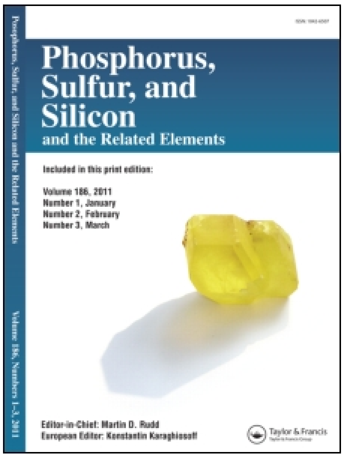


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

RELATIVE STABILITIES OF $XSiH_2B_5H_8$ (X = H, SiH_3, Cl) SILYLPENTABORANE(9)S: SYNTHESIS OF CHLOROSILYL- AND DISILANYL-PENTABORANES

Thomas C. Geisler[a]; Neil P. Soice[a]; Arlan D. Norman[a]
[a] Department of Chemistry and Biochemistry, Universiry of Colorado, Boulder, Colorado

To cite this Article Geisler, Thomas C. , Soice, Neil P. and Norman, Arlan D.(1998) 'RELATIVE STABILITIES OF $XSiH_2B_5H_8$ (X = H, SiH_3, Cl) SILYLPENTABORANE(9)S: SYNTHESIS OF CHLOROSILYL- AND DISILANYL-PENTABORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 132: 1, 123 — 133

To link to this Article: DOI: 10.1080/10426509808036980

URL: http://dx.doi.org/10.1080/10426509808036980

Phosphorus Sulphur and Silicon, Vol. 132 pp. 123–133
Reprints available directly from the publisher
Photocopying permitted by license only

RELATIVE STABILITIES OF $XSiH_2B_5H_8$ (X = H, SiH_3, Cl) SILYLPENTABORANE(9)S: SYNTHESIS OF CHLOROSILYL- AND DISILANYL-PENTABORANES

THOMAS C. GEISLER, NEIL P. SOICE and ARLAN D. NORMAN*

(Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309)

(Received 17 November 1997; Revised 4 January 1997 In final form 4 January 1998)

Reaction of LiB_5H_8 with Si_2H_5Cl in Et_2O at −45°C yields μ-$Si_2H_5B_5H_8$ (**10**), which in Et_2O at 25°C isomerizes to 2-$Si_2H_5B_5H_8$ (**11**). At 120°C in the gas phase, **11** undergoes conversion to an **11**/1-$Si_2H_5B_5H_8$ (**12**) mixture. The three disilanylpentaborane(9) isomers have been separated by high-vacuum fractional distillation. Reaction of 1- $SiH_3B_5H_8$ with BCl_3 yields 1-$(ClSiH_2)B_5H_8$ (**9**). The new silylpentaboranes have been characterized by spectral data. Thermal equilibration of the μ-, 2- and 1-isomers of $SiH_3B_5H_8$, $(ClSiH_2)B_5H_8$ and $Si_2H_5B_5H_8$ in a static reactor at 120°C and in a flow reactor at 350°C and 425°C results in 1- and 2-isomer mixtures. The 1-isomer for all compounds studied is favored at all temperatures. The measured equilibrium constants (K) range from; 8.8 ± 0.4 ($SiH_3B_5H_8$) and 7.3 ± 0.4 ($Si_2H_5B_5H_8$) at 120°C to 1.6 ± 0.4 ($SiH_3B_5H_8$), 1.3 ± 0.2 ($Si_2H_5B_5H_8$) and 2.2 ± 0.6 [$(ClSiH_2)B_5H_8$] at 425°C. These are discussed in terms of substituent conjugative effects.

