Formation of Silylcarbaboranes from 1,2-Bis(trimethylsilyl)pentaborane(9)

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By way of an apparent carbon-insertion process, 1,2-bis(trimethylsilyl)pentaborane(9) gives, on flash thermolysis, a number of *C*-silyl derivatives of the smallest known carbaborane, 1-H_3Si-1,5-$C_2B_3H_3$, 1-MeH_2Si-1,5-$C_2B_3H_4$, 2-Me-1-(H_3Si)-1,5-$C_2B_3H_3$, as well as an equilibrium mixture of 2- and 4-methyl derivatives of CB_5H_7. A total carbaborane yield of *ca.* 40 mol % has been obtained. Temperature-dependent n.m.r. studies on the *B*-methyl isomers of CB_5H_7 show a fast bridge-hydrogen tautomerism at *ca.* 100 °C. A substituent chemical-shift effect has been calculated for Me_3Si and H_3Si groups on all positions of the pentaborane(9) cage.

ALTHOUGH *C*-silyl derivatives are known for many of the six- to twelve-atom *closo*-carbaborane polyhedra,[1] none have been reported for the smallest cage, $C_2B_3H_5$. Attempts in this laboratory to prepare $[C_2B_3H_4]^-$ and $[C_2B_3H_3]^{2-}$, logical precursors to *C*-substituted derivatives, from $C_2B_3H_5$ by the methods [1] employed for the higher carbaboranes have not succeeded. In the course of flash-thermolysis studies on substituted boron hydrides,[2] we report the preparation of three *C*-silyl derivatives of $C_2B_3H_5$ from 1,2-bis(trimethylsilyl)pentaborane(9). In addition, *B*-methyl derivatives of CB_5H_7 as well as the parent compound are formed as by-products. Also, because good yields of 1,5-$C_2B_3H_5$ were experienced on flash thermolysis of 1,2-$Me_2B_5H_7$,[2] we have attempted a similar conversion of 1,2-$(H_3Si)_2$-B_5H_7 to the cage $Si_2B_3H_5$.

EXPERIMENTAL

Materials.—Preparation of μ-Me_3Si-B_5H_8, 1-$(Me_3Si)B_5H_8$, 2-$(Me_3Si)B_5H_8$, μ-H_3Si-B_5H_8, 2-$(H_3Si)B_5H_8$, and 1-(H_3Si)-B_5H_8 was carried out as reported earlier.[3] We note, however, that a better yield of 1-$(H_3Si)B_5H_8$ was obtained by heating 2-$(H_3Si)B_5H_8$ to 135 rather than 150 °C.

μ-*Silyl*-1-*silylpentaborane*(9).—Butyl-lithium (10·3 mmol) in hexane was syringed into a flask (250 cm^3); the hexane was removed by vacuum distillation and replaced by diethyl ether (25 cm^3) which had been dried over Li[AlH_4]. 1-Silylpentaborane(9) [10·5 mmol with a trace impurity of 2-$(H_3Si)B_5H_8$] was condensed into the flask and the reactants warmed to −30 °C over a period of 2 h with constant stirring. Chlorosilane (13·0 mmol) was then condensed into the flask and the temperature allowed to rise to −18 °C with constant stirring over a period of 2 h. Fractionation of the products through traps at −22, −43, −78, and −196 °C was carried out while keeping the reaction flask at −18 °C until most of the ether had been removed, after which it was allowed to warm up slowly to room temperature. The *product* 1,μ-$(H_3Si)_2B_5H_7$ (2·5 mmol, 25%) was found in both the −22 and −45 °C traps.

