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# Organosilyl and Silylorgano Derivatives of 2,3-$C_2B_4H_8$. Conversion of *B*-($ClMe_2SiCH_2$)$C_2B_4H_7$ to *B*-$ClMe_2SiCH_2$ Derivatives of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$

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The bridged silyl derivative of the *nido*-dicarbahexaborane(8), $\mu$-$ClCH_2SiMe_2$-$C_2B_4H_7$, is prepared from the reaction of $ClCH_2SiMe_2Cl$ with the 2,3-$C_2B_4H_7^-$ ion. Mild heating converts the bridge derivative to a basal terminally substituted Si–B bonded isomer. A 1,2 shift of the carboranyl unit from the silicon to the methylene carbon atom is catalyzed with aluminum chloride under ambient conditions to yield 4-($ClMe_2SiCH_2$)$C_2B_4H_7$. A similar shift giving a mixture of 4- and 5-($ClMe_2SiCH_2$)$C_2B_4H_7$ is observed without a catalyst at 150 °C. Flash thermolysis of ($ClMe_2SiCH_2$)$C_2B_4H_7$ gives silylorgano derivatives of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$. Boron-11-decoupled proton NMR data for all the above compounds as well as methyl derivatives of 2,3-$C_2B_4H_8$ are obtained and correlated.

## Introduction

Silylpentaboranes of the type ($ClCH_2SiR_2$)$B_5H_8$ can be encouraged to rearrange to the C–B bonded ($ClR_2SiCH_2$)$B_5H_8$ derivatives; and insertion of the methylene carbon into the boron cage is observed with the latter compound under flash thermolysis conditions to give *nido*-$CB_5H_9$ (as well as *closo*-$CB_5H_7$ by $H_2$ elimination) and $R_2Si(Cl)H$.[1] It was with this in mind that we wished to carry out similar chemistry on the *nido*-2,3-$C_2B_4H_8$.

It is possible to rearrange bridge-bonded silyl derivatives of *nido*-2,3-dicarbahexaborane(8) such as $\mu$-$R_3Si$-$C_2B_4H_7$, prepared from $R_3SiCl$ and the 2,3-$C_2B_4H_7^-$ ion, to a neighboring B-terminal position,[2,3] although similar bridge derivatives of *nido*-2,3-$Me_2$-2,3-$C_2B_4H_6$ fail to do so.[4] Studies in our laboratories have resulted in the successful preparation of the bridge derivative $\mu$-$ClCH_2SiMe_2$-$C_2B_4H_7$ and rearrangement of the bridge derivative to the B terminally substituted isomer. Additional chemistry of these compounds is also reported.

## Experimental Section

**Apparatus.** Due to the generally low volatility of most materials in this work (approximately 1 Torr), it was preferable, when possible, to carry out the manipulations in high-vacuum apparatus attached externally to the usual standard high-vacuum system.

**Materials.** Tetrahydrofuran was dried over sodium and distilled prior to use. (Chloromethyl)dimethylchlorosilane, dried over molecular sieves, was obtained from PCR Inc.; sodium hydride–oil dispersion, from Alfa Inorganics; and aluminum chloride, from Matheson Coleman and Bell. 2,3-Dicarbahexaborane(8) was prepared by previously known methods.[5]

**Nuclear Magnetic Resonance (Table I).** Proton spectra were recorded on Varian A-60 and HA-100 spectrometers. The boron-11 spectra were obtained at 32.1 MHz using the Varian HA-100 instrument. Decoupled proton spectra at 100 MHz were observed while irradiating at 32.1 MHz using the Nuclear Magnetic Resonance Specialties Model HD-60 spin decoupler, modified for use with the HA-100, and the General Radio Model 1061 frequency synthesizer with a power booster provided by the Electronic Navigation Industries Model 320L RD power amplifier. Proton-decoupled $^{11}B$ spectra at 32.1 MHz were observed while irradiating at 100 MHz using the above-mentioned system.

The boron-11 chemical shift data are reported relative to boron trifluoride–ethyl etherate and were obtained using boron trichloride, $\delta$ −46.8 ppm, as a secondary standard. The proton chemical shifts are reported relative to tetramethylsilane, $\tau$ 10.00, and were obtained using $CHCl_3$, THF, or TMS as internal standards.

The gas-phase **infrared spectra** were recorded on a Beckman Acculab 3 spectrometer.

**Mass spectra** were recorded on a Varian CH-5 high-resolution mass spectrometer.

**$\mu$-(Chloromethyl)dimethylsilyl-2,3-dicarbahexaborane(8), $\mu$-$ClCH_2Me_2Si$-$C_2B_4H_7$ (I).** (Chloromethyl)dimethylsilyl chloride (4.00 mmol) was vacuum distilled at −196 °C into a reaction vessel containing 3.64 mmol of freshly prepared sodium 2,3-heptahydrodicarbahexaborate, $Na^+C_2B_4H_7^-$, in tetrahydrofuran, prepared according to a previously described method.[2] The contents were warmed to 0 °C and then shaken every 5 min for a duration of 45 min.[6] The product was isolated by first passing the reaction mixture volatiles through traps at −45 and −196 °C. The −45 °C trap contained I and a small amount of unreacted (chloromethyl)dimethylsilyl chloride which was removed by passing the materials through traps at −23 and −196 °C, isolating the $\mu$-silyl-carborane in the former. The product is a colorless liquid with a vapor pressure of less than 1 Torr at 25 °C; yield 2.10 mmol (58%).

**5-(Chloromethyl)dimethylsilyl-2,3-dicarbahexaborane(8), 5-($ClCH_2Me_2Si$)$C_2B_4H_7$ (II).** Typically, 1.5 mmol of I was quantitatively converted to the terminally substituted carborane by heating at 60 °C for 30 h in a sealed glass reaction vessel equipped with an NMR tube side arm. Progress of conversion was monitored by $^{11}B$ NMR. A portion was transferred into a separate NMR tube containing $CHCl_3$ for the purpose of obtaining a $^1H$ NMR spectrum. The remainder was used for the formation of III and IV.

