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CONTRIBUTION TO THE CHEMISTRY OF BORON
LI*. (SILYLAMINO)BORANES BY CLEAVAGE OF BORON–HALOGEN BONDS WITH HEPTAMETHYLDISILAZANE

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SUMMARY

Treatment of various mono-, di- and trihaloboranes with heptamethyldisilazane leads to stepwise replacement of halogen by the (trimethylsilyl)methylamino group. The silylaminoboranes $Me_3Si–NMe–BR_2$ (R = Me, Ph, Me_2N) can be prepared by reaction of $(Me_3Si)_2NMe$ and the corresponding monohaloborane. Depending on the conditions the dihaloboranes $PhBCl_2$ and $MeBBr_2$ on treatment with heptamethyldisilazane afford the borazines (RBNMe), the bis(silylamino)boranes $RB(NMe–SiMe_3)_2$ or the novel chain compounds $Me_3Si–NMe–BR–NMe–BR–NMe–SiMe_3$ (R = Ph, Me), besides trimethylhalosilanes.

All the boron halides BF_3, BCl_3 and BBr_3 form 1/1 adducts with $(Me_3Si)_2NMe$ at low temperatures. Whilst the BF_3 adduct decomposes directly into $(FBNMe)_3$ and Me_3SiF, the BCl_3 and BBr_3 adducts yield *B*-haloborazines (XBNMe) via the thermally unstable (silylamino)boranes $X_2B–NMe–SiMe_3$. With an excess of $(Me_3Si)_2NMe$ the products are $FB(NMe–SiMe_3)_2$ and $ClB(NMe–SiMe_3)_2$, but with BBr_3 the tris(silylamino)borane $B(NMe–SiMe_3)_3$ is obtained.

INTRODUCTION

The reaction of silylamines with boron halides according to eqn. (1) was first described in 1950 by Burg and Kuljian[1], who observed the elimination of a silyl halide in this reaction and the formation of a (silylamino)borane, *i.e.* a compound having a Si–N–B unit. (Silylamino)boranes are potentially valuable synthetic reagents, as has been demonstrated by their applicability to the preparation of diborylamines[2,3] and other boron–nitrogen compounds[4,5].

Although cleavage of a silicon–nitrogen bond by a boron halide is a fairly general reaction (for a review see ref. 4), no systematic studies have previously been made and the scope of this reaction has not been fully explored. We report here in some detail on the behaviour of one single aminosilane, heptamethyldisilazane

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[*] For part L see ref. 29.

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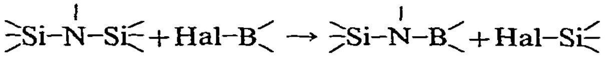
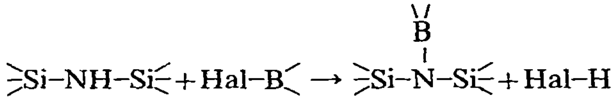
towards a series of mono-, di- and trihaloboranes. This aminosilane was chosen since this molecule has no NH groups and so side-reactions involving hydrogen halide elimination, as shown in eqn. (2), were precluded. Such eliminations have been reported by Wells and Collins in the reaction of boron trichloride with hexamethyldisilazane[6-8].



$$\geq\mathrm{Si{-}\overset{|}{N}{-}Si}\leq+\mathrm{Hal{-}B}< \;\rightarrow\; \geq\mathrm{Si{-}\overset{|}{N}{-}B}<+\mathrm{Hal{-}Si}\leq \quad (1)$$



$$\geq\mathrm{Si{-}NH{-}Si}\leq+\mathrm{Hal{-}B}< \;\rightarrow\; \geq\mathrm{Si{-}\overset{\overset{\backslash/}{B}}{\overset{|}{N}}{-}Si}\leq+\mathrm{Hal{-}H} \quad (2)$$

