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BORON INSERTION REACTIONS

IV. THE SYNTHESIS OF 1- AND 2-$[(CH_3)_3M^{IV}]$-μ-$[(CH_3)_2B]B_5H_7$ (M^{IV} = Si, Ge)

DONALD F. GAINES and JEFFREY ULMAN

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

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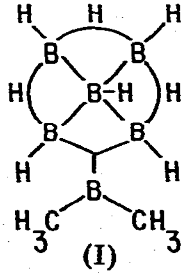
Summary

Anions derived from 1- and 2-$[(CH_3)_3M^{IV}]B_5H_8$ by proton abstraction react with $(CH_3)_2BCl$ to produce 1- and 2-$[(CH_3)_3M^{IV}]$-μ-$[(CH_3)_2B]B_5H_7$ (M^{IV} = Si, Ge). Spectroscopic evidence indicates that the $(CH_3)_2B$ moiety occupies a bridging position between two boron atoms in the base of the pentaborane(9) pyramid. When the $(CH_3)_3M^{IV}$ substituent is in a 2-position it appears to be attached to a boron atom adjacent to the bridging $(CH_3)_2B$ group. These new B_5H_9 derivatives do not undergo the expected rearrangement to a corresponding hexaborane(10) derivative, whereas μ-$[(CH_3)_2B]B_5H_8$ itself rearranges readily.

Part II of this series [1] described the preparation of μ-$[(CH_3)_2B]B_5H_8$ (I) according to eqn. 1. This unusual borane is best described as a derivative of

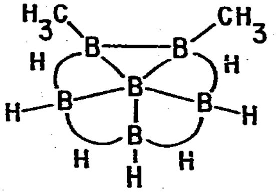
$$LiB_5H_8 + (CH_3)_2BCl \rightarrow \mu\text{-}[(CH_3)_2B]B_5H_8 + LiCl \quad (1)$$

B_5H_9 in which a bridge hydrogen has been replaced by a bridging dimethylboryl group, $(CH_3)_2B$:



(I)

The boron of the $(CH_3)_2B$ group in I is bound to the pentaborane(9) cage via a single three-center two-electron bond and is considered to be three-coordinate and thus formally sp^2 hybridized. Rearrangement of I occurs in the presence of weak Lewis bases such as diethyl ether. Insertion of the $(CH_3)_2B$ boron atom into the polyhedral framework and concurrent migration of a CH_3 group to a neighbouring boron atom produces a hexaborane(10) derivative, 4,5-$(CH_3)_2$-B_6H_8. The boron framework in this compound is a pentagonal pyramid, and the CH_3 groups are on adjacent basal boron atoms. In addition there are four rapidly tautomerizing bridge hydrogens around the base of the pyramid [2]:



In this report we describe the synthesis of trimethylsilyl and trimethylgermyl derivatives of I. The unexpected structures indicated for these derivatives and their resistance to rearrangement to hexaborane(10) derivatives raise new questions regarding the primary factors that establish the most stable configurations for nido borane derivatives.

Results and discussion

Pentaborane(9) derivatives containing Group IV and bridging dimethylboryl substituents have been synthesized by the general reactions depicted in eqns. 2 and 3.

$$2\text{-}[(CH_3)_3M^{IV}]B_5H_8 + n\text{-}C_4H_9Li \rightarrow Li^+2\text{-}[(CH_3)_3M^{IV}]B_5H_7^- + C_4H_{10} \qquad (2)$$

$$Li^+2\text{-}[(CH_3)_3M^{IV}]B_5H_7^- + (CH_3)_2BCl \rightarrow$$

$$2\text{-}[(CH_3)_3M^{IV}]\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7 + LiCl \qquad (3)$$

(II: M^{IV} = Si
III: M^{IV} = Ge)

The reactions were carried out in diethyl ether in the temperature range —30 to —78°C. The apically-substituted isomer 1-$[(CH_3)_3Si]$-μ-$[(CH_3)_2B]B_5H_7$ (IV) was also prepared according to the above equations, using 1-$[(CH_3)_3Si]B_5H_8$ [3] in place of the 2-$[(CH_3)_3Si]B_5H_8$ [4]. Yields of II have been as high as 76%, while the yields for III and IV have typically been in the range of 45-50%. These new derivatives are stable liquids at room temperature in the absence of air and moisture. Their vapor pressures are less than 1 torr at room temperature and decrease in the order IV > II > III. The elemental compositions II-IV have been established using high resolution mass spectroscopy, and their structures deduced primarily on the basis of their ^1H and ^{11}B NMR spectra. In each case the mass and infrared spectral data are consistent with the structural conclusions.

