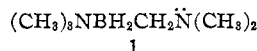


CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTH DAKOTA,
VERMILLION, SOUTH DAKOTA 57069**(Trimethylamine-borylmethyl)dimethylamine, a Strong Base**BY N. E. MILLER^{1a} AND D. L. REZNICEK^{1b}

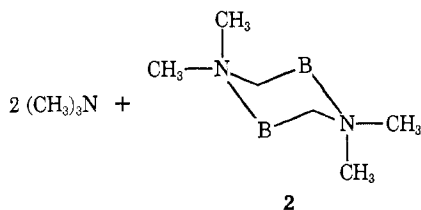
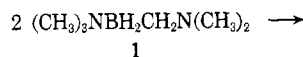
Received August 7, 1968

(Trimethylamine-borylmethyl)dimethylamine is a liquid of low volatility and strong basicity. It is a good nucleophile and forms a stable adduct with diborane. It has been used to form new classes of borane cations.

The characterization and some chemistry of the recently communicated² (trimethylamine-borylmethyl)dimethylamine, **1**, are reported here. **1** is a clear



mobile liquid that freezes at -26 to -24° . It slowly decomposes at room temperature into trimethylamine and dimethylaminomethylborane cyclic dimer, **2**.³



The conformation of **2** has not been determined. It is drawn in the chain form to show its relation to cyclohexane. This decomposition prevents rigorous purification. Fractional condensation methods actually enhance the amount of **2** present because **1** only slowly volatilizes. Fortunately, **1** can be trapped as pure as 98% directly from the reaction flask in which it is made.

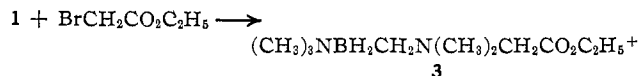
In considering the chemistry of **1** it is helpful to view it as trimethylamine with one carbon bearing a trimethylamine-boryl $[(\text{CH}_3)_3\text{NBH}_2-]$ substituent.⁴ Any difference in the chemistry of the amine function of **1** and trimethylamine, then, may reasonably be associated with the electrical and steric effects of the trimethylamine-boryl radical.

1 is completely miscible in water, forming strongly basic solutions that are stable for several days. An estimate of pK_b was made from potentiometric titration data.⁵ This estimate, while not precise, does show **1** to be at least 1 and probably 2 pK units stronger

than trimethylamine, and consequently implies a greater electron density on the amine nitrogen of **1**. The notion that trimethylamine-boryl is strongly electron releasing, ostensibly by inductive electron drift, is therefore established on a sound experimental basis. This electron release has also been implicated⁶ in the chemistry of $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_3$, which may be viewed as derived from dimethyl sulfide by replacement of one methyl by trimethylamine-boryl.

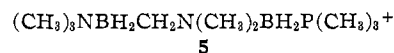
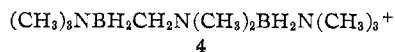
As might be expected, **1** readily forms a borane adduct, $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$, in an exothermic reaction with diborane. This adduct is a white, crystalline solid of sufficient thermal stability to be purified by vacuum sublimation with good recovery.

Nucleophilic reaction of **1** and ethyl bromoacetate led to the borane cation **3**. **3** represents a new type



of borane cation in which the base portion has functional substitution. Good kinetic stability in aqueous acid or neutral solution was observed, and **3** is readily handled for characterization as its sparingly soluble hexafluorophosphate salt. In alkali the carbethoxy group is hydrolyzed, but the BH_2 moiety is only very slowly attacked (less than 1% hydrogen evolution in 1.5 hr in 0.5 M alkali). Clearly, functional substitution on the base portion of borane cations is possible. The effects of such substitution are presently being studied.

Another new class of borane cations in which two boron atoms are separated by a two-membered bridge was established using **1** as a base. [(Trimethylamine-borylmethyl)dimethylamine]trimethylaminodihydroboron(1+), **4**, and the analogous trimethylphosphine-containing cation **5** were synthesized using a modifica-



tion of Douglass' reaction;⁷ the borane adduct of **1** was monoiodinated in chloroform and the iodine was sub-

(1) (a) Author to whom inquiries should be addressed at the University of South Dakota; (b) National Science Foundation Trainee, 1966-1968.

