747. *The Relative Stabilities of some Complexes of Dimethyl-amino-silanes and -methanes with Lewis Acids*

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Bis-, tris-, and tetrakis-dimethylaminosilane all give borane adducts, but only $SiH_2(NMe_2)_2$ forms a complex with trimethylborane. The corresponding base, bisdimethylaminomethane, yields 1 : 2, 1 : 1, and 1 : 2 complexes with borane, trimethylborane, and iodosilane, respectively. The stoicheiometries and relative stabilities of these and some related adducts are discussed in terms of steric and π-bonding effects. Borane adducts of $SiH_2(NMe_2)_2$ and $SiH(NMe_2)_3$ readily decompose giving dimethylaminoboranes.

Silicon–nitrogen compounds are usually weaker bases [1] than the corresponding carbon compounds; this is commonly attributed to p_π–d_π N $\longrightarrow$ Si dative π-bonding,[2] which makes the lone-pair electrons on nitrogen less available for donation. Thus, trimethylborane forms a weaker complex with *N*-dimethylaminosilane than with trimethylamine,[3] and trisilylamine, unlike trimethylamine, forms no stable adducts with borane,[4,5] trimethyl-borane,[3,4] trimethylaluminium,[6] or iodosilane.[7] Possible reference acids are limited, since attempts to use hydrogen halides or boron and aluminium trihalides have almost invariably resulted [8] in cleavage of the Si–N bond. Most of such studies have been made with compounds that contain one or more silicon atoms attached to each nitrogen; much less has been reported about compounds with more than one nitrogen attached to each silicon. A solid adduct $SiCl_2(NMe_2)_2,2HCl$ has been described,[9] and a recent careful study of base strengths by measurements of heats of mixing [10] included $SiMe_2(NHEt)_2$. Such compounds must offer considerable steric hindrance to Lewis acids other than the proton.

The dimethylaminosilanes $SiH_{4-n}(NMe_2)_n$, recently prepared,[11] provide a complete

[1] E. A. V. Ebsworth, " Volatile Silicon Compounds," Pergamon, Oxford, 1963, ch. 5.
[2] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 332; H. H. Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.
[3] S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, 1954, **76**, 4631.
[4] A. B. Burg and E. S. Kuljian, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.
[5] J. M. Gamboa, *Anales real Soc. españ. Fis. Quim.*, 1950, **46B**, 699.
[6] S. Sujishi and H. M. Manasevit, U.S. Dept. Comm., P.B. Report 143, p. 572 (*Chem. Abs.*, 1961, **55**, 17,333).
[7] B. J. Aylett, unpublished results.
[8] S. Sujishi and S. Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447; H. Grosse-Ruyken and R. Kleesaat, *Z. anorg. Chem.*, 1961, **308**, 122.
[9] R. Cass and G. E. Coates, *J.*, 1952, 2347.
[10] S. W. Jarvie and D. Lewis, *J.*, 1963, 1073.
[11] B. J. Aylett and L. K. Peterson, *J.*, 1964, 3429.

series in which silicon has an increasing number of nitrogen ligands, and where steric effects are minimised. The stoicheiometry and relative stability of some of their adducts have been studied in an attempt to clarify the effects of π-bonding.

RESULTS AND DISCUSSION

The observed adducts are listed in the Table, together with an indication of their volatility. Results obtained with bisdimethylaminomethane, and the reported adducts of N-dimethylaminosilane and trimethylamine are also included for comparison. Attempts to prepare more fully substituted dimethylaminomethanes were unsuccessful; from an examination of space-filling models, they seem unlikely to exist.

Observed adducts

Base	Ref.	Acid	Reacting ratio/temp.*	Remarks
$SiH_3 \cdot NMe_2$	3, 6	BH_3	$1:1/-80°$	——
		BMe_3	$1:1/-78°$	V. p., 11 mm./$-27°$
$SiH_2(NMe_2)_2$	This work	BH_3	$1:2/-84°$; $1:1$	Volatile at 20°
		BMe_3	$1:1/-84°$	V. p., 7 mm./$-25°$
		SiH_3I	—	Reacts further
$SiH(NMe_2)_3$	This work	BH_3	$1:2/-135°$; ?$1:1$	Volatile at 20°
		BMe_3	—	No reaction
$Si(NMe_2)_4$	This work	BH_3	$1:1/-135°$	Slightly dissociated at $-135°$
		BMe_3	—	No reaction
$CH_3 \cdot NMe_2$	12	BH_3	$1:1$/R.T.	V. p., 2 mm./20°
	13	BMe_3	$1:1$/R.T.	V. p., 1·4 mm./20°
	14	SiH_3I	$1:1$/R.T.; $2:1$/R.T.	Almost involatile at 20°
$CH_2(NMe_2)_2$	This work	BH_3	$1:2/20°$	,, ,, ,,
		BMe_3	$1:1/-84°$	V. p., 8 mm./19°
		SiH_3I	$1:2/20°$	Almost involatile at 20°

