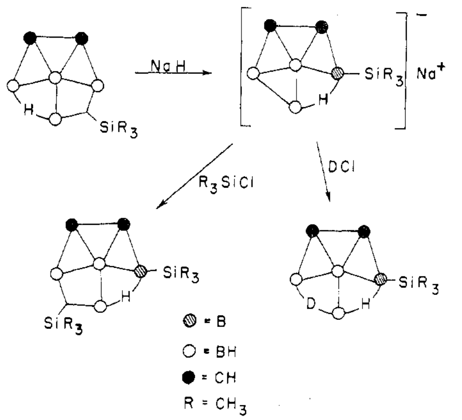

Figure 3. Reaction sequence for the formation of bridge, terminal-disubstituted derivatives from μ-$(CH_3)_3SiC_2B_4H_7$.

Treatment of the analogous germanium compound, μ-$(CH_3)_3GeC_2B_4H_7$, with NaH followed by reaction with $(CH_3)_3SiCl$ in an attempt to prepare μ-$(CH_3)_3$Ge-μ'-$(CH_3)_3$-$SiC_2B_4H_6$, yields a slightly volatile material whose nmr and mass spectra are suggestive of a bis(carboranyl) species of composition $(C_2B_4H_6)_2GeSi_2(CH_3)_8$. The expected bridge-disubstituted compound has not been found, and the reaction is evidently complicated both by the cleavage of some Ge-CH_3 links and by incomplete cage deprotonation (only 30% of the expected volume of H_2 is produced in the reaction with NaH).

The μ-$(CH_3)_3$Sn- and μ-$(CH_3)_3PbC_2B_4H_7$ carboranes are only slightly reactive toward sodium hydride, even at room temperature. This result is quite consistent with the previous observations that deprotonation of the bridged trimethylsilyl and trimethylgermyl compounds is accompanied by bridge-

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(6) Attachment of the terminally bonded ligand to B(4) is assumed because (1) thermal rearrangement of μ-$(CH_3)_3SiC_2B_4H_7$ yields the 4-substituted isomer quantitatively[2] and base-induced isomerization would be expected to proceed similarly, and (2) the nearly identical ^{11}B nmr chemical shifts of the two basal B-H groups (Figure 2a) are difficult to reconcile with a μ,5 isomer, in which either B(4)-H or B(6)-H, but not both, would be adjacent to the bridging $(CH_3)_3Si$ group. Of the two remaining possible isomers, the ^{11}B nmr spectrum of the μ(4,5),4 isomer would be expected to exhibit an unusually sharp singlet arising from the substituted B(4) atom, which would be adjacent to only one other boron [*i.e.*, B(1)] and thus would experience minimal B-B quadrupolar broadening (similar effects have been noted previously, *e.g.*, in μ,μ'-$SiH_2(C_2B_4H_7)_2$[7]). Since the terminal B-Si singlet is actually rather broad, the spectrum appears more consistent with substitution at the μ(5,6),B(4) positions. Finally, the μ(5,6),4-$[(CH_3)_3Si]_2C_2B_4H_6$ isomer is the most plausible from a steric standpoint since the bulky ligand groups are well separated.

(7) A. Tabereaux and R. N. Grimes, *J. Amer. Chem. Soc.*, 94, 4768 (1972).

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

to-terminal isomerization and that the tin and lead analogs fail to rearrange even on heating. Thus, if rearrangement to the terminal B(4)-substituted isomer is actually a necessary precondition for bridge deprotonation, the inability of the tin- and lead-bridged compounds to isomerize would explain their near-inertness toward hydride ion.

From this and other work, it is clear that the chemical behavior of $C_2B_4H_8$ derivatives is markedly influenced by the location of substituents on the cage. In contrast to our own observation[2] that μ-$(CH_3)_3SiC_2B_4H_7$ isomerizes quantitatively and rapidly to the 4-substituted isomer at 175°, Wallbridge and Savory have found that C,C'-$(CH_3)_2$-μ-$(CH_3)_3SiC_2B_4H_5$ decomposes at 80° with no evidence of rearrangement.[3b] Moreover, these workers observed no H_2 evolution on treatment of the latter compound with NaH, a remarkable result in view of our finding that μ-$(CH_3)_3SiC_2B_4H_7$ is easily and quantitatively bridge deprotonated by this reagent (see above). Although they did observe thermal rearrangement of C,C'-$(CH_3)_2$-μ-$(CH_3)_3GeC_2B_4H_5$ to a terminally bonded isomer at 140° in 7 days,[3b] the same bridged compound was found to be stable at 80°; at this temperature, μ-$(CH_3)_3GeC_2B_4H_7$ rearranged quantitatively within 3 hr in our study.[2] Since the C-bonded methyl groups are unlikely to affect sterically either μ-to-4 isomerization or bridge deprotonation, the explanation presumably lies in the influence of the methyl groups on the electronic structure of the cage. In view of the delocalized bonding in this pseudo-aromatic cage framework, such an effect is not unreasonable but much further study is clearly warranted.