1,2-*Disilylpentaborane*(9).—A sample of 1,μ-$(H_3Si)_2B_5H_7$ (2·5 mmol) was condensed into an ampoule together with diethyl ether (*ca.* 10 cm^3) and left standing overnight. The reaction was monitored by observing changes in the ^{11}B n.m.r. spectrum. The products were fractionated through traps at −22, −45, and −196 °C. The *product* 1,2-$(H_3Si)_2B_5H_7$ (80% yield) was obtained from the −22 and −45 °C traps. A small amount of involatile yellow polymer remained in the reaction vessel and the −196 °C trap was shown to contain the ether solvent together with a small amount of silane. The mass-spectroscopic cut-off was at *m/e* 124, $[^{28}Si_2{}^{11}B_5{}^{1}H_{13}]^+$, with an intensity of 10% of the base peak at *m/e* 91.

μ-*Trimethylsilyl*-1-*trimethylsilylpentaborane*(9).— Butyl-lithium (30·5 mmol) in hexane was syringed into a flask

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[1] R. N. Grimes, 'Carboranes,' Academic Press, New York, 1970; T. Onak, 'Organometallic Chemistry,' ch. 4, vol. 1—3, *Specialist Periodical Report*, The Chemical Society, London, 1971—1974.

[2] E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, 1971, **10**, 2770.

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

previously purged with dry nitrogen. The hexane was distilled off and replaced with dry diethyl ether (40 cm^3). A mixture of 1- and 15% 2-(Me$_3$Si)B$_5$H$_8$ (32 mmol) was condensed into the reaction flask and the reactants allowed to warm to −10 °C with constant stirring over a period of 2 h. Chlorotrimethylsilane (34 mmol) was then distilled into the reaction flask and the reactants allowed to warm to *ca.* 0 °C over a period of another 2 h. The products were then vacuum fractionated through traps at 0, −22, −45, and −196 °C. Some unchanged (Me$_3$Si)B$_5$H$_8$ and Me$_3$SiCl were found in the last three traps and the *product* 1,μ-(Me$_3$Si)$_2$B$_5$H$_7$ was found in the 0 °C trap. It should be noted that preferential bridge substitution of 1-(Me$_3$Si)B$_5$H$_8$ rather than the 2-derivative had occurred, for the −22 °C trap contained the monosilyl starting material enriched (50%) with the 2-isomer.

1,2-Bis(trimethylsilyl)pentaborane(9).—The 1,μ-(Me$_3$Si)$_2$-B$_5$H$_7$ prepared as described above was combined with hexamethylenetetramine and warmed to 85 °C. The reaction was monitored by ^{11}B n.m.r. spectroscopy and rearrangement was shown to be practically complete in 5 h. Fractionation through 0 and −196 °C gave 1,2-(Me$_3$Si)$_2$B$_5$H$_7$ (2·18 g, 10·3 mmol) in the 0 °C trap. The mass spectrum contained a cut-off at *m*/*e* 208 corresponding to the [^{28}Si$_2$^{12}C$_6$^{11}B$_5$^{1}H$_{25}$]$^+$ ion.

Flash Thermolysis of 1,2-(Me$_3$Si)$_2$B$_5$H$_7$.—Low-pressure dynamic transfer of 1,2-(Me$_3$Si)$_2$B$_5$H$_7$ (10·3 mmol) through a hot quartz tube at 575 °C was accomplished by constantly vacuum pumping (over a 24 h period) the reactant while it was kept in a bath at *ca.* 15 °C. The products (*ca.* 18 mmol) were trapped at −196 °C and subsequently fractionated by cold-column vacuum distillation. A product analysis of the fractions obtained from both types of fractionation is summarized in Table 1. Carbaboranes, not heretofore reported in the literature, were removed from the cold column at the following temperatures: 1-H$_3$Si-1,5-C$_2$B$_3$H$_4$, −90 to −100; *B*-MeCB$_5$H$_6$, −86 to −90; 1-MeH$_2$Si-1,5-C$_2$B$_3$H$_4$ and 2-Me-1-(H$_3$Si)-1,5-C$_2$B$_3$H$_3$, −83 °C. Careful refractionation of the latter mixture gave partial separation, the *B*-Me compound being the less volatile of the two isomers.

