Organosilyl- and Silylorgano-pentaboranes: Monocarbahexaboranes from 2-[(Chlorodimethylsilyl)methyl]pentaborane(9)

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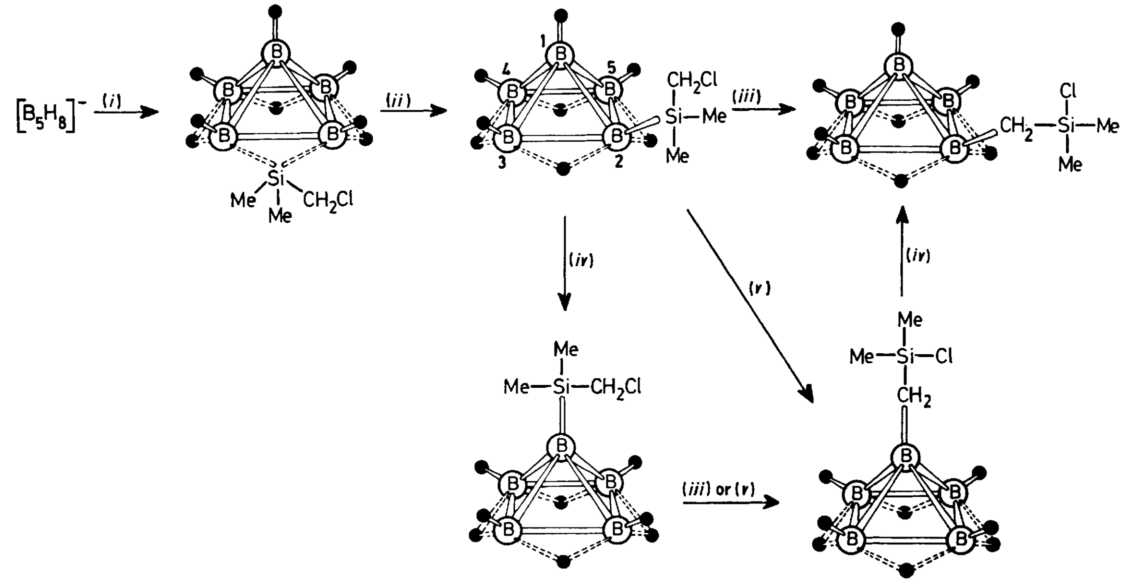
Bridge and terminally substituted pentaborane(9) derivatives of the type $[(ClCH_2)Me_2Si]B_5H_8$ have been prepared. Rearrangement of both the 1- and 2-terminally substituted pentaborane compounds to the carbon-attached isomers, 1-'and 2-$[(ClMe_2Si)CH_2]B_5H_8$, is accomplished with the use of $AlCl_3$ as catalyst. Flash thermolysis of 2-$[(ClMe_2Si)CH_2]B_5H_8$ yields $SiMe_2ClH$ (48%), B_5CH_9 (4.2%), and B_5CH_7 (9.4%) as the major volatile products. Alkylation of B_5H_9 with $SiMe_3(CH_2Cl)$ in the presence of $AlCl_3$ gives 1-MeB_5H_8 and $SiMe_3Cl$ in quantitative amounts, whereas use of $Si(CH_2Cl)Cl_3$ as the alkylating agent gives only 1-$[(Cl_3Si)CH_2]B_5H_8$.

ALL the silicon-attached pentaborane isomers, μ-, 1-, and 2-H_3Si and Me_3Si, have previously been prepared and characterized.[1] Similar silylpentaboranes having functional groups (usually halogens) on the silicon atom have also been reported;[2,3] however, no functionalities have been placed on the carbon atom of the organosilylpentaboranes. Also, except for $(Cl_2BCH_2)B_5H_8$ and $(B_5H_8CH_2)B_5H_8$,[4] no functionalities have been placed on the organo-group of organopentaboranes.[5] Because a model compound of the type $(R_3SiCH_2)B_5H_8$ [analogous to that proposed to be an intermediate in the conversion of bis(trimethylsilyl)pentaborane into silylcarbaboranes][6] was desired, we attempted to synthesize silylorganopentaboranes both from the rearrangement of [(chloromethyl)silyl]pentaboranes and from the Friedel–Crafts alkylation of pentaborane with $SiR_3(CH_2Cl)$.