Preparation of μ,μ'-Bis(carboranyl)silanes. The existence of numerous $C_2B_4H_8$ derivatives containing group IV atoms in bridging positions suggested that this structural principle might be extended to μ,μ'-bis(carboranyl) compounds in which a single metal atom is bridge-bonded to two carborane cages, with two of the sp^3 tetrahedral orbitals on the heteroatom involved in separate three-center, two-electron B–M–B bonds. Since models suggested that bulky organic ligands on the heteroatom would be subject to severe steric constraints, the first reaction to be examined was that of the carborane anion with dichlorosilane, which gives the desired compound in good yield (a preliminary communication[7] on this work has appeared). The mass spectrum of the product (Table IV)

$$2Na^+C_2B_4H_7^- + SiH_2Cl_2 \rightarrow \mu,\mu'\text{-}SiH_2(C_2B_4H_7)_2 + 2NaCl$$

is consistent with a bis(dicarbahexaboranyl)silane, and the ^{11}B nmr spectrum (Figure 4a) contains only B–H doublets, thus eliminating terminal B–Si bonds. The infrared spectrum (Table III) contains a split B–H stretching band near 2600 cm^{-1}, a characteristic feature of the vibrational spectra of all known heteroatom-bridged $C_2B_4H_8$ derivatives[2,3b] (conversely, the spectra of derivatives lacking bridge substitution exhibit only a singlet in the B–H stretching region). Since the proton nmr spectrum (Figure 5) exhibits distinct singlets, each of area 2, corresponding to the two types of C–H groups, C–Si links are also ruled out and the bridge-substituted structure is established.

As is indicated in Figure 6, two geometric isomers are possible, a consequence of the fact that the $C_2B_4H_7^-$ ion lacks a plane of symmetry and exists in two enantiomorphic forms. The μ,μ'-$SiH_2(C_2B_4H_7)_2$ isomers are not expected to have significantly different ^{11}B nmr spectra, since in both isomers each boron atom in one cage has a magnetically equivalent counterpart in the other; indeed, the spectrum gives no indication of the presence of more than one bridged species. However, since the silylene protons are equivalent in isomer A but not in B, the two compounds should be distinguishable in the proton nmr spectrum, and the H–Si region of the spectrum does indeed contain an apparent small doublet corresponding to isomer B, partially overlapping a large singlet attributed to A. Thus it appears that isomer A is predominant although the evidence is not conclusive. The indicated preference for the formation of A can be accounted for in terms of the slightly more favorable spacial arrangement of the two cages relative to each other in A.

Table IV. Partial Mass Spectrum of μ,μ'-$SiH_2(C_2B_4H_7)_2$ at 15 eV[a]

m/e	Rel intens	m/e	Rel intens
182[b]	5.8	175	81.2
181	7.4	174	53.3
180	33.7	173	27.8
179	57.2	172	16.2
178	72.1	171	16.2
177	81.3	170	7.4
176	100.0	169	6.5

[a] Intense groupings are also observed with cutoffs at m/e 105 and 76, corresponding to $SiH_2C_2B_4H_7^+$ and $C_2B_4H_8^+$, respectively.
[b] Assigned to the $^{30}Si^{12}C_4{}^{11}B_8{}^1H_{16}{}^+$ parent ion.

Pyrolysis of μ,μ'-$SiH_2(C_2B_4H_7)_2$ at 100° in CS_2 solution yields quantitatively the terminally B-substituted isomer 4,4'-$SiH_2(C_2B_4H_7)_2$. The mass spectrum of this compound is essentially identical, in the parent region, with that of the μ,μ' isomer, but the ^{11}B nmr spectrum (Figure 4b) contains a singlet of area 1 superimposed on a broad doublet of area 2, indicative of terminal substitution. Although technically the spectrum could be reconciled with either the 4,4'- or 5,5'-substituted isomer,[9-11] the 4,4' structure is favored in view of the close similarity of the ^{11}B nmr spectrum to that of 4-$SiH_3C_2B_4H_7$[2] and the fact that 4-$SiH_3C_2B_4H_7$ is formed on pyrolysis as described below.

At 150° μ,μ'-$SiH_2(C_2B_4H_7)_2$ decomposes to give *closo*-$C_3B_5H_7$,[12] 4-$SiH_3C_2B_4H_7$, $C_2B_4H_8$, and solid products, thus paralleling the decomposition[2] of μ- or 4-$SiH_3C_2B_4H_7$ and suggesting that the initial process (after isomerization to the 4,4' species) is the cleavage of an Si–B bond to form 4-$SiH_3C_2B_4H_7$ and $C_2B_4H_8$.