REACTIONS OF MONOHALOBORANES

It has been found that treatment of dimethylboron bromide, diphenylboron chloride or bis(dimethylamino)boron chloride with an equimolar quantity of heptamethyldisilazane leads to the expected mono(silylamino)borane in good yield according to eqn. (3). Therefore the Si–N bonds of the disilazane can be cleaved stepwise,

$$\mathrm{R_2BX+Me_3Si{-}NMe{-}SiMe_3 \longrightarrow R_2B{-}NMe{-}SiMe_3+Me_3SiX} \quad (3)$$

$$\mathrm{R = Me, Ph, Me_2N;\; X = Cl, Br}$$

since it has already been reported[5] that dimethylboron bromide and heptamethyldisilazane react in a 2/1 mole ratio to give bis(dimethylboryl)methylamine, $(\mathrm{Me_2B})_2$-NMe, and a similar stepwise cleavage has also been observed in the interaction of boron halides with hexamethyldisilazane[2,9,10]. In contrast, our attempts to prepare bis(diphenylboryl)methylamine, $(\mathrm{Ph_2B})_2\mathrm{NMe}$, by the reaction of diphenylboron chloride and heptamethyldisilazane in a 2/1 mole ratio were unsuccessful*. The ^{11}B and ^{1}H NMR spectra of the solid product were consistent with the formation of a mixture of triphenylboron and *B*-triphenyl-*N*-trimethylborazine. This does not preclude the possibility that bis(diphenylboryl)amine is an unstable intermediate in reaction (4), since it is well known that diborylamines are thermodynamically unstable with respect to a disproportionation into a borazine and a borane[3].

$$\mathrm{6\,Ph_2BCl+3\,Me_3Si{-}NMe{-}SiMe_3 \longrightarrow (PhBNMe)_3+3\,BPh_3+6\,Me_3SiCl} \quad (4)$$

REACTIONS OF DIHALOBORANES

The reaction of a dihaloborane with heptamethyldisilazane can lead to a variety of products due to the inherent difunctional nature of both reagents. Thus it is known[11] that equimolar quantities of phenylboron dichloride and heptamethyldisilazane react to give *B*-triphenyl-*N*-trimethylborazine and trimethylsilyl chloride. In addition to confirming this result—which implies that $\mathrm{PhClB{-}NMe{-}SiMe_3}$ is unstable at room temperature—we have found that methylboron dibromide and heptamethyldisilazane in a 1/1 mole ratio react quantitatively as shown in eqn. (5) to

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* Contrary to this result $(\mathrm{Ph_2B})_2\mathrm{NH}$ was obtained from diphenylboron chloride and hexamethyldisilazane (unpublished observations by H. Nöth and W. Regnet).

produce hexamethylborazine and trimethylsilyl bromide. Again no MeBrB–NMe–SiMe$_3$ could be isolated or detected.

$$3\ MeBBr_2 + 3\ Me_3Si{-}NMe{-}SiMe_3 \rightarrow (MeBNMe)_3 + 6\ Me_3SiBr \qquad (5)$$

It was anticipated that a reaction between (diethylamino)boron dichloride and heptamethyldisilazane would proceed according to eqn. (6), because aminoboron halides are generally less reactive than organoboron halides. Indeed a nearly quantitative yield of the silyl chloride was obtained along with a colourless liquid of ap-

$$Et_2NBCl_2 + Me_3Si{-}NMe{-}SiMe_3 \rightarrow Et_2N{-}BCl{-}NMe{-}SiMe_3 + Me_3SiCl \qquad (6)$$

proximate composition Et$_2$N–BCl–NMe–SiMe$_3$, but the complex proton NMR spectrum of the liquid indicated that the formulation was incorrect. The liquid gradually deposited a solid on standing at room temperature. This result is somewhat unexpected since Geymayer *et al.*[12–15] showed that a number of (silylamino)boranes of type (Me$_3$Si)$_2$N–BCl–NR$_2$ (R = ethyl, isopropyl, cyclohexyl, phenyl) are perfectly stable for 24 hours at 240°, while (Me$_3$Si)$_2$NBCl$_2$ decomposes readily, and one would not expect that the replacement of one trimethylsilyl group by a methyl group would greatly increase the tendency for trimethylhalosilane elimination.