SCHEME (*i*) $SiMe_2(CH_2Cl)Cl$, $-Cl^-$; (*ii*) OEt_2; (*iii*) $AlCl_3$; (*iv*) hmt; (*v*) heat

RESULTS AND DISCUSSION

The bridged silylpentaborane, μ-$[(ClCH_2)Me_2Si]B_5H_8$, prepared in 61% yield from $[B_5H_8]^-$ ion and $SiMe_2(CH_2Cl)Cl$, rearranged to the 2-substituted analogue in the presence of diethyl ether. The 2-isomer, in turn, was converted to the 1-isomer by use of a catalytic amount of hexamethylenetetramine (hmt), Scheme. In the presence of $AlCl_3$ both 1- and 2-$[(ClCH_2)Me_2Si]B_5H_8$ underwent a 1,2 shift of the boron cage from the silicon to the methylene carbon to give 1- and 2-$[(ClMe_2Si)CH_2]B_5H_8$, respectively, in which the position of attachment at the polyboron cage site has not changed. The B_5H_8 cage apparently has a much greater migratory aptitude than a methyl group for there was no evidence that $(ClEtMeSi)B_5H_8$ is formed as a side product in this rearrangement. The apex-substituted C–B isomer, 1-$[(ClMe_2Si)CH_2]B_5H_8$, was also obtained directly from the 2-$[(ClCH_2)Me_2Si]B_5H_8$ by heating to 100 °C.

Attempts to prepare compounds with a Si–C–B_5 linkage by a modified Friedel–Crafts alkylation[5] of B_5H_9 with $SiMe_2(CH_2Cl)Cl$ or with $SiMe_3(CH_2Cl)$ resulted instead in a quantitative yield of 1-MeB_5H_8 [equations (1) and (2)]. There is a high probability that alkylation of

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[1] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1968, **90**, 6617; 1967, **89**, 4249; *Inorg. Chem.*, 1971, **10**, 1094.

[2] D. F. Gaines and J. Ullman, *Inorg. Chem.*, 1974, **13**, 2792.

[3] T. C. Geisler and A. D. Norman, *Inorg. Chem.*, 1970, **9**, 2167; 1972, **11**, 2549.

[4] E. R. Altwicker, G. E. Ryschkewitsch, A. B. Garrett, and H. H. Sisler, *Inorg. Chem.*, 1964, **3**, 454.

[5] See original references to work in T. Onak, ' Organoborane Chemistry,' Academic Press, New York, 1975, pp. 196—202.

[6] J. B. Leach, G. Oates, S. Tang, and T. Onak, *J.C.S. Dalton*, 1975, 1018.

B_5H_9 by the chlorosilane reagent is taking place, as

$$SiMe_3(CH_2Cl) + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}MeB_5H_8 + SiMe_3Cl \quad (1)$$

$$SiMe_2(CH_2Cl)Cl + B_5H_9 \xrightarrow{AlCl_3} 1\text{-}MeB_5H_8 + SiMe_2Cl_2 \quad (2)$$

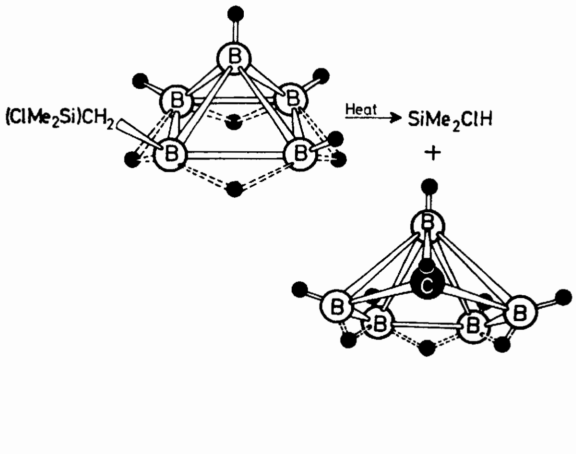
might be expected [equation (3)], but that the intermediate (silylmethyl)pentaborane product undergoes rapid Si–C cleavage with HCl [equation (4)] under the

$$SiR_3(CH_2Cl) + B_5H_9 \xrightarrow{AlCl_3} [(R_3Si)CH_2]B_5H_8 + HCl \quad (3)$$

$$HCl + [(R_3Si)CH_2]B_5H_8 \xrightarrow{AlCl_3} 1\text{-}MeB_5H_8 + SiR_3Cl \quad (4)$$