**4-(Chlorodimethyl)silylmethyl-2,3-dicarbahexaborane(8), 4-($ClMe_2SiCH_2$)$C_2B_4H_7$ (III).** Typically, to 1.00 mmol of II at −196 °C was added aluminum chloride (5–20 mol %) by sublimation. The reaction vessel, containing an NMR tube side arm, was sealed off and the −196 °C bath removed. Shortly after the silylcarborane became a liquid and in contact with the catalyst, heat was evolved. The alkyl-substituted carborane III was vacuum-pumped out of the reaction vessel at 0 °C and condensed in a −45 °C trap, through which passed a small amount of $C_2B_4H_8$ (approximately 0.03 mmol), the latter being trapped at −196 °C. A small amount (approximately 0.05 mmol) of a very viscous, involatile yellow liquid, which was not characterized, remained in the vessel. The desired product, 4-($ClMe_2SiCH_2$)$C_2B_4H_7$, yield 0.92 mmol (92%), is a colorless liquid with a vapor pressure of approximately 1 Torr and gives a mass spectrum with a parent peak at *m/e* 182, assigned to $^{35}Cl^{28}Si^{12}C_5{}^{11}B_4{}^1H_{15}$, and other peaks corresponding to P − $CH_3$ (*m/e* 167), P − $C_2H_5$ (153), P − $(CH_3)_2$ (152), P − Cl (147), and P − $CH_2C_2B_4H_7$ (93). Relative intensities indicated that the ease of loss of groups about silicon is Me and ($C_2B_4H_7$)$CH_2$ over Cl.

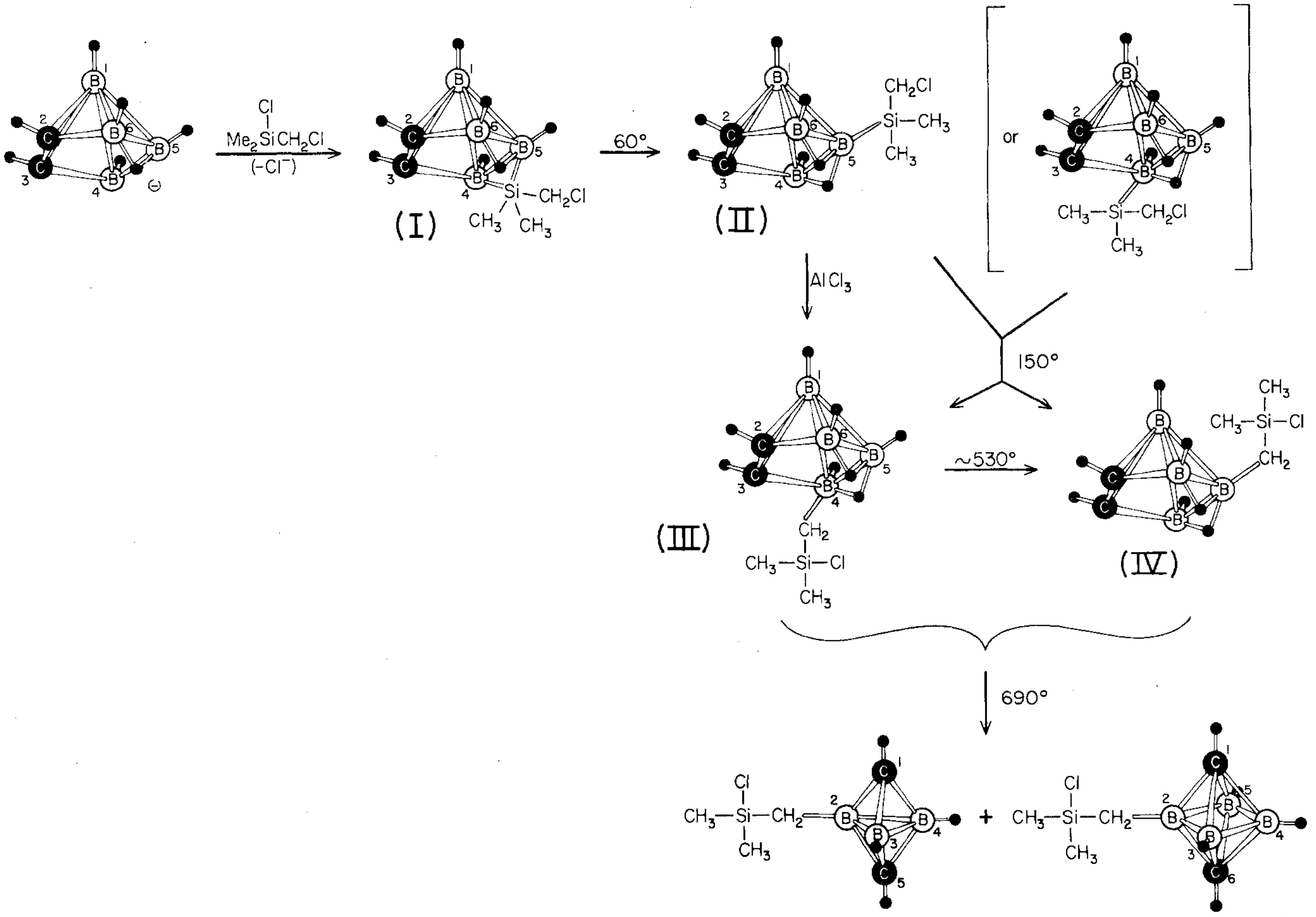
**III and 5-($ClMe_2SiCH_2$)$C_2B_4H_7$ (IV).** Approximately 0.1 mmol of II was heated for 4.5 h at 150 °C in a sealed NMR tube. The volatile contents were subsequently transferred to a fresh NMR tube, leaving behind a brown-yellow residue. Both the $^{11}B$ and $^1H\{^{11}B\}$ spectra of the volatile fraction (ca. 0.05 mmol) are consistent with a 2:1 ratio of both III and IV (see Results and Discussion). Further heating at 150 °C for another 4 h does not alter the mixture ratio.