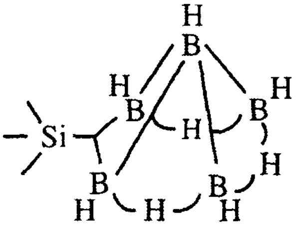
Keywords: pentaborane(9)s; silylpentaborane(9)s; silyl-substituents

INTRODUCTION

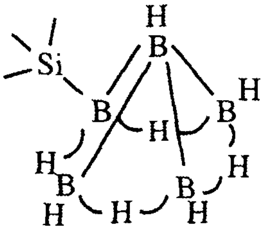
The silylpentaborane(9)s, $SiH_3B_5H_8$, [1, 2] $Me_3SiB_5H_8$ [1-3], and $SiF_3B_5H_8$ [4] were reported previously and shown to exist as three isomers in which the silyl groups occupy the bridging (μ-), 2- and 1-positions on the pentaborane(9) cage, **1-3**, respectively. [5] For these compounds it was determined that the order of

---

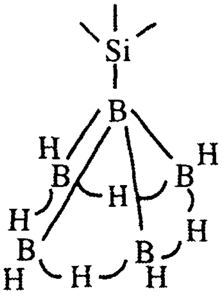
*Corresponding author.



1 (μ-isomer)



2 (2-isomer)



3 (1-isomer)

relative thermodynamic stability for the isomers is 1- > 2- > μ. [2, 4, 5] Further, it was shown that at equilibrium only the 2- and 1-isomers are present in detectable amounts and that the 1-isomer is favored.

As an extension of the silylpentaborane(9) studies, and because silicon/boron hydrides offer potential as Si/B/N and Si/B/C/N ceramics precursors, [6, 7] it became of interest to determine if different substituents on the silyl group, eg. $XSiH_2B_5H_8$, would impart electronic differences large enough to influence the equilibrium properties. To this end we have prepared μ-, 2- and 1-isomers of $Si_2H_5B_5H_8$ and 1-$ClSiH_2B_5H_8$ which along with our previously reported 2- and μ- $(ClSiH_2)B_5H_8$ [8] and the μ-, 2- and 1-isomers of $SiH_3B_5H_8$ [1-3] provide a series of $(XSiH_2)B_5H_8$ (X = H, SiH_3 and Cl) compounds in which we can study and compare thermal equilibration properties. The results of our study follow.

EXPERIMENTAL

Apparatus and Materials

All manipulations were carried out in standard vacuum-line apparatus. [9] Boron-11 NMR spectra were obtained on Varian HA-100 (32.1 MHz) and

VXR300S (96.3 MHz) spectrometers, respectively. Chemical shifts (downfield = $+\delta$) were measured relative to external $B(OMe)_3$ or BBr_3 and are given relative to $BF_3 \cdot OEt_2$. ^1H NMR spectra were obtained at 100.0 MHz on a Varian HA-100 spectrometer. Mass spectra (EI) were obtained with Varian MAT CH-5 and VG 7070 EQ-HF spectrometers. Unless specified otherwise, the M^+ ions reported refer to the largest peak in the parent ion envelope. IR spectra (4000 − 400 cm^{-1}) were obtained on gaseous samples using a Beckman 4250 spectrometer. Melting points were determined using the magnetic plunger technique. [9] Vapor pressure vs. temperature data were obtained in an all-glass immersible tensimeter which had been predried with SiH_3Br before use. Samples were frozen to −196°C between pressure measurements to minimize decomposition.

Elemental analyses for H, Cl and B were conducted by wet chemical techniques. [10] Hydrogen was determined as hydrolytic H_2 by hydrolysis of weighed samples; evolved H_2 was measured using a calibrated Toepler pump. [9] Chloride was determined by titration with standard $AgNO_3$ solution. The end point was determined potentiometrically using a silver-wire indicating electrode and a glass reference electrode. [11] Boron was determined potentiometrically as $B(OH)_3$ with standard NaOH solution using the equivalent pH method. [10]

Chlorodisilane [12], μ-$SiH_3B_5H_8$(**4**), [2] 2-$SiH_3B_5H_8$(**5**), [2] 1-$SiH_3B_5H_8$(**6**), [3] μ-$(ClSiH_2)B_5H_8$(**7**), [8] 2-$(ClSiH_2)B_5H_8$(**8**) [8] and LiB_5H_8 solutions [13, 14] were prepared and purified as described previously. Boron trichloride (Matheson Co.) was purified by routine fractional condensation techniques. Diethyl ether was distilled from $LiAlH_4$ prior to use.