In contrast to the rapid reaction of $Na^+C_2B_4H_7^-$ with SiH_2Cl_2 at 0°, the reaction with $(CH_3)_2SiCl_2$ is extremely sluggish even at 25° and gives no detectable μ,μ'-$[(CH_3)_2Si](C_2B_4H_7)_2$ although a trace of μ-$[(CH_3)_2SiH]C_2B_4H_7$ is produced. The implication that the methyl groups bonded to silicon sterically inhibit formation of the bis(carboranyl) species has been further examined with other organosilicon reagents. The reaction of $Na^+C_2B_4H_7^-$ with CH_3SiCl_2H proceeds rapidly at 0°, yielding μ-$[CH_3SiH_2]C_2B_4H_7$ but no bis(carboranyl) derivative. Presumably μ-$[CH_3SiClH]C_2B_4H_7$

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(9) Careful comparison of the available ^{11}B nmr spectra of alkyl[10] and halogen[11] derivatives of $C_2B_4H_8$ with those of the terminally substituted silyl, trimethylsilyl, and trimethylgermyl $C_2B_4H_8$ derivatives[2,7] tends to support the assignment of 4 substitution for these compounds. Thus, the spectra of mono- and trimethyl $C_2B_4H_8$ derivatives indicate that attachment at B(5) results in a downfield shift of 12–13 ppm for the B(5) resonance; substitution at B(4), on the other hand, produces a shift of only 3–6 ppm for B(4). The 4-$ClC_2B_4H_7$ and 4-$BrC_2B_4H_7$ compounds exhibit a similar effect. On this basis, the spectra of the $R_3MC_2B_4H_7$ and $SiH_2(C_2B_4H_7)_2$ species appear more consistent with 4 rather than 5 substitution (the spectrum of parent $C_2B_4H_8$ contains resonances at δ +0.6 [B(4,6)–H], +3.3 [B(5)–H], and +50.5 ppm [B(1)–H]). Second, the spectra of 2-SiH_3- and 2-$GeH_3B_5H_8$[8] show that these ligands produce an *increase* in δ for the substituted boron atom. If this effect is applicable to $SiH_3C_2B_4H_7$,[2] in which the singlet resonance appears at δ +2.1, 4 substitution again appears more probable.

(10) T. Onak, D. Marynick, P. Mattschei, and G. Dunks, *Inorg. Chem.*, 7, 1754 (1968).

(11) J. R. Spielman, G. B. Dunks, and R. Warren, *Inorg. Chem.*, 8, 2172 (1969).

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

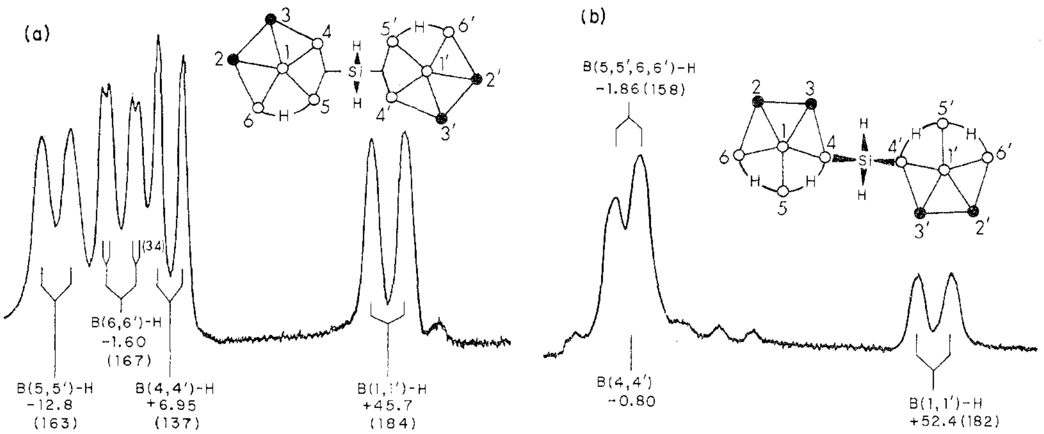


Figure 4. The 32.1-MHz ^{11}B nmr spectra of (a) μ,μ'-$SiH_2(C_2B_4H_7)_2$ and (b) 4,4-$SiH_2(C_2B_4H_7)_2$ in CS_2 solutions. Data are given as in Figure 2.

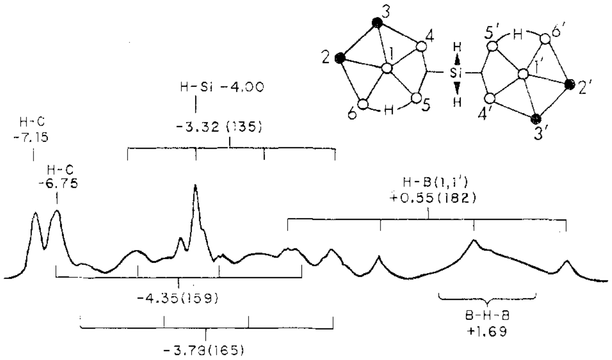


Figure 5. The 100-MHz ^1H nmr spectrum of μ,μ'-$SiH_2(C_2B_4H_7)_2$ in CS_2 solution. Chemical shifts are relative to $(CH_3)_4Si$ and coupling constants are in parentheses.

