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Synthesis of Bis(pentaboranyl)-Group IV Compounds

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Reactions of LiB_5H_8 with $RCH_3M^{IV}Cl_2$ (M^{IV} = Si, R = H, CH_3; M^{IV} = Ge, R = CH_3) at low temperature in diethyl ether solution produce the bis(pentaboranyl)-group IV compounds $(B_5H_8)_2M^{IV}RCH_3$. In $(B_5H_8)_2SiHCH_3$ both B_5H_8 units are bound at their basal terminal positions (2) to silicon, and the compound is isolated as a mixture of two isomers that appear to differ from one another only in the relative orientations of the B_5H_8 groups. In $(B_5H_8)_2Si(CH_3)_2$, however, one B_5H_8 group is bonded at a bridging site (μ) to silicon while the other B_5H_8 unit is bonded at a 2 position to the silicon. In $(B_5H_8)_2Ge(CH_3)_2$, a mixture of μ,2'-$(B_5H_8)_2Ge(CH_3)_2$ and 2,2'-$(B_5H_8)_2Ge(CH_3)_2$ is obtained. Three previously unreported pentaboranyl-group IV compounds, 2-$HCH_3ClSiB_5H_8$, $(CH_3)_2HSiB_5H_8$, and $(CH_3)_2HGeB_5H_8$, were also isolated from these reactions. Several reactions of bis(pentaboranyl) species are described and compared with similar reactions of $R_3M^{IV}B_5H_8$.

Introduction

The discovery that a bridge hydrogen, as a proton, can be removed from pentaborane(9) by treatment with a base[1] has led to the preparation of a number of B_5H_9 derivatives containing a group IV moiety (other than carbon) bridging two basal borons *via* a three-center, two-electron bond (eq 1).[2]

$$LiB_5H_8 + R_3M^{IV}X \rightarrow \mu\text{-}R_3M^{IV}B_5H_8 + LiX \tag{1}$$

M^{IV}	R
Si	H, CH_3, C_2H_5
Ge	H, CH_3, C_2H_5
Sn, Pb	CH_3

It was found that interaction with weak Lewis bases causes an irreversible intramolecular rearrangement of the Si and Ge derivatives, μ-$R_3M^{IV}B_5H_8$, to occur. In the rearrangement the group IV moiety moves from a bridge position to a terminal (2) position on a basal boron atom. The apically substituted (1) derivatives are prepared by treating the μ or 2 isomers with stronger Lewis bases such as 2,6-lutidine or hexamethylenetetramine or by gas-phase thermolysis at 150°.[3]

Within the last few years, Grimes, *et al.*, have prepared carborane derivatives similar to several of the B_5H_9 derivatives mentioned above (eq 2).[4] Savory and Walbridge have also

$$MC_2B_4H_7 + R_3M^{IV}Cl \rightarrow \mu\text{-}R_3M^{IV}C_2B_4H_7 + MCl \tag{2}$$

(M = Na or Li)

M^{IV}	R
Si,Ge	H, CH_3
Sn, Pb	CH_3

reported Si and Ge derivatives of the dimethyl compound 2,3-$(CH_3)_2C_2B_4H_7$.[5] A bis(carboranyl)silane μ,μ'-SiH_2-$(C_2B_4H_7)_2$, in which a silicon atom simultaneously occupies bridging positions on two $C_2B_4H_7$ moieties, has been reported recently by Tabereaux and Grimes.[6] Studies in our laboratory have resulted in the preparation of several bis(pentaboranyl) compounds $(B_5H_8)_2M^{IV}RCH_3$ (M^{IV} = Si, R = H, CH_3; M^{IV} = Ge, R = CH_3). Similar species in which two pentaboranyl groups are bonded to carbon are known.[7]

Experimental Section

Procedures and Instrumentation. All reactions were carried out on a vacuum line using standard techniques.[8] Infrared spectra were recorded on a Perkin-Elmer 700 infrared spectrometer in the gas phase (unless otherwise noted). Proton and boron-11 nmr spectra were obtained on Varian XL-100 (^1H at 100 MHz and ^{11}B at 32.1 MHz), Varian HR-220 (^1H at 220 MHz and ^{11}B at 70.6 MHz), and Bruker WH-270 (^1H at 270 MHz and ^{11}B at 86.7 MHz) instruments. Mass spectra were obtained using an AEI MS-9 mass spectrometer.

Materials. Diethyl ether was distilled from $LiAlH_4$ immediately before use. *n*-Butyllithium in pentane solution (from Matheson Coleman and Bell), Na-K alloy (from MSA Research Corp.), methyldichlorosilane (from PCR, Inc.), and dimethyldichlorogermane (from Alfa Inorganics) were used as received. Dimethyldichlorosilane, from laboratory supplies, was distilled under N_2 just before use.