1-$(ClSiH_2)B_5H_8$ (9)

Boron trichloride (0.024 mL, 0.30 mmol) and 1-$SiH_3B_5H_8$ (0.188 g 1.47 mmol) were condensed into a 25 mL reaction tube at −196°C and slowly warmed to 25°C with occasional shaking. After 30 min, volatile materials were fractionally condensed through a −95°C trap into a −196°C trap. The −196°C trap contained traces of B_2H_6, $BHCl_2$ and B_2H_5Cl. [15] High-vacuum column distillation of the −95°C condensate yielded unreacted 1-$SiH_3B_5H_8$ (0.58 mmol) and **12** (0.107 g, 0.84 mmol; 57% yield). Mp −41.3 ± 0.1°C. 0°C vapor tension = 0.5 ± 0.05 Torr. Owing to the thermal instability of **12**, vapor tension data above 0°C were not obtained. ^{11}B NMR (CS_2): δ 58.0 (s, 1B; B_1), 12.4 (d, 4B, J = 168 Hz; $B_{2\text{-}5}$). ^1H NMR (CS_2): δ 4.78 (q, 2H, J = 10.4 Hz; SiH_2), 2.66 (d, 4H, J = 168 Hz; BH_t), −1.67 (br s, 4H; BH_μ). M^+ ($^{11}B_5^{28}Si^{37}ClH_{10}^+$): m/e, 130. IR (gaseous, KBr): 2615(s; BH_t), 2165(vs; SiH), 1855(w; BH_μ), 1495(w), 1410(w), 1060(w), 960(sh), 955(m), 950(sh), 885(m), 835(s), 675(w), 530(m) cm^{-1}. *Anal.* Calcd. for B_5SiClH_{10}: H, 7.89; Cl, 27.8. Found: H, 7.89; Cl, 28.7.

μ-$Si_2H_5B_5H_8$ (10)

Chlorodisilane (0.193 g, 2.01 mmol) was condensed at −196°C into a 100 mL flask containing LiB_5H_8 (1.77 mmol) in Et_2O. The reactants were warmed slowly to −45°C. After 10 min at −45°C, volatile reaction materials were removed and passed through traps at 0°C and −45°C. The **10** condensed at −45°C, typically along with 5-10% of **11**. High-vacuum distillation [9] of the **10**/**11** mixture yielded pure **10** (0.17 g, 1.4 mmol, 80% yield). Mp −81.1 ± 0.2°C. 0°C vapor tension = 0.7 ± 0.05 Torr. Attempts to obtain vapor tension data above 0°C were unsuccessful due to sample thermal instability. ^{11}B NMR (CS_2): δ 50.1 (d, 1B, J = 177 Hz; B_1), 12.4 (d, 4B, J = 156 Hz; $B_{2\text{-}5}$). ^1H NMR (CS_2): δ 4.03 (br mult., 2H; SiH_2), 3.51 (br t, 3H, J = 2.9 Hz; SiH_3). B-H ^1H resonances were not well enough resolved to be assigned. M^+ ($^{11}B_5^{28}Si_2H_{13}{}^+$): m/e, 124. IR (gaseous, KBr): 2620(s; BH_t), 2160(s; SiH), 1820(w; BH_μ), 1400(m), 1110(w), 1025(w). 935(m), 880(s), 840(w), 800(m), 755(s), 665(w), 615(m) cm^{-1}. *Anal.* Calcd. for $B_5Si_2H_{13}$: H, 7.67. Found: H, 7.72.

2-$Si_2H_5B_5H_8$ (11)

A sample of **10** (0.134 g, 1.09 mmol) was dissolved in Et_2O (5 mL) and allowed to stand at 25°C for 4 h. High-vacuum column fractional distillation yielded pure **11** (0.12 g, 0.98 mmol, 73% yield). Mp −92.0 ± 0.1°C. 0°C vapor tension = 0.70 ± 0.05 Torr. ^{11}B NMR (CS_2): δ 50.3 (d, 1B, J = 174 Hz; B_1), 13.8 (s, 1B; B_2), 6.6 (d, 1B, J = 124 Hz; B_4), 11.2 (d, 2B, J = 168 Hz; $B_{3,5}$). ^1H NMR (CS_2): 3.27 (comp. mult., 5H). B-H ^1H resonances were not resolved enough to be assigned. M^+ ($^{11}B_5^{28}Si_2H_{13}{}^+$): m/e, 124. IR (gaseous, KBr): 2610(s; BH_t), 2150(s; SiH), 1810(w; BH_μ), 1625(w), 1495(w), 1450(w), 1400(m), 1285(w), 1020(w), 935(m), 880(w), 810(w), 780(w), 740(s), 665(m), 610(w), 515(w) cm^{-1}. *Anal.* Calcd. for $B_5Si_2H_{13}$: H, 7.67. Found: H, 7.57.