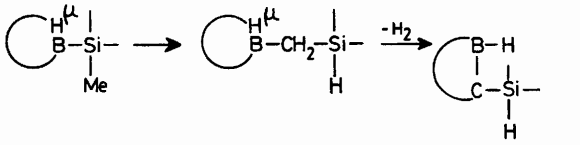
conditions of the reaction. This is based on a separate control experiment in which 1-$[(ClMe_2Si)CH_2]B_5H_8$ (prepared by the method shown in the Scheme), when subjected to HCl in the presence of $AlCl_3$, cleaved to give 1-MeB_5H_8 and $SiMe_2Cl_2$. In still another control experiment, it is noted that HCl cleavage of the Si–C bond did not take place in the absence of the $AlCl_3$ catalyst. Interestingly, use of $Si(CH_2Cl)Cl_3$ as the Friedel–Crafts alkylating reagent resulted in nearly quantitative yield of 1-$[(Cl_3Si)CH_2]B_5H_8$ with no evidence of products, *i.e.* $SiCl_4$ and 1-MeB_5H_8, expected from Si–C bond cleavage. This difference in reaction for the trichlorosilane is attributed, in part, to a change in the Si–C bond polarity in the direction of inhibiting electrophilic attack by HCl.

Flash thermolysis of 2-$[(ClMe_2Si)CH_2]B_5H_8$ gave a moderate yield of volatile material, the major products being the parent carbapentaboranes B_5CH_9 and B_5CH_7, as well as the silicon compound $SiMe_2ClH$. There was also evidence for a B_5CH_9 derivative, probably (B- or C-?) $(ClMe_2Si)B_5CH_8$, as well as very small amounts of a substituted $B_4C_2{}^{1,6}H_6$ and the parent $B_3C_2{}^{1,5}H_5$. Because B_5CH_9 can lead to B_5CH_7 under the conditions of the experiment, it seems reasonable to suggest that an initial step in this flash-thermolysis reaction could be a simple hydrogen transfer from the methylene carbon to silicon with concomitant cleavage of the Si–C bond and incorporation of the resulting HC unit into the base of the pyramidal boron cage [equation (5)].



(5)

As previously reported,[6] flash thermolysis of the bis(silyl)pentaborane, 1,2-$(Me_3Si)_2B_5H_7$, gives a substantial yield of small cage carbaboranes. On the basis of known organosilicon rearrangements, it was suggested that methylene insertion of one of the methyl carbon atoms may well precede carbon incorporation into the boron cage [equation (6)]. Because we now find that



(6)

2-$[(ClMe_2Si)CH_2]B_5H_8$ can be converted into B_5C carbaboranes, the first step in (6), leading to an $SiCH_2$–B linkage, now seems even more probable in the earlier study.[6] It is suggested that the step in which the methylene carbon is incorporated into the boron cage can either entail simple H_2 loss together with hydrogen (bridge ?) migration to a cage boron atom to give a *C*-silylcarbaborane [6] as in equation (6), or hydrogen transfer from carbon to the silicon atom with C–Si bond cleavage to give, *e.g.* equation (5), the *C*-unsubstituted carbaborane as observed in the present study. In both cases elimination of geminal groups about the carbon atom (*i.e.* H,H to give H_2; or H,$SiMe_2Cl$ to give $SiMe_2ClH$) is involved.

Mass Spectra.—The weak parent peak (m/e 170) of both 1- and 2-$[(ClCH_2)Me_2Si]B_5H_8$, together with substantial peaks observed at m/e 121 and 107, indicates that loss of CH_2Cl and B_5H_8 occurs more readily than loss of a methyl fragment. The facile loss of CH_2Cl from Si–CH_2Cl appears to be a common phenomenon, as can be seen from a study of the substituted silicon series $SiMe_{3-x}(CH_2Cl)Cl_x$ (Table 1). With both the 1- and 2-isomers of $[(ClMe_2Si)CH_2]B_5H_8$, loss of either methyl or $CH_2B_5H_8$ fragments from the silicon is preferred over loss of chlorine.

EXPERIMENTAL

Physical Measurements.—Positive-ion mass spectra (Table 1) were recorded using a Varian CH-5 high-resolution mass spectrometer. N.m.r. chemical-shift data (Table 2) for the protons were obtained using tetramethylsilane (τ 10.00) as internal standard. Boron-11 chemical-shift data (Table 2) were obtained using boron trichloride, δ −46.8 p.p.m. relative to boron trifluoride–diethyl ether, as external secondary standard. Both ^1H (100.0 MHz) and ^{11}B (32.1 MHz) n.m.r. spectra were recorded using a Varian HA-100 spectrometer. Boron-11-decoupled proton spectra and proton-decoupled ^{11}B n.m.r. spectra were obtained as outlined earlier.[7] Gas-phase i.r. spectra were recorded on a Beckman IR-acculab 3 instrument.