* Temperature at which excess of acid was removed. (R.T. = room temperature.)

The stoicheiometries of corresponding adducts of substituted silanes and methanes are generally the same, and reflect the size of the acid. Thus, bisdimethylaminosilane and bisdimethylaminomethane both formed 1 : 2 adducts with borane, but 1 : 1 adducts with the larger trimethylborane (approximate molar volumes of these acids are 30 and 90 ml., respectively). By the criterion of volatility,[15] the substituted methanes are more basic. Only borane adducts could be prepared with tris- and tetrakis-dimethylaminosilane; that from the latter was extremely weak.

Examination of models confirmed that sterically unhindered dispositions were possible for all the observed adducts. $Si(NMe_2)_4,2BH_3$ appeared possible if the dimethylamino-groups were suitably arranged, but could not be prepared. It was also clear that, because of the larger size of silicon, adducts of substituted silanes were less crowded than similar adducts of methanes. Simple considerations of electronegativity also suggest that Si–N compounds should be more basic than C–N compounds. It appears that Si–N dative π-bonding is sufficiently important to overcome both these factors.

Bisdimethylaminomethane retained dimethylamine very strongly, but trimethylamine could easily be removed, presumably because hydrogen-bonding was not then possible. Acetic anhydride effectively removed the secondary amine. The physical properties of bisdimethylaminomethane were those of a normal unassociated liquid. With trimethyl-borane as a reference acid, bisdimethylaminomethane was shown to be a somewhat weaker base than trimethylamine in two ways. The dissociation constant (K_p) for

[12] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.
[13] H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435.
[14] B. J. Aylett, H. J. Eméleus, and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 187.
[15] F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101.

$CH_2(NMe_2)_2,BMe_3$ at 54° was 0·12 atm., while that of NMe_3,BMe_3 at the same temperature [13] is 0·017.   Also, in a competitive experiment, the equilibrium

$$CH_2(NMe_2)_2,BMe_3 + NMe_3 \rightleftharpoons NMe_3,BMe_3 + CH_2(NMe_2)_2 \qquad (1)$$
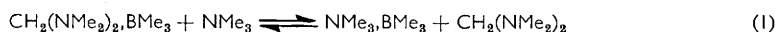
was shown to lie at least 85% to the right.   The relative base strengths of bisdimethylaminomethane and trimethylamine in aqueous solution are not known; in a corresponding pair of bases, bisdiethylaminomethane [16] is, however, about as strong as triethylamine.[17] The displacement reaction (1) is thus probably a reflection of steric strain in the bisdimethylaminomethane–trimethylborane adduct.   It is interesting that bisdimethylaminomethane formed a 1 : 2 adduct so readily with the relatively large molecule iodosilane (approx. molar vol., 80 ml.).   Tetramethylhydrazine, the corresponding ditertiary amine without a bridging methylene group between nitrogen atoms, will form only a 1 : 1 adduct with iodosilane under the same conditions.[18]

When bisdimethylaminosilane–trimethylborane reacted with trimethylamine in a competitive experiment, the reaction

$$SiH_2(NMe_2)_2,BMe_3 + NMe_3 \longrightarrow NMe_3,BMe_3 + SiH_2(NMe_2)_2 \qquad (2)$$
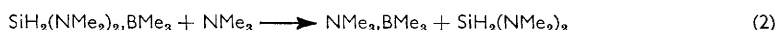
proceeded completely from left to right.   Comparison of reactions (1) and (2) confirms that bisdimethylaminomethane is a stronger base than bisdimethylaminosilane.   Comparison of iodosilane adducts could not be made, as this acid reacted irreversibly with bisdimethylaminosilane, probably suffering disproportionation.   Weak bases are known to bring this about.[19]   Diborane also reacted slowly and irreversibly with bis- and trisdimethylaminosilane below 0°.   In the first case, dimethylaminoborane and silane were isolated as major products, in amounts closely corresponding to the equation

$$2SiH_2(NMe_2)_2,BH_3 \longrightarrow 2BH_2NMe_2 + SiH_4 + SiH_2(NMe_2)_2$$
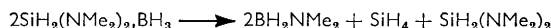
Trisdimethylaminosilane produced a complex mixture that was shown to consist of various dimethylaminoboranes and dimethylaminosilanes.   Similar reactions of borane adducts of dialkylaminodialkylsilanes and dialkylaminotrialkylsilanes have been reported.[20]