More interesting than the reactions of equimolar amounts of dihaloboranes with heptamethyldisilazane are those in which the disilazane is present in excess. The products obtained by the interaction of 1 mole of phenylboron dichloride with 2.4 moles of heptamethyldisilazane were bis[(trimethylsilyl)methylamino]phenylborane, PhB(NMe–SiMe$_3$)$_2$, and the more condensed species Me$_3$Si–NMe–BPh–NMe–BPh–NMe–SiMe$_3$. The yield of trimethylchlorosilane was virtually quantitative. Under these conditions there are thus two competing reactions (6) and (7). It is likely that the very reactive PhBCl–NMe–SiMe$_3$, which has not yet been isolated, is a common intermediate in the reactions. It can be assumed that its reaction with excess

$$PhBCl_2 + Me_3Si{-}NMe{-}SiMe_3 \rightarrow PhB(NMe{-}SiMe_3)_2 + 2\ Me_3SiCl \qquad (6)$$

$$2\ PhBCl_2 + 3\ Me_3Si{-}NMe{-}SiMe_3 \rightarrow Me_3Si{-}NMe{-}BPh{-}NMe{-}BPh{-}NMe{-}SiMe_3 + 4\ Me_3SiCl \qquad (7)$$

disilazane produces PhB(NMe–SiMe$_3$)$_2$ which in turn interacts with PhB(Cl)–NMe–SiMe$_3$ to yield the solid, air stable, crystalline compound MeN(BPh–NMe–SiMe$_3$)$_2$ which may be distilled unchanged under high vacuum at 160°. Yields up to 68% of this new "diborylamine" can be obtained if the stoichiometry of the reaction corresponds to eqn. (7). Again trimethylsilyl chloride is produced quantitatively, and additional products are PhB(NMe–SiMe$_3$)$_2$ (7%) and (PhBNMe)$_3$ (3%).

Reactions of the type (6) and (7) are probably general for organoboron dihalides since when methylboron dibromide was treated with two molar equivalents of heptamethyldisilazane there was quantitative evolution of trimethylbromosilane and MeN(BMe–NMe–SiMe$_3$)$_2$ was formed in low yield. The other reaction products were (MeBNMe)$_3$ and probably MeB(NMe–SiMe$_3$)$_2$, as suggested by the NMR spectra, but these could not be separated from one another.

REACTIONS OF BORON TRIHALIDES

Burg and Kuljian[1] had shown that BF_3 and BCl_3 form 1/1 adducts with $N(SiH_3)_3$ of which the BCl_3 adduct decomposed more readily than $BF_3 \cdot N(SiH_3)_3$ with H_3SiX elimination. Since then a number of other adducts of boron trihalides and various aminosilanes have been observed, and the products of decomposition of the adducts with (disilylamino)boranes are (monosilylamino)boranes and/or borazine derivatives[4].

It has now proved possible to isolate several classes of compounds from the reaction of boron trihalides with heptamethyldisilazanes by employing various conditions. Thus, equimolar quantities of the disilazane and BF_3, BCl_3 and BBr_3 apparently react initially at low temperatures to give 1/1 adducts and the thermal stability in respect to Me_3SiX elimination decreases in the order $(Me_3Si)_2NMe \cdot BF_3 > (Me_3Si)_2NMe \cdot BCl_3 > (Me_3Si)_2NMe \cdot BBr_3$.

The adduct of heptamethyldisilazane with BF_3 decomposes into trimethylfluorosilane and *B*-trifluoro-*N*-trimethylborazine as shown in eqn. (8). The possible intermediate compound $F_2B{-}NMe{-}SiMe_3$ could not be isolated or detected in this decomposition. In contrast, the BCl_3 and BBr_3 adducts eliminate Me_3SiX slowly at low temperatures to give the corresponding (silylamino)boron dihalides as represented in eqn. (9). Quantitative studies of this decomposition, involving measuring the amount of Me_3SiX evolved in a given time from suspensions of the two adducts in pentane at −78°, −46°, −23° and 0°, showed that the decomposition of the BBr_3 adduct was always more rapid than of that with BCl_3. The compounds $Cl_2B{-}NMe{-}SiMe_3$ and $Br_2B{-}NMe{-}SiMe_3$ were isolated as colourless mobile liquids which decomposed rapidly at room temperature to the *B*-trihalo-*N*-trimethylborazine and the corresponding trimethylsilyl halide. The formation of $(ClBNMe)_3$ from the reaction