LiB_5H_8 + HCH_3SiCl_2. (a) **2,2'-$(B_5H_8)_2SiHCH_3$** was prepared by warming an ether solution of 18 mmol of HCH_3SiCl_2 and approximately 36 mmol of LiB_5H_8 from −78 to −20° over 1.5 hr and then maintaining it at −20° for an additional 1 hr. A white precipitate became noticeable at −40° and grew heavier as the reaction proceeded. The product was purified by high-vacuum distillation into a U-shaped storage tube at 0° followed by a U-tube trap at −196°. A small amount of $B_{10}H_{14}$ distilled through the 0° U tube. The yield of 2,2'-$(B_5H_8)_2SiHCH_3$ was approximately 50% based on LiB_5H_8. It had no measurable vapor pressure at 25° and condensed as a glass at −196°. Its infrared spectrum was obtained as a thin film at −196°. Absorptions occurred at 2980 (w) and 2950 (vvw) (C–H stretch), 2605 (s) (B–H stretch), 2135 (w) (Si–H stretch), 1840 (w, br) (B–H–B), 1405 (s), 1260 (w), 1035 (w), 965 (w), 935 (m), 890 (m), 865 (w), and 830 (m, br) cm^{-1}. The mass spectrum exhibited a cutoff at *m/e* 170. An exact measurement on this peak gave an observed *m/e* value of 170.2270; calcd for $(^{11}B_5H_8)_2{}^{28}SiH^{12}CH_3$, 170.2265.

(b) **2-$HCH_3ClSiB_5H_8$** was also obtained from the above reaction in yields of 8–10%. It was purified by high-vacuum distillation through a −30° trap and by condensation in a −50° trap. This compound showed signs of decomposition within 0.5 hr at room temperature, turning yellow and showing changes in its infrared spectrum. The major decomposition product was 2-$H_2CH_3SiB_5H_8$. A gas-phase infrared spectrum of 2-$HCH_3ClSiB_5H_8$ showed absorptions at 3000 (w) and 2960 (vw) (C–H), 2625 (s) (B–H), 2210 (sh) and 2160 (s) (Si–H), 1815 (w, br) (B–H–B), 1415 (m), 1370 (sh), 1275 (mw), 1115 (mw), 1050 (w), 990 (sh), 950 (ms), 890 (s), 865 (sh), 775 (mw), 745 (mw), and 685 (mw) cm^{-1}. The mass spectrum exhibited a cutoff at *m/e* 144, corresponding to $HCH_3{}^{37}Cl^{28}Si^{11}B_5H_8$. An exact measurement on the 142 peak gave an observed *m/e* value of 142.0792; calcd for $^{12}CH_3{}^{37}Cl^{28}Si^{10}B^{11}B_4H_8$, 142.0791.

μ,2'-$(B_5H_8)_2Si(CH_3)_2$ was prepared by condensing 22 mmol of $(CH_3)_2SiCl_2$ onto a diethyl ether solution of approximately 44 mmol of LiB_5H_8 at −196°. The temperature of the reaction mixture was raised to −78°, was allowed to rise from −78 to −20° over 1.5 hr,

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(1) (a) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 89, 3375 (1967); (b) R. A. Geanangel and S. G. Shore, *ibid.*, 89, 6771 (1967).

(2) (a) D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 89, 4249 (1967); (b) *ibid.*, 90, 6617 (1968).

(3) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, 10, 1094 (1971).

(4) M. L. Thompson and R. N. Grimes, *Inorg. Chem.*, 11, 1925 (1972); A. Tabereaux and R. N. Grimes, *ibid.*, 12, 792 (1973).

(5) C. G. Savory and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 918 (1972).

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

(7) E. R. Altwicker, G. E. Ryschkewitsch, A. B. Garrett, and H. H. Sisler, *Inorg. Chem.*, 3, 454 (1964).

(8) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

and was then maintained at −20° for another 1.5 hr. The product was isolated in yields of about 10% by high-vacuum distillation at ambient temperature followed by condensation in a U-shaped storage tube at 0°. Its mass spectrum exhibited a cutoff at *m/e* 183 corresponding to $(^{11}B_5H_8)_2{}^{28}Si(^{12}CH_3)_2$. An exact measurement on the 182 peak gave an observed *m/e* value of 182.2492; calcd for $(^{10}B^{11}B_4H_8)_2{}^{28}Si(^{12}CH_3)_2$, 182.2494.

Small amounts of μ- and 2-$(CH_3)_2HSiB_5H_8$, identified by their mass spectra, were also obtained from the above reaction. The mixture of isomers was stirred with diethyl ether for several hours to give pure 2-$(CH_3)_2HSiB_5H_8$, with infrared spectrum absorptions at 2995 (w) and 2940 (vw) (C–H stretch), 2625 (s) (B–H stretch), 2140 (s) (Si–H stretch), 1840 (w) (B–H–B), 1405 (m), 1265 (m), 1045 (vw), 940 (m), 885 (s), 840 (m), 770 (w), and 730 (w) cm^{-1}. Comparison of this spectrum with those of 2-$(CH_3)_3SiB_5H_8$ and 2-$H_3SiB_5H_8$ [2b] confirms the identity of this product.