1-$Si_2H_5B_5H_8$ (12)

A sample of **11** (0.125 g, 1.02 mmol) was heated in a 1-L bulb at 120°C. After 14 h, reaction contents were removed and found to consist of a **12**/**11** mixture (6:1 mol ratio). High vacuum column distillation yielded **12** (0.95 g, 0.77 mol, 77% yield). Mp −63.9 ± 0.2°C). 0°C vapor tension = 0.75 ± 0.05 Torr. ^{11}B NMR (CS_2): δ 61.2 (s, 1B; B_1), 12.9 (d, 4B, J = 167 Hz; $B_{2\text{-}5}$). ^1H NMR (CS_2): 3.20 (compl. mult., 5H, J = 2.5 Hz; SiH_2 and SiH_3), 2.54 (br d, 4H, J = 166 Hz; BH_t), −2.11 (br s, 4H; BH_μ). M^+ ($^{11}B_5^{28}Si_2H_{13}{}^+$): m/e, 124. IR (gaseous, KBr): 2615(s; BH_t), 2150(s; SiH), 1850(w; BH_μ), 1790(w), 1490(w), 1405(w), 1050(w), 940(m), 880(m), 865(m), 815(w), 770(w), 740(s), 670(w), 525(w) cm^{-1}. *Anal.* Calcd. for $B_5Si_2H_{13}$: H, 7.67. Found: H, 7.57.

Thermal Equilibration Reactions

Thermal equilibrations were carried out under both static and flow conditions. Static thermolyses of the $SiH_3B_5H_8$ (**4**-**6**) and $Si_2H_5B_5H_8$ (**10**-**12**) isomers were conducted in 500 mL or 1-L sealed Pyrex bulbs in an oven at temperatures maintained to ±2°C. Experiments were carried out optimally at 120°C. In each case, the reactor was dried thoroughly before the reaction. Thermolyses of chlorosilylpentaborane(9)s (**7**-**9**) were not carried out in static reactors because during the time needed to vaporize the compounds, extensive disproportionation to $SiH_3B_5H_8$ and $Cl_2SiHB_5H_8$ occured.

Flow reactions were accomplished in a single-pass apparatus, in which the reactant silylpentaborane was passed slowly at low pressures (ca. 1 Torr; flow rates between 0.6 and 2.3 mmol/h) through a Pyrex reactor tube (12 mm O.D by 28 cm length) heated with a heat tape. Conditions were varied in each case so as to minimize reactant decomposition and to insure equilibration of the product mixtures. The reactor was insulated to maintain a constant temperature; the reactor temperature was monitored by a thermocouple to within ±5°C. Reactions were carried out at 350 and 425°C. The system was pumped continously during each experiment in order to remve H_2 from the system. After reaction materials passed the heated reactor they were collected in a −196°C trap, then separated and analyzed.

Static and flow thermolyses typically were carried out under conditions, as shown for example for $SiH_3B_5H_8$ isomers, as listed in Table I. Upon completion of each reaction, volatile reaction materials were separated by high-vacuum column distillation. No attempt was made to analyze involatile reaction residues. Reaction products were characterized by comparison of their physical and/or spectral properties with literature values. In each experiment, the recovered silylpentaboranes were a mixture of 1- and 2-isomers. In no case was any of the μ-isomers seen.