$$3\,(Me_3Si)_2NMe \cdot BF_3 \rightarrow (MeNBF)_3 + 6\,Me_3SiF \tag{8}$$

$$(Me_3Si)_2NMe \cdot BX_3 \rightarrow Me_3Si{-}NMe{-}BX_2 + Me_3SiX \tag{9}$$

$$3\,X_2B{-}NMe{-}SiMe_3 \rightarrow (XBNMe)_3 + 3\,Me_3SiX \tag{10}$$

$$X = Cl, Br$$

of equimolar amounts of BCl_3 and $(Me_3Si)_2NMe$ has already been noted by Abel *et al.*[11], but the latter did not report on the adduct and $Cl_2B{-}NMe{-}SiMe_3$.

It is still not clear whether the decomposition of $Cl_2B{-}NMe{-}SiMe_3$ is an intra- or intermolecular process, but it has been established[11] that BCl_3 can react with Me_3SiNEt_2 to give $B(NEt_2)_3$ and therefore successive cleavage of Si–N bonds of different molecules can occur. Since the two Si–N bonds in disilazane can be cleaved stepwise, the first being cleaved more readily than the second, it was thought that a dihalo[(trimethylsilyl)methylamino]borane might react more rapidly with another molecule of heptamethyldisilazane than with itself or another molecule of $X_2B{-}NMe{-}SiMe_3$. Reactions of the boron halides with more than one molar equivalent of heptamethyldisilazane confirmed the above mentioned reactivity order $BF_3 < BCl_3 < BBr_3$ with respect to Si–N bond cleavage. Thus, when BF_3 and heptamethyldisilazane were allowed to react in a 1/2 mole ratio the compound $FB(NMe{-}SiMe_3)_2$ was obtained, although in poor yield. In contrast, $ClB(NMe{-}SiMe_3)_2$ was readily obtained by reaction (12). However, when BBr_3 reacted with two moles of heptamethyldisi-

$$BF_3+2\ (Me_3Si)_2NMe \rightarrow FB(NMe{-}SiMe_3)_2+2\ Me_3SiF \qquad (11)$$

$$Cl_2B{-}NMe{-}SiMe_3+(Me_3Si)_2NMe \rightarrow ClB(NMe{-}SiMe_3)_2+Me_3SiCl \qquad (12)$$

$$BBr_3+3\ (Me_3Si)_2NMe \rightarrow B(NMe{-}SiMe_3)_3+3\ Me_3SiBr \qquad (13)$$

lazane essentially all the boron bromine bonds were cleaved, and the monobromo compound $BrB(NMe{-}SiMe_3)_2$ could not be isolated. The greater reactivity of boron tribromide towards heptamethyldisilazane was further demonstrated by the production of the tris(silylamino)borane $B(NMe{-}SiMe_3)_3$ in high yield in a reaction according to eqn. (13). A similar experiment using BCl_3 indicated rapid reaction of two B–Cl bonds, whilst reaction with the third Cl atom took place only very slowly under forcing conditions.

The (silylamino)borane $B(NMe{-}SiMe_3)_3$ has previously been obtained —although contaminated with some of the borazine derivative $(Me_3Si{-}NMe{-}B{-}NMe)_3$—in 42% yield from BBr_3 and three moles of $Me_3Si{-}NMeLi$ in ether[16], and is now more readily accessible by the process described here. It is a third example of a tris(silylamino)borane, the other two being $B[NHSiEt_3]_3$[10] and $(Me_3Si)_2NB(NHSiMe_3)_2$[8]. Attempts to prepare $B[N(SiMe_3)_2]_3$ were unsuccessful[12,13], and a model indicates the considerable steric strain in such a compound.