**Flash Thermolysis of III and IV.** Low pressure (≤1 Torr) flash thermolysis of 4-($ClMe_2SiCH_2$)$C_2B_4H_7$ was carried out using a quartz-tube system previously described.[7] Pumping out of a 0 °C bath and through the tube at 250 °C and at 360 °C in two separate experiments gave back unchanged starting material. An attempt at 530 °C was indicated by $^{11}B$ NMR to partially isomerize III (ca. 25%) to the 5 isomer (IV) which was reflected by a noticeable downfield side shoulder on the C-substituted B(4) resonance and the appearance of bridge hydrogen coupling on the remaining basal doublet (see

**Table I.** $^{11}B$ and $^1H$ NMR Data

| Compd | Groups | $^{11}B$ [$BF_3 \cdot Et_2O = 0$] ($J$/Hz) | Pattern and rel area | $^1H$ [TMS = 10.00] ($J$/Hz) | Pattern and rel area |
|---|---|---|---|---|---|
| $\mu$-$ClCH_2Me_2Si$-$C_2B_4H_7$ (I) | B(1)–H | +47.1 (176) | Doublet 1 | 10.88 | Singlet[b] 1 |
| | B(4)–H | +2.8 (124) | Doublet 1 | 6.62 | Singlet[b] 1 |
| | B(5)–H | −9.1 (158) | Doublet 1 | 6.07 | Singlet[b] 1 |
| | B(6)–H | −0.8 (164) ($J_{B-H_\mu} = 35$) | Doublet 1 | 6.33 | Singlet[b] 1 |
| | $CH_3$ | | | 9.56, 9.76 | Singlet 6 |
| | $CH_2$ | | | 7.06 | Singlet 2 |
| | C(2,3)–H | | | 3.24, 3.56 | Singlet 2 |
| | $H_\mu$(5,6) | | | 12.43 | Br Singlet 1 |
| 5-($ClCH_2Me_2Si$)$C_2B_4H_7$ (II) | B(1)–H | +51.3 (181) | Doublet 1 | 11.01 (181) | Quartet[c] 1 |
| | B(5)–Si | +0.5 | Singlet 1 | | |
| | B(4,6)–H | −0.9 ($J_{B-H_\mu} \approx 35$) | Doublet 2 | 6.32 (154) | Quartet[c] 2 |
| | $CH_3$ | | | 9.70 | Singlet 6 |
| | $CH_2$ | | | 7.14 | Singlet 2 |
| | C(2,3)–H | | | 3.40 | Singlet 2 |
| | $H\mu$(4,5) | | | 12.17 | Broad Singlet 2 |
| | $H\mu$(5,6) | | | | |
| 4-($ClMe_2SiCH_2$)$C_2B_4H_7$ (III) | B(1)–H | +51.8 (179) | Doublet 1 | 10.82 (180) | Quartet[c] 1 |
| | B(4)–C | −8.1 | Singlet 1 | | |
| | B(5,6)–H | +2.2 (148) | Doublet 2 | 6.56 (152) | Quartet[c] 2 |
| | $CH_3$ | | | 9.51 | Singlet 6 |
| | $CH_2$ | | | 9.17 | Singlet 2 |
| | C(2,3)–H | | | 3.83 | Singlet 2 |
| | B(4,5)–$H_\mu$ | | | 11.46 | Singlet[f] 1 |
| | B(5,6)–$H_\mu$ | | | 11.86 | Singlet[f] 1 |
| 5-($ClMe_2SiCH_2$)$C_2B_4H_7$[e] (IV) | B(1)–H | +52.1 (179) | Doublet 1 | 10.8 | Singlet[b] 1 |
| | B(5)–C | −10.5 | Singlet 1 | | |
| | B(4,6)–H | +2.6 (148) ($J_{B-H_\mu} = 38$) | Doublet 2 | 6.5 | Singlet[b] 2 |
| | $CH_3$ | | | 9.5 | Singlet 6 |
| | $CH_2$ | | | 9.2 | Singlet 2 |
| | C(2,3)–H | | | 3.7 | Singlet 2 |
| | B(4,5)–$H_\mu$ | | | 11.5 | Singlet[b] 2 |
| | B(5,6)–$H_\mu$ | | | | |
| 2-$ClMe_2SiCH_2$-1,5-$C_2B_3H_4$ | B(2)–C | −9.4 | Singlet 1 | | |
| | B(3,4)–H | −8.0 (168) | Doublet 2 | 5.89 (176) | Quartet[c] 2 |
| | $CH_3$ | | | 9.66 | Singlet 6 |
| | $CH_2$ | | | 9.30 | Singlet 2 |
| | C(1,5)–H | | | 4.80 | Singlet 2 |
| 2-$ClMe_2SiCH_2$-1,6-$C_2B_4H_5$ | B(2)–C | +9.6 | Singlet 1 | | |
| | B(3,5)–H | +17.3 (188) | Doublet 2 | 8.02 | Singlet[b] 2 |
| | B(4)–H | +23.1 (192) | Doublet 1 | 8.12 | Singlet[b] 1 |
| | $CH_3$ | | | 9.55 | Singlet 6[d] |
| | $CH_2$ | | | 9.78 | Singlet 2[d] |
| | C(1,6)–H | | | 6.90 | Singlet 2 |
| $C_2B_4H_8$[a] | B(1)–H | | | 11.02 | Singlet[b] 1 |
| | B(4,5,6)–H | | | 6.48 | Singlet[b] 3 |
| | C(2,3)–H | | | 3.68 | Singlet 2 |
| | B–$H_\mu$ | | | 12.20 | Singlet[b] 2 |
| 4-$MeC_2B_4H_7$[a] | B(1)–H | | | 10.83 | Singlet[b] 1 |
| | B(5,6)–H | | | 6.50 | Singlet[b] 2 |
| | $CH_3$ | | | 9.28 | Singlet 3 |
| | C(2,3)–H | | | 3.83 | Singlet 2 |
| | B(4,5)–$H_\mu$ | | | 11.54 | Singlet[b] 1 |
| | B(5,6)–$H_\mu$ | | | 11.88 | Singlet[b] 1 |
| 5-$MeC_2B_4H_7$[a] | B(1)–H | | | 10.83 | Singlet[b] 1 |
| | B(4,5)–H | | | 6.50 | Singlet[b] 2 |
| | $CH_3$ | | | 9.28 | Singlet 3 |
| | C(2,3)–H | | | 3.83 | Singlet 2 |
| | B(4,5)–$H_\mu$ | | | 11.54 | Singlet[b] 2 |
| | B(5,6)–$H_\mu$ | | | | |
| C-$MeC_2B_4H_7$[a] | B(1)–H | | | 10.89 | Singlet[b] 1 |
| | B(4,5,6)–H | | | 6.66 | Singlet[b] 3 |
| | $CH_3$ | | | 7.88 | Singlet 3 |
| | C(3)–H | | | 4.04 | Singlet 1 |
| | B(4,5)–$H_\mu$ | | | 12.21 | Singlet[b] 2 |
| | B(5,6)–$H_\mu$ | | | | |
| 1-$MeC_2B_4H_7$[a] | B(4,5,6)–H | | | 6.45 | Singlet[b] 3 |
| | $CH_3$ | | | 10.53 | Singlet 3 |
| | C(2,3)–H | | | 3.58 | Singlet 2 |
| | B–$H_\mu$ | | | 11.89 | Singlet[b] 2 |