RESULTS AND DISCUSSION

Silylpentaborane(9) Syntheses

Preparation of the three isomeric disilanyl (Si_2H_5-) substituted pentaborane(9)s is effected readily in reactions analogous to those described for the SiH_3- and Me_3Si- substituted pentaboranes. [1-3] Reaction of LiB_5H_8 in Et_2O with Si_2H_5Cl

TABLE I Typical $SiH_3B_5H_8$ Thermal Equilibration Experiments

Exp.	Reactant(mmol)	Conditions[a]	Percent Reactant(s) Consumed	Recovered Isomer Ratio (1:2)	Decomposition Products(mmol)
1	1-$SiH_3B_5H_8$ (1.32 mmol)	flow 1.04 mmol/h 425°C	79 Si_2H_6 (0.007)[c]	1.5:1.0	SiH_4 (0.01),[a] B_5H_9 (0.10)[b]
2	1-$SiH_3B_5H_8$ (2.40)	flow 1.11 mmol/h 350°C	25	1.9:1.0	SiH_4 (0.01)[a], B_5H_9 (0.08)[b]
3	2-$SiH_3B_5H_8$ (1.34)	flow 0.60 mmol/h 425°C	68 B_6H_{10} (trace)[d]	1.7:1.0	SiH_4 (0.02)[a], B_5H_9 (0.12)[b],
4	2-$SiH_3B_5H_8$ (2.22)	flow 0.60 mmol/h 350°C	14	1.7:1.0	SiH_4 (0.02)[a], B_5H_9 (0.07)[b]
5	μ-$SiH_3B_5H_8$ (2.70)	flow 1.62 mmol/h 350°C	17 Si_2H_6 (0.003)[c]	2.0:1.0	SiH_4 (0.02)[a], B_5H_9 (0.07)[b],
6	μ-$SiH_3B_5H_8$ (3.23)	flow 1.29 mmol/h 425°C	61 Si_2H_6 (0.10)[c], B_6H_{10} (0.35)[d]	1.6:1.0	SiH_4 (0.14)[a], B_5H_9 (0.23)[b],
7	μ-$SiH_3B_5H_8$ (1.00)	static 12 h 120°C	2	8.5:1.0	not measured

[a] Ref.[21]. [b] Ref.[23]. [c] Ref.[22]. [d] Ref.[30].

$$Si_2H_5Cl \;+\; LiB_5H_8 \longrightarrow LiCl \;+\; Y\text{-}Si_2H_5B_5H_8$$
$$(\mathbf{10},\ Y = \mu;\ \mathbf{11},\ Y = 2)$$

at −45°C for 10 minutes yields an approximately 9:1 (mole ratio) mixture of μ- and 2-$Si_2H_5B_5H_8$ (**10** and **11**; eqn. 1). During longer reaction periods, a larger percentage of **11** was observed, however, in no case was it possible to obtain exclusively **10** from these reaction mixtures. Pure **10** was obtained only after repeated high-vacuum column distillations. Conversion of **10** to 2-$Si_2H_5B_5H_8$ (**11**) in essentially quantitative yield (>90%) occured in Et_2O solution during 4 hours at 25°C. The 1-$SiH_3B_5H_8$ (**12**) is the most thermodynamically stable isomer; it is obtained by gaseous phase thermolysis of either **10** or **11**. The most efficient preparative conditions involve thermolysis of **11** at ca. 120°C for 12-14 hours. This allows sufficient time for conversion to **12** and also results in minimal thermal decomposition of the disilanylpentaboranes. The $Si_2H_5B_5H_8$ isomers behavior parallels closely that of other known silylpentaboranes, [2-4] in that the order of thermodynamic stability is μ- $\ll$ 2- < 1-.

Chlorosilyl-substituted pentaboranes are readily prepared from reactions of the $SiH_3B_5H_8$ isomers with BCl_3. The isomers μ-$(ClSiH_2)B_5H_8$ (**7**) and 2-$(ClSiH_2)B_5H_8$ (**8**) were reported previously; [8] the 1-$(ClSiH_2)B_5H_8$ (**9**) was prepared for the first time in this study. All isomers (Y = μ-, 1- and 2-) react essentially quantitatively at moderate temperatures (eqn 2) and in the absence of catalysts. Halogenation occurs exclusively at the silicon. Only traces of products such as SiH_4, SiH_3Cl and B_5H_9 were seen, presumably the result of HCl cleavage of Si-B bonds. Under reaction conditions using quantities of BCl_3 equal to or slightly greater than that required for monohalogentation, there was no evidence for formation of di or tri-chlorinated products of any of the three $SiH_3B_5H_8$ isomers. No evidence for halogenation of the B_5 cage was observed; however, it is known that at higher temperatures (120°C) in the presence of catalysts, the BCl_3/B_5H_8 reaction yields the six boron product 1-$(Cl_2B)B_5H_8$. [16]