TABLE 1

Products from the flash thermolysis of 1,2-(Me$_3$Si)$_2$B$_5$H$_7$

Compound	Quantity/mmol
Me$_3$SiH	6·36
Me$_2$SiH$_2$	0·80
MeSiH$_3$	4·04
B$_2$H$_6$	1·35
1,1-Me$_2$B$_2$H$_4$	0·03
Me$_3$B$_2$H$_3$	1·01
CB$_5$H$_7$	1·16
1-H$_3$Si-1,5-C$_2$B$_3$H$_4$	0·78
2,4-C$_2$B$_5$H$_7$	0·11
B-MeCB$_5$H$_6$	1·60
1-MeH$_2$Si-1,5-C$_2$B$_3$H$_4$	0·26
2-Me-1-(H$_3$Si)-1,5-C$_2$B$_3$H$_3$	0·16
*	0·50

* A mixture of lower volatility compounds (see Experimental section).

The mass-spectroscopic cut-off for the *B*-MeCB$_5$H$_6$ mixture was at *m*/*e* 88, [^{12}C$_2$^{11}B$_5$^{1}H$_9$]$^+$, with an intensity of 30% of the base peak at *m*/*e* 86. The cut-off for 1-H$_3$Si-1,5-C$_2$B$_3$H$_4$ at *m*/*e* 92 corresponds to [^{28}Si^{12}C$_2$^{11}B$_3$^{1}H$_7$]$^+$ and had an intensity of 17% of the base peak at *m*/*e* 90. Both 1-MeH$_2$Si-1,5-C$_2$B$_3$H$_4$ and the isomeric 2-Me-1-(H$_3$Si)-1,5-C$_2$B$_3$H$_3$ had the expected cut-off at *m*/*e* 106. In addition to the products listed in Table 1 there was mass-spectroscopic and ^{11}B n.m.r. evidence for 2-Me$_2$HSi-2-CB$_5$H$_8$ (*m*/*e* 134 cut-off; H–^{11}B doublets at δ +49·8, +2·6, and −18·2 p.p.m. in *ca.* 2 : 2 : 1 area ratio) and 1-(Me$_3$Si)B$_5$H$_8$ (*m*/*e* 136 cut-off with a base peak at *m*/*e* 121; large H–^{11}B doublet, δ +12·1, and smaller singlet, δ +57·4 p.p.m.). Also mass-spectroscopic data on two very small fractions showed cut-offs corresponding to Me$_2$CB$_5$H$_5$ and (Me$_2$HSi)C$_2$B$_3$H$_4$; the ^{11}B n.m.r. spectrum of Me$_2$CB$_5$H$_5$ was consistent with that expected for a mixture of all *B*-dimethyl isomers and like other CB$_5$H$_7$ derivatives[2] showed a temperature dependence.

Physical Measurements.—Positive-ion mass spectra were recorded using a Varian CH-5 high-resolution mass spectrometer. N.m.r. chemical-shift data for the protons were obtained using tetramethylsilane (τ 10·00) as external standard. ^{11}B 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. ^{1}H (100·0 MHz) N.m.r. spectra were recorded using a Varian HA 100 spectrometer (Table 3). Boron-11 decoupled spectra were obtained with a Nuclear Magnetic Resonance Specialties HD-60 spin-decoupler attachment, modified for use with HA 100. The radiation frequency (*ca.* 32·1 MHz) was controlled by a Hewlett–Packard 200 CD wide-range oscillator. Another 200 CD oscillator drove a pseudo-random binary-noise generator whose output was used to phase shift the radiation frequency. This signal amplified by an Electronic Navigation Industries 320L RF power