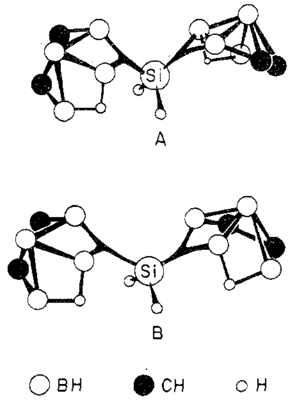
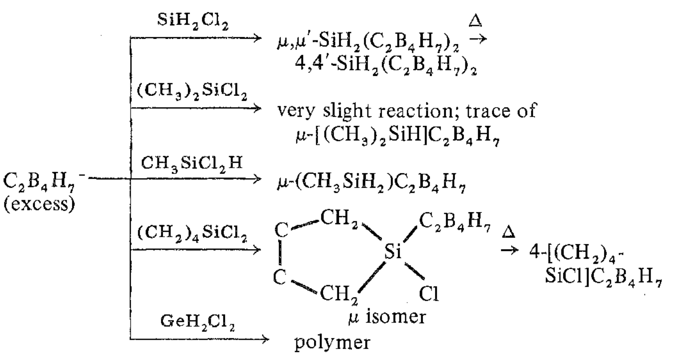


Figure 6. Proposed structures of the two possible geometric isomers of μ,μ'-$SiH_2(C_2B_4H_7)_2$.

Scheme I



is formed initially, with subsequent reduction of the Si-Cl bond by interaction with excess $C_2B_4H_7^-$ ion.

Treatment of the $C_2B_4H_7^-$ anion with cyclotetramethylenedichlorosilane at 23° in THF yields μ-$[(CH_2)_4SiCl]C_2B_4H_7$, with no evidence of the bis(carboranyl) compound (in this case the Si-Cl bond is not hydrogenated, probably as a consequence of steric hindrance by the bulky tetramethylene ring). Again, thermal rearrangement to the 4-substituted derivative is observed at 220°. (See Scheme I.)

The reaction of $Na^+C_2B_4H_7^-$ with dichlorogermane somewhat surprisingly yields only a nonvolatile reddish black air-stable polymer.

Experimental Section

General Procedures. The techniques and instrumentation used were identical with those described in a previous paper.[2] All work was conducted in a Pyrex system, either *in vacuo* or under a nitrogen atmosphere.

Materials. Sodium dicarbahexaborate(1−) $[Na^+C_2B_4H_7^-]$ solution in tetrahydrofuran was prepared from NaH and $C_2B_4H_8$ as described previously[2] and was filtered under N_2 prior to use. Pentaborane(9), silane, chloromethane (all from Matheson), trimethylbromostannane, trimethylchlorosilane, trimethylchlorogermane, dimethyldichlorosilane, tetrachlorogermane (all from Alfa), cyclotetramethylenedichlorosilane (PCR), and methyldichlorosilane (PCR) were used as received but were checked by ir spectroscopy before use. Acetylene (Matheson) was distilled through a trap at −128° to remove less volatile impurities. Sodium hydride (61% dispersion in mineral oil, from Metal Hydrides, Inc.) was washed several times with *n*-hexane in an N_2 atmosphere to remove the oil. Tetrahydrofuran (Eastman) was dried over lithium aluminum hydride and distilled *in vacuo* immediately prior to use. Dimethyl ether (Matheson) was dried over lithium aluminum hydride at −78°. Hydrogen chloride was generated from reagent grade NaCl and H_2SO_4 and distilled through a −128° trap. Deuterium chloride was prepared from D_2O and benzoyl chloride by the method of Brown and Groot[13] and was passed through a trap at −128°, and its ir spectrum was checked before use. Dichlorosilane was prepared by the gas-phase reaction of silane and hydrogen chloride over aluminum chloride at room temperature for 7 days and was purified by fractionation through traps at −63, −112, and −196°; the SiH_2Cl_2 was retained at −112°. Dichlorogermane was prepared similarly from germane (GeH_4) and HCl, the product being fractionated through traps at −23, −78, and −196° with the GeH_2Cl_2 condensing at −78°. The germane was obtained from the reaction of tetrachlorogermane with lithium aluminum hydride as described in the literature.[14] Trimethyllead chloride was prepared from tetramethyllead and HCl by the method of Heap and Saunders.[15]

μ-$(CH_3)_3SnC_2B_4H_7$. A THF solution containing 3.20 mmol of $Na^+C_2B_4H_7^-$ was added to 3.88 mmol of $(CH_3)_3SnBr$ in THF at −196° *in vacuo*, after which the contents were warmed to 23° and stirred for 1 hr. The products were fractionated repeatedly through

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(13) H. D. Brown and G. Groot, *J. Amer. Chem. Soc.*, 64, 2223 (1942).