(2) N. E. Miller, *J. Am. Chem. Soc.*, **88**, 4284 (1966).

(3) N. E. Miller and E. L. Muettterties, *Inorg. Chem.*, **3**, 1196 (1964).

(4) The amine nomenclature was used here rather than the adduct name, trimethylamine-dimethylaminomethylborane, because the latter obscures the functional group and makes the nomenclature of derivatives very difficult.

(5) Lack of ultraviolet or visible absorption of **1** or its conjugate acid, along with instability in the presence of platinum black, precludes direct spectral measurement of the buffer ratio or precise measurement of hydrogen ion activity.

(6) R. J. Rowatt and N. E. Miller, *J. Am. Chem. Soc.*, **89**, 5509 (1967).

(7) (a) J. E. Douglass, *ibid.*, **86**, 5431 (1964); (b) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967).

TABLE I

INFRARED ABSORPTION^a

$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, neat	2950 m, multiplet, 2800 w, 2750 m, 2330 m, bd, 2250 vw, 1450 s, bd, 1410 m, 1400 m, 1320 m, 1250 s, 1175 s, doublet, 1155 s, 1100 s, 1035 m, doublet, 985 m, doublet, 935 w, 920 w, 885 m, 840 s, 770 m, 730 m
$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}^+\text{PF}_6^-$	3260 m, 2360 w, bd, 2300 w, 2270 vw, 1335 vw, 1255 w, 1190 vw, 1175 m, 1155 w, 1130 vw, 1105 m, 1055 w, 990 m, 970 w, 840 s, bd, 745 w
$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$	3010 m, doublet, 2360 s, 2320 s, 2270 s, 1320 w, 1260 w, doublet, 1215 vw, 1185 m, 1170 s, 1155 s, 1110 w, 1010 m, 995-985 m, doublet, 945 vw, 900 w, 850 s, 830 m
$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5^+\text{PF}_6^-$	3010 vw, doublet, 2380 m, 2300 w, 2260 vw, 1750 s, 1450 m, 1410 m, 1390 w, 1380 vw, 1365 vw, 1340 m, 1270 vw, 1250 s, 1210 s, 1160 s, 1105 m, 1050 m, 1040 m, 985 m, 945 m, 820 s, bd
$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{N}(\text{CH}_3)_3^+\text{PF}_6^-$	2450 w, bd, 2350 w, bd, 2300 w, 1415 w, 1320 w, 1310 w, 1240 m, 1200 m, 1180 m, 1160 m, 1135 vw, 1120 w, 985 m, 835 s, bd
$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{P}(\text{CH}_3)_3^+\text{PF}_6^-$	2420 m, 2370 m, 2280 w, 1405 m, 1320 m, 1310 w, 1245 w, 1220 w, 1190 m, 1160-1150 m, 1090 m, 1020 w, 975 m, bd, 840 s, bd
$[(\text{CH}_3)_2\text{NCH}_2\text{BH}_2]_2$ (2)	2395 m, 2330 s, doublet, 2290 m, doublet, 2240 m, doublet, 1345 w, 1300 w, 1260 w, 1185 s, doublet, 1120 m, 1105 m, 1035 m, 1005 m, 975 m, 920 m, 840 m, 775 m

^a All but the first compound were run as mineral oil mulls on a Perkin-Elmer 237 B. The absorptions listed are in cm^{-1} and represent the major bands except those in common with or shouldering on those of mineral oil. Abbreviations: s, strong; m, moderate; w, weak; vw, very weak; bd, broad.

sequently displaced with trimethylamine or trimethylphosphine. These cations exhibited excellent aqueous stability. A great number of extensions of this class are possible.

Attention is also directed to the conjugate acid of **1**, $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}^+$, as representing a new class of borane cations. In a formal sense this cation can be considered as derived from the tautomer ylide base of trimethylamine, $:\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}$. This cation can be recovered from 1 *N* aqueous base in good yield after 1 week, illustrating that it is more stable toward hydrolysis than cations with the secondary amine directly bonded to boron.⁸

That the thermal stability of **1** is greatly enhanced whenever the amine function is complexed, even by weak hydrogen bonding in aqueous solution, raises an interesting question concerning the thermal dissociation of **1**. Is the dative boron-nitrogen bond inherently weak or is there an ancillary process assisting its dissociation by an intra- or intermolecular attack which requires mobility of the unshared electrons of the amine function? An investigation of the kinetic details of the dissociation would be instructive here.