TABLE 2

^{11}B N.m.r. data

Compound	Boron type	δ [a]/p.p.m. obs.	δ [a]/p.p.m. calc.
1,μ-(H$_3$Si)$_2$B$_5$H$_7$	B(1),	+57·2	+57·5
	B(2), B(3) B(4), B(5)	+11·2 (150)	+11·3
1,2-(H$_3$Si)$_2$B$_5$H$_7$	B(1)	+56·7	+56·9
	B(2)	+13·2	+13·4
	B(3), B(5)	+10·2 (*ca.* 170)	+9·6
	B(4)	+6·0 (*ca.* 170)	+5·5
1,μ-(Me$_3$Si)$_2$B$_5$H$_7$	B(1),	+51·1	+52·9
	B(2), B(3)	+7·4 (*ca.* 155)	+8·4
	B(4), B(5)	+11·9 (*ca.* 155)	+12·7
1,2-(Me$_3$Si)$_2$B$_5$H$_7$	B(1)	+54·7	+55·8
	B(2)	+9·0	+9·3
	B(3), B(5)	+11·1 (120—160)	+10·6
	B(4)	+7·5—8·5 (150—180)	+7·7
1-H$_3$Si-1,5-C$_2$B$_3$H$_4$	B(2)—B(4)	−6·5 (196)	
1-MeH$_2$Si-1,5-C$_2$B$_3$H$_4$	B(2)—B(4)	−6·4 (190)	
2-Me-1-(H$_3$Si)-1,5-C$_2$B$_3$H$_3$	B(2)	−12·8	
	B(3), B(4)	−10·9 (185)	
2-Me-1-CB$_5$H$_6$ [b]	B(2)	+3·5	
	B(3), B(5)	+12·5 (173)	
	B(4)	+17·8 (178)	
	B(6)	−4·0 (173)	

[a] With respect to F$_3$B·OEt$_2$ (δ 0 p.p.m.); values of the coupling constant (*J*/Hz) are given in parentheses. [b] At 110 °C.

amplifier was then applied to the HA 100 probe which had been double tuned for decoupling. Conversely, decoupled ^{11}B spectra at 32·1 MHz were observed while irradiating with the heteronuclear-decoupling apparatus equipped with 100 MHz modules. Gas-phase i.r. spectra were recorded on a Beckman IR-Acculab 3. The compounds $(MeH_2Si)C_2B_3H_4$, 2-Me-1-$(H_3Si)C_2B_3H_3$, 1,μ- and 1,2-$(H_3Si)_2B_5H_7$ all exhibited a strong band in the Si–H stretching region of 2 145—2 180 cm^{-1}, all the reported pentaborane and carbaborane derivatives exhibited strong absorption in the B–H(terminal) stretching region of 2 605—2 622 cm^{-1}, and $MeCB_5H_6$, $(MeH_2Si)C_2B_3H_4$, and 2-Me-1-$(H_3Si)C_2B_3H_3$ showed bands in the methyl C–H stretching region of 2 817—2 978 cm^{-1}. Both 1,μ- and 1,2-$(Me_3Si)_2B_5H_7$ were too involatile for gas-phase spectra.

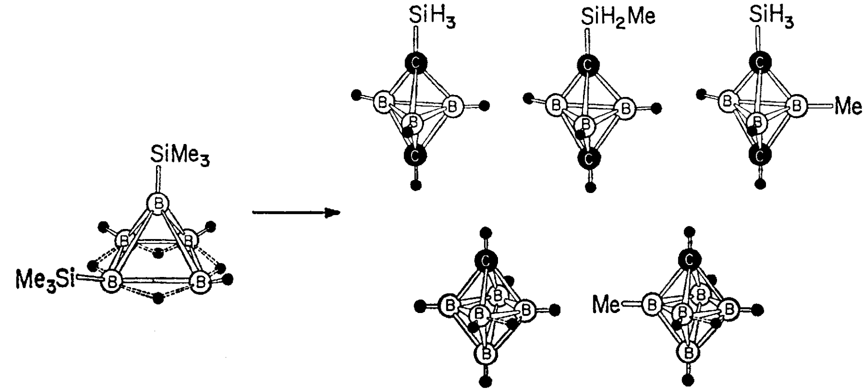


FIGURE 1 Major carbaborane products from the flash thermolysis of 1,2-$(Me_3Si)_2B_5H_7$