Materials.—Pentaborane(9) was obtained from Callery Chemical Company, and the organosilicon compounds from PCR Inc. The silicon compounds were distilled from molecular sieves prior to use. All the materials were handled using conventional high-vacuum techniques.

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[7] T. Onak, K. Gross, J. Tse, and J. Howard, *J.C.S. Dalton*, 1973, 2633.

TABLE 1

Mass spectra (partial)

Compound	P [a]	$P - CH_2Cl$	$P - CH_3$	$P - Cl$	$P - B_5H_8$	$P - CH_2B_5H_8$
2-$[(ClCH_2)Me_2Si]B_5H_8$	<1 (170)	16.0 (121)	<1 (155)	<1 (135)	100.0 (107)	[20.9] [b] (93)
1-$[(ClCH_2)Me_2Si]B_5H_8$	<1 (170)	100.0 (121)	12.0 (155)	<1 (135)	29.2 (107)	[37.9] [b] (93)
2-$[(ClMe_2Si)CH_2]B_5H_8$	2.2 (170)	1.1 (121)	28.0 (155)	2.4 (135)	8.9 (107)	100.0 (93)
1-$[(ClMe_2Si)CH_2]B_5H_8$	9.4 (170)	1.0 (121)	100.0 (155)	13.8 (135)	7.3 (107)	82.1 (93)
$Si(CH_2Cl)Cl_3$	12.3 (182)	100.0 (133)		8.8 (147)		
$SiMe(CH_2Cl)Cl_2$	4.3 (162)	100.0 (113)	5.5 (147)	1.9 (127)		
$SiMe_2(CH_2Cl)Cl$	2.4 (142)	100.0 (93)	3.5 (127)	5.4 (107)		
$SiMe_3(CH_2Cl)$	1.0 (122)	100.0 (73)	6.2 (107)			

[a] The percentage of the base peak is reported with the *m/e* value in parentheses. Naturally occurring polyisotopic spectra were observed but the peaks in each envelope cited here represent the mass calculated using the ^{35}Cl, ^{12}C, ^{1}H, ^{11}B, and ^{28}Si isotopes. [b] B_5H_8 loss accompanied by loss of CH_2 from SiMe or $Si(CH_2Cl)$ to give a SiH or SiCl species.

TABLE 2

Nuclear magnetic resonance data

Compound	Group	^{11}B [a,b]	^{1}H [b,c]
μ-$[(ClCH_2)Me_2Si]B_5H_8$	B^1–H	45.4 (d) (174) [1]	9.2 (q) (176) [1]
	B^{2-5}–H	9.4 (d) (145) [4]	7.5 (q) (155) [4]
	CH_3		9.5 (s) [6]
	CH_2		7.1 (s) [2]
	$H^{\mu(3,5)}$		12.6 (vbr, s) [2]
	$H^{\mu(4)}$		11.9 (vbr, s) [1]
2-$[(ClCH_2)Me_2Si]B_5H_8$	B^1–H	49.8 (d) (173) [1]	9.5 (q) (173) [1]
	B^2–Si	13.1 (s) [1]	
	$B^{3,5}$–H	10.7 (d) (*ca.* 160) [2]	7.2 (q) (*ca.* 160) [3]
	B^4–H	7.2 (d) (*ca.* 160) [1]	
	CH_3		9.8 (s) [6]
	CH_2		7.2 (s) [2]
	$H^{\mu(2,5)}$		12.5 (vbr, s) [2]
	$H^{\mu(3,4)}$		11.9 (vbr, s) [2]
1-$[(ClCH_2)Me_2Si]B_5H_8$	B^1–Si	58.2 (s) [1]	
	B^{2-5}–H	12.7 (d) (169) [4]	7.6 (q) (166) [4]
	CH_3		9.9 (s) [6]
	CH_2		7.2 (s) [2]
	H^{μ}		12.3 (vbr, s) [4]
2-$[(ClMe_2Si)CH_2]B_5H_8$	B^1–H	50.2 (d) (164) [1]	9.5 (q) (171) [1]
	B^2–C	−1.5 (s) [1]	
	$B^{3,5}$–H	13.2 (d) (156) [2]	7.6 (q) (156) [3]
	B^4–H	18.2 (d) (156) [1]	
	CH_3		9.5 (s) overlapped [8]
	CH_2		9.5 (s)
	$H^{\mu(2,5)}$		11.4 (vbr, s) [2]
	$H^{\mu(3,4)}$		12.3 (vbr, s) [2]
1-$[(ClMe_2Si)CH_2]B_5H_8$	B^1–C	44.6 (s) [1]	
	B^{2-5}–H	13.8 (d) (164) [4]	7.6 (q) (161) [4]
	CH_3		9.8 (s) [6]
	CH_2		10.1 (s) [2]
	H^{μ}		12.1 (vbr, s) [4]
1-$[(Cl_3Si)CH_2]B_5H_8$	B^1–C	43.1 (s) [1]	
	B^{2-5}–H	11.7 (d) (160) [4]	7.6 (q) [4]
	CH_2		9.5 (s) [d] [2]
	H^{μ}		12.2 (vbr, s) [4]