The ^{11}B NMR spectrum of III, shown in Fig. 1, illustrates in part the basis

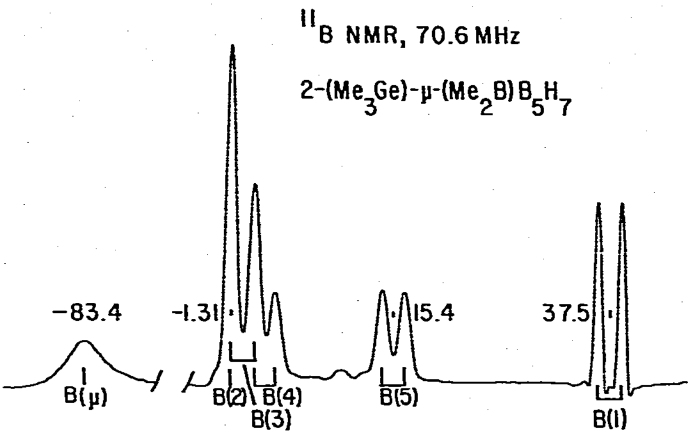


Fig. 1. The 70.6 MHz ^{11}B NMR spectrum of 2-[$(CH_3)_3$Ge]-μ-[$(CH_3)_2$B]B_5H_7 (III) with line narrowing. Selected chemical shifts are shown relative to $BF_3 \cdot O(C_2H_5)_2$.

of the structural assignments for II-IV. The broad singlet at very low field in Fig. 1 (−83.4 ppm referenced to $BF_3 \cdot O(C_2H_5)_2 = 0$) is indicative of the sp^2 hybridized boron of the bridging $(CH_3)_2B$ group. The singlet at −1.3 ppm corresponds to B(2), on which the $(CH_3)_3Ge$ substituent resides. The remaining four doublet resonances arise from the remaining four unique boron environments. Each resonance is a doublet as a result of J coupling of each boron to its attached terminal hydrogen. Though the highest field resonance is most certainly due to B(1), the absolute assignments for the three remaining resonances are tentative. The ^{11}B NMR spectrum of II is very similar to that of III and indicates the same molecular geometry. In the spectrum of IV, however, the highest field resonance, arising from B(1), is a singlet, thus confirming that apical substitution of the $(CH_3)_3Si$ group is retained throughout the reaction sequence in the synthesis of IV. These ^{11}B NMR spectra, tabulated in Table 1, do not allow one to distinguish between structures for II and III in which the $(CH_3)_2B$ bridging group is adjacent to the terminal Group IV substituent, and structures in which the $(CH_3)_2B$ bridging group is not adjacent to the boron bearing the Group IV substituent. On the basis of the ^{1}H NMR spectra of II and III, and comparisons of these spectra with those of I and IV, more definite conclusions can be reached regarding the positional relationships between the μ-$(CH_3)_2B$ and $(CH_3)_3M^{IV}$ groups in II and III. The ^{1}H NMR spectra of II and III exhibit two separate resonances for the CH_3 groups of the $(CH_3)_2B$ moiety at ambient temperature (see Fig. 2 and Table 2). In contrast the ^{1}H NMR spectra of I and IV contain a single resonance for the $(CH_3)_2B$ moiety at ambient temperature [1]. At lower temperatures, however, the CH_3 groups in I become non-equivalent. These data suggest the presence of a significantly higher barrier to rotation of the $(CH_3)_2B$ group in II and III, compared to that in I and IV. If it is assumed that this rotation barrier is largely steric, then the $(CH_3)_2B$ and $(CH_3)_3M^{IV}$ groups are most likely adjacent in II and III, as indicated by the proposed structure for II shown in Fig. 3. The formation of these sterically crowded derivatives is undoubtedly a result of specific bridge proton abstraction adjacent to the more electron rich Group IV substituent in the 2-[$(CH_3)_3M^{IV}$]B_5H_8 reactants. There