[a] These compounds were rerun for this study; ref 5, 19, and 28 report spectra taken on earlier instruments without the present advantage of high rf-power decoupling. [b] Pattern with $^{11}B$ decoupling. [c] Recorded on the A-60 only. [d] Presumed since the intensities could not be directly obtained from the spectrum due to lesser amounts of III and 2-$ClMe_2SiCH_2$-1,5-$C_2B_3H_4$ present. [e] Because of overlap with $^1H$ NMR peaks due to III, $^1H$ values for IV are reliable only to the nearest 0.1 ppm and the intensities are assumed. [f] Broad and unresolved.



Results and Discussion).[3,4,8-10] Subsequently, 0.75 mmol of the 4 and 5 isomer mixture was passed through the tube at 690 °C, having been pumped out of a trap at 0 °C for 3.5 h and at 25 °C for 20 min. The products were trapped at −196 °C and subsequently passed through traps at −45, −78, −130, and −196 °C. The −196 °C trap contained a mixture of diborane and HCl, the major component. The −130 °C trap contained a mixture of 1,6-dicarbahexaborane(6), chlorodimethylsilane,[11] both identified by infrared and NMR spectroscopy, and a boron-containing species thus far not conclusively identified but indicated to be a haloalkylmonoboron species by its $^{11}$B NMR chemical shift (singlet at $\delta$ −53.8) and a strong infrared absorption at 870 cm$^{-1}$ indicative of a B–Cl bond.[12] The materials in the −78 and −45 °C traps were combined and subjected to cold-column[13] fractionation. Pure 2-(chlorodimethyl)silylmethyl-1,5-dicarbapentaborane(5), 2-ClMe$_2$SiCH$_2$-1,5-C$_2$B$_3$H$_4$, was collected at −57 to −63 °C. The product, a colorless liquid, gave a mass spectrum with a parent peak at *m/e* 168 assigned to $^{35}$Cl$^{28}$Si$^{12}$C$_5$$^{11}$B$_3$$^1$H$_{12}$. Other significant peaks were P − CH$_3$ (*m/e* 153), P − Cl (133), and P − CH$_2$C$_2$B$_3$H$_4$ (93). The remaining fraction consisted of approximately a 2:1 mixture of 2-ClMe$_2$SiCH$_2$-1,6-C$_2$B$_4$H$_5$ and 4-(ClMe$_2$SiCH$_2$)C$_2$B$_4$H$_7$ as well as trace amounts of the above dicarbapentaborane. The mass spectrum of the mixture exhibits the envelope in the *m/e* 178–184 region skewed to the *m/e* 180 parent cutoff peak due to the predominance of 2-ClMe$_2$SiCH$_2$-1,6-C$_2$B$_4$H$_5$ ($^{35}$Cl$^{12}$C$_5$$^{28}$Si$^{11}$B$_4$$^1$H$_{13}$) with peaks due to P − CH$_3$ (*m/e* 165), P − Cl (145), and P − CH$_2$C$_2$B$_4$H$_5$ (93) also observed. This spectrum and that of 2-ClMe$_2$SiCH$_2$-1,5-C$_2$B$_3$H$_4$ show that the ease of group loss about Si is similar to that of III. An alternative compound to 2-ClMe$_2$SiCH$_2$-1,6-C$_2$B$_4$H$_5$ possessing a mass spectral parent peak at *m/e* 180 is the Si-substituted ClMe$_2$SiC$_3$B$_4$H$_7$ tricarbaheptaborane species formally derived from H$_2$ elimination coupled with C insertion into the carborane cage. In light of the known chemical behavior of 2,3-C$_2$B$_4$H$_8$ under flash thermolysis conditions and the similarities in the $^{11}$B and $^1$H NMR spectra for the compound in question and 2-Me-1,6-C$_2$B$_4$H$_5$,[14a] we choose to attribute the *m/e* parent peak to the 1,6-C$_2$B$_4$H$_6$ derivative. Throughout the workup minor amounts of some material(s) exhibiting $^1$H NMR resonances in the methyl region were present, possibly including trace amounts of Me$_3$SiCl ($\tau$ 9.55).[14b] The isolated thermolysis products and their respective yields are given in Table II.