A comparison of the base strengths of the dimethylaminosilanes, $SiH_{4-n}(NMe_2)_n$, must take into account both steric and electronic effects; while steric effects will lower the base strength as n increases, there is also the possibility that the π-bonding ability of silicon will alter as more nitrogen ligands are involved.   Clearly, when trimethylborane is the reference acid, the stability of the complexes decreases very markedly as n increases from 2 to 4.   When the much smaller borane is used, the dissociation pressure depends critically on the combining ratio.   With an accurate mole ratio of 1 : 0·95 (base : acid) in each case, the vapour pressure of the bis- and tris-dimethylaminosilane adducts at −64° were 1·7 (by interpolation) and 1·8 mm., respectively.   Since steric effects will undoubtedly be present to reduce relatively the base strength of tridimethylaminosilane, the closely similar dissociation pressures imply that π-bonding is weaker in this compound than in bisdimethylaminosilane.   If an even smaller reference acid could be found, it might be possible to reverse the order of base strength.   Unfortunately, H⁺ cleaves the Si–N bond in these compounds.[11]

A group theoretical treatment by Eyring *et al.*[21] suggests that a tetrahedrally co-ordinated atom with accessible *d*-orbitals can form two strong and three weak π-bonds with the ligands.   This does not, of course, imply a necessary discontinuity of behaviour when more than two π-bonding ligands are attached, and attempts to demonstrate such a

[16] T. D. Stewart and J. G. Aston, *J. Amer. Chem. Soc.*, 1926, **48**, 1642.
[17] J. E. Ablard, D. S. McKinney, and J. C. Warner, *J. Amer. Chem. Soc.*, 1940, **62**, 2181.
[18] B. J. Aylett, *J. Inorg. Nuclear Chem.*, 1958, **5**, 292.
[19] B. J. Aylett, *J. Inorg. Nuclear Chem.*, 1960, **15**, 87.
[20] H. Nöth, *Angew. Chem.*, 1960, **73**, 371; *Z. Naturforsch.*, 1961, **16**b, 618.
[21] H. Eyring, J. Walter, and G. E. Kimball, " Quantum Chemistry," Wiley, New York, 1944.

discontinuity in series such as $Ph_xMe_{3-x}Si\cdot C_6H_4\cdot CO_2H$ have failed.[22]　Although there has been some recent controversy as to the actual orbitals used,[23] Cruickshank [24] has discussed a wide range of S–O, P–O, and Si–O compounds in terms of two molecular π-orbitals around each tetrahedral centre.　If we extend his arguments to $SiH_2(NMe_2)_2$ and $SiH(NMe_2)_3$, it seems likely that the lone-pair electrons of all the nitrogen atoms will combine with one silicon $3d$-orbital, so that delocalisation is as extensive as possible.　In that case, the (valence bond) π-bond order in these two compounds will be $\frac{1}{2}$ and $\frac{1}{3}$, respectively, in agreement with deductions made earlier.　Uncertainties in this simple approach include: (*a*) the orientation of the methyl groups with respect to the SiN_2 or SiN_3 framework, and (*b*) the importance of changes in the effective nuclear charge seen by the $3d$-orbitals [25] as the ligands alter.　Both these factors will markedly affect π-overlap.

<center>EXPERIMENTAL</center>

Manipulations were carried out in a high-vacuum system in the absence of mercury, or in a dry-box filled with nitrogen.

Bisdimethylaminomethane.—Preparation.　Henry's method [26] was used; the crude product was dried successively with potassium hydroxide and calcium hydride, and distilled.　The fraction boiling between 80 and 83° was chiefly bisdimethylaminomethane, but tenaciously retained traces of dimethylamine.　Treatment with acetic anhydride for 12 hr. at room temperature and further fractionation gave a tensiometrically homogeneous sample (v. p. 23·6 mm./0°).