TABLE 1

^{11}B NMR SPECTRAL RESULTS

Compound	Assignment	δ	J(Hz) (±5)
B_5H_9 [e]	B(1)	+51.8	176
	B(2-5)	+12.5	160
μ-[$(CH_3)_2B$]B_5H_8 [a, d] (I)	B(1)	+33.3	175
	B(4, 5)	+4.4	162
	B(2,3)	+10.4	162
	$(CH_3)_2B$	−96.5	
2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 [a] (II)	B(1)	+36.6	175
	B(5)	+15.7	157
	B(3, 4)	+1.0	150
	B(2)	−1.3	
	$(CH_3)_2B$	−84.8	
2-[$(CH_3)_3Ge$]-μ-[$(CH_3)_2B$]B_5H_7 [a, b] (III)	B(1)	+37.5	174
	B(5)	+15.4	157
	B(4) [c]	+2.2	146
	B(3) [c]	−0.1	173
	B(2)	−1.3	
	$(CH_3)_2B$	−83.4	
1-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 [a] (IV)	B(1)	+41.2	
	B(4, 5)	+9.6	182
	B(2, 3)	+2.5	160
	$(CH_3)_2B$	−94.5	
6-$CH_3B_5CH_6$	B(2, 3) [c]	+18.7	180
	B(4, 5) [c]	+9.4	180
	B(6)	−17.2	

[a] Spectrum obtained at 32.1 MHz. [b] Spectrum obtained at 70.6 MHz. [c] These assignments are not definite and may be interchanged. [d] Ref. 1. [e] Ref. 5.

is a remote possibility that the hindered rotation of the $(CH_3)_2B$ group in II and III is a result of unidentified electronic effects, in which case the above arguments would be somewhat tenuous.

TABLE 2

^{1}H NMR SPECTRAL RESULTS [a]

Compound	Terminal B—H [b]	Bridge B—H	M^{IV}—CH_3	B—CH_3
2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 (II)	7.19	11.8	9.87	8.87
2-[$(CH_3)_3Ge$]-μ-[$(CH_3)_2B$]B_5H_7 (III)	6.95 7.43	11.8 12.2	9.75	8.90 9.20
1-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 (IV)	7.34	11.4 12.0	9.85	8.77

[a] Chemical shifts relative to tetramethylsilane at τ 10.0. Spectra were obtained at 100 MHz. [b] Basal and apical resonances could not be distinguished.

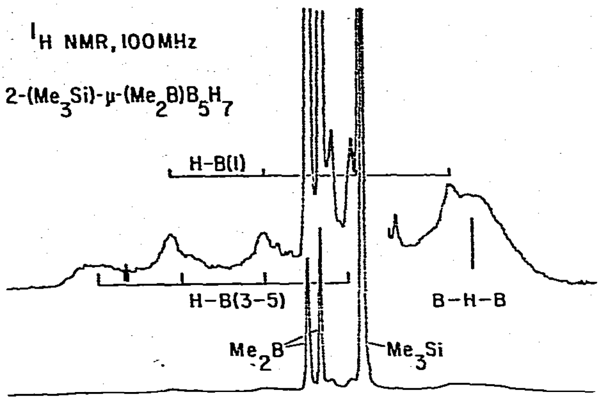


Fig. 2. The 100 MHz NMR spectrum of 2-[(CH$_3$)$_3$Si]-μ-[(CH$_3$)$_2$B]B$_5$H$_7$ (II) at power settings to emphasize the B-H hydrogens (upper) and the methyl hydrogens (lower). See Table 2 for chemical shift data.

On inspection of Table 1 it is apparent that several trends in ^{11}B chemical shift changes can be related to the position of substitution on the B$_5$H$_9$ framework. For example, the B(1) resonance for all derivatives having a bridging μ-(CH$_3$)$_2$B group occurs between 10 and 18 ppm downfield from the B(1) resonance in B$_5$H$_9$. This is in contrast to the more general observation [5] that substitution of R$_3$M^{IV} groups for terminal or bridge hydrogen atoms in the base of the B$_5$H$_9$ pyramid do not cause significant changes (i.e., less than 2 ppm) in the chemical shift of the B(1) resonance. A second example is the change in the chemical shift of the μ-(CH$_3$)$_2$B boron resonance. In II and III the shifts are -84.8 and -83.4 ppm, respectively, whereas in I and IV, the shifts are -96.5 and -94.5 ppm, respectively. The presence of a terminal (CH$_3$)$_3$M^{IV} group on B(2) thus gives rise to an upfield shift of the μ-{CH$_3$)$_2$B resonance of about 10 ppm compared to either the unsubstituted I or the B(1) substituted IV. The current state of development of the theory of ^{11}B chemical shifts is inadequate to explain these apparent trends.