The proton and boron NMR data of the new compounds reported in this study are shown in Table 1. They will be discussed in detail along with other material in a subsequent report. But it should be noted at this stage that comparison of these [(trimethylsilyl)methylamino]boranes with the related (dimethylamino)boranes indicate a weaker B–N bond in the (silylamino)boranes; this would be expected as a

TABLE 1

NUCLEAR MAGNETIC RESONANCE DATA FOR VARIOUS (SILYLAMINO)BORANES

Compound	$\delta(^1H)$[a] (ppm)					$\delta(^{11}B)$[b] (ppm)
	$(CH_3)_3Si$	$SiNCH_3B$	BCH_3	BPh	BNMeB	
$Me_3SiNMeBCl_2$	−0.26	−2.77				−33.5 (−30.8)
$Me_3SiNMeBBr_2$	−0.33	−2.90				−28.8 (−25.7)
$Me_3SiNMeBMe_2$	−0.27	−2.77	−0.43			−51.2 (−44.6)
$Me_3SiNMeB(NMe_2)_2$[c]	−0.05	−2.45				−28.7 (−27.3)
$Me_3SiNMeBPh_2$	−0.55	−3.40		−7.74m		−48.0
$(Me_3SiNMe)_2BF$	−0.12	−2.61				−25.4 (−21.8)
	−0.14	−2.62				
	Δ=0.017	Δ=0.012				
$(Me_3SiNMe)_2BCl$	−0.21	−2.66				−32.9 (−27.9)
$(Me_3SiNMe)_2BPh$	−0.04	−2.78		−7.36m		−39.5 (−32.4)
$(Me_3SiNMe)_3B$	−0.22	−2.60				−33.8 (−27.3)
$(Me_3SiNMeBPh)_2NMe$	+0.24	−2.69		−7.30 −7.49	−2.43	−39.6
$(Me_3SiNMeBMe)_2NMe$	−0.15	−2.47	−0.38		−2.59	−41.1

[a] For ^1H NMR data $\delta(Me_4Si)=0$; m=multiplet. [b] For ^{11}B NMR data $\delta(BF_3 \cdot Et_2O)=0$; in parentheses $\delta(^{11}B)$ of corresponding boron compounds[17] in which the Me_3Si groups have been replaced by Me groups. [c] $\delta[N(CH_3)_2]$ −2.56 ppm.

result of competition by the silicon atom with the boron atom for the nitrogen's lone pair in back-bonding.

EXPERIMENTAL

General

Solvents were dried by conventional methods. All reactions were carried out in a high-vacuum apparatus or in an inert atmosphere. The trimethylsilyl chloride or bromide evolved in the experiments was identified on the basis of its infrared spectrum.

Analyses. Nitrogen was determined by the Kjeldahl method, chloride and bromide potentiometrically with silver nitrate, and boron as boric acid by titration with mannitol after the sample had been decomposed with sulphuric acid and hydrogen peroxide. Boron in the presence of fluorine was analysed by mannitol titration after addition of aluminium sulphate. The carbon and hydrogen analyses were generously performed by Dr. H. Klamberg of these laboratories to whom we extend our thanks.

Spectra. Infrared spectra were recorded on a Perkin Elmer Model 225 grating spectrophotometer, and peak positions were calibrated against polystyrene. The nuclear magnetic resonance spectra were obtained by means of a Varian Associates H.A. 100 instrument. Methylene chloride (with $\delta = -5.80$ ppm referred to tetramethylsilane) was used as internal standard for the proton resonance spectra, and boron trifluoride diethyletherate served as external standard for the boron-11 resonance studies.

Reagents. Heptamethyldisilazane was prepared from trimethylsilyl chloride and methylamine[18]. Dimethylboron bromide and methylboron dibromide were obtained by treatment of boron tribromide with tetramethyltin in the appropriate molar ratio[19-21] and phenylboron dichloride from boron trichloride and tetraphenyltin[22]. Diphenylboron chloride was prepared from bis(diphenylboron) oxide by a modification of the procedure of Lappert *et al.*[23]. Bis(dimethylamino)boron chloride and (dimethylamino)boron dichloride were isolated from the redistribution reactions between tris(dimethylamino)boron and boron trichloride[24,25]. (Diethylamino)boron dichloride was prepared analogously[25].