μ,2′- and 2,2′-$(B_5H_8)_2Ge(CH_3)_2$ were prepared by condensing 17.3 mmol of $(CH_3)_2GeCl_2$ onto a diethyl ether solution of 40 mmol of LiB_5H_8 at −196°. The solution was warmed to −65° and stirring begun. The temperature was allowed to rise to −35° over 1 hr, during which time a heavy white precipitate formed. The temperature was then maintained at −30° for an additional 1.5 hr. The $(B_5H_8)_2Ge(CH_3)_2$ distilled very slowly *in vacuo* and was isolated in 20% yield by condensation into a U-shaped storage tube at 0°. Because the mass spectrum of $(B_5H_8)_2Ge(CH_3)_2$ showed a very weak parent envelope, exact *m/e* matching was accomplished using a $P - 15$ peak. The observed *m/e* value was 213.1708; calcd for $(^{10}B^{11}B_4H_8)_2{}^{74}GeCH_3$, 213.1709. Peaks at *m/e* 101, 103, and 105, corresponding to $(CH_3)_2{}^{70}Ge$, $(CH_3)_2{}^{72}Ge$, and $(CH_3)_2{}^{74}Ge$, confirmed the presence of the $Ge(CH_3)_2$ group in the molecule.

Another product, distilling through a −22° trap and condensing in a −36° trap, was obtained in 14% yield. It was identified as a mixture of μ- and 2-$(CH_3)_2HGeB_5H_8$ by infrared and ^1H and ^{11}B nmr spectroscopy. Stirring the mixture in diethyl ether for 6 hr allowed pure 2-$(CH_3)_2HGeB_5H_8$ to be obtained. Some decomposition occurred during this time, as evidenced by a white deposit in the flask. The infrared spectrum of 2-$(CH_3)_2HGeB_5H_8$ contains absorptions at 3015 (w) and 2955 (vw) (C–H stretch), 2625 (s) (B–H stretch), 2050 (s) (Ge–H stretch), 1845 (w) (B–H–B), 1410 (m), 1260 (vw), 1045 (vw), 980 (vw), 940 (w), 900 (w), 845 (s), and 770 (vw) cm^{-1}.

2,2′-$(B_5H_8)_2SiHCH_3$ + $N(CH_3)_3$. 2,2′-$(B_5H_8)_2SiHCH_3$ (0.60 mmol) and $N(CH_3)_3$ (3.0 mmol), which had been purified by distillation through a −95° trap, were condensed into the reactor. The reactor was kept at −78° for 1 hr, during which time a white solid formed. Excess $N(CH_3)_3$, amounting to 1.15 mmol, was removed. The reaction stoichiometry thus indicated formation of a 3:1 complex. The complex was soluble in CH_2Cl_2 but insoluble in $(C_2H_5)_2O$.

2,2′-$(B_5H_8)_2SiHCH_3$ + Hexamethylenetetramine. Several crystals of sublimed hexamethylenetetramine were placed in an nmr tube, which was then attached to the vacuum line and evacuated. A volume of 2,2′-$(B_5H_8)_2SiHCH_3$ sufficient to observe a spectrum was condensed in, and the nmr tube sealed. It was stored at room temperature for 30 hr. The sample turned slightly yellow during this time but no change was observed in its ^{11}B nmr spectrum.

2,2′-$(B_5H_8)_2SiHCH_3$ + $NaBH_4$. In a nitrogen-filled glove bag, 5 mmol of $NaBH_4$ was placed in a 100-ml round-bottom flask. The flask was then cooled to −78°, and a THF solution of 1.45 mmol of 2,2′-$(B_5H_8)_2SiHCH_3$ was added. The flask was fitted with a stopcock adapter, attached to a vacuum line, and evacuated. The solution was stirred at 24° for 18 hr. Only traces of CH_3SiH_3 and noncondensable gases were produced. THF was then evaporated and 5 ml of freshly distilled diglyme was added. This solution was stirred at 24° for 5 hr, but again only very small amounts of CH_3SiH_3 and noncondensable gases were formed.

2,2′-$(B_5H_8)_2SiHCH_3$ + $LiAlH_4$. A THF solution of 2.64 mmol of 2,2′-$(B_5H_8)_2SiHCH_3$ was mixed with excess $LiAlH_4$ in a 100-ml flask as described in the $NaBH_4$ reaction. The reactants were stirred at room temperature for 21.5 hr. A trace of CH_3SiH_3 was formed. The flask was then heated to 50–60° for 12 hr, resulting in the formation of 0.2 mmol of CH_3SiH_3.

2,2′-$(B_5H_8)_2SiHCH_3$ + Br_2. A diethyl ether solution of 0.918 mmol of 2,2′-$(B_5H_8)_2SiHCH_3$ was mixed with a small excess of Br_2 at room temperature for 15 min, HBr and unreacted Br_2 were removed, and the nonvolatile residue was transferred to a vacuum sublimator. A slightly yellow solid was collected at 70°. Its ^{11}B nmr spectrum indicated that Br substitution occurred at the apical position on each B_5H_8 moiety.

Pyrolysis Experiments on 2,2′-$(B_5H_8)_2SiHCH_3$. (a) An *n*-butyl ether solution of 0.83 mmol of 2,2′-$(B_5H_8)_2SiHCH_3$ was heated in an nmr tube at 100° for 1.5 hr. The solution was deep yellow at this time, indicating that considerable decomposition occurred. The ^{11}B nmr spectrum, however, showed a single peak just above the high-field doublet at 50.2 ppm, indicating that some isomerization to 1,2′- or 1,1′-$(B_5H_8)_2SiHCH_3$ may also have occurred.