Attempts were made to prepare 2-(H$_3$Si)-μ-[(CH$_3$)$_2$B]B$_5$H$_7$, but were frustrated by the reaction of n-C$_4$H$_9$Li with 2-(H$_3$Si)B$_5$H$_8$ to produce both the desired 2-(H$_3$Si)B$_5$H$_7^-$ and what appears to be 2-(C$_4$H$_9$SiH$_2$)B$_5$H$_8$. The latter could not

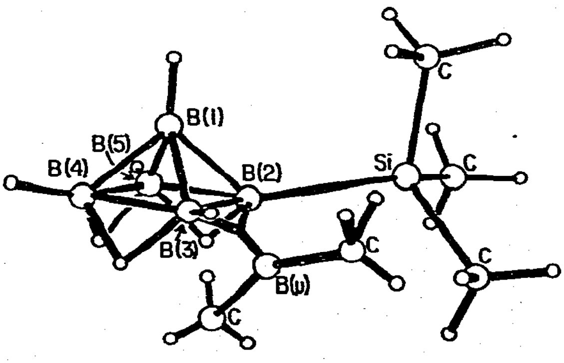


Fig. 3. The proposed structure of 2-[(CH$_3$)$_3$Si]-μ-[(CH$_3$)$_2$B]B$_5$H$_7$ (II) and its germanium analog (III).

be separated from the desired 2-(H_3Si)-μ-$[(CH_3)_2B]B_5H_7$. The synthesis of 2-$[(CH_3)_2HSi]$-μ-$[(CH_3)_2B]B_5H_7$ was successful, but the product is not stable enough at ambient temperature to be conveniently investigated. The primary isolated decomposition product is 2-$[(CH_3)_2SiH]B_5H_8$.

Chemical studies

By analogy with the rearrangement of I to 2,3-dimethylhexaborane(10) in the presence of the weak Lewis base diethyl ether, it appeared reasonable to expect substituted I derivatives to undergo a similar rearrangement. However, neither diethyl ether not the stronger Lewis bases dimethyl ether and hexamethylenetetramine caused a rearrangement of 2-$[(CH_3)_3Si]$-μ-$[(CH_3)_2B]B_5H_7$. A possible rationale for the failure to obtain a B_6 species is the hindrance to the insertion of the dimethylboryl moiety into the B_5 framework by the adjacent bulky trimethylsilyl group. 1-$[(CH_3)_3Si]$-μ-$[(CH_3)_2B]B_5H_7$, in which the trimethylsilyl group is remote from the dimethylboryl moiety, was therefore allowed to interact with diethyl ether. Surprisingly, no hexaborane derivatives were produced. Apparently, some effects other than, or in addition to, steric ones are operating to block the insertion process. The trimethylsilyl moiety apparently exerts an as yet undefined electronic effect that makes the compound less susceptible to attack by the Lewis base. It should be noted, however, that reaction of either 1- or 2-$[(CH_3)_3Si]B_5H_7^-$ anion with $H_2BCl \cdot OEt_2$ produces small amounts of the hexaborane(10) derivative 1-$[(CH_3)_3Si]B_6H_9$ as the only boron insertion product [6].

Reaction of 2-$[(CH_3)_3Si]$-μ-$[(CH_3)_2B]B_5H_7$ with trimethylamine at —78°C produced a 1/1 complex, which decomposed when warmed to —30°C. There was no reaction with triethylphosphine at —78°C, but when the reaction mixture was warmed to room temperature an intractable yellow oil formed.