Reaction of dimethylboron bromide with heptamethyldisilazane (1/1 *mole ratio*)

Onto 17.85 g (101.8 mmole) of heptamethyldisilazane cooled in liquid air were condensed 12.29 g (101.7 mmole) of dimethylboron bromide and the mixture was warmed slowly to room temperature, with stirring, and allowed to stand for 2 days. The clear liquid thus obtained was twice fractionated in a nitrogen atmosphere at atmospheric pressure to give 13.70 g (89.5 mmoles, 88%) of trimethylsilyl bromide and 10.56 g (73.8 mmoles, 73%) of the compound $Me_3SiNMeBMe_2$ as a clear, colourless, mobile liquid b.p. 129.5–131.5°/747 mm. (Found: B, 7.1; N, 8.9. $C_6H_{18}BNSi$ calcd.: B, 7.6; N, 9.8%.) According to both ^1H and ^{11}B NMR spectra the sample contained no impurities.

Reaction of diphenylboron chloride with heptamethyldisilazane (1/1 *mole ratio*)

To 6.32 g (31.5 mmoles) of diphenylboron chloride cooled to −78° in a nitrogen-filled flask were added 6.91 ml (5.50 g, 31.4 mmoles) of heptamethyldisilazane.

The mixture was warmed to room temperature and agitated to dissolve the solid halide and then heated under reflux at 100° for 3 h to ensure completion of the reaction After the mixture had cooled to room temperature the flask was evacuated via a liquid-air-cooled trap to condense out trimethylsilyl chloride (3.36 g, 30.9 mmoles, 99%). The liquid residue which was involatile at room temperature was fractionated under reduced pressure to give the compound $Me_3SiNMeBPh_2$ (7.11 g, 26.6 mmoles, 85%) as a clear, colourless somewhat viscous liquid of b.p. 140°/0.1 mm. (Found: B, 4.0; N, 5.4. $C_{16}H_{22}BNSi$ calcd.: B, 4.0; N, 5.2%.)

Reaction of diphenylboron chloride with heptamethyldisilazane (2/1 *mole ratio*)

Heptamethyldisilazane (2.44 g, 13.9 mmoles) was added to diphenylboron chloride (5.62 g, 28.0 mmoles). The mixture was held at room temperature for 2 weeks and then the evolved trimethylsilyl chloride (1.20 g, 11.0 mmoles) was distilled off under reduced pressure. After an additional 24 h at 200° a total of 3.05 g (28.1 mmoles) of trimethylsilyl chloride had been evolved, but the solid reaction product, after vacuum sublimation at 120°, gave ^1H and ^{11}B NMR spectra indicating the presence of a mixture of triphenylboron and *N*-trimethyl-*B*-triphenylborazine (^{11}B NMR: two peaks of equal heights at −66.4 and −37.7 ppm).

A similar experiment in which the reaction mixture was held at 140° for 4 weeks yielded 98% of the anticipated quantity of trimethylsilyl chloride, but again the NMR spectra gave no evidence for the formation of $(Ph_2B)_2NMe$.

Reaction of bis(dimethylamino)boron chloride with heptamethyldisilazane (1/1 *mole ratio*)

A mixture of 9.62 g (71.6 mmoles) of bis(dimethylamino)boron chloride and 12.56 g (71.6 mmoles) of heptamethyldisilazane was heated under reflux for 3h. The liquid reaction product was fractionated, first at atmospheric pressure and then under reduced pressure to give 7.55 g (69.5 mmoles, 97%) of trimethylsilyl chloride and 3.6 g (18.1 mmoles, 25%) of the compound $Me_3SiNMeB(NMe)_2$ as a clear colourless liquid, b.p. 65–66°/8 mm. (Found: B, 5.2; N, 21.2. $C_8H_{24}BN_3Si$ calcd.: B, 5.4; N, 20.9%.)