**Table II.** Compounds from the Flash Thermolysis of 5- and 4-(ClMe$_2$SiCH$_2$)C$_2$B$_4$H$_7$ (IV and III) (0.75 mmol)

| Compd | Quantity, mmol | Compd | Quantity, mmol |
|---|---|---|---|
| HCl | 0.12 | 1,6-C$_2$B$_4$H$_6$ | 0.01 |
| B$_2$H$_6$ | 0.03 | 2-ClMe$_2$SiCH$_2$-1,5-C$_2$B$_3$H$_4$ | 0.24 |
| Haloalkylborane | 0.02 | 2-ClMe$_2$SiCH$_2$-1,6-C$_2$B$_4$H$_5$ | 0.03 |
| SiHMe$_2$Cl | 0.03 | 4-(ClMe$_2$SiCH$_2$)C$_2$B$_4$H$_7$ | 0.01 |

## Results and Discussion

**Synthesis and Structures of Organosilyl and Silylorgano Derivatives of 2,3-C$_2$B$_4$H$_8$.** Making use of a general preparative method for the synthesis of Si-bridged polyboranes,[1-4,15,16] the addition of (chloromethyl)dimethylchlorosilane to a THF solution of Na$^+$C$_2$B$_4$H$_7^-$ at 0 °C results in a 58% yield of the bridge-substituted silylcarborane with the carbon-attached halogen intact.

$$\mathrm{ClCH_2Me_2SiCl + Na^+C_2B_4H_7^-} \xrightarrow[-\mathrm{NaCl}]{\mathrm{THF}} \underset{\mathrm{I}}{\mu\text{-}\mathrm{ClCH_2Me_2Si\text{-}C_2B_4H_7}}$$

The $^{11}$B and $^1$H NMR spectra of I (Table I) are consistent with the silyl group bonded to two adjacent basal boron atoms in a three-center bond. The $^{11}$B NMR spectrum (Figure 1a) consists of a high-field doublet, negating apical substitution, and, in the low-field basal region, one B–H doublet exhibiting only terminal coupling and two overlapping doublets, one of which exhibits terminal and bridge hydrogen coupling and the other only terminal coupling. The highest field basal doublet is assigned to B(4); the two remaining doublets are assigned to B(6) and B(5), respectively. The latter B(5,6) assignment is based on previous $^{11}$B NMR results,[2-4] concerning similar bridging derivatives, which show that the B(5) resonance is

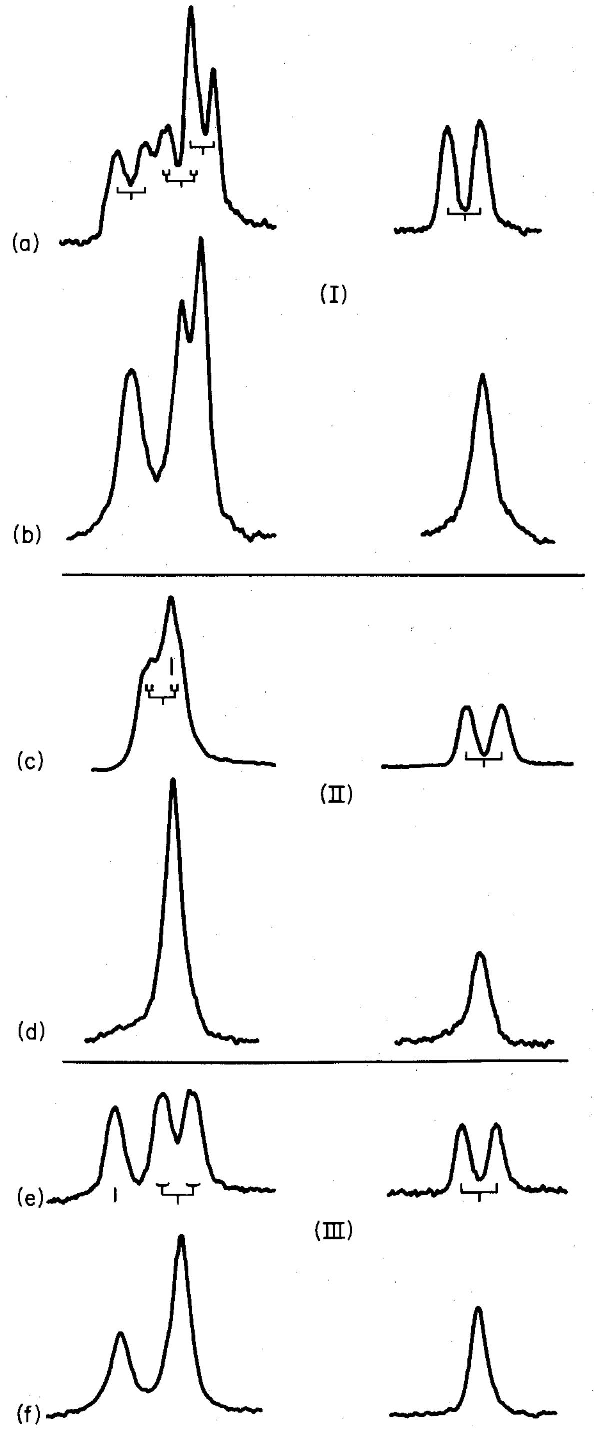


**Figure 1.** The 32.1-MHz $^{11}B$ spectra: I, $\mu$-$ClCH_2Me_2Si$-$C_2B_4H_7$ [(a) undecoupled and (b) with $^1H$ decoupling]; II, 5-$(ClCH_2Me_2Si)C_2B_4H_7$ [(c) undecoupled and (d) with $^1H$ decoupling]; III, 4-$(ClMe_2SiCH_2)C_2B_4H_7$ [(e) undecoupled and (f) with $^1H$ decoupling].