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

(15) R. Heap and B. C. Saunders, *J. Chem. Soc.*, 2983 (1949).

a −12° trap, which retained only μ-$(CH_3)_3SnC_2B_4H_7$ (0.520 g, 66% yield). The mass spectrum exhibits a cutoff at *m/e* 229 (intensity 13% of base peak) assigned to $^{124}Sn^{12}C_4{}^{11}B_4{}^{1}H_{13}{}^{+}$, a fragment formed by loss of a CH_3 group from the molecular ion. The cutoff group profile (base peak *m/e* 223) is consistent with the calculated intensities based on natural isotope distribution. The materials passing through −12° consisted of THF, $C_2B_4H_8$, and $(CH_3)_3SnBr$.

μ-$(CH_3)_3PbC_2B_4H_7$. A THF solution of $Na^+C_2B_4H_7{}^-$ (2.80 mmol) was added to 2.90 mmol of $(CH_3)_3PbCl$ in THF, and the reaction and work-up were conducted exactly as in the μ-$(CH_3)_3SnC_2B_4H_7$ synthesis. The product condensing at −12° was μ-$(CH_3)_3PbC_2B_4H_7$ (0.640 g, 70% yield). The mass spectroscopic cutoff is at *m/e* 313 (intensity 75% of base peak) assigned to $^{208}Pb^{12}C_4{}^{11}B_4{}^{1}H_{13}{}^{+}$ which is formed by loss of CH_3 from the parent ion. The cutoff group profile (base peak *m/e* 312) is consistent with calculated intensities, with some hydrogen loss evident.

Thermolysis of μ-$(CH_3)_3Sn$- and μ-$(CH_3)_3PbC_2B_4H_7$. A neat liquid sample of μ-$(CH_3)_3SnC_2B_4H_7$ in a standard Pyrex 5-mm tube was heated 1 hr at 100°, 1.5 hr at 120°, and 1.5 hr at 175° with no change in the ^{11}B nmr spectrum. After an additional 16 hr at 180°, glpc and ir spectra indicated that ~30% of the sample had been converted to $C_2B_4H_8$ and $(CH_3)_3SnH$ while the remainder of the original compound was unchanged. Following another 16 hr at 220°, all of the compound had decomposed to the same volatile products and dark nonvolatile residue.

A sample of neat μ-$(CH_3)_3PbC_2B_4H_7$ in a similar tube was converted to $C_2B_4H_8$, $(CH_3)_3PbH$, and dark solids in 48 hr at room temperature, while in a separate experiment the compound decomposed completely in 1.5 hr at 120°.

Reaction of μ-$(CH_3)_3SnC_2B_4H_7$ with DCl. A mixture of 3.13 mmol of DCl and 2.90 mmol of the carborane at −196° was warmed to 23° and stirred for 1 hr after which the volatiles were fractionated through −23°, which retained $(CH_3)_3SnCl$ (2.81 mmol), and −128°, which retained $C_2B_4H_7D$ (2.03 mmol). The latter product is deuterated in the bridge position only, as shown by its ^{11}B nmr and ir spectrum.[16]

Reaction of μ-$(CH_3)_3PbC_2B_4H_7$ with HCl. In a procedure identical with the preceding experiment, 0.319 mmol of μ-$(CH_3)_3PbC_2B_4H_7$ and 0.300 mmol of HCl were warmed from −196 to 23°, at which temperature a white precipitate formed rapidly. After 1 hr at 23° the reactor contained $C_2B_4H_8$ (0.300 mmol) and no other volatiles. The white solid was identified as $(CH_3)_3PbCl$ from its ir spectrum.

Reaction of μ-$(CH_3)_3GeC_2B_4H_7$ with HCl. The same technique as in the above reactions was used to study a reaction between 0.128 mmol of the carborane[2] and 0.380 mmol of HCl. After 1 hr at room temperature, fractionation yielded 0.206 mmol of HCl (passed −112°, condensed −196°), a mixture of $C_2B_4H_8$ and $(CH_3)_3GeCl$ (condensed −45°, not measured), and 0.068 mmol of μ-$(CH_3)_3GeC_2B_4H_7$ (condensed −23°).

Reaction of μ-$(CH_3)_3SiC_2B_4H_7$ with HCl. Using the above procedure, a mixture of 2.40 mmol of HCl and 2.10 mmol of the carborane[2] was warmed from −196 to +23° and maintained at the latter temperature for 1 hr with stirring. Fractionation yielded 2.10 mmol of HCl, 0.35 mmol of a mixture of $C_2B_4H_8$ and $(CH_3)_3SiCl$, and 1.82 mmol of the original carborane.