Since $[(CH_3)_3Si]$-μ-$[(CH_3)_2B]B_5H_7$ did not isomerize to a B_6 pyramidal species by the action of base, a high-temperature method of effecting the conversion was investigated. The gas phase pyrolysis of 2-$[(CH_3)_3Si]$-μ-$[(CH_3)_2B]$-B_5H_7 at 260° yielded a complex mixture of products, but no B_6 species were isolated. The most interesting product was the previously unknown B_5CH_7 derivative, 6-$CH_3B_5CH_6$. The only other known methyl derivative of B_5CH_7 was obtained in low yield from the pyrolysis of 1-ethylpentaborane, and has the methyl group bonded to the carbon atom [7]. The ^{11}B NMR spectrum of 6-$CH_3B_5CH_6$ (Table 1) is very similar to that of the parent B_5CH_7 [8]. The low-field doublet in the spectrum of the parent B_5CH_7 has collapsed to a singlet due to methyl substitution at B(6), and has also been shifted downfield by more than 15 ppm. Low and high resolution mass spectroscopy confirmed the identity of 6-$CH_3B_5CH_6$.

Experimental

Reactants and solvents

Diethyl ether, isopropyl ether, tetrahydrofuran (each stored over $LiAlH_4$), and dichloromethane (stored over 3 Å molecular sieves) were distilled immediately prior to use. 2-$R_3M^{IV}B_5H_8$ [4] (M^{IV} = Si, R = H, CH_3; M^{IV} = Ge, R = CH_3), 1-$(CH_3)_3SiB_5H_8$ [3], and dimethylboron chloride (from boron trichloride and tetramethyltin [9]) were prepared by published methods. n-Butyllithium in pentane solution was obtained from Foote Mineral Co. The pentane was evaporated and a new solvent added for all reactions. Trimethylamine, dimethyl ether, boron trichloride, and hydrogen chloride were obtained from Matheson Gas Co. and purified by trap-to-trap distillations. Hexamethylenetetramine (freshly sublimed), triethylphosphone (dried over calcium hydride), and trimethylchlorosilane (distilled under nitrogen) were obtained from laboratory supplies. Other reagents were obtained from standard commercial sources and were used as received.

Instrumentation

Vacuum line techniques [10] were used throughout in handling volatile, air-sensitive materials. Infrared spectra (gas phase unless otherwise noted) were recorded on a Perkin—Elmer model 700 infrared spectrometer. NMR spectra were obtained on Varian HA-100, XL-100 (^1H at 100 MHz, ^{11}B at 32.1 MHz), and HR-220 (Indiana University) (^1H at 220 MHz, ^{11}B at 70.6 MHz) instruments. Mass spectra were obtained using an AEI-MS9 mass spectrometer.

Synthesis of $[(CH_3)_3M^{IV}]$*-µ-*$[(CH_3)_2B]B_5H_7$

2-Trimethylsilyl-µ-dimethylborylpentaborane(9) (II). This was prepared by the reaction of the 2-$(CH_3)_3SiB_5H_7^-$ ion with $(CH_3)_2BCl$. Original reactions were run on a 10 mmol scale, and it was later found that the reactions could be scaled up without difficulty. A convenient method of preparing II proceeded in the following manner. Two current reactions were run in 100 ml flasks fitted with high-vacuum Teflon stopcocks and containing Teflon covered magnetic stirring bars. In each flask, 26 mmol of 2-$(CH_3)_3SiB_5H_8$ were condensed onto a frozen diethyl ether solution of 25 mmol of n-butyllithium at —196°C. The general reaction procedure involved warming the reaction mixture to —70°C, then from —70 to —35°C over 1.5 h, with magnetic stirring, and then maintaining —35°C for an additional 1 h. The solution of 2-$(CH_3)_3SiB_5H_7^-$ was then cooled to —196°C and 25 mmol of $(CH_3)_2BCl$ was condensed onto it. The reaction was then effected using the above general reaction procedure. Purification of II was accomplished by high-vacuum distillation through a —10°C trap and by condensation in a —30°C trap. The combined yield of II from two such reactions was 6.70 g, 38.3 mmol (76.6%). Product II is a liquid with a vapor pressure of less than 1 torr at 24°C. Infrared spectra obtained in carbon disulfide solution and as a thin film at —196°C were virtually identical. Absorptions for II occur at 2980m, 2955(sh), and 2915w (C—H stretch), 2605s and 2550(sh) (B—H stretch), 1835w (B—H—B), 1410m, 1315(sh), 1300s, 1260(sh), 1245s, 1170w, 1135w, 1100(sh), 1085m, 1060s, 1005w, 985w, 925m, 855(sh), 835s, 825(sh), 760w, 750w, 730w, 690w, and 675w cm^{-1} (± 10 cm^{-1}). High resolution mass spectral measurement gave an observed parent *m/e* value of 176.2051; 2-$[(^{12}CH_3)_3{}^{28}Si]$-µ-$[(^{12}CH_3)_2{}^{11}B]^{11}B_5H_7$ calcd.: 176.2049. The overall fragmentation pattern was as expected based on previous investigations [1, 3, 4]. Other characterization data are in Tables 1 and 2.