Within the limits of our experimental data, no difference was observed in the rate of BCl_3 halogenation of 2- and 1-$SiH_3B_5H_8$. Both react quantitatively within 30 minutes between 0°C and room temperature. However, the μ-$SiH_3B_5H_8/BCl_3$ reaction is incomplete even after 4 hours at 45°C. In contrast to the

$$Y\text{-}SiH_3B_5H_8 \xrightarrow{BCl_3} Y\text{-}(ClSiH_2)B_5H_8$$
$$(\mathbf{8},\ Y = \mu;\ \mathbf{9},\ Y = 1;\ \mathbf{10},\ Y = 2)$$

silylpentaboranes, SiH_4 undergoes no reaction with BCl_3. [17] Thus, from our data, limited conclusions can be made about the effect of pentaboranyl substitution on the halogenation of a silyl group. It appears that pentaboranyl-group substitution markedly enhances the reactvity of the SiH_3 moiety towards BCl_3. The increased effectiveness of a terminal B_5H_8 group over a μ-B_5H_8 unit is apparent also. However, until more data are available, speculation as to the basis of the reactivity differences seems unjustified.

Characterization of **9** and **10-12** is based on elemental analysis and spectral (mass, IR and NMR) data. For **9** and **10-12**, parent mass spectral molecular ions are seen at m/e 130 and 126, respectively. All show both teminal B-H and Si-H and bridge μ B-H stretching absorptions, in the 2600-2620, 2140-2190 and 1810-1860 cm^{-1} regions. [18-23] Isomers **9-10** show a distinct SiH_2 group ^1H NMR resonance. For **10-12**, complex ^1H NMR spectral multiplets of relative area 5 are seen for the Si_2H_5 groups. Isomer identification is most clear from the ^{11}B NMR spectral data; the spectra for the **9** and **10-12** series are very similar to those reported earlier for the $SiH_3B_5H_8$ isomers. [1-3, 8, 24, 25] The 2-$Si_2H_5B_5H_8$ (**11**) exhibits the expected four resonances in relative areas 1:2:1:1 attributable to the apical (B_1) and basal (B_2, $B_{3,5}$ and B_4) boron atoms. [25-27] Like other pentaboranes, the high field doublet is assigned to B_1. The 1-isomers (**9** and **12**) show two resonances, a singlet and a doublet, of relative area 1:4 due to the substituted boron B_1 and the four equivalent basal boron BH groups (B_{2-5}). The μ-$Si_2H_5B_5H_8$ (**10**) shows two resonances, an area 1 doublet from the apical boron (B_1) and an area 4 doublet assigned to the basal (B_{2-5}) borons. At the field strengths employed, the chemical shift difference between the $B_{2,3}$ and $B_{4,5}$ atom types are not great enough to be allow their differentiation.

Thermal Equilibrations

The $SiH_3B_5H_8$, $Si_2H_5B_5H_8$ and $(ClSiH_2)B_5H_8$ isomers were subjected to static and flow reactor thermolyses in order to effect isomer interconversion and equilibration. Experimental details for a series of typical $SiH_3B_5H_8$ thermolyses are shown in Table I. Static reactor reactions of **4-5** and **10-12** were typically carried out for 8-24 hours at 120°C, a temperature at which equilibration could be achieved without excessive sample decomposition. Equilibrations at higher temperatures, 350 and 425°C were examined in the flow apparatus. At these temperatures, significant decomposition occurred; however, because the reactant time in the hot zone was short, equilibration could be achieved without complete decomposition of the reactants. In each system, attainment of equilibrium was recognized by the fact the product isomer ratio remained constant irrespective of the starting silylpentaborane isomer.