usually broader than those of B(4) and B(6) and lacks bridge coupling resolution; and, in general, the chemical shifts for unsubstituted borons are similar to those of the parent. The B(5) broadness can be attributed, at least in part, to significant $^{11}B(1)$–$^{11}B(5)$ coupling.[17] The $^1H\{^{11}B\}$-decoupled spectrum of I exhibits two cage C–H resonances. Two methyl resonances are also observed presumably due to the lack of rotational symmetry about an axis passing through the silicon and bisecting the B(4)–B(5) bond. The methyl chemical shift difference (0.2 ppm) is of similar magnitude with those found for the diastereotopic methyl groups (0.16–0.31 ppm) in various 1-isopropyl-*o*-carboranes.[18] All three basal B–H resonances are observed and are assignable upon selective $^{11}B$ decoupling. The effect of Si bridge substitution on the adjacent bridge hydrogen resonance is to move it upfield (+0.23 ppm) relative to the parent $C_2B_4H_8$. A similar trend has generally been observed for bridging Si derivatives of $B_5H_9$[1,15,16] but for those of $C_2B_4H_8$ and 2,3-$C_2Me_2B_4H_6$ there are examples of downfield,[3,4] upfield,[2] and no chemical shift movement at all.[2]

At 60 °C, $\mu$-$ClCH_2Me_2Si$-$C_2B_4H_7$ (I) rearranges irreversibly to a terminally substituted silylcarborane (II). The conversion temperature is much lower than that reported[2] (175 °C) in the similar rearrangement of $\mu$-$Me_3Si$-$C_2B_4H_7$ and the time required (0.5 h) indicates the conversion could have been carried out more slowly at a lower temperature. It is doubtful, however, that at 60 °C the $\mu$-trimethylsilyl analogue would rearrange without requiring an inordinate amount of time. In related work[4] Wallbridge reported that a similar thermal rearrangement of $\mu$-$Me_3Ge$-2,3-$C_2Me_2B_4H_5$ gives 5-$(Me_3Ge)C_2Me_2B_4H_5$. On the other hand, he found that $\mu$-$Me_3Si$-2,3-$C_2Me_2B_4H_5$ and similar compounds fail to thermally isomerize but instead decompose to the parent carborane, alkylsilane, and polymeric species.

The $^{11}B$ spectrum (Figure 1c) of II is consistent with either 4- or 5-$(ClCH_2Me_2Si)C_2B_4H_7$. The substituted boron atom singlet nestled in with remaining basal resonances negates alkyl substitution at boron.[2,19] We judge that the partial overlap of the unsubstituted and substituted basal boron resonances renders the low degree of bridge hydrogen coupling resolution (Figure 1c) unreliable as a potential diagnostic factor in differentiating between the 4 and 5 isomers. Our observance of only one bridge hydrogen resonance in the $^1H\{^{11}B\}$-decoupled NMR spectrum of II (line width ca. 16 Hz) is highly suggestive of B(5) Si substitution for II. This assignment is not totally unambiguous, however, since accidental overlap of two chemical shifts cannot be ruled out. Such behavior has been observed for 1,2-$(Me_3Si)_2B_5H_7$[20] (almost complete overlap) and bridging $Me_2Ge(B_5H_8)_2$ compounds.[16] Previous $^1H$ spectra for 4-$XC_2B_4H_7$ (X = Cl, Br, I)[8] and terminally substituted $R_3SiC_2B_4H_7$ (R = H, Me) derivatives assigned to the 4 isomer[2] lack boron decoupling and hence show only a single broad bridge hydrogen resonance. The structural assignments for the latter series were made on the basis of the $-SiR_3$ group's migration to the carbon atoms upon further heating of the proposed 4 isomer. We note with interest the rather large B(4) chemical shift difference between 4-$(Me_3Si)C_2B_4H_7$ ($\delta$ −3.2) and $\mu$(5,6),4-$(Me_3Si)_2C_2B_4H_6$ ($\delta$ −10.9)[3] which presumably is due to a substantial change in the B(4) electronic environment upon further substitution elsewhere in the molecule. The existence of only one observable methyl resonance in II is also consistent with the 5 isomer although the lack of diastereotopic methyl groups (see above) is judged not to be a valid criterion for structural assignment since the interaction of steric and electronic effects cannot be evaluated.

The effect of terminal silyl substitution in II on the adjacent bridge hydrogens' chemical shift is to leave it virtually unchanged from that of the parent (see Table I). With respect to this observation it should be noted that the literature contains examples of upfield[2] and downfield[3] movement for $C_2B_4H_8$ silane derivatives of similar type and upfield movement[1,15,16] for $B_5H_9$ compounds.

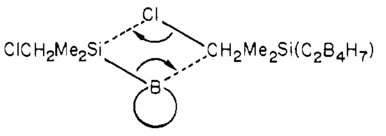
A 1,2 shift of both the carborane cage and the chlorine atom along the silicon–methylene–carbon bond of II is effected by a catalytic amount of $AlCl_3$, giving 4-$(ClMe_2SiCH_2)C_2B_4H_7$ (III). This rearrangement is a specific example of the more generally known process[21] which involves migration of an alkyl

$$R'R_2SiCH_2Cl \xrightarrow{AlCl_3} ClR_2SiCH_2R'$$

group from silicon to a neighboring electron-deficient carbon atom. The enthalpy for such a process is calculated[22] to be about −28 kcal/mol with much of the driving force derived from the formation of the strong Si–Cl bond. The lack of methyl migration when R′ is a boron or carborane cage suggests that the heat evolved for the process involving Si–Z (Z = B, C) and C–Cl bond breaking and C–Z and Si–Cl bond making is greater for Z = B than when Z = C. The observance of only the 4 isomer suggests that the rearrangement of II is kinetically controlled since no amount of 5-$(ClMe_2SiCH_2)C_2B_4H_7$ (indicated to be thermally more stable by its partial formation from III under flash thermolysis at conditions of 530 °C) was detected.