μ,4-$[(CH_3)_3Si]_2C_2B_4H_6$. A 3.03-mmol sample of μ-$(CH_3)_3SiC_2B_4H_7$ was added to excess sodium hydride (which had been washed with *n*-hexane to remove mineral oil) in THF at 25°. Following evolution of noncondensable gas, the solution was filtered to remove NaCl, and excess $(CH_3)_3SiCl$ was condensed into the filtrate at −196°. Upon warming to 25° a white precipitate appeared within 10 min. After stirring for 1 hr the volatiles were separated by fractionation. The product, a colorless liquid with a vapor pressure of <1 Torr at 25° was collected at −23° and characterized as μ(5,6),4-$[(CH_3)_3Si]_2C_2B_4H_6$. The mass spectrum contains a cutoff at *m/e* 222 corresponding to the $^{30}Si^{28}Si^{12}C_8{}^{11}B_4{}^{1}H_{24}{}^{+}$ parent ion, and the profile in the parent region is in agreement with an SiB_4 species. Also evident are prominent peak groupings corresponding to the successive loss of four methyl groups and of a trimethylsilyl group. The compound was structurally characterized from spectroscopic data as described in the text.

μ-D,4-$(CH_3)_3SiC_2B_4H_6$. A 1.5-mmol quantity of μ-$(CH_3)_3SiC_2B_4H_7$ was added to excess sodium hydride (previously washed with *n*-hexane) in THF. Approximately 1.2 mmol of noncondensable gas was evolved at 25°. Following filtration most of the solvent was pumped off and 1.75 mmol of DCl was added to the filtrate at −196°. On warming to room temperature a white solid formed immediately. Distillation of the volatiles through −23 and −45° traps, with several passes through the latter trap to remove all of the solvent, gave μ-D,4-$(CH_3)_3SiC_2B_4H_6$ (1.2 mmol, 80% yield). Deuteration exclusively at bridge positions is indicated by the ^{11}B (Table I, Figure 2b) and ^{1}H nmr spectra (Table II), which are virtually identical with those of 4-$(CH_3)_3SiC_2B_4H_7$[2] except for the apparent absence of B–H bridge coupling in the ^{11}B spectrum of the deuterated compound (minor differences are attributed to the presence of CS_2 solvent in the latter case). The ^{11}B nmr spectrum (Figure 2b) is more consistent with the μ(5,6)-D,4-$(CH_3)_3Si$ structure than the alternative μ(4,5)-D,4-$(CH_3)_3Si$ isomer, in that the latter compound would be expected to exhibit B(6)–H coupling, which is not observed. However, deuterium exchange between both bridging positions is also a possibility which the available data do not exclude. The infrared spectrum is virtually identical with that of 4-$(CH_3)_3SiC_2B_4H_7$[2] except for diminished intensity of the B–H–B stretching band due to partial bridge deuteration.

Reaction of μ-$(CH_3)_3GeC_2B_4H_7$ with NaH followed by $(CH_3)_3SiCl$. A 3.83-mmol sample of μ-$(CH_3)_3GeC_2B_4H_7$[2] was added to excess hexane-washed sodium hydride in THF. Approximately 1.2 mmol of noncondensable gas was evolved, after which the solution was filtered and 5.8 mmol of $(CH_3)_3SiCl$ was condensed into the filtrate at −196°. On warming the flask to room temperature a white precipitate slowly formed. The mixture was stirred for 1 hr, after which the volatiles were fractionated through traps at 0, −23, −45, and −196°. The condensate in the 0° trap was a colorless liquid, vp <1 Torr at 25°, which could be slowly distilled *in vacuo*. The mass spectrum contains a high mass cutoff at *m/e* 406 and a grouping from *m/e* 391 to 406 whose intensities approximately correspond to those calculated for a $(C_2B_4H_6)_2GeSi_2(CH_3)_8$ species. The significant infrared bands are at 3020 (m) (cage C–H), 2940 (s), 2910 (s), 2845 (s) (all alkyl C–H), 2600 (s) (B–H), 1900 (m, b) (B–H bridge), 1360 (m), 1250 (s), 1095 (s), 970 (m), 955 (m), 860 (s), 830 (s), 745 (s), and 690 (s) cm^{-1}. No significant absorptions appear in the 2000–2400-cm^{-1} Si–H and Ge–H stretching region. The proton nmr spectrum contains a single cage C–H band at δ −6.25 ppm relative to $(CH_3)_4Si$, B–H quartets at −3.45 (J = 156 Hz) and +0.92 ppm (180 Hz), an intense CH_3 peak at −0.50 ppm, and a broad B–H–B hump centered at +1.78 ppm. The 32.1-MHz ^{11}B nmr spectrum in CS_2 contains a broad singlet of area 1 at δ −9.3 ppm relative to $BF_3\cdot O(C_2H_5)_2$, a doublet of area 2 centered at +2.9 ppm (J = 153 Hz) with each peak of the doublet further split ($J \approx 35$ Hz), and a doublet of area 1 centered at +53.0 ppm (J = 184 Hz). From the simplicity of the spectrum and its similarity to that of μ,4-$(CH_3)_3Si_2C_2B_4H_6$ (Figure 2a), a symmetric structure containing two 4-$(CH_3)_3SiC_2B_4H_6$ units linked to a central $Ge(CH_3)_2$ group *via* B(5)–Ge–B(6) three-center bonds is suggested. The low-field singlet is then assigned to B(4)–Si, the low-field doublet to B(5,6)–H with fine splitting by the adjacent bridge hydrogen, and the high-field doublet to B(1)–H.