TABLE 3

^1H N.m.r. data

Compound	τ [a]		
1,μ-$(H_3Si)_2B_5H_7$	1-H_3Si μ-H_3Si	7·0, 6·1	
	H_tB (all)	7·6	
	H_μ (near)	12·4	
	H_μ (far)	12·0	
1,2-$(H_3Si)_2B_5H_7$	1-H_3Si 2-H_3Si	6·9	
	H_tB (all)	7·5	
	H_μ (near) H_μ (far)	12·4, 12·0	
1,μ-$(Me_3Si)_2B_5H_7$	1-Me_3Si μ-Me_3Si	10·1, 9·7	
	H_tB (all)		
	H_μ (near)	12·7	
	H_μ (far)	12·4	
1,2-$(Me_3Si)_2B_5H_7$	1-Me_3Si 2-Me_3Si	10·0	
	H_tB (all)	7·6	
	H_μ (near) H_μ (far)	12·3—12·5	
1-H_3Si-1,5-$C_2B_3H_4$	H_3Si	6·9	[$J(^{29}SiH)$ *ca.* 100]
	HB	7·2	[$J(^{11}BH)$ *ca.* 190]
	HC	5·3	
1-MeH_2Si-1,5-$C_2B_3H_4$	H_2Si	6·0	[$J(H_2SiMe)$ 3—4]
	MeSi	10·0	[$J(MeSiH_2)$ 3—4]
	HB	6·5	[$J(^{11}BH)$ 187]
	HC	4·5	
2-Me-1-(H_3Si)-1,5-$C_2B_3H_3$	H_3Si	6·2	[$J(^{29}SiH)$ *ca.* 98]
	MeB	10·0	
	HB	6·3	[$J(^{11}BH)$ *ca.* 185]
	HC	4·8	
B-Me-1-CB_5H_6 [b]	MeB	9·7	
	HC	7·6	
	H_μ	14 (broad)	
	$H_t(6)$	7·9	
	$H_t(3)$—$H_t(5)$	8·2	[$J(H_1H_6)$ 12·5]

[a] With respect to $SiMe_4$ (τ 10·00); coupling constants (J/Hz) are given in square brackets. [b] At 110 °C.

RESULTS AND DISCUSSION

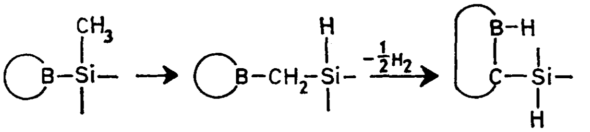
Preparation of Disilylpentaboranes.—Taking advantage of previous chemistry[3] carried out on the preparation and rearrangement of monosilyl derivatives of pentaborane(9), we found that a bridge-hydrogen position of 1-$(R_3Si)B_5H_8$ (R = H or Me) could be easily replaced with another R_3Si group. Rearrangement of

$$\begin{tikzcd}
B_5H_9 \arrow[r, "(i)"] & {[B_5H_8]^-} \arrow[r, "(ii)"] & \mu\text{-}R_3Si\text{-}B_5H_8 \arrow[r] & 2\text{-}(R_3Si)B_5H_8 \arrow[d, "(1)"] \\
 & 1,2\text{-}(R_3Si)_2B_5H_7 & 1,\mu\text{-}(R_3Si)_2B_5H_7 \arrow[l] & 1\text{-}(R_3Si)B_5H_8 \arrow[l, "{(i),(ii)}"']
\end{tikzcd}$$

(*i*), BuLi; (*ii*), R_3SiCl

the second bridge-silyl group to one of the basal-terminal positions in the presence of a Lewis base occurred only slightly more slowly than rearrangement of the monosilyl derivative. In this regard the trimethylsilyl group was more reluctant to rearrange than the parent silyl and this may be attributed to steric repulsions in the transition state of the rearrangement.