The substituted boron atom singlet downfield from the basal borons observed in the $^{11}B$ NMR spectrum (Figure 1e) for III reflects carbon substitution.[19] The existence of two bridge proton resonances in the $^{1}H\{^{11}B\}$-decoupled NMR spectrum of III is also consistent with 4-$(ClMe_2SiCH_2)C_2B_4H_7$. Following what seems to be the general rule (see below and Table II) alkyl substitution on the cage moves both the adjacent and, to a lesser degree, the far bridging hydrogen chemical shifts substantially downfield from that of the parent. The methylene group protons exhibit the expected[1] upfield shift upon rearrangement. Only one C–H resonance is observed for III contrary to what might be expected since the bulky silylmethyl substituent at the 4 position seemingly ought to result in significantly different magnetic fields at each C–H site, especially in light of I exhibiting two C–H resonances when the bulky substituent is further removed from the C–H hydrogens. Similar anomalous results[8] involving 4-$IC_2B_4H_7$ (separation of C–H resonances) and 4-I-2,3-$C_2Me_2B_4H_5$ (no separation of Me resonances) suggest overriding electronic factors may cause apparent equivalence in III.

While the $AlCl_3$-catalyzed rearrangement of II to give III presumably involves only one Si center, it is tempting to suggest that the small amount of nonvolatile viscous material present with III in the rearrangement mixture arises from an alternative intermolecular pathway like that proposed for the thermal rearrangement of $ClMeSiH_2$ and related systems.[23] One can envision a pathway involving a silicon center and a methylene carbon attached to a neighboring Si center bridged by a chlorine and a basal boron of the carborane cage.



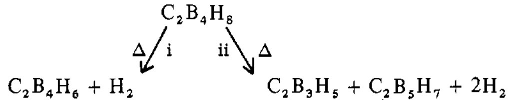
Subsequent exchange would initially give $(C_2B_4H_7)$-$CH_2Me_2Si(C_2B_4H_7)$ (presumably viscous) and $ClMe_2SiCH_2Cl$. The lack of an $^{1}H$ NMR signal attributable to the formation of $ClMe_2SiCH_2Cl$ in the mixture seemingly precludes this specific exchange although a similar one may account for the side product(s) present.

The appearance of the small amount of $C_2B_4H_8$ along with the formation of III presumably occurs prior to rearrangement should trace amounts of moisture hydrolyze the silylcarborane[2] or occur via cleavage of the B–Si bond[24] by HCl generated from small amounts of $AlCl_3{\cdot}H_2O$ during sublimation. At 150 °C II thermally undergoes a 1,2 shift giving an approximate 2:1 mixture of 4- and 5-$(ClMe_2SiCH_2)C_2B_4H_7$ (III and IV). The $^{11}B$ NMR spectrum of the mixture exhibits a downfield shoulder ($\delta$ −10.5) on the C-substituted B(4) atom resonance and this shoulder is attributed to the C-substituted B(5) atom. Such a downfield movement is also noted[19] in going from 4- to 5-$MeC_2B_4H_7$. The $^{1}H\{^{11}B\}$-decoupled spectrum of the mixture exhibits the expected bridge hydrogen resonances due to III with the lower field peak exhibiting increased intensity due to overlap with the bridge hydrogens of IV. Such an overlap at the lower field peak is expected as all the hydrogens involved are adjacent to a C-substituted B atom. Similar behavior is again noted for the $MeC_2B_4H_7$ compounds.[19]

In light of the partial rearrangement of III to IV at 530 °C under flash thermolysis conditions, the observance of no III:IV ratio change upon further heating at 150 °C indicates II is directly converted at the lower temperature to IV and does not proceed via III.

**Conversion of III and IV to Carboranes.** The 4-$(ClMe_2SiCH_2)C_2B_4H_7$ molecule is reasonably stable and only at 530 °C does it partially rearrange to the 5 isomer (IV). The $^{11}B$ NMR spectrum of the 5 isomer exhibits a new low-field resonance ($\delta$ −10.5) and an easily resolvable $J_{B-H_\mu}$ doublet for each member of the unsubstituted basal boron doublet (4,6 positions). The appearance of well-defined bridge hydrogen coupling is consistent with each of the unsubstituted basal borons being adjacent to only one bridge hydrogen. In addition to the possibly detectable line-broadening contribution from $^{11}B$–$^{11}B$ coupling (see above), previous $^{11}B$ spectra for $C_2B_4H_8$ derivatives[3,8,9,10] and $CB_5H_9$ and its derivatives[25] show that the degree of basal boron–bridge hydrogen coupling resolution depends directly upon whether the boron atom is adjacent to two (less resolution) or one (more resolution) bridge hydrogen. Using the B–$H_\mu$ doublet as a criterion for structural assignment seems to work only in the positive sense; that is, if it is not observed, it is not necessarily structurally diagnostic (e.g., the B(4)–C boron in III is adjacent to one bridge hydrogen but no B–$H_\mu$ doublet is observed). The appearance of highly resolved B–$H_\mu$ coupling though, upon partial intramolecular rearrangement of III at 590 °C, strongly suggests the B(4,6) borons in the rearranged product are now unsubstituted, implying B(5) substitution in this case.

The array of recovered products from the successful flash thermolysis at 690 °C suggests that $ClMe_2SiCH_2C_2B_4H_7$ undergoes thermolytic changes via three or more different pathways. The high yield of 2-$ClMe_2SiCH_2$-1,5-$C_2B_3H_4$ suggests the preferred pathway is rapid $BH_3$ elimination. The elimination of a borane unit could account for the presence of $B_2H_6$, which perhaps could also react with an organosilicon moiety giving a side product presumed to be a haloalkylmonoboronic species exhibiting a $^{11}B$ NMR chemical shift at $\delta$ −53.8 and B–Cl bond stretching frequency in the infrared spectrum. In light of previous work concerning the thermolysis of the parent 2,3-$C_2B_4H_8$[5,26,27] the most striking feature of the flash thermolysis of III/IV is the absence of any 2,4-$C_2B_5H_7$ or derivatives thereof. The low-pressure flow pyrolysis of $C_2B_4H_8$ gives, at optimum conditions, $C_2B_4H_6$ (approximately 20%) resulting from $H_2$ elimination, $C_2B_3H_5$ (approximately 40%), and $C_2B_5H_7$ (approximately 40%), the latter two compounds presumably being derived from a redistribution reaction (ii) involving two molecules of the parent nido system.