(b) A 2.86-mmol sample of 2,2′-$(B_5H_8)_2SiHCH_3$ was heated at 220–250° for 10 min in the liquid phase, during which time much decomposition occurred. Volatile products were removed and a considerable quantity of H_2 was produced. The reaction vessel was continuously evacuated for 2 hr while being heated at 230–260°. Very little H_2 was produced after the first hour. Traces of B_2H_6 and methyldiboranes were obtained, but the major volatile products were B_5H_9, CH_3SiH_3, 1-$H_2CH_3SiB_5H_8$, and 2-$H_2CH_3SiB_5H_8$.

(c) A 0.95-mmol amount of 2,2′-$(B_5H_8)_2SiHCH_3$ was distilled through a Pyrex tube packed loosely with Pyrex wool and heated at 180 ± 5° for 8 hr. Only traces of B_5H_9 and CH_3SiH_3 were produced and no decomposition products were seen on the Pyrex wool. An ^{11}B nmr spectrum showed essentially all the starting material recovered unchanged.

2-$HCH_3ClSiB_5H_8$ + Na–K Alloy. Excess sodium–potassium alloy was placed in a dry reaction flask in an N_2-filled glove bag. The flask was attached to the vacuum line and evacuated, and several milliliters of THF and 1.2 mmol of 2-$HCH_3ClSiB_5H_8$ were condensed into it at −196°. The flask was then warmed to −60° and from −60 to −20° over 1.5 hr with no change in the appearance of the solution. The solution was then stirred at between −10 and 0° for an additional 1.5 hr, during which time the solution took on a purple-gray color. Most of the $HCH_3ClSiB_5H_8$ was subsequently recovered and no noncondensable gases were produced. The only other volatile product was a trace of CH_3SiH_3.

LiB_5H_8 + 2-$H_2ClSiB_5H_8$. The synthesis of $(B_5H_8)_2SiH_2$ was attempted by addition of $B_5H_8^-$ to 2-$H_2ClSiB_5H_8$, which was prepared from 2-$H_3SiB_5H_8$ and BCl_3 by the method of Geisler and Norman.[9] The reactants, 5.5 mmol of 2-$H_2ClSiB_5H_8$ and a diethyl ether solution of 9 mmol of LiB_5H_8, were then warmed from −78 to −40° over 1 hr and kept at −40 ± 3° for an additional 1.5 hr. A white precipitate was present in the solution, but no $(B_5H_8)_2SiH_2$ was obtained, and the only volatile boron-containing product was B_5H_9.

Results and Discussion

The method of synthesis of the bis(pentaboranyl)silanes and -germanes followed the reaction scheme in eq 3. All re-

$$2LiB_5H_8 + RCH_3M^{IV}Cl_2 \rightarrow (B_5H_8)_2M^{IV}RCH_3 + 2LiCl \tag{3}$$

M^{IV}	R
Si	H, CH_3
Ge	CH_3

actions were carried out at low temperature (−20 to −78°) in diethyl ether solutions. The silicon compounds were prepared using either a 1:1 or 2:1 LiB_5H_8:RCH_3SiCl_2 ratio, with no significant difference in yields. Three previously unreported pentaboranyl-group IV compounds, 2-$HCH_3ClSiB_5H_8$ (eq 3, R = H), $(CH_3)_2HSiB_5H_8$ (eq 3, R = CH_3), and $(CH_3)_2HGeB_5H_8$, were also isolated in fair yields from these reactions.

2,2′-$(B_5H_8)_2SiHCH_3$, 2,2′-methylsilenebis(pentaboranyl) (I), was obtained in yields of about 50% based on LiB_5H_8. It is a colorless liquid of low volatility that can be distilled slowly under high vacuum. The 32.1-MHz ^{11}B nmr spectrum, Figure 1, contains a high-field doublet at +50.2 ppm, which upon ^1H decoupling, collapses to a singlet. The apical boron atoms on the two B_5H_8 groups, which give rise to this high-field resonance, are thus shown to be magnetically equivalent, indicating that the methylsilene group is bonded at the same position on each B_5H_8 cage. Decoupling the lower field multiplet of the spectrum shows it to consist of a low-field doublet and a more intense doublet, which is partially overlapped on the high-field side by a singlet. The singlet indicates terminal, rather than bridging, substitution of the silene group on the B_5H_8 cages, and the occurrence of a doublet at +50.2 ppm eliminates apical substitution. We

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(9) T. C. Geisler and A. D. Norman, *Inorg. Chem.*, 9, 2167 (1970).