TABLE II Observed Silylpentaborane Isomer Ratios and Mean Equilibrium Constants

Reactant Compound	Isomer	1-:2- Isomer Ratio 120°C[a]	350°C[b]	425°C[b]
$SiH_3B_5H_8$	μ-	n.m.[c]	2.0 ± 0.2	1.6 ± 0.2
	2-	8.5 ± 0.2	n.m.	1.7 ± 0.2
	1-	9.1 ± 0.2	1.9 ± 0.3	1.5 ± 0.2
Mean K		8.8 ± 0.4	1.9 ± 0.4	1.6 ± 0.4
$Si_2H_5B_5H_8$	μ-	n.m.	1.5 ± 0.2	n.m.
	2-	7.1 ± 0.2	1.3 ± 0.2	n.m
	1-	7.4 ± 0.3	1.7 ± 0.2	1.3 ± 0.2
Mean K		7.3 ± 0.4	1.5 ± 0.4	1.3 ± 0.2
$(ClSiH_2)B_5H_8$	μ-	n.m.	3.5 ± 0.2	2.9 ± 0.3
	2-	n.m	n.m	2.2 ± 0.3
	1-	n.m.	3.0 ± 0.2	1.6 ± 0.3
Mean K		3.3 ± 0.04	2.2 ± 0.6	

[a]Measured to ± 2.0°C. [b]Measured to ± 5.0°C. [c]Not measured.

Thermolyses of the silylpentaborane isomers results in rearrangements ultimately to an equilibrium mixture of the 1- and 2-isomers. Equilibrium ratios as obtained from thermolysis of each isomer along with mean equilibrium constants (K) at each temperature are shown in Table II. Except in the case of $(ClSiH_2)B_5H_8$, the equilibrium ratios shown are average values of at least two experiments obtained from equilibration of each isomer at the conditions given. Data for $(ClSiH_2)B_5H_8$ result from only one experiment. In thermolyses of the 2-isomer, equilibration was typically achieved faster than with the μ-isomers, presumably because the μ-isomer must first rearrange to the 2-isomer, which subsequently reacts to the final 2- and 1-isomer equilibrium mixture. [28]

At 120°C, the relative order of 1-:2- equilibrium constants for the silylpentaboranes we studied is $Si_2H_5 < SiH_3$. When our data are considered along with the value of 3.3 at 120°C for $Me_3SiB_5H_8$ reported earlier, [4] we surmise that at 120°C the K's increase as $Me_3SiB_5H_8 < Si_2H_5 < SiH_3$. At 350 and 425°C, we observed a 1-:2- equilibrium constant order increasing as $Si_2H_5 < SiH_3 < SiH_2Cl$, assuming that we can consider the small differences observed between the values for $SiH_3B_5H_8$ and $Si_2H_5B_5H_8$ as statistically significant. Thus overall we conclude that the 1-: 2-isomer ratio increases in the order $Me_3SiB_5H_8 < Si_2H_5 < SiH_3 < (ClSiH_2)B_5H_8$.

Some observations can be made concerning (i) the relative stability of the 1- and 2-isomers of the $X\text{-}SiH_2B_5H_8$ ($X = Cl, H, SiH_3$) series ($ClSiH_2B_5H_8$, $SiH_3B_5H_8$, $Si_2H_5B_5H_8$) and the previously studied $Me_3SiB_5H_8$[4] and (ii) the effect of the X substitutents on the equilibrium constants. Firstly, the 1-:2- equilibrium constants for the $SiH_3B_5H_8$, $Si_2H_5B_5H_8$, $(ClSiH_2)B_5H_8$ series decrease with increasing temperature. This is consistent with the fact that the 2- to