$$\begin{tikzcd} & C_2B_4H_8 \arrow[dl, "\Delta"', "i"] \arrow[dr, "ii"', "\Delta"] & \\ C_2B_4H_6 + H_2 & & C_2B_3H_5 + C_2B_5H_7 + 2H_2 \end{tikzcd}$$

$C_2B_5H_7$ is known to be stable up to 700 °C in a flow system[26] and a $ClMe_2SiCH_2$ derivative of this closo carborane, should it have formed during the pyrolysis of III/IV, is not expected to be less stable than the obtained derivatives of $C_2B_3H_5$ and $C_2B_4H_6$. Apparently, with III/IV the $BH_3$ elimination step is so rapid that a productive bimolecular collision involving two molecules of III/IV is not possible. This may account for no detectable quantity of the $C_2B_5H_7$ (or a derivative) in the product mixture should a bimolecular collision be required for the production of a $C_2B_5$ carborane. A second pathway followed to a lesser extent by III/IV is the elimination of R–H (R = H, $CH_2SiMe_2Cl$), analogous to reaction i, giving 1,6-$C_2B_4H_6$ and 2-$ClMe_2SiCH_2$-1,6-$C_2B_4H_5$. The 1,2 isomers are not observed since any produced would be converted to the more stable 1,6 isomer at the high temperature used.[5,27] The presence of small amounts of $HSiClMe_2$, confirmed by $^1H$ NMR, indicates III/IV may have followed a third pathway, that of C insertion, presumably giving initially a tricarbaheptaborane species, $C_3B_4H_8$. The failure to detect such a species with both mass and NMR spectral methods seems to reflect the instability of the carborane, at least at 690 °C. It is interesting to note that the mass spectroscopic pattern for compound III exhibits a substantial peak at $m/e$ 87 assigned to $^{12}C_3{}^{11}B_4{}^1H_7$, perhaps reflecting a tendency of $(ClMe_2SiCH_2)C_2B_4H_7$ to insert carbon to a minor extent. Alternately, this may be a result of the production of $^+CH_2{-}C_2B_4H_5$.

**$^1H\{^{11}B\}$-Decoupled Nuclear Magnetic Resonance Spectra of $2,3\text{-}C_2B_4H_8$ and Its Methyl Derivatives.** $^1H$ NMR data have previously been published for $2,3\text{-}C_2B_4H_8$,[5,28] *C*-$MeC_2B_4H_7$,[5] and the *B*-$MeC_2B_4H_7$ isomers.[19] The lack of $^{11}B$ decoupling in these data precluded the establishment of a precise proton chemical shift trend resulting from alkyl substitution. In the present work it is noted that *B*-methyl substitution at any position moves the bridge hydrogen chemical shifts downfield (Table I). Apical methyl substitution exhibits an effect on the $B{-}H_\mu$ group equivalent to that of a basal substituted methyl group on the shift of the far bridge hydrogen ($\Delta\tau = -0.3$ ppm). The effect of a methyl group on the adjacent bridge hydrogen is more pronounced ($\Delta\tau = -0.7$ ppm). *C*-Methyl substitution exhibits no measurable bridge hydrogen shift relative to the parent $C_2B_4H_8$. The effects of methyl substitution on the other cage proton chemical shifts are apparent from the previous work and our new results only confirm them.

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**Registry No.** I, 61916-29-8; II, 61916-30-1; III, 61916-31-2; IV, 61916-32-3; $2\text{-}ClMe_2SiCH_2\text{-}1,5\text{-}C_2B_3H_4$, 61916-33-4; $2\text{-}ClMe_2SiCH_2\text{-}1,6\text{-}C_2B_4H_5$, 61966-87-8; $C_2B_4H_8$, 18972-20-8; $4\text{-}MeC_2B_4H_7$, 21107-31-3; $5\text{-}MeC_2B_4H_7$, 21107-32-4; $C\text{-}MeC_2B_4H_7$, 34228-46-1; $1\text{-}MeC_2B_4H_7$, 21107-30-2; $Na^+C_2B_4H_7^-$, 38117-50-9; $ClCH_2Me_2SiCl$, 1719-57-9.

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# Polarography of Some p-Block Elements in Anhydrous Hydrogen Fluoride

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The polarography of the p-block elements In(III), Tl(I), Pb(II), Cd(II), As(III), Sb(III), Bi(III), and the halides in anhydrous hydrogen fluoride has been investigated using a Teflon dropping mercury electrode and an all Kel-F vacuum line. Data obtained are compared with those reported previously for Sn(II) in HF and with corresponding values for aqueous solution systems and the differing roles of the two solvents are discussed, hydrogen fluoride appearing the simpler solvent. The effects of simple solvation and fluoro complexation on the reversibility of reduction processes in HF are also discussed.

## Introduction

Anhydrous hydrogen fluoride (AHF) undergoes self-ionization to give very simple and mobile anionic and cationic species.[2] Having a large dielectric constant the solvent is potentially very useful for effecting dissolution of ionic compounds, particularly fluorides. Because of its volatility and its corrosive and toxic properties, specialized vacuum systems have been used for its manipulation. The majority of physical studies in AHF have been largely confined to conductivity,[3] spectroscopy,[4,5] and, more recently, cryoscopic measurements.[6,7] Prior to the last few years, electrochemical studies were few in number and mainly limited to potentiometry.[8,9] The earliest reports of polarographic investigations in hydrogen fluoride gave details of work which was essentially exploratory since the solvent was not truly anhydrous and the polarograms were not reproducible.[10]

Although polarographic measurements have yielded much information about aqueous solution chemistry and the nature of electrode processes, the conventional use of this technique in fluoride media was largely precluded because of the dissolution of the glass capillaries by the strongly acidic solvent. However, with the use of an all Kel-F vacuum system in conjuction with a Teflon dropping mercury electrode (DME), reliable polarographic parameters may be obtained for metal