[a] δ($OEt_2{\cdot}BF_3$) 0 p.p.m. [b] *J* values (in Hz) in parentheses, relative area of pattern in square brackets. [c] τ($SiMe_4$) 10. [d] On selective decoupling of the basal borons the CH_2 group resonance exhibited a partially resolved 1 : 1 : 1 : 1 quartet pattern (*J* 6.3 Hz) similar to that observed for 1-MeB_5H_8 [J. B. Leach and T. Onak, *J. Magnetic Resonance*, 1971, **4**, 30] and assigned to *H*–C–*B*^{1} coupling.

Reaction of $[B_5H_8]^-$ *Ion with* $SiMe_2(CH_2Cl)Cl$.—To $[B_5H_8]^-$ (53 mmol) in diethyl ether, prepared in the standard manner [8] by a low-temperature reaction of B_5H_9 with butyl-lithium, was added freshly distilled $SiMe_2(CH_2Cl)Cl$ (54 mmol) while keeping the ion solution at −196 °C. The mixture was warmed to −78 °C with a bath of acetone–solid CO_2 surrounding the reaction flask. With constant stirring (1 h) the contents of the flask were allowed to attain −30 °C, complete solubility of all the materials in the diethyl ether occurring. On warming the mixture to −20 °C a white precipitate (LiCl) formed; the contents of the flask were stirred for another hour when the temperature had risen to −15 °C. An ice-bath was placed around the flask and most of the solvent was removed. A quantity of material approximately equal to the amount of diethyl ether originally used to prepare the ion was vacuum distilled from the reaction mixture, and the remainder of the material was transferred to a cold column [9] for fractionation. Keeping the cold column below −40 °C resulted in the removal of a small amount of diethyl ether; increasing the temperature of the column to −10 °C removed mostly the starting compound $SiMe_2(CH_2Cl)Cl$ (2.8 mmol). The bulk of the desired product, μ-$[(ClCH_2)Me_2Si]B_5H_8$ (32.3 mmol, 61% yield), was obtained when the temperature of the column was increased slowly from −10 °C to room temperature. The early portion of this last fraction appeared, from ^{11}B n.m.r. (Table 2), to contain a small amount of the 2-isomer.

Rearrangement of μ- *to* 2-$[(ClCH_2)Me_2Si]B_5H_8$.—A mixture of μ-$[(ClCH_2)Me_2Si]B_5H_8$ (11.6 mmol) and diethyl ether (4 cm^3) was allowed to stand at room temperature in a glass ampoule equipped with a 4-mm side tube for taking n.m.r. measurements. After 2.5 h the ^{11}B n.m.r. spectrum (Table 2) of the mixture indicated that complete rearrangement to 2-$[(ClCH_2)Me_2Si]B_5H_8$ had occurred. Vacuum fractionation of the mixture gave the product (11.6 mmol) in a −22 °C trap and diethyl ether in a −196 °C trap.

Rearrangement of 2- to 1-$[(ClCH_2)Me_2Si]B_5H_8$.—A mixture of 2-$[(ClCH_2)Me_2Si]B_5H_8$ (3.3 mmol) and a catalytic amount of hexamethylenetetramine (hmt) was allowed to stand at room temperature for 4 d. The volatile fraction was found to be 1-$[(ClCH_2)Me_2Si]B_5H_8$ (2.3 mmol, 74% yield) by ^{11}B and ^1H n.m.r. (Table 2) as well as by mass-spectroscopic analysis (Table 1).