2-Trimethylgermyl-µ-dimethylborylpentaborane(9) (III). This was prepared from 2-$(CH_3)_3GeB_5H_7^-$ and $(CH_3)_2BCl$ by the general procedure above. It was isolated in yields of 45-50% after high vacuum distillation at ambient temperature and condensation in a —10°C trap. It has no measurable vapor pressure at 24°C.High resolution mass spectral measurement gave an observed parent *m/e* value of 222.1508; $2\text{-}[(^{12}CH_3)_3{}^{74}Ge]\text{-}\mu\text{-}[(^{12}CH_3)_2{}^{11}B]^{11}B_5H_7$ calcd.: 222.1499. Other characterization data are in Tables 1 and 2.

1-Trimethylsilyl-µ-dimethylborylpentaborane(9) (IV). This was prepared by condensing 6.0 mmol of $(CH_3)_2BCl$ onto a frozen diethyl ether solution of 5.0 mmol of $1\text{-}(CH_3)_3SiB_5H_7^-$, prepared from $1\text{-}(CH_3)_3SiB_5H_8$ and $n\text{-}C_4H_9Li$, at —196°C. The method of preparation followed the general procedure used in the synthesis of II. Product IV was purified by distillation through a —22°C trap and by condensation in a —36°C trap, and was obtained in a yield of 0.39 g, 2.2 mmol, 44%. It is a liquid with a vapor pressure of less than 1 torr at 24°C. Its gas phase infrared spectrum showed absorptions at 2965w and 2915vw (C—H stretch), 2610m and 2585(sh) (B—H stretch), 1840vw (B—H—B), 1400w, 1335w, 1260w, 1040w(br), 955w, 865m, 850m, and 755w cm^{-1} ($\pm 10\ cm^{-1}$). Other characterization data are in Tables 1 and 2.

Attempted synthesis of $2\text{-}(H_3Si)\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$. The reaction of 11.8 mmol of $2\text{-}H_3SiB_5H_8$ with 12 mmol of $n\text{-}C_4H_9Li$ was run according to the general procedure above. The reaction flask was cooled to —196°C and opened to a section of the vacuum line prior to condensing in the $(CH_3)_2BCl$. A significant quantity of H_2 was produced in the ensuing reaction. The H_2 was removed, 11.6 mmol of $(CH_3)_2BCl$ were condensed in, and reaction was effected by the above general procedure. The contents of the flask were removed and partially separated by trap-to-trap distillation. The 32.1 MHz ^{11}B NMR spectrum of the fraction condensing in a —36°C trap indicated that this fraction consisted of two compounds. One group of resonances was assigned to $2\text{-}(H_3Si)\text{-}\mu\text{-}[(CH_3)_2B]\text{-}B_5H_7$ on the basis of their similarity in appearance to the resonances in the spectra of the other $2\text{-}(R_3M^{IV})\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$ species. The other group of resonances was similar to that expected for $2\text{-}H_3SiB_5H_8$. However, the two compounds were inseparable by trap-to-trap fractionation. The significant quantity of H_2 produced in the reaction of $2\text{-}H_3SiB_5H_8$ with $n\text{-}C_4H_9Li$ suggests that this latter material is $2\text{-}[H_2(C_4H_9)Si]B_5H_8$. The difficulty of separating $2\text{-}(H_3Si)\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$ from the suspected $2\text{-}[H_2(C_4H_9)Si]B_5H_8$ and the decomposition of $2\text{-}(H_3Si)\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$ that occurred during distillation discouraged attempts to isolate pure $2\text{-}(H_3Si)\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$.

2-Dimethylsilyl-µ-dimethylborylpentaborane(9), $2\text{-}[(CH_3)_2HSi]\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$. This compound was prepared from 6 mmol of $2\text{-}[(CH_3)_2HSi]B_5H_7^-$ and 6 mmol of $(CH_3)_2BCl$ by the above general procedure, and was obtained in a yield of approximately 18% (0.18 g, 1.1 mmol) by room temperature distillation and condensation in a —30°C trap. No hydrogen was evolved in the reaction of $2\text{-}[(CH_3)_2HSi]B_5H_8$ and $n\text{-}C_4H_9Li$ and there was no evidence for a reaction between the $(CH_3)_2HSi$- group and $n\text{-}C_4H_9Li$.