Reaction of phenylboron dichloride with heptamethyldisilazane (1/1 *mole ratio*)

To 6.02 g (37.9 mmoles) of phenylboron dichloride were added 6.62 g (37.7 mmoles) of heptamethyldisilazane and the mixture was allowed to stand at room temperature for 3 weeks, during which time white crystals were slowly precipitated. The mixture was evacuated via a liquid-air-cooled trap and 7.91 g (72.8 mmoles, 96%) of trimethylsilyl chloride were collected. The involatile solid reaction product, which was essentially chloride free, was recrystallised from benzene to give *N*-trimethyl-*B*-triphenylborazine as small needles, m.p. 267° (lit.[26] 270°). (Found: B, 9.1; N, 11.3. $C_{21}H_{24}B_3N_3$ calcd.: B, 9.2; N, 12.0%.)

Reaction of methylboron dibromide with heptamethyldisilazane (1/1 *mole ratio*)

Methylboron dibromide (7.10 g, 38.2 mmoles) was condensed onto heptamethyldisilazane (6.76 g, 38.5 mmoles) which was cooled to −193°. The solid mixture was warmed to −78° when a very vigorous reaction took place after a few minutes to give a colourless liquid containing a little white solid. The mixture was warmed slowly to room temperature and after 2 days 11.49 g (75.1 mmoles, 98%) of trimethylsilyl bromide were condensed out from the product, held at 0°, into a liquid-air-cooled trap. The solid product was sublimed at 40° under high vacuum and a portion recrystallised from pentane at −78° to give hexamethylborazine[27] as white needles, m.p. 97–98°. (Found: B, 19.1; N, 24.4. $C_6H_{18}B_3N_3$ calcd.: B, 19.7; N, 25.5%.)

Reaction of (diethylamino)boron dichloride with heptamethyldisilazane (1/1 *mole ratio*)

To 5.4 g (35.1 mmoles) of (diethylamino)boron dichloride were added 7.7 ml (6.2 g, 35.1 mmoles) of heptamethyldisilazane and the mixture was allowed to stand for 12 h at room temperature and finally heated for 20 min to 150°. After the mixture had been cooled to 0°, trimethylsilyl chloride (4.4 g, 40.2 mmoles) was condensed out into a trap cooled in liquid air. The liquid reaction mixture was fractionated under reduced pressure to give 3.4 g of a cloudy liquid b.p. 48–50°/0.3 mm, which, on redistillation from a trap held at room temperature into one cooled in liquid air yielded a colourless, initially clear, liquid, $Me_3SiNMeBClNEt_2$. (Found: B, 5.2; Cl, 16.4; N, 12.3. $C_8H_{22}BClN_2Si$ calcd.: B, 4.9; Cl, 16.1; N, 12.7%.) The clear liquid became cloudy on standing for a few hours at room temperature, and the complex proton NMR spectrum indicated that the liquid was not the pure compound $Me_3SiNMeB(Cl)NEt_2$.

Reaction of phenylboron dichloride with heptamethyldisilazane (1/2.4 *mole ratio*)

Heptamethyldisilazane (25.37 g, 144.6 mmoles) was condensed onto phenylboron dichloride (9.50 g, 59.8 mmoles) cooled to −78° and the mixture warmed over a 1-h period to room temperature and allowed to stand for 2 weeks. The material which was readily volatile at room temperature was then condensed into a liquid-air-cooled trap and fractionation of the condensate gave 13.02 g (119.6 mmoles, 100%) of trimethylsilyl chloride and 7.06 g (40.3 mmoles) of unreacted heptamethyldisilazane. The reaction product, consisting of a mixture of solid and liquid was heated to 120° under high vacuum when a cloudy colourless liquid distilled out. Redistillation of the latter gave 7.63 g (26.1 mmoles, 44%) of the compound $(Me_3SiNMe)_2BPh$ as a clear colourless liquid, b.p. 73–75°/0.001 mm. (Found: B, 3.6; N, 9.5. $C_{14}H_{29}BN_2Si_2$ calcd.: B, 3.7; N, 9.6%.)