Rearrangement of 2-$[(ClCH_2)Me_2Si]B_5H_8$ *to* 2-$[(ClMe_2Si)CH_2]B_5H_8$.—A mixture of 2-$[(ClCH_2)Me_2Si]B_5H_8$ (9.14 mmol) and a catalytic amount of freshly sublimed aluminium chloride was allowed to warm from −190 °C to room temperature in a sealed glass tube. An exothermic reaction ensued which was moderated with a cold bath. A ^{11}B n.m.r. spectrum (Table 2), taken after 1 h, indicated that complete rearrangement to the 2-$[(ClMe_2Si)CH_2]B_5H_8$ had occurred. Vacuum fractionation through a series of cold traps gave 2-$[(ClMe_2Si)CH_2]B_5H_8$ (−22 °C trap, 8.39 mmol, 92% yield), 2-MeB_5H_8 (−65 and −196 °C traps, *ca.* 0.05 mmol), $SiMe_2(CH_2Cl)Cl$ (−65 and −196 °C traps, 0.30 mmol), and a trace amount of $SiMe_2Cl_2$ in the −196 °C trap.

Rearrangement of 1-$[(ClCH_2)Me_2Si]B_5H_8$ *to* 1-$[(ClMe_2Si)CH_2]B_5H_8$.—*Catalyzed by* $AlCl_3$. A mixture of 1-$[(ClCH_2)Me_2Si]B_5H_8$ (0.83 mmol) and a catalytic amount of freshly sublimed $AlCl_3$ was allowed to warm, in a sealed n.m.r. tube, from −190 °C to room temperature. An exothermic reaction ensued which was moderated with a cold bath. After several minutes a ^{11}B n.m.r. spectrum was recorded and indicated that the rearrangement to 1-$[(ClMe_2Si)CH_2]B_5H_8$ (Table 2) was complete. Vacuum fractionation through a series of cold traps gave 1-$[(ClMe_2Si)CH_2]B_5H_8$ (−45 °C trap, 0.43 mmol, 52% yield), $SiMe_2(CH_2Cl)Cl$ (−78 °C trap, 0.05 mmol), and in the −196 °C trap a mixture of 1-MeB_5H_8 (0.09 mmol), $SiMe_2Cl_2$ (0.09 mmol), and $SiMe_3Cl$ (0.10 mmol).

Thermal reaction. In another n.m.r. tube was sealed 1-$[(ClCH_2)Me_2Si]B_5H_8$ (1.49 mmol) which was heated at 120 °C for 17 h. Vacuum fractionation through a series of cold traps gave 1-$[(ClMe_2Si)CH_2]B_5H_8$ (−45 °C trap, 0.75 mmol, 50% yield), and a mixture of more volatile products (0.19 mmol) in the −196 °C trap in which 1-MeB_5H_8, from ^{11}B and ^1H n.m.r., is probably one of the major components. Remaining behind as a viscous involatile residue was a material (0.38 mmol) which had the ^{11}B n.m.r. pattern of an apex-substituted pentaborane with a singlet at δ 44.4 p.p.m. and a doublet of higher intensity at δ 13.4 p.p.m. (146 Hz).

Rearrangement of 2-$[(ClCH_2)Me_2Si]B_5H_8$ *to* 1-$[(ClMe_2Si)CH_2]B_5H_8$.—A sealed n.m.r. tube containing 2-$[(ClCH_2)Me_2Si]B_5H_8$ was warmed first at 55—60 °C for 65 h, after which a ^{11}B n.m.r. spectrum revealed no change, and then at 100 °C for 30 h. After the final heating period the ^{11}B and ^1H n.m.r. spectra of the sample were coincidental with those of 1-$[(ClMe_2Si)CH_2]B_5H_8$ (Table 2) with no other resonances present. A mass spectrum of the product was, within experimental error, identical to that of 1-$[(ClMe_2Si)CH_2]B_5H_8$ (Table 1).