Flash Thermolysis of Disilylpentaboranes.—Flash thermolysis of 1,2-$(Me_3Si)_2B_5H_7$ produced an unusually high yield (*ca.* 40 mol %) of a carbaborane mixture as compared to previous[2] thermolysis reactions carried out on other boron hydride derivatives. The major carbaborane products included three silyl derivatives of the *closo*-carbaborane 1,5-$C_2B_3H_5$ (all three compounds together representing *ca.* one third of the total carbaborane mixture) and *B*-methyl derivatives of CB_5H_7 as well as the parent compound (*ca.* two thirds of the total carbaborane mixture, Figure 1). Both of these carbaborane systems, appearing as the parent compound, were also observed as major carbaborane products in the thermolysis reaction of 1,2-$Me_2B_5H_7$.[2] In the present case, however, it is surprising to find a silyl group attached to the carbaborane carbon of the products rather than to a boron atom of $C_2B_3H_5$ in that the starting material for this reaction contained silyl groups on the cage borons of *nido*-B_5H_9. Both this and the loss of methyl carbons on the silyl group in this transformation lead one to suspect that a rearrangement of the sort outlined in equation (2) may be responsible for the silyl $C_2B_3H_5$ derivatives.[4]



(2)

Because *closo*-1,5-$C_2B_3H_5$ is obtained in reasonably good yield from the thermolysis of 1,2-$Me_2B_5H_7$, it was thought that a cage silaborane (*e.g.* $Si_2B_3H_5$) might be obtained from 1,2-$(H_3Si)_2B_5H_9$. Subjecting the latter compound to minimal flash-thermolysis conditions gave, however, only a poor yield of products including 1-$(H_3Si)B_5H_8$ and B_5H_9 and no substantial evidence of a cage silaborane.

^{11}B *N.M.R. Spectra.—Pentaborane derivatives.* Using previously reported chemical shifts [3] for the monosilyl derivatives of pentaborane, it appears possible to develop chemical-shift additivity formulae [5] to predict ^{11}B n.m.r. chemical shifts for polysubstituted derivatives. For basal and apical boron atoms this can be expressed by the relations (3) and (4), where $\sigma_{a\mu}$ is the effect of a bridge

$$\delta\ (^{11}\text{B apex}) = 53{\cdot}1 + \sigma_{ac} + \sigma_{ab} + \sigma_{a\mu} \quad (3)$$

$$\delta\ (^{11}\text{B base}) = 13{\cdot}4 + \sigma_{bc} + \sigma_{bt} + \sigma_{bn} + \sigma_{ba} + \sigma_{b\mu} + \sigma_{b\mu'} \quad (4)$$

substituent on an apical boron, $\sigma_{b\mu}$ that of a bridge substituent on a neighbouring basal boron, and $\sigma_{b\mu'}$ that of a bridge substituent on a ' far ' basal boron; all other contributions are as defined earlier.[5] Values (in p.p.m.) for each of the individual contributions as calculated from the monosilyl derivatives are as below:

Substituent	σ_{ac}	σ_{ab}	σ_{bc}	σ_{bt}	σ_{bn}
H_3Si	+6·9	−3·1	+1·6	−6·3	−2·2
Me_3Si	+4·9	−2·2	−3·6	−5·2	−2·3
Substituent	σ_{ba}	$\sigma_{a\mu}$	$\sigma_{b\mu}$	$\sigma_{b\mu'}$	
H_3Si	−1·6	−2·5	−0·5	−0·5	
Me_3Si	−0·5	−5·1	−4·5	−0·2	

The agreement of the calculated values using equations (3) and (4) with the experimentally obtained values for the disilyl derivatives (Table 2) is acceptable when considering the difficulty in determining ^{11}B chemical shifts to an accuracy greater than ±1 p.p.m. It is interesting to note that the two largest effects in the silyl groups, σ_{ac} and σ_{bt}, are opposite in sign to those found for alkyl substituents.[5] For bridge SiH_3-substituted B_5H_9 derivatives the ^{11}B n.m.r. spectra did not distinguish between the two different basal-boron nuclei. In an investigation to see if this was due to fluxional motion of the SiH_3 group, a low-temperature study on μ-H_3Si-B_5H_8 at −140 °C in a Freon solvent did not resolve the low-field doublet. We conclude that this is therefore probably due to accidental overlap of basal ^{11}B resonances rather than fluxional behaviour.