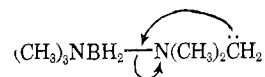
Synthesis.—The preparation of **1** from bis(trimethylamine)dihydroboron(1+) chloride proceeds in fair but erratic yield by treatment with 1.5 molar equiv of butyllithium in hydrocarbon solvent at room temperature. With less (1.0 molar equiv) or more (2.0 molar equiv) butyllithium the cyclic dimer **2** or a lithium-substituted derivative of **1**² is obtained. Apparently the physical state of the borane cation salt is also critical since better yields are more often (but not always) achieved using anhydrous salt prepared by pumping on the hydrate rather than the chloroform solvate.

Unpredictable conversions even with ostensibly

(8) T. A. Shegoleva, V. D. Sheludyakov, and B. M. Mikhailov, *Zh. Obshch. Khim.*, **35**, 1066 (1963); *J. Gen. Chem. USSR*, **35**, 1070 (1963). These authors report the half-life of $[(\text{CH}_3)_2\text{NH}]_2\text{BH}_2^+\text{Cl}^-$ in 0.6 *M* NaOH to be 0.66 min.

identical conditions made the search for optimum conditions very frustrating and discouraged serious attempts to obtain material balances. It was established, however, that the original cation was consumed in the reaction and that there was little or no lithium hydride produced. The reaction mixture is complex, and it is believed that there are still two or three major unidentified products.

Because the stoichiometry and mechanism are obscure, formal yields cannot be calculated; more than one borane cation may be required to produce one boron-carbon bond. A reasonable speculation for the initial step is that butyllithium abstracts a proton to form a charge-compensated carbanion $[(\text{CH}_3)_3\text{NBH}_2\text{N}(\text{CH}_3)_2\text{CH}_2^-]$. This species may then rearrange by intra- or intermolecular processes to form **1**. In the absence of kinetic data only the net process can be symbolized



The conversion to **1** was usually less than 25%, based upon total boron charged. Attempts to improve the conversion by increasing the temperature or duration of the reaction or by addition of a catalyst (trimethylamine) were unsuccessful. An alternate route is being sought.

Spectra.—Infrared spectra of **1** or its derivatives (Table I) show characteristic broad and structured BH stretching bands near 2350 cm^{-1} . This is a little lower frequency than observed for borane cations with exclusive B-N bonding but typical of simple boranes with concomitant B-C bonding. The conjugate acid of **1** as the hexafluorophosphate salt has an NH stretching absorption at 3260 cm^{-1} which is strong and sharp, characteristic of tertiary ammonium salts without hydrogen bonding.

TABLE II
 PROTON NMR CHEMICAL SHIFT DATA

Compound ^a	Resonances ^b			Intensity ratio ^c
	-N(CH ₃) ₃	-N(CH ₃) ₂	Other	
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂	2.60	2.13	-CH ₂ -, 1.66	1.51:1
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ H ⁺ PF ₆ ⁻ in CH ₂ Cl ₂	2.60	Doublet, 2.86, <i>J</i> = 5 cps		
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ H ⁺ PF ₆ ⁻ in D ₂ O	2.58	2.76		1.5:1
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ BH ₃	2.54	2.50		9:6:1.8:1.9:2.8
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ CH ₂ CO ₂ C ₂ H ₅ ⁺ PF ₆ ⁻	2.60	3.20	-CH ₂ CO ₂ C ₂ H ₅ , 3.96 -CH ₂ CH ₃ , 4.26 <i>J</i> = 7 cps	
			-CH ₂ CH ₃ , 1.30	
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ BH ₂ N(CH ₃) ₃ ⁺ PF ₆ ⁻	2.58	2.71	NBN(CH ₃) ₃ , 2.83	9:5.8:10
(CH ₃) ₃ NBH ₂ CH ₂ N(CH ₃) ₂ BH ₂ P(CH ₃) ₃ ⁺ PF ₆ ⁻	2.56	Doublet, 2.72, <i>J</i> = 1.5 cps	-P(CH ₃) ₃ , doublet, 1.52, <i>J</i> _{POCH} = 12 cps	9:6:8.7

^a The first compound was run as a 75% solution in tetramethylsilane. Compound 2 in D₂O was referenced with Na⁺(CH₃)₃SiCH₂-CH₂CH₂SO₃⁻. All other compounds were run in methylene chloride with tetramethylsilane reference. ^b In ppm downfield from reference. ^c Ratio is in order of the resonances as listed in this table.