Rearrangement of 1- *to* 2-$[(ClMe_2Si)CH_2]B_5H_8$.—A mixture of 1-$[(ClMe_2Si)CH_2]B_5H_8$ (0.40 mmol) and a catalytic quantity of hmt was heated at 71 °C for 17 h. Vacuum fractionation of the mixture indicated that nearly all the volatile material passed through a 0 °C trap and was collected in a −47 °C trap. A ^{11}B n.m.r. spectrum (Table 2) of the material in the latter trap was that of 2-$[ClMe_2Si)CH_2]B_5H_8$ (0.35 mmol, 88% yield).

Friedel–Crafts Methylation of B_5H_9 *using* $SiMe_3(CH_2Cl)$.—Into a 5-mm n.m.r. tube was condensed 1.25 mmol each of $SiMe_3(CH_2Cl)$ and B_5H_9 as well as a catalytic amount of $AlCl_3$. The tube was sealed and left overnight at room temperature. During this time the ^1H n.m.r. singlet (CH_2) resonance at τ 7.5 (external $SiMe_4$) disappeared and left only CH resonances in the τ 9—10 region. The ^{11}B n.m.r. spectrum exhibited a singlet at 43.9 and a 1 : 1 doublet at 12.5 p.p.m. The tube was opened and fractionated through traps at −78 and −190 °C. The trap at −78 °C contained no measurable amount of material and that at −190 °C contained an equimolar mixture (2.40 mmol) of 1-MeB_5H_8 and $SiMe_3Cl$ identified by i.r., mass, and ^{11}B and ^1H n.m.r. spectroscopy.[10-15]

In a separate n.m.r. tube a mixture of 0.74 mmol each of $SiMe_3(CH_2Cl)$ and B_5H_9 together with a catalytic amount of

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$AlCl_3$ was kept at room temperature for 45 min when the bridge region of the ^{11}B-decoupled ^1H n.m.r. spectrum exhibited two resonances *ca.* 0.25 p.p.m. apart.[14] The area of the two resonances indicated that methylation of the apex of B_5H_9 was *ca.* 40% complete. A cold-column fractionation of the mixture gave $SiMe_3Cl$ (0.30 mmol), B_5H_9 (0.44 mmol), 1-MeB_5H_8 (0.32 mmol), and $SiMe_3(CH_2Cl)$ (0.439 mmol). There was no evidence of a product with the formula $[(Me_3Si)CH_2]B_5H_8$.

Friedel–Crafts Methylation of B_5H_9 *using* $SiMe_2(CH_2Cl)Cl$.—Into a 5-mm n.m.r. tube was condensed 0.54 mmol each of $SiMe_2(CH_2Cl)Cl$ and B_5H_9 and a catalytic amount of $AlCl_3$. The tube was sealed and left overnight at room temperature. The ^{11}B n.m.r. spectrum indicated that only *ca.* 10% of the B_5H_9 had reacted at the end of this time. After heating to 75 °C for 16 h the ^{11}B n.m.r. spectrum exhibited very little change in the doublet at δ 12.7 p.p.m. but the doublet at 52 p.p.m. attributed to the apex B–H of B_5H_9 had disappeared and was replaced by a singlet at δ 44 p.p.m. The proton spectrum (external $SiMe_4$) exhibited a broad singlet at τ 10.0, a very broad peak at τ 12.2, and a 1 : 1 : 1 : 1 quartet at τ 7.6 (*J* 170 Hz), all attributed to 1-methylpentaborane,[14] as well as a strong singlet at τ 9.3 attributed to $SiMe_2Cl_2$.[15] The area of the methyl resonance of $SiMe_2Cl_2$ was twice that of the methyl resonance of 1-MeB_5H_8. No further change in the ^{11}B spectrum occurred when the sample was heated at 110 °C for 2 h.

Formation of 1-$[(Cl_3Si)CH_2]B_5H_8$ *from the* $AlCl_3$*-catalyzed Reaction of* B_5H_9 *with* $Si(CH_2Cl)Cl_3$.—Into a dry 5-mm n.m.r. tube was added $Si(CH_2Cl)Cl_3$ (0.14 g, 0.75 mmol), a catalytic quantity of $AlCl_3$, and B_5H_9 (0.75 mmol). The tube was sealed and monitored by both ^1H and ^{11}B n.m.r. After heating the sample to 90 °C for 21 h some change in the n.m.r. spectra had occurred, and after 50 h at 110 °C the apex doublet in the ^{11}B n.m.r. of B_5H_9 at δ 53 p.p.m. had completely disappeared and was replaced by a singlet at δ 43.1 p.p.m. Cold-column fractionation of the product mixture gave 1-$[(Cl_3Si)CH_2]B_5H_8$ (−25 °C to ambient, 0.65 mmol) and at lower temperature trace quantities of $BMeCl_2$, $SiCl_4$, and BCl_3. A mass spectrum of 1-$[(Cl_3Si)CH_2]B_5H_8$ exhibited an envelope of peaks in the parent region of *m/e* 205—214 with the maximum intensity at *m/e* 210. The ^{11}B and ^1H n.m.r. spectra are given in Table 2.