The solid product was then pumped under dynamic high vacuum conditions and warmed to approximately 90° to remove the adhering traces of $(Me_3SiNMe)_2BPh$ and finally distilled under dynamic high vacuum from an oil bath held at 160° using an air condensor. The material distilled as a clear colourless viscous liquid which gradually crystallised to a white solid mass, m.p. 94°. In this way were obtained 5.13 g (12.5 mmoles, 42%) of the compound $Me_3SiNMeBPhNMeBPhNMeSiMe_3$. (Found: C, 61.3; H, 8.8; B, 5.6; N, 9.9. $C_{21}H_{37}B_2N_3Si_2$ calcd.: C, 61.6; H, 9.1; B, 5.3; N, 10.3%.)

Reaction of phenylboron dichloride with heptamethyldisilazane (2/3 *mole ratio*)

Phenylboron dichloride (13.92 g, 87.6 mmoles) was allowed to react with heptamethyldisilazane (23.01 g, 131.2 mmoles) as in the previous experiment, except that the products were separated after only a 4-day reaction period. From the reaction mixture were obtained 19.02 g (175 mmoles, 100%) trimethylsilyl chloride, 1.87 g (6.4 mmoles, 7%) of $(Me_3SiNMe)_2BPh$ and 12.15 g (29.7 mmoles, 68%) of Me_3Si-

NMeBPhNMeBPhNMeSiMe$_3$. After the above products had been distilled from the reaction mixture white, needle-shaped crystals were sublimed at 200° under high vacuum from the brown oily residue. The crystals were washed with a little dry hexane to remove adhering Me$_3$SiNMeBPhNMeBPhNMeSiMe$_3$, and were identified by comparison with an authentic sample as *N*-trimethyl-*B*-triphenylborazine (0.32 g, 0.92 mmoles, 3%). No unreacted heptamethyldisilazane was recovered from the reaction products.

Reaction of methylboron dibromide with heptamethyldisilazane (1/2 *mole ratio*)

Onto 53.36 g (304.0 mmoles) of well-stirred heptamethyldisilazane cooled to −78° was condensed a total of 28.26 g (152.2 mmoles) of methylboron dibromide in five portions. After each addition the mixture was warmed slowly to approximately −20° in order to cause all the white solid (1/1 adduct) to pass into solution. The liquid mixture was left for 24 h at −78°, then slowly warmed to room temperature and allowed to stand for 2 weeks. The products were then submitted to fractional distillation, first at atmospheric pressure and then at successively reduced pressures. In this way were obtained (in decreasing order of volatility), 46.10 g (301.0 mmoles, 99%) of trimethylsilyl bromide, 18.93 g (107.9 mmoles) of unreacted heptamethyldisilazane, 8.09 g of a fraction, b.p. 80–110°/0.5 mm, which could not be separated into its components but which, on the basis of its infrared and NMR spectra, was a mixture of (Me$_3$SiNMe)$_2$BMe and hexamethylborazine, and as a final fraction 3.25 g (11.4 mmoles, 15%) of the compound Me$_3$SiNMeBMeNMeBMeNMeSiMe$_3$, as a clear colourless liquid, b.p. 68–73°/0.27 mm. (Found: B, 7.0; N, 14.4. $C_{11}H_{33}B_2N_3Si_2$ calcd.: B, 7.6; N, 14.7%.)

Similar experiments in which the reacting mole ratios of methylboron dibromide to heptamethyldisilazane were 2/3 and 1/3.2 gave somewhat poorer yields of the compound Me$_3$SiNMeBMeNMeBMeNMeSiMe$_3$, namely 11% and 13% respectively.

Reaction of boron trifluoride with heptamethyldisilazane (1/1 *mole ratio*)

Boron trifluoride (1052 cc SPT, 47.0 mmoles) was condensed onto heptamethyldisilazane (8.24 g, 47.0 mmoles) cooled to −78°. After 3 h the white solid adduct thus produced was warmed slowly to room temperature when the pressure in the system gradually increased and the solid slowly dissolved to give a colourless liquid. Three weeks later the mixture was cooled to −23° and connected to a trap cooled in liquid air when 7.87 g (85.4 mmoles, 91%) of trimethylsilyl fluoride were obtained, which was identified on the basis of its vapour pressure at 0° (v.p. 394 mm). The solid reaction product was resublimed under vacuum to give 2.49 g (14.1 mmoles, 90%) of