Physical Properties.—A number of samples, when cooled in liquid nitrogen, set to a glass-like solid that melted in a Stock apparatus below −140°.　The density of the liquid was 0·751 g./ml. at 20° (lit.,[26] 0·749 g./ml. at 17°).

Saturated vapour pressures, measured with glass tensimeters, are given below:

Temp.	0·0°	5·2°	7·9°	9·8°	12·3°	15·8°	28·2°	33·0°	36·2°
P (mm.) ...	23·6	31·9	37·2	40·6	46·4	54·3	100·7	125·0	144·0
Temp.	41·0°	44·6°	46·0°	49·6°	53·4°	58·5°	60·0°	64·3°	65·3°
P (mm.) ...	172·2	201·5	209	243	283	336	356	403	423
Temp.	66·2°	67·5°	71·0°	72·5°	74·9°	68·0°	53·0°	28·0°	
P (mm.) ...	435	456	508	537	569	468 *	280 *	104 *	

<center>* Decreasing temperature.</center>

The values above 28·2° determine the equation: $\log P$ (mm.) $= 7\cdot611 - 1688/T$.　The extrapolated b. p. is 84° [lit., 85° (Henry [26]); 90—95° (Klages *et al.*[27])], the latent heat of vaporisation is 7·71 kcal. mole^{-1} and Trouton's constant is 21·6 cal. deg.$^{-1}$ mole^{-1}.

Infrared spectrum.　A Hilger H800 spectrometer was used to obtain spectra of samples in the gas phase.　The following band centres (in cm.$^{-1}$) were recorded: 2960vs, 2825vs, 2775vs, 1450s, 1385m, 1280s, 1215s, 1085sh, 1050vs, 903w, 865m, 790w, 770w.　These values may be compared with Raman shifts obtained by Kahovec [28] in the same range: 2982vs, 2945vs, 2902m, 2810s, 2762vs, 2718w, 2660w, 1468vs, 1444vs, 1385m, 1308m, 1281vw, 1210s, 1144m, 1098m, 1042s, 1017m, 926m, 860s, 716w.　The symmetry of $CH_2(NMe_2)_2$ cannot be greater than C_{2v} (ignoring methyl hydrogen atoms).　As expected, therefore, there are a large number of coincidences.

Reaction of Bisdimethylaminomethane with Trimethylborane.—In a typical experiment, bisdimethylaminomethane (0·386 mmole) and trimethylborane (1·785 mmoles) reacted together in the gas phase.　Immediately the vapours mixed, fern-like translucent crystals were formed. The mixture remained at room temperature for 30 min., and was then cooled to −84°; excess of trimethylborane (1·363 mmoles) was the only volatile product at that temperature.　The combining ratio $CH_2(NMe_2)_2$: BMe_3 (mean of 3 expts.) was 1 : 1·04.

[22] J. Chatt and A. A. Williams, *J.*, 1956, 688; cf. D. E. Webster, *J.*, 1960, 5132.
[23] D. P. Craig and N. L. Paddock, *J.*, 1962, 4118; M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J.*, 1960, 2423; F. A. Cotton, *J.*, 1960, 5269.
[24] D. W. J. Cruickshank, *J.*, 1961, 5486.
[25] D. P. Craig and E. A. Magnusson, *J.*, 1956, 4895.
[26] L. Henry, *Bull. Acad. roy. Belg.*, 1893, [3], **26**, 200; *Ber.*, 1893, **26**, R934.
[27] F. Klages, G. Nober, F. Kircher, and M. Bock, *Annalen*, 1941, **547**, 1.
[28] L. Kahovec, *Acta Physica Austriaca*, 1948, **1**, 307.

Physical Properties of Bisdimethylaminomethane–Trimethylborane.—The m. p. was 22°. Saturated vapour pressures, measured in an all-glass tensimeter, are given below:

Temp.	18·8°	29·1°	36·8°	41·5°	49·3°	55·0°	59·6°	66·5°	71·0°
P (mm.)	7·5	15·7	27·5	33·0	55·8	78·0	103	148	192
Temp.	76·3°	81·1°	86·1°	91·1°	96·1°	86·1°	57·3°	34·0°	22·2°
P (mm.)	247	312	370	456	547	409 *	119 *	49 *	35 *

* Decreasing temperature.