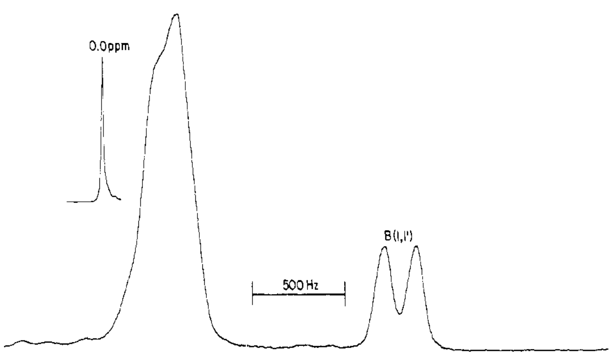

Figure 1. The 32.1-MHz ^{11}B nmr spectrum of 2,2'-$(B_5H_8)_2SiHCH_3$ [$BF_3 \cdot O(C_2H_5)_2$ reference at 0.0 ppm].

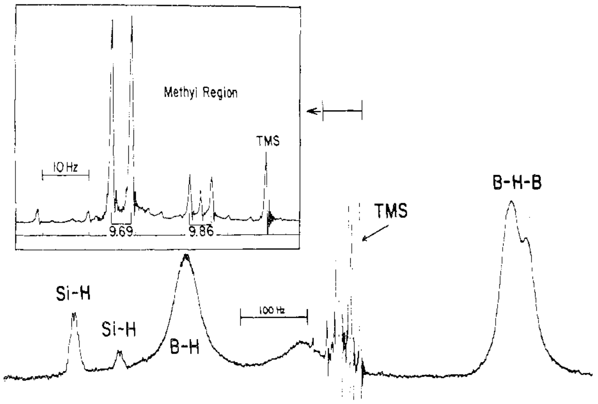

Figure 2. The 100-MHz ^1H nmr spectrum of 2,2'-$(B_5H_8)_2SiHCH_3$ (^{11}B decoupled). The insert shows an expansion of the methyl region just below TMS.

can thus conclude that the compound obtained is the 2,2' isomer. The low-field doublet can be assigned to B(4) and B(4'). This downfield shift of the boron atom trans to the substituted boron is similar to that observed for the pentaboranylsilanes, 2-$R_3SiB_5H_8$.

The 100-MHz ^1H nmr spectrum of I, Figure 2, allows more exact conclusions to be made concerning its geometry. The silicon hydrogen resonance is split into a quartet by the methyl hydrogens. There are not one but two quartets in the spectrum, one at τ 5.69 and the other at τ 6.38. Coupling of the methyl hydrogens with the hydrogen atom on silicon results in a doublet. The spectrum shows two doublets at τ 9.69 and 9.86, having relative areas approximately equal to the relative areas of the quartets. The product thus appears to be a mixture of unequal amounts of two isomers of $(B_5H_8)_2SiHCH_3$, possibly differing in the relative positions in space of the two pentaborane moieties. It was determined from building models of several possible isomers that the most likely structures, from steric considerations, are those shown in Figure 3. That two static structures can be isolated indicates that a significant barrier to the rotation of the B_5H_8 groups around the silicon atom exists in the molecule. Attempts to rotate the groups in a model of the molecule produce a number of configurations having the bulky B_5H_8 groups and CH_3 group in close proximity. The suggested static structures are those in which the groups appear to interact the least.

See also Tables I and II for nmr spectral results.

μ,2'-$(B_5H_8)_2Si(CH_3)_2$, μ,2'-dimethylsilenebis(pentaboranyl) (II), a colorless liquid of very low volatility, was produced in yields of approximately 10%. The low yield is probably due to the difficulty in fitting two CH_3 and two B_5H_8 groups around the silicon atom. The ^{11}B nmr spectrum at 32.1 MHz shows two doublets in the region assigned to the apical borons on the B_5 cages, one centered at 47.5 and the other at 50.1 ppm. The two resonances indicate that the $(CH_3)_2$-Si group is bonded at different positions on the B_5H_8 cages, making the apical boron atoms nonequivalent. The multiplet at about +10 ppm is difficult to interpret. A higher frequency spectrum at 70.6 MHz, Figure 4, however, resolves this multiplet sufficiently to allow interpretation of the grouping with more confidence. Although there is considerable overlap among the peaks, there appear to be a doublet at +8.33, a singlet at +9.55, and two more doublets at +10.7 and +12.8 ppm. The relative areas of these peaks are approximately 3:1:2:2. These interpretations support the structure shown in Figure 5 with the $(CH_3)_2Si$ group bonded at the 2 position on one pentaborane cage and at a bridging position on the other. The 100-MHz ^1H nmr spectrum of II, unlike that of I, shows only one methyl resonance. It is likely, there-

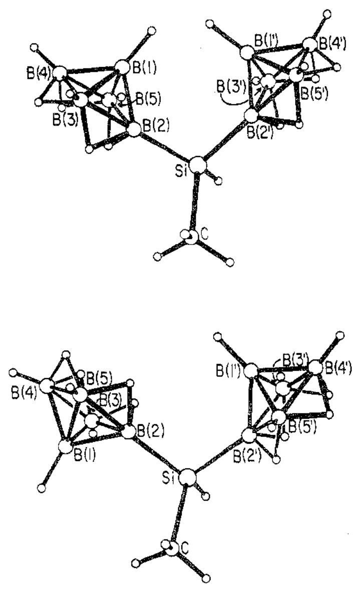

Figure 3. Suggested structures for the two least sterically hindered conformers of 2,2'-$(B_5H_8)_2SiHCH_3$.