Reaction of HCl *with* 1-$[(ClMe_2Si)CH_2]B_5H_8$.—(*a*) *Without* $AlCl_3$. A mixture of 1-$[(ClMe_2Si)CH_2]B_5H_8$ (0.15 mmol) and dry HCl (0.38 mmol) in a sealed n.m.r. tube was allowed to stand at room temperature for 3 d and then heated at 80 °C for 19 h. Both ^{11}B and ^1H n.m.r. spectra of the mixture indicated no change had occurred. Fractionation of the mixture using −30 {1-$[(ClMe_2Si)CH_2]B_5H_8$} and −196 °C traps (HCl) gave the unchanged starting materials.

(*b*) *With* $AlCl_3$. A catalytic quantity of $AlCl_3$ was sealed into a side-arm attached to an n.m.r. tube. Both 1-$[(ClMe_2Si)CH_2]B_5H_8$ (0.058 mmol) and HCl (0.058 mmol) were condensed into the n.m.r. tube before sealing. After standing for 24 h at room temperature a ^1H n.m.r. spectrum indicated the build-up of $SiMe_2Cl_2$ (τ 9.20).[15] After vacuum fractionation of the mixture through traps at −25, −130, and −190 °C only the −130 °C bath contained a measurable amount of material. A ^{11}B n.m.r. spectrum of this material was consistent with that[14] of 1-MeB_5H_8, and a mass spectrum indicated the presence of both MeB_5H_8[12] and $SiMe_2Cl_2$. The ^1H n.m.r. spectrum was consistent with a nearly equimolar mixture of 1-MeB_5H_8[14] and $SiMe_2Cl_2$.[15]

Reaction of HCl *with* 2-$[(ClMe_2Si)CH_2]B_5H_8$.—(*a*) *Without* $AlCl_3$. A mixture of 0.36 mmol each of 2-$[(ClMe_2Si)CH_2]B_5H_8$ and dry HCl in a sealed n.m.r. tube was allowed to stand at room temperature for 2 d and then heated at 80 °C overnight (*ca.* 16—20 h). Both the ^1H and ^{11}B n.m.r. spectra of the mixture indicated no change had occurred. Fractionation of the mixture using −30 {2-$[(ClMe_2Si)CH_2]B_5H_8$} and −196 °C traps (HCl) gave the unchanged starting materials.

(*b*) *With* $AlCl_3$. The above mixture was recondensed into a 4-mm n.m.r. tube containing $AlCl_3$ (7.4 mg). The tube was sealed and heated to 80 °C for 24 h. The ^{11}B and ^1H n.m.r. spectra of the sample at the end of this heating period were essentially that of the starting materials except for a small ^1H singlet which appeared at τ 9.2 ($SiMe_2Cl_2$).[15] After heating to 120 °C for *ca.* 6 h the peak at τ 9.2, $SiMe_2Cl_2$, grew to nearly half the intensity of the slightly broader *H*–C resonance at τ 9.5—9.6, the latter assigned to a mixture of 2-$[(ClMe_2Si)CH_2]B_5H_8$ (Table 2) and 2-MeB_5H_8.[14] The remainder of the ^1H spectrum and the ^{11}B n.m.r. pattern were consistent with a nearly 1 : 1 ratio of the two pentaborane derivatives.

Conversion of 2-$[(ClMe_2Si)CH_2]B_5H_8$ *into Carbaboranes.*—A slow low-pressure transfer of 2-$[(ClMe_2Si)CH_2]B_5H_8$ (6.59 mmol) through a hot quartz tube at 570 °C was accomplished by vacuum transfer of the reactant from a trap. The volatile products were condensed at −196 °C and subsequently fractionated by cold-column distillation.[9] The products were identified as $SiMe_2ClH$ (3.18 mmol),[16] $B_3C_2{}^{1,5}H_5$ (0.034 mmol),[17] B_5CH_7 (0.63 mmol),[17,18] and B_5CH_9 (0.28 mmol).[19]

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