1-isomerization is exothermic and that the 1-isomer is more thermodynamically stable. [4, 28] Although trends can be seen, the data are not good enough to allow us to calculate reliable ΔH and ΔS data parameters for the reactions. Secondly, it is interesting that the 1-:2- equilibrium quotient order of $Me_3SiB_5H_8 < Si_2H_5 < SiH_3 < SiH_2Cl$ is consistent with what might be expected based on an analysis of substituent effects and their origins in pentaboranes reported earlier by Ulman and Fehlner.[29] These authors considered XB_5H_8 pentaborane(9)s (X = halogen, CH_3 and SiH_3) and concluded that isomer preference is a result of both conjugative (π) and inductive (σ) effects. In the $SiH_3B_5H_8$ isomers, conjugative effects involving backbonding from the B_5 cage to Si appear especially significant and are more important in the 1- than in the 2-isomer. In the series we examined, the substituents varied are not directly bonded to the B_5 cage, so the effects are secondary. However, if the effect in the $XSiH_2B_5H_8$ series of going from electron donating to electron withdrawing substituents, as $(Me_3)\text{-}SiB_5H_8 < SiH_3\text{-}SiH_2\ (Si_2H_5) < H\text{-}SiH_2 < Cl\text{-}SiH_2$, is to progressively lower the Si acceptor d-orbital energy and increase the degree of backbonding in the 1- isomer more than the 2- isomer, the 1-:2- stability order would increase as $Me_3SiB_5H_8 < Si_2H_5 < SiH_3 < (ClSiH_2)B_5H_8$, as we observe. To further probe the effect of substituents on silylpentaborane isomer stabilities, a broader range of derivatives must be studied; these are planned for the future.

Acknowledgements

Support of this work by National Science Foundation grants (GP-23575 and CHE-7604290) is gratefully acknowledged.

References

[1] D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968).
[2] D. F. Gaines and T. V. Iorns, *Inorg. Chem..*, **10**, 1094 (1971).
[3] D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 4249 (1967).
[4] A. B. Burg, *Inorg. Chem.*, **13**, 1010 (1974).
[5] S. G. Shore, *Boron Hydride Chemistry*, Academic Press, San Franciso, 1975.
[6] R. Riedel, A. Kienzle, L. Ruwish, W. Dressler, J. Bill and F. Aldinger, *Nature*, **382**, 796 (1996).
[7] K. Komeya, M. Matsui, in *Materials Science and Technology*, Vol. 11, R. W. Cahn, P. Haasen, E. J. Kramer, eds, VCH, Weinheim, 1994, p. 517.
[8] T. C. Geisler and A. D. Norman, *Inorg. Chem.*, **9**, 2167 (1970).
[9] D. F. Shriver, M. A. Drezdzon *The Manipulation of Air-Sensitive Compounds*; 2nd ed, McGraw Hill: New York, 1986.
[10] *Scotts Standard Method of Chemical Analysis*, 6th ed., Part B, 1963, p. 2405.
[11] H. F. Walton, *Principles and Methods of Chemical Analysis*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1964.
[12] D. M. Goge and E. F. Barker, *J. Chem. Phys.*, **7**, 455 (1939).

[13] D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 3375 (1967).
[14] R. A. Geanangel and S. G. Shore, *J. Am. Chem. Soc.*, **89**, 6771 (1967).
[15] R. C. Lord and E. Nielson, *J. Chem. Phys.*, **19**, 1 (1951).
[16] D. F. Gaines, J. A. Heppert, D. E. Coons and M. W. Jorgenson, *Inorg. Chem.*, **21**, 3662 (1982).
[17] C. H. Van Dyke and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **35**, 1503 (1963).
[18] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, NY, 1963.
[19] J. J. Miller, M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 4501 (1959).
[20] W. E. Keller, H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).
[21] C. H. Tindahl, J. W. Straley and H. N. Nielson, *Phys. Rev.*, **62**, 151 (1942).
[22] G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).
[23] H. J. Hrostewski and G. C. Pimental, *J. Am. Chem. Soc.*, **76**, 998 (1954).
[24] D. F. Gaines and J. Ulman, *Inorg. Chem.*, **13**, 2792 (1974).
[25] J. B. Leach, G. Oates, S. Tang, T. Onak, *J. Chem. Soc. Dalt.*, 1018 (1975).
[26] D. K. Srivastava, N. P. Rath and L. Barton, *Organometallics*, **11**, 2263 (1992).
[27] B. H. Goodreau and J. T. Spencer, *Inorg. Chem.*, **31**, 2612 (1992).
[28] J. A. Heppert and D. F. Gaines, *Inorg. Chem.*, **22**, 3155 (1983).
[29] J. A. Ulman and T. P. Fehlner, *J. Am. Chem. Soc.*, **98**, 1119 (1976).
[30] R. Schaeffer, *Progess in Boron Chemistry*, Vol. 1, Pergamon Press, New York, NY, 1964, p. 417.