The proton nmr spectrum of **1** is complicated by coincident peaks of impurities (trimethylamine and **2**), and satisfactory intensity ratios were not obtained. The chemical shifts and assignments are in Table II. The protonated hexafluorophosphate salt of **1** in methylene chloride shows a doublet N(CH₃)₂ resonance split by the NH proton, *J* = 5 cps. In D₂O or water the doublet collapses to a sharp singlet, so it appears that rapid proton exchange obtains here (for reasonable values of *T*₂ the lifetime of a spin state is much less than 0.1 sec⁹). Other spectral data are summarized in Tables I and II.

Experimental Section

Reagent grade solvents were employed. Chloroform was rendered anhydrous by distillation from phosphorus pentoxide. Pentane and hexane were freed of olefins by long stirring over sulfuric acid followed by separation and distillation. Diborane was obtained from Callery Chemical Co., Callery, Pa., and was stored at -78°. Vacuum line preparations and manipulations were carried out in a line equipped with Delmar-Urry needle valves and O-ring joints (Delmar Scientific Co., Maywood, Ill). The pumping train was capable of producing a vacuum better than 10⁻⁵ mm routinely.

Synthesis of 1.—Of many conditions tried those described in the following typical preparation seemed to be best.

In a 50-ml two-necked reaction flask attached to the vacuum line *via* a U trap was placed a near crystalline paste of [(CH₃)₃N]₂-BH₂Cl made by adding small amounts of chloroform to the wet chloride salt. The salt was rendered anhydrous under high vacuum without agitation and was then weighed, 1.219 g, 7.34 mmol. Dry pentane, about 5 ml, was added, and the hard, porous chunks were broken with a spatula. At room temperature, under nitrogen, 4.1 ml of 2.72 *M* butyllithium in hexane (11.0 mmol) was added dropwise from a syringe into the stirred slurry until there was noticeable warming. The reaction flask was then cooled to 20° and the remainder of the butyllithium was added; the total time was about 0.25–0.5 hr. The mixture was stirred an additional 0.5 hr and the solvent was removed under vacuum *via* a -35° trap, leaving a semisolid residue. The trap temperature was lowered to -78° and the residue was pumped for 1 hr at room temperature before slowly heating to 70°. Pumping was continued at 70° until no additional product was collected in the trap.

A rough separation of **1** from **2** can be made at this point by warming the trap, whereupon the lower ring of solid melts and flows away from **2** present in an upper ring around the trap. In this preparation work-up, the trap contents were removed with a mixture of about 5 ml of ether and 5 ml of water (**2** dissolves in ether and **1** in water). The water layer was acidified and treated with about 0.5 ml of saturated ammonium hexafluorophosphate solution. Upon cooling (0°) and scratching, a paste of crystalline (CH₃)₃NBH₂CH₂N(CH₃)₂H⁺PF₆⁻ formed. The solid was separated by filtration and vacuum dried (owing to its high solubility **1** should not be washed with water). The white solid product was recrystallized from ethanol-water; yield 384 mg. A sample from a different preparation having an identical infrared spectrum was analyzed. *Anal.* Calcd for (CH₃)₃NBH₂CH₂N(CH₃)₂-H⁺PF₆⁻: C, 26.1; H, 7.3; N, 10.1; P, 11.2. Found: C, 26.2; H, 7.4; N, 10.6; P, 11.5.¹⁰ Hydrolytic hydrogen determinations² gave 7.3 × 10⁻³ and 7.1 × 10⁻³ mmol/mg in good agreement with 7.25 × 10⁻³ mmol/mg calculated.