Table I. 32.1-MHz ^{11}B Nmr Spectral Results

Compd	Assignment	δ,[a] ppm	J,[b] Hz
2,2'-$(B_5H_8)_2SiHCH_3$	B(1)	+50.2	175
	B(2–5,2'–5')	+11.1	
μ,2'-$(B_5H_8)_2Si(CH_3)_2$[c]	B(1')	+50.1	183
	B(1)	+47.5	187
	B(4,5)	+12.8	147
	B(2,3)	+10.7	156
	B(2')	+9.55	
	B(3'–5')	+8.33	173
μ,2'- and 2,2'-$(B_5H_8)_2Ge(CH_3)_2$[d]	B(1')	+52.0	182
	B(1)	+49.3	191
	B(4,5)	+14.1	138
	B(2,3)	+12.6	165
	B(2')	+11.4	
	B(3'–5')	+10.1	207
2-$HCH_3ClSiB_5H_8$	B(1)	+51.2	176
	B(2)	+14.5	
	B(3,5)	+12.3	144
	B(4)	+7.5	160
2-$(CH_3)_2HGeB_5H_8$	B(1)	+53.2	175
	B(2,3,5)	+13.8	
	B(4)	+11.1	

[a] Relative to $BF_3 \cdot O(C_2H_5)_2$ at +0.0 ppm. [b] Overlap of peaks due to B(2–5) occurs for all the compounds and the J values are thus approximate. [c] Chemical shifts from the 70.6-MHz spectrum. [d] Chemical shifts from the 86.7 MHz spectrum.

Table II. 100-MHz ^1H Nmr Spectral Results

	Chem shifts^a (J, Hz)				
Compd	Basal B-H	Apex B-H	Bridge B-H-B	M^{IV}-H	M^{IV}-CH_3
2,2'-$(B_5H_8)_2SiHCH_3$	+7.40 (155)	+9.13	+12.30 +12.54	+5.69 +6.38	+9.69 (4.2) +9.86 (4.8)
μ,2'-$(B_5H_8)_2Si(CH_3)_2$	+7.59 (153)		+12.15 +12.45		+9.84
μ,2'- and 2,2'-$(B_5H_8)_2Ge(CH_3)_2$	+7.32 (157)	+9.08	+12.35		+9.39 +9.55
2-$(CH_3)_2HGeB_5H_8$	+7.37 (163)	+9.02	+12.20 +12.45	+6.25 (4.3)	+9.65 (3.7)

^{a} τ values relative to tetramethylsilane at +10.0.

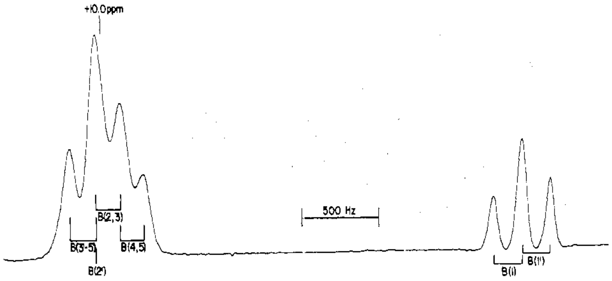

Figure 4. The 70.6-MHz line-narrowed ^{11}B spectrum of μ,2'-$(B_5H_8)_2Si(CH_3)_2$.

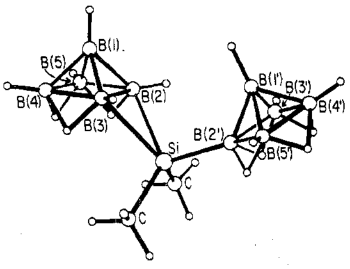

Figure 5. A proposed molecular structure of μ,2'-$(B_5H_8)_2Si(CH_3)_2$.

fore, that not more than one isomer is obtained for II.

$(B_5H_8)_2Ge(CH_3)_2$, dimethylgermenebis(pentaboranyl) (III), was obtained in approximately 20% yield. Its 86.7-MHz ^{11}B nmr spectrum indicates that III is a mixture of μ,2'- and 2,2'-$(B_5H_8)_2Ge(CH_3)_2$ isomers. The multiplet in the apical boron region consists of two overlapping doublets which, unlike those in the spectrum of II, are of unequal intensity. The lower field, less intense doublet is assigned to the B(1) atom of the B_5H_8 group having the $(CH_3)_2Ge$ substituted in the μ position. The more intense doublet is assigned to the B(1) atom of the B_5H_8 groups having the $(CH_3)_2Ge$ substituent in the 2 position. These assignments are based on the observation that in the $R_3M^{IV}B_5H_8$ compounds the apical boron resonance occurs at a higher field when the R_3M^{IV} group occupies a 2 position than when it occupies a μ position on the pentaborane cage.[2b] If only μ,2'-$(B_5H_8)_2Ge(CH_3)_2$ were produced, the two doublets would be equally intense. Since the higher field doublet is more intense than the low-field doublet, we can conclude that 2,2'-$(B_5H_8)_2Ge(CH_3)_2$ was also produced. The 100-MHz ^1H nmr spectrum of III, Figure 6, supports this conclusion. Two distinct singlets are observed for the equivalent methyl groups on the germanium atom. Again by comparison with spectra of $R_3M^{IV}B_5H_8$ compounds, the singlet at τ 9.39 ppm is assigned to the methyl groups of μ,2'-$(B_5H_8)_2Ge(CH_3)_2$ and the resonance at τ 9.55 ppm to the methyls of the 2,2' isomer.