Attempted Reaction of μ-$(CH_3)_3Sn$- and μ-$(CH_3)_3PbC_2B_4H_7$ with NaH. A solution of 1.0 mmol of μ-$(CH_3)_3SnC_2B_4H_7$ with excess sodium hydride in THF was stirred at 25° for 0.5 hr with virtually no indication of reaction; 0.08 mmol of noncondensable gas was measured, but fractionation of the volatiles yielded only starting material and solvent. A similar experiment with μ-$(CH_3)_3PbC_2B_4H_7$ (0.147 mmol) and NaH (2.08 mmol) in THF for 0.5 hr gave 0.03 mmol of noncondensable gas but no other volatile products, and a substantial part of the original carborane was recovered.

μ,μ'-$SiH_2(C_2B_4H_7)_2$. Dichlorosilane (3.72 mmol) was condensed into a reactor containing 7.44 mmol of $Na^+C_2B_4H_7{}^-$ in THF at −196°. The reactor was warmed to room temperature and stirred for 0.5 hr, during which a white precipitate formed rapidly. Fractionation of the volatiles through a −23° trap gave clear viscous condensate which was slowly distillable *in vacuo*. The yield of product was ~2 mmol (54%).

Thermolysis of μ,μ'-$SiH_2(C_2B_4H_7)_2$. (a) A 1.0-mmol sample in CS_2 solution in a standard 5-mm Pyrex nmr tube was heated at 100° for 1 hr. The nearly quantitative conversion to 4,4′-$SiH_2(C_2B_4H_7)_2$ was evidenced by ^{11}B and ^{1}H nmr and further supported by ir and mass spectra. (b) In another experiment, a 1.0-mmol sample of the neat liquid was heated at 150° for 1.25 hr, after which the reactor was opened and the volatile contents were separated by glpc,[2] which yielded 0.195 mmol of $C_2B_4H_8$, 0.098 mmol of $C_3B_5H_7$, and 0.071 mmol of 4-$SiH_3C_2B_4H_7$. A considerable quantity of nonvolatile yellow residue remained in the reactor.

Reaction of $Na^+C_2B_4H_7{}^-$ with $(CH_3)_2SiCl_2$. Dimethyldichlorosilane (3.5 mmol) was condensed at −196° into a reactor containing 10.1 mmol of $Na^+C_2B_4H_7{}^-$ in THF solution. The solution was slowly warmed to room temperature and maintained there for 1 hr, during which there was little evidence of reaction, and volatiles were fractionated through a trap at −23°. The condensate consisted of a trace

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

of material whose ir and mass spectra were suggestive of μ-[$(CH_3)_2$SiH]$C_2B_4H_7$ although definitive characterization was not possible due to the extremely small quantity obtained. The material passing through the −23° trap was $(CH_3)_2SiCl_2$, in a quantity approximately equal to the starting amount, and solvent.

Reaction of $Na^+C_2B_4H_7^-$ with CH_3SiHCl_2. Methyldichlorosilane (3.0 mmol) was condensed at −196° into a reactor containing 7.0 mmol of $Na^+C_2B_4H_7^-$ in THF. The flask was warmed to room temperature, at which point a white precipitate immediately formed. After 0.5 hr the volatiles were fractionated to give a clear liquid (~2 mmol) which passed a −23° trap but was retained at −45°. This material exhibits a vapor pressure of 7.0 Torr at 23° and was characterized as μ-[CH_3SiH_2]$C_2B_4H_7$ from its ^{11}B and ^1H nmr, ir, and mass spectra. The mass spectrum contains a cutoff at *m/e* 122 corresponding to the $^{30}Si^{12}C_3{}^{11}B_4{}^1H_{12}{}^+$ parent ion and a profile compatible with an SiB_4 species. The ir B–H stretching band near 2600 cm^{-1} is split, characteristic of bridge-substituted species (see above), and Si–H (2158 cm^{-1}) and cage C–H (3040 cm^{-1}) bands are also present (Table III). The bridged structure is also supported by the ^{11}B nmr spectrum (Table I) which contains only doublets, arising from terminal B–H groups, and by the ^1H nmr spectrum (Table II).

Reaction of $Na^+C_2B_4H_7^-$ with $(CH_2)_4SiCl_2$. Cyclotetramethylenedichlorosilane (3.24 mmol, 0.501 g) was condensed into a reactor containing 6.65 mmol of $Na^+C_2B_4H_7^-$ in THF at −196°. The reactor was warmed to 23° and maintained at that temperature for 16 hr, during which a white precipitate gradually formed. Fractionation of the volatiles through a trap at −23° gave ~2 mmol of a clear viscous liquid product having a vapor pressure of <1 Torr at 23°, which was purified by distillation *in vacuo* with mild heating. The material was characterized as μ-[$(CH_2)_4SiCl$]$C_2B_4H_7$ from its mass spectrum, which contains a cutoff at *m/e* 198 corresponding to the $^{30}Si^{37}Cl^{12}C_6{}^{11}B_4{}^1H_{15}{}^+$ parent ion and a profile in close agreement with the calculated intensities. The ^{11}B and ^1H nmr spectra (Tables I and II) exhibit the usual features for a bridged $C_2B_4H_8$ derivative (see above) but the ^1H nmr spectrum also contains separate methylene peaks corresponding to the two types of CH_2 group in the organic ring (Table II). Again, the split B–H ir stretching band (~2600 cm^{-1}) is characteristic of a bridge-substituted derivative. No significant ir bands appear in the Si–H stretching region (Table III).