Many reaction variants were tried in efforts to improve the yield: trimethylamine was introduced to improve the basicity of the butyllithium; the mixture was heated during and/or after the addition of butyllithium to near 60°; long reaction times near 24 hr were used; the iodide form of the borane cation was employed. The addition of trimethylamine had no apparent effect, but the other variants decreased the yield. The pot residue after product removal varied from one preparation to another between a semisolid and a white, hard solid. The residues dissolved completely in water with little gas evolution, and the solution precipitated no material on addition of saturated ammonium hexafluorophosphate. The solution evolved considerable gas upon acidification, suggestive of the presence of borohydride-like ions.

The structure of **1** was confirmed by decomposition into **2** and trimethylamine. A 55.0-mg sample was heated 3 hr at 120° in a sealed ampoule. After cooling to -78°, the ampoule was opened to the vacuum line. The material volatile at -78° was removed and found to be 0.404 mmol of trimethylamine (identified by its infrared spectrum). The residue amounted to 29.5 mg, 0.208 mmol of **2**, identified by its infrared spectrum. From these data a composition of 7.34 × 10⁻³ mmol of trimethylamine/mg of compound and 3.79 × 10⁻³ mmol of **2**/mg of compound is calculated. These values represent 96 and 98% of the theoretical values, 7.69 × 10⁻³ and 3.85 × 10⁻³ mmol/mg, respectively.

(CH₃)₃NBH₂CH₂N(CH₃)₂BH₃.—Diborane, 0.362 mmol measured as a gas, was condensed onto 76.2 mg (0.584 mmol) of **1** contained in a 50-ml reaction vessel. On warming, a white solid

(9) Method of M. Takeda and E. Stejskal in "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press Ltd., London, 1965, p 490.

(10) Analyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, West Germany, and Midwest Microlab Inc., Indianapolis, Ind.

was produced in an exothermic reaction which commenced near -78° . The mixture was allowed to stand at room temperature for 15 min and the volatile products were removed. Noncondensable gas (about 0.03 mmol) and 0.090 mmol of diborane (identified by its infrared spectrum) were obtained. Thus the stoichiometry was $1:\text{BH}_3 = 1.07$. The adduct was sublimed under high vacuum at $80-100^{\circ}$ to give 43.4 mg of white crystalline solid, mp $106-109.5^{\circ}$. *Anal.* Calcd for $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$: C, 50.1; H, 15.4. Found: C, 49.4; H, 15.0. The hydrolytic hydrogen value found, 3.43×10^{-2} mmol/mg, also agreed well with the calculated value of 3.47×10^{-2} mmol/mg.

The adduct from another preparation was sublimed with 74% recovery.

Titration of $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{H}^+\text{PF}_6^-$.—A 43.7-mg sample was dissolved in 20.0 ml of water and titrated with 0.0975 *N* sodium hydroxide under nitrogen using a glass electrode standardized at pH 9 and a Beckman expanded-scale pH meter. A blank containing 20.0 ml of deionized water was similarly titrated. Estimation of pK_b was made from the titrant volume difference between the salt solution and blanks at pH 9.5, 10.0, and 10.5. The equation employed was $K_b = K_w(V_{ep} - \Delta V)/10^{-pH\Delta V}$, where V_{ep} is the theoretical volume of 1 equiv of base. Values obtained were 17×10^{-3} , 8×10^{-3} , and 5×10^{-3} . Similar results were obtained using 0.02 *N* sodium hydroxide.

It was found that 1 could be extracted into hexane from 0.1–1 *N* base. The distribution coefficient in 1 *N* base at 25.0° was determined as 2.2 ± 0.1 , $D = [1]_{\text{aqueous}}/[1]_{\text{hexane}}$. A solution of 1 in hexane was prepared by extracting a solution of the conjugate acid of 1 in 1 *N* base. The concentration of the resulting hexane solution was determined by stirring an aliquot vigorously with deionized water and titrating under nitrogen. A 5.00-ml aliquot of the hexane solution was equilibrated with 1.00 ml of 1 *N* sodium hydroxide and the concentration of 1 in hexane was again determined. The decrease of 1 in the hexane phase was used to calculate the concentration of 1 in the aqueous phase. In experiments without the borane salt it was established that hexane by itself carries no basic material after shaking with 1 *N* sodium hydroxide and separating.