They determine the equation: $\log P$ (mm.) $= 10\cdot27 - 2747/T$ from 20 to 80°. Clearly, some irreversible change occurred at the highest temperatures. The apparent extrapolated b. p. of the adduct is 99°, its latent heat of vaporisation is 12·6 kcal. mole^{-1}, and Trouton's constant is 33·8 cal. deg.$^{-1}$ mole^{-1}.

The unsaturated vapour pressure of 0·119 mmole of adduct in a tensimeter (vol. 320 ml.) was 14·2 mm. at 54°, thus $K_p = 0\cdot12$ atm.

Reaction of Bisdimethylaminomethane–Trimethylborane with Trimethylamine.—The adduct was allowed to react with a slight deficiency of trimethylamine at room temperature for 1 hr.; fractionation of the volatile products indicated that 85% of the ditertiary amine had been displaced. This reaction was used to separate traces of dimethylamine (formed, *e.g.*, by hydrolysis) from bisdimethylaminomethane; addition of excess of trimethylborane to this mixture, followed by excess of trimethylamine, gave a mixture of solid $NHMe_2,BMe_3$ and NMe_3,BMe_3 (both of low volatility) together with easily separable NMe_3 and $CH_2(NMe_2)_2$.

Reaction of Bisdimethylaminomethane with Diborane.—When bisdimethylaminomethane (0·184 mmole) and excess of diborane (0·676 mmole) were mixed in the gas phase, a white smoke was immediately produced. This slowly settled on the walls of the vessel, together with translucent crystals; 0·495 mmole of diborane were recovered, giving a combining ratio $CH_2(NMe_2)_2 : BH_3$ of 1 : 1·98. The adduct was involatile *in vacuo* at room temperature, but sublimed slowly above about 70°.

Reaction of Bisdimethylaminomethane with Iodosilane.—When bisdimethylaminomethane (0·771 mmole) and iodosilane (2·242 mmoles) reacted together in the gas phase for 30 min., no hydrogen or silane was detected, and the sole volatile compound was excess of iodosilane (0·689 mmole). The white solid also produced had the composition: $CH_2(NMe_2)_2$–2·01 SiH_3I; it was almost involatile at room temperature.

Reaction of Bisdimethylaminosilane with Trimethylborane.—When bisdimethylaminosilane (0·366 mmole) and trimethylborane (0·806 mmole) reacted together in a 1-l. vessel, all the products were gaseous at room temperature. When part of the vessel was cooled to $-84°$, a white solid was formed, and 0·433 mmole of trimethylborane were recovered. The composition of the adduct was therefore: $SiH_2(NMe_2)_2$–0·96 BMe_3. In a small sealed tube, it melted at $-11°$. Vapour-pressure measurements of bisdimethylaminosilane–trimethylborane below its m. p. showed that considerable negative deviations from Raoult's law occur at low temperatures.

Reaction of Bisdimethylaminosilane–Trimethylborane with Trimethylamine.—A slight excess of trimethylamine was added to the adduct, and the whole allowed to warm to room temperature. After 1 hr., fractionation showed that displacement of bisdimethylaminosilane was complete. This reaction was used to purify bisdimethylaminosilane from traces of dimethylamine or trimethylborane (neither of which could be removed by fractional condensation) in a similar way to that described for bisdimethylaminomethane.

Reaction of Bisdimethylaminosilane with Diborane.—When bisdimethylaminosilane (0·267 mmole) and diborane (0·527 mmole) reacted together in the gas phase at room temperature, a fine white solid was formed. Part of the reaction vessel was then cooled to $-84°$ for 1 hr., and excess of diborane (0·263 mmole) was removed. The composition of the solid was therefore $SiH_2(NMe_2)_2$–1·97 BH_3. This adduct was readily volatile; its fractional condensation at $-84°$ trapped an approximately 1 : 1 adduct, whilst diborane passed through.