Attempted Isomerization of 2,2'-$(B_5H_8)_2SiHCH_3$. The pentaborane derivatives μ-$R_3M^{IV}B_5H_8$ (M^{IV} = Si, Ge; R = H,

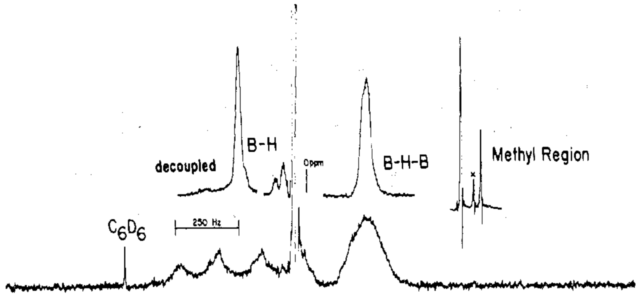

Figure 6. The 100-MHz ^1H nmr spectrum of μ,2'- and 2,2'-$(B_5H_8)_2Ge(CH_3)_2$. The upper plot shows the ^{11}B-decoupled spectrum and expansion of the methyl region just below TMS (τ 10.0).

CH_3, C_2H_5) were found to rearrange to their 2 isomers in the presence of weak Lewis bases, while stronger Lewis bases such as hexamethylenetetramine (HMTA), or gas-phase thermolysis, converted μ- or 2-$R_3SiB_5H_8$ to their 1 isomers.[3] By contrast, 2,2'-$(B_5H_8)_2SiHCH_3$ remained unaffected by HMTA after 30 hr at room temperature. When its vapor was passed through a Pyrex tube heated to 180°, traces of B_5H_9 and CH_3SiH_3 were produced, but essentially all the starting material was recovered. In another experiment a di-n-butyl ether solution of 2,2'-$(B_5H_8)_2SiHCH_3$ was heated in an nmr tube at 100° for 1.5 hr. Although considerable decomposition of the sample occurred, the ^{11}B nmr spectrum showed a single peak just upfield of the high-field doublet of the starting material,[10] suggesting the presence of either 1,2'-$(B_5H_8)_2SiHCH_3$ or 1,1'-$(B_5H_8)_2SiHCH_3$.

Chemical Studies. The 2,2'-$(B_5H_8)_2SiHCH_3$ is less affected by $LiAlH_4$ or $NaBH_4$ than is μ- or 2-$R_3SiB_5H_8$. For example, when μ-$(CH_3)_3SiB_5H_8$ was stirred with $LiAlH_4$ in THF for 3 hr at room temperature, a 91% yield of $(CH_3)_3SiH$ was obtained,[2b] whereas a similar experiment with the bis(pentaboranyl)silane produced only a trace of CH_3SiH_3, and heating to 50-60° did not produce a significant quantity of CH_3SiH_3. Similar results were obtained using $NaBH_4$ as the hydride source. Reaction of 2,2'-$(B_5H_8)_2SiHCH_3$ with bromine, on the other hand, appears to be analogous to the bromination of μ-$(CH_3)_3SiB_5H_8$,[2b] producing a sublimable solid whose ^{11}B nmr spectrum indicates the formula 1,1'-Br_2-2,2'-$(B_5H_7)_2SiHCH_3$. The appearance of the downfield multiplet is essentially unchanged from that of the parent compound, while the doublet at +50.2 ppm collapses to a singlet and is shifted downfield by about 15 ppm. This chemical shift of approximately +35 ppm is similar to that of 1-BrB_5H_8,[11] 1-Br-2-$CH_3B_5H_7$,[12] and 1-Br-μ-$(CH_3)_3$-

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[10] The singlet assigned to the apical boron atom in 1-$H_3SiB_5H_8$ and 1-$(CH_3)_3SiB_5H_8$ occurs at slightly higher field than the doublet in their μ or 2 isomers.[3]

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SiB_5H_7.[2b] The formation of a 3:1 complex with $(CH_3)_3N$ at −78° compares with 2:1 adducts of $(CH_3)_3N$ with B_5H_9,[13] $CH_3B_5H_8$,[12,14] 2-$H_3SiB_5H_8$,[15] and 2-$H_5Si_2B_5H_8$[15] and 1:1 adducts of $(CH_3)_3N$ with 1- or 2-$CH_3B_5H_8$.[16] A 3:1 adduct was obtained when $(CH_3)_3N$ was mixed with 2-$(ClSiH_2)B_5H_8$.[15]