In several titrations of solutions of 1 in water with 0.02 *N* hydrochloric acid, differential titration curves, $\Delta pH/\Delta V$ vs. volume, exhibited maxima near pH 7.0.

$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5^+\text{PF}_6^-$.—A mixture of 0.26 g of 1 and 0.22 ml of ethyl bromoacetate in 5 ml of ether rapidly became cloudy, precipitating a clear oil which slowly crystallized. The bromide salt so obtained was dissolved in water and converted to the hexafluorophosphate by addition of excess ammonium hexafluorophosphate. The slightly soluble hexafluorophosphate was recrystallized from hot water; 0.33 g of white crystals, 46% yield; mp $70-74^{\circ}$. *Anal.* Calcd for $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5^+\text{PF}_6^-$: C, 33.2; H, 7.2; N, 7.7; B, 3.0. Found: C, 34.0; H, 7.2; N, 7.8; B, 2.2.

$(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{N}(\text{CH}_3)_3^+\text{PF}_6^-$ and $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{P}(\text{CH}_3)_3^+\text{PF}_6^-$.—To a stirred solution of 311 mg (2.12 mmol) of $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ in 5 ml of dry chloroform was added dropwise a solution of 269 mg (1.06 mmol) of I_2 in 20 ml of chloroform. The mixture was stirred 15 min more after hydrogen evolution ceased. Then 2.11 mmol of trimethylamine was added and the clear solution was allowed to stand overnight. Solvent was removed and the resulting oil (iodide salt) was converted to the hexafluorophosphate salt; 490 mg, 80% yield. Recrystallization from hot water (10 mg/ml) gave white crystals, mp $103-104^{\circ}$. *Anal.* Calcd for $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{N}(\text{CH}_3)_3^+\text{PF}_6^-$: C, 31.2; H, 8.7; N, 12.1; B, 6.2. Found: C, 31.5; H, 8.5; N, 12.0; B, 6.1.

Similarly, from 319 mg of $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$, 218 mg of iodine, and 2.28 mmol of trimethylphosphine, after work-up, was obtained 537 mg of crude $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{P}(\text{CH}_3)_3^+\text{PF}_6^-$. Recrystallization from hot water gave 267 mg of pure material, mp $123-124^{\circ}$. *Anal.* Calcd for $(\text{CH}_3)_3\text{NBH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_2\text{P}(\text{CH}_3)_3^+\text{PF}_6^-$: C, 29.7; H, 8.3; N, 7.7; B, 5.9; P, 17.0. Found: C, 29.8; H, 8.6; N, 7.9; B, 5.8; P, 16.9.

Acknowledgment.—Partial support of this work by a grant from the National Science Foundation is sincerely appreciated.

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A Study of the Bonding in Group IV Amines

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Received August 6, 1968

N-Methyl C^{13} -H coupling constants and relative basicities were measured for the compounds $(\text{CH}_3)_2\text{MN}(\text{CH}_3)_2$ and $\text{M}[\text{N}(\text{CH}_3)_2]_4$, where $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{and Sn}$. The coupling constants for the trimethyl series varied in the order $\text{Si} > \text{Ge} = \text{C} > \text{Sn}$ and for the tetrakis series in the order $\text{Si} > \text{C} > \text{Ge} \gtrsim \text{Sn}$. The relative basicities in both series varied in the order $\text{Ge} > \text{Si}$. The trends are interpreted as indicative of a decrease in $(p-d)\pi$ overlap from silicon to tin, with the major change occurring between silicon and germanium.

The bonding in silylamines has been a subject of considerable concern and numerous publications ever since the discovery of the planarity and low basicity of trisilylamine. Although there has been a recent flourish of experiments resulting in agnostic interpreta-

tion,² it is generally conceded that the chemical and physical peculiarities of silylamines as compared to organic amines are a result of $(p-d)\pi$ bonding. The bonding in other group IV amines has received much

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(2) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **6**, 108 (1967); E. W. Randall and J. J. Zuckerman, *J. Am. Chem. Soc.*, **90**, 3167 (1968).