Properties of Bisdimethylaminosilane–Borane.—A sample of the 1 : 1 adduct was prepared from stoicheiometric amounts of reagents and sealed in a small tube. The m. p. (rapid heating) was 10°. Vapour pressures (in mm.) of various combining ratios are shown below:

	V. p./$-97°$	V. p./$-87°$	V. p./$-64°$
$SiH_2(NMe_2)_2$–0·93 BH_3	0·4	0·5	1·3
$SiH_2(NMe_2)_2$–0·97 BH_3	1·9	2·0	2·2
$SiH_2(NMe_2)_2$–0·99 BH_3	—	8·2	8·6

At $-46°$ and above, slow irreversible decomposition occurred. After several days, a sample of the monoborane adduct (0·254 mmole) in a small sealed tube at room temperature had produced some large glistening crystals. The tube was then heated to 120° for 12 hr.; the contents were all gaseous at this temperature. The products were then fractionated to yield (*a*) hydrogen (trace), (*b*) silane (0·119 mmole), (*c*) an inseparable mixture held at $-96°$ that contained boron, silicon, hydrolysable hydrogen, and dimethylamino-groups, and (*d*) impure dimethylamino-borane (0·235 mmole; m. p. 62—65°; v. p. 8·8 mm./19° (lit.,[29] m. p., 75°; v. p. 9·1 mm./23°). Hydrolysis of (*d*) with 2N-hydrochloric acid at 100° gave a ratio of hydrolysable hydrogen to boron of 2·01 : 1 (Calc. for Me_2NBH_2, 2·00 : 1).

Reaction of Bisdimethylaminosilane with Iodosilane.—When bisdimethylaminosilane (0·241 mmole) reacted with iodosilane (0·683 mmole) in the gas phase for 15 min., no hydrogen was formed. The products consisted of (*a*) iodosilane (0·495 mmole), (*b*) a liquid, held at $-64°$ (v. p. 21 mm./22°), which liberated iodine on standing, and (*c*) an involatile white solid.

Reaction of Trisdimethylaminosilane and Tetrakisdimethylaminosilane with Trimethylborane.— In neither case was any adduct formed, even at $-78°$. Trimethylborane could be recovered quantitatively at this temperature. Vapour-pressure measurements at low temperatures showed no significant negative deviations from Raoult's law.

Reaction of Trisdimethylaminosilane with Diborane.—Trisdimethylaminosilane (0·224 mmole) and diborane (0·552 mmole) reacted together in the gas phase to form a fine white powder. This solid readily sublimed *in vacuo*, and was allowed to mature at $-135°$ for 1 hr. Unused diborane (0·318 mmole) was recovered at this temperature, showing the solid to have the composition $SiH(NMe_2)_3$–2·09 BH_3. Recovery of diborane at higher temperatures yielded solids with less borane, *e.g.*, $SiH(NMe_2)_3$–1·76 BH_3 at $-64°$. Decomposition supervened above about $-40°$, and a pure 1 : 1 adduct could not be obtained in this way.

Trisdimethylaminosilane–Borane.—A sample of composition $SiH(NMe_2)_3$–0·95 BH_3 prepared by direct mixing showed the following vapour pressures:

Temp.	$-97°$	$-84°$	$-64°$	$-45°$	$-23°$	$-97°$
V. p. (mm.)	1·5	1·6	1·8	2·5	5·1	2·2

Slight decomposition was evidenced at $-23°$. The sample (0·339 mmole) was sealed in a small tube under the same conditions as bisdimethylaminosilane–borane. The products were: hydrogen (trace), silane (0·058 mmole), and a mixture of volatile compounds, which was partly liquid and partly solid at room temperature; this mixture could not be quantitatively separated. Estimations of boron, silicon, and hydrolysable hydrogen, infrared spectra, and known volatilities were consistent with the presence of bisdimethylaminosilane and bisdimethyl-aminoborane[30] in the more volatile fractions and of trisdimethylaminosilane and dimethyl-aminoborane in the less volatile.

Reaction of Tetrakisdimethylaminosilane with Diborane.—Tetrakisdimethylaminosilane (0·252 mmole) and diborane (0·283 mmole) were condensed together and allowed to reach equilibrium at $-135°$ for $\frac{1}{4}$ hr. Diborane (0·160 mmole) was rapidly recovered at this temperature, corresponding to a solid composition of $Si(NMe_2)_4$–0·99 BH_3. There was no evidence for a 1 : 2 adduct. Diborane could be slowly removed from the solid, held at $-135°$, by evacuation; the composition of the residue was $Si(NMe_2)_4$–0·77 BH_3 (after 1 hr.) and $Si(NMe_2)_4$–0·65 BH_3 (after 2 hr.).

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[29] A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, 1949, **71**, 3451.
[30] A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, 1951, **73**, 955.