Carbaboranes.—The ^{11}B n.m.r. assignment for the *B*-methyl derivative of CB_5H_7 isolated from thermolysis of 1,2-$(Me_3Si)_2B_5H_7$ was substantially easier to make at 110 °C than at room temperature. For at the higher temperature a fast bridge-proton tautomerization converted the static mixture of 2-Me (*ca.* 25%) and 4-Me (*ca.* 75%) isomers to a single compound, 2-Me-1-CB_5H_6, on the n.m.r. time scale (Figure 2). *Trans*-upfield (*ca.* 3·4 p.p.m.) and contiguous downfield (*ca.* 11 p.p.m.) shifts were observed for the tautomerized isomer, and are very similar to those observed for the structural relative *nido*-B_5H_9.[5] When the heated sample was cooled to ambient conditions the ^{11}B n.m.r. pattern changed to that of the original mixture (lower temperatures down to −80 °C did not further change the pattern), indicating that an equilibrium ratio of *B*-methyl isomers was produced originally from the flash-thermolysis reaction. During this ^{11}B n.m.r. study a very small singlet at δ −19 p.p.m. prevailed and might be attributed to a small quantity of a 6-Me-1-CB_5H_6; the higher-field 2,3,4,5 B–H resonances of such a compound are probably masked by the greater quantity of

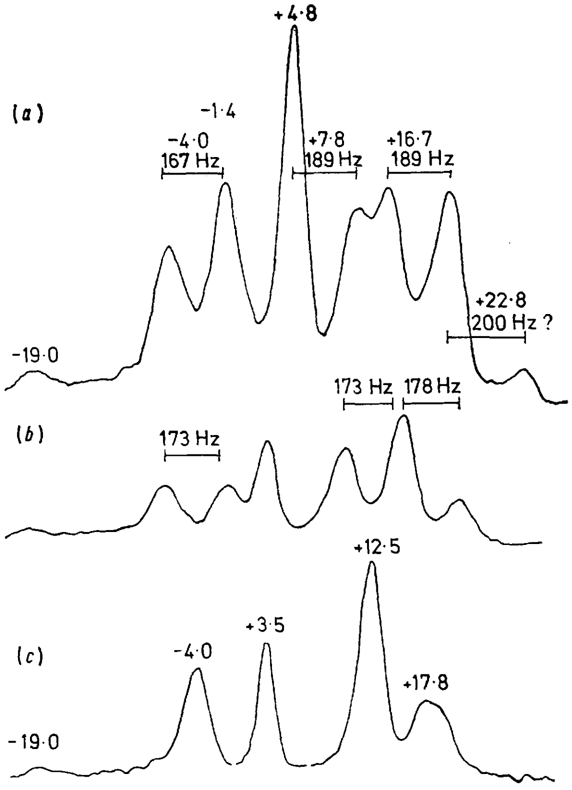


FIGURE 2 Temperature-dependent ^{11}B n.m.r. spectra for 2-(and/or 4-)$MeCB_5H_6$ at (*a*) 20, (*b*) 110, and (*c*) 110 °C (^{1}H decoupled)

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[4] Methylene-group rearrangement has been previously observed in organosilicon compounds (G. Fritz, J. Grobe, and D. Kummer, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 349).

[5] P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 1970, **9**, 1430.

both the other *B*-methyl isomers and therefore positive identification was not possible.

The positional assignment of 2-Me-1-$(H_3Si)C_2B_3H_3$ rather than 1-Me-2-$(H_3Si)C_2B_3H_3$ is based on the observation of a methyl-proton resonance at τ *ca.* 10·0, in the region expected for a B–Me group;[6] a methyl group on the cage carbon atom would be expected at somewhat lower field, τ *ca.* 8·1—8·5.[7]

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