Thermolysis of μ-[$(CH_2)_4SiCl$]$C_2B_4H_7$. A sample of ~1.0 mmol of the carborane was sealed into a 5-mm Pyrex nmr tube and heated at 220° with periodic monitoring of the ^{11}B nmr spectrum. After 2.5 hr the essentially quantitative conversion to 4-[$(CH_2)_4SiCl$]-$C_2B_4H_7$ was evident from the nmr spectrum (Table I), which is very similar to that of other B(4)-substituted $C_2B_4H_8$ derivatives (see above and earlier references[2,7]). The ^1H nmr (Table II) and infrared spectra (Table III) further support the assigned structure.

Reaction of $Na^+C_2B_4H_7^-$ with GeH_2Cl_2. A solution of $Na^+C_2B_4H_7^-$ (7.0 mmol in THF) was filtered into an evacuated Pyrex reactor and cooled to −196°. Dichlorogermane (3.5 mmol) was condensed into the reactor, which was then warmed to −30°. At this temperature the solution quickly became dark red. After 0.5 hr at −30° the volatiles were fractionated through a series of traps at −23, −45, −63, and −196°, but no products other than solvent and a trace of $C_2B_4H_8$ were detected. The nonvolatile material remaining in the reactor was reddish black and crystalline in appearance, apparently air stable, and insoluble in CCl_4, hexane, methanol, and water. The infrared spectrum contains a B–H band but no Ge–H absorption, and the broad, poorly resolved peaks are suggestive of a polymeric structure.

Registry No. Silane, 7803-62-5; chloromethane, 74-87-3; trimethylbromostannane, 1066-44-0; trimethylchlorosilane, 1066-45-1; trimethylchlorogermane, 1529-47-1; dimethyldichlorosilane, 75-78-5; tetrachlorogermane, 10038-98-9; cyclotetramethylenedichlorosilane, 2406-33-9; methyldichlorosilane, 75-54-7; dichlorosilane, 4109-96-0; dichlorogermane, 15230-48-5; trimethyllead chloride, 1520-78-1; [$Na^+C_2B_4H_7^-$], 38117-50-9; [μ-$(CH_3)_3SnC_2B_4H_7$, 38117-56-5; μ-$(CH_3)_3PbC_2B_4H_7$, 38117-57-6; $C_2B_4H_7D$, 38118-31-9; μ-4-[$(CH_3)_3Si$]$_2C_2B_4H_6$, 38117-58-7; μ-D,4-$(CH_3)_3SiC_2B_4H_6$, 38194-33-1; $(C_2B_4H_6)_2GeSi_2(CH_3)_8$, 37239-40-0; μ,μ'-$SiH_2(C_2B_4H_7)_2$, 38117-59-8; μ-[$(CH_3)_2SiH$]$C_2B_4H_7$, 38117-60-1; μ-[CH_3SiH_2]$C_2B_4H_7$, 38117-61-2; μ-[$(CH_2)_4SiCl$]$C_2B_4H_7$, 38117-62-3; 4,4′-$SiH_2(C_2B_4H_7)_2$, 37889-52-4.

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Identification of an Unstable Nonaborane (B_9H_{13}) in the Gas Phase

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A nonaborane, B_9H_{13}, is shown to be formed as a transient intermediate in the pyrolysis of $B_9H_{13}L$ compounds in reactors directly coupled to a mass spectrometer. Identification is based upon the temperature dependence, time dependence, and ligand dependence of the mass spectra. Low-voltage spectra and exact mass measurements were used to support the identification. The reaction of B_9H_{13} with $B_9H_{13}L$ to yield $B_{18}H_{20}L$, the reaction of B_9H_{13} with H_2 to yield B_9H_{15}, and the reaction of the pyrolysis products of $B_9H_{13}S(CH_3)_2$ with various boranes to yield an unusual product are reported.

The chemistry of compounds containing boron is marked by numerous examples of the importance of the Lewis acid-base concept.[2] This is particularly evident in the formal systemization of the reactions of the boron hydrides.[3] Although it is expected that intermediates produced in the reactions of boron hydrides will conform to the already established principles of the field, the identification and characterization of these unstable species can be very helpful in further developing our understanding of the reactivity of the parent compounds. Indeed, many times the progress in understanding reaction mechanisms is coupled to the progress in characterization of the important reaction intermediates.

In borane chemistry the problem of intermediates and mechanism is compounded by the reactivity of the molecular

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