Attempted rearrangements of $[(CH_3)_3M^{IV}]\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$

Diethyl ether. 5 mmol of $2\text{-}[(CH_3)_3Si]$-, 1.5 mmol of $1\text{-}[(CH_3)_3Si]$-, and 1 mmol of $2\text{-}[(CH_3)_3Ge]\text{-}\mu\text{-}[(CH_3)_2B]B_5H_7$ were each stirred with about 5 ml of diethyl ether for periods of from 5 to 24 h. Slight decomposition occurred via loss of the $(CH_3)_2B$ moiety, but no isomerization or other reaction occurred.

Dimethyl ether. 1.7 mmol (0.30 g) of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 and 3.3 mmol of $(CH_3)_2O$ were maintained at —78°C for several hours and then at room temperature overnight. In neither case did rearrangement or reaction occur.

Hexamethylenetetramine (HMTA). About 0.7 g (4 mmol) of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 and 0.1 g (0.7 mmol) of HMTA were allowed to stand in an NMR tube for 14 h at room temperature. No change occurred other than slight decomposition of II to 2-$(CH_3)_3SiB_5H_8$.

Trimethylamine. 0.3 g (1.7 mmol) of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 and 3.3 mmol of $N(CH_3)_3$, which had been purified by distillation through a —95°C trap and by condensation at —196°C, were allowed to interact for 1 h at —78°C, during which time a white solid formed. Excess $N(CH_3)_3$, 2.0 mmol, was removed at —78°C. The reaction stoichiometry suggests that the white solid is a 1/1 complex of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 with $N(CH_3)_3$. Warming the complex to —30°C caused its decomposition to an intractable yellow oil.

Triethylphosphine. 0.3 g (1.7 mmol) of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 and 3.5 mmol of $P(C_2H_5)_3$, which had been dried over CaH_2, were allowed to interact at —78°C for several hours with no reaction occurring. The reactants were then maintained at room temperature for a few hours, during which time an intractable yellow oil formed.

Pyrolysis of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7. Approximately 2.3 g (13 mmol) of 2-[$(CH_3)_3Si$]-μ-[$(CH_3)_2B$]B_5H_7 were evaporated and passed through a Pyrex tube at 260° ± 5°C during 13.5 h. Products were condensed in a U-shaped receiving trap at —196°C, and noncondensable gases were collected and measured using a Toepler pump. About 11 mmol of noncondensable gases were produced. Condensable products, separated by trap-to-trap fractionations on the vacuum line, included diborane, tetramethyldiborane, trimethylboron, trimethylsilane, 1- and 2-[$(CH_3)_3Si$]B_5H_8, and a small amount of μ-[$(CH_3)_2B$]B_5H_8. Some starting material was recovered. Traces of a very low volatility product showed signs of decomposition within 1 h when warmed to room temperature. The fraction distilling through a —50°C trap and condensing in a —84°C trap was further purified on a low temperature spinning band column. The first fractions collected from the column consisted of traces of tetramethyldiborane, trimethylboron, and trimethylsilane, followed by the largest fraction, which was identified on the basis of its ^{11}B NMR and mass spectra as a previously unknown isomer of B_5CH_7, 6-$CH_3B_5CH_6$. The latter was obtained in approximately 14% yield. Its mass spectrum exhibited a cutoff at $m/e = 88$, and an exact measurement on this peak gave an observed m/e value of 88.1173; 6-$^{12}CH_3$-$^{11}B_5{}^{12}CH_6$ calcd.: 88.1170. The infrared spectrum of 6-$CH_3B_5CH_6$ showed absorptions at 3040(sh), 3020(sh), 2980m, 2930m (C—H stretch), 2630vs (B—H stretch), 1440w, 1340s, 1255(sh), 1220ms, 1150w, 1095m, 950ms, 910m, 840w, and 770w cm^{-1} (± 10 cm^{-1}). The last fractions collected consisted of 1- and 2-$(CH_3)_3SiB_5H_8$ and traces of a compound whose infrared spectrum indicated it to be CB_5H_9 [11].

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