Pentaboranyl-Group IV Compounds. Reaction between LiB_5H_8 and HCH_3SiCl_2 produced, in addition to 2,2′-$(B_5H_8)_2SiHCH_3$, the pentaborane(9) derivative 2-$HCH_3ClSiB_5H_8$. The 32.1-MHz ^{11}B nmr spectrum verifies that the silyl group occupies a terminal position on the base of the B_5H_9 pyramid. 2-$HCH_3ClSiB_5H_8$ is unstable at room temperature with respect to decomposition to 2-$H_2CH_3SiB_5H_8$. The reactions of LiB_5H_8 with $(CH_3)_2SiCl_2$ and with $(CH_3)_2GeCl_2$ gave the pentaboranyl-group IV compounds μ- and 2-$(CH_3)_2HSiB_5H_8$ and μ- and 2-$(CH_3)_2HGeB_5H_8$, respectively. No compounds of the type $(CH_3)_2ClM^{IV}B_5H_8$ were isolated. Pure 2-$(CH_3)_2HM^{IV}B_5H_8$ was obtained by stirring the mixture of bridge and terminal isomers in diethyl ether. Identity of these compounds was confirmed by ^1H and ^{11}B nmr, infrared, and mass spectra.

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Registry No. 2,2′-$(B_5H_8)_2SiHCH_3$, 52570-92-0; 2-$HCH_3ClSiB_5H_8$, 52570-93-1; μ,2′-$(B_5H_8)_2Si(CH_3)_2$, 52718-63-5; μ,2′-$(B_5H_8)_2Ge(CH_3)_2$, 52570-94-2; 2,2′-$(B_5H_8)_2Ge(CH_3)_2$, 52570-95-3; 2,2′-$(B_5H_8)_2SiHCH_3 \cdot 3N(CH_3)_3$, 52570-96-4; 1,1′-$Br_2$-2,2′-$(B_5H_7)_2SiHCH_3$, 52570-97-5; 2-$(CH_3)_2HGeB_5H_8$, 52570-98-6; HCH_3SiCl_2, 75-54-7; $(CH_3)_2SiCl_2$, 75-78-5; $(CH_3)_2GeCl_2$, 1529-48-2; LiB_5H_8, 34370-18-8; ^{11}B, 14798-13-1; 2-$(CH_3)_2HSiB_5H_8$, 52570-99-7.

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Basicity of Substituted Difluorophosphines

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The previously unreported compounds PF_2-*i*-Pr, $PF_2Et \cdot BH_3$, and PF_2-*t*-Bu·BH_3 have been prepared and characterized by ^1H, ^{19}F, and ^{11}B nmr and ir spectroscopy and *PVT* molecular weights, as well as by stoichiometric data. A series of base displacement reactions established the base strengths toward borane as PF_2-*t*-Bu $\lesssim$ $PF_2Et > PF_2C{\equiv}CMe \lesssim PF_2Me > PF_2NMe_2 > PF_2O$-*i*-Pr $> PF_2OEt > PF_2OMe > PF_2OTfet \lesssim PF_2SMe > PF_3 > PF_2Cl > PF_2Br$. The basicity order is not mirrored by the series of values for the J_{PB} coupling constants or ν_{BH} stretching frequencies. The J_{PB} coupling constant peaks at $PF_2N(CH_3)_2$ and then decreases as basicity increases and decreases. Although no overall correlations were evident, cases where the subject correlation is apparent are discussed. Association involving PF_2R (R = carbon group, H) compounds is proposed as a reason for the failure of general correlations.

Introduction

Comparison of the Lewis base strength of phosphines toward boron Lewis acids is somewhat difficult because of the many different methods that have been used to establish orders. Some of the various methods include gas-phase dissociation data, displacement methods, competition experiments, studies of the volatility of addition compounds, and calorimetric heats of reaction.[1-8] Recently a great interest has been aroused in the basicity of certain phosphines toward borane and in correlations of spectroscopic properties of borane adducts and basicity orders established by displacement equilibria methods.

The high base strength of PF_2OCH_3 and $PF_2N(CH_3)_2$ when compared to PF_3 was initially explained in terms of basicity enhancement of the phosphorus by the formation of a dative π bond between the nitrogen or oxygen electron pairs and the vacant orbitals of the phosphorus.[9] Since this effect would be absent in PF_2CH_3, the recent observation that PF_2CH_3 is a stronger base than $PF_2N(CH_3)_2$ may require that basicity parameters be revised.[2,10] Generally the relative displacement order toward BH_3 of PF_2X ligands where X is a member of the second row (C, N, O, F) follows an electronegativity order; however, examination of other PF_2X compounds shows that electronegativity-basicity correlations immediately fail PF_2NMe_2 and PF_2OMe from stronger adducts[2] with borane than PF_2SMe and the basicity order is $PF_3 > PF_2Cl > PF_2Br$ toward BH_3.[11]

Several workers have published rather elegant correlations of spectroscopic properties of borane adducts with displacement equilibria basicity orders. Attempts have been made

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[10] The position of PF_2Me as the strongest base in the series PF_2X (X = Me, OMe, NMe_2, SMe) has been attributed to the possible combination of both σ-electron donation and hyperconjugation effects.[2] From our work it is evident that a hyperconjugation effect is probably not involved since PF_2-*t*-Bu is more basic than PF_2Me toward BH_3. The high basicity must be attributed to a strong σ-donation of the methyl group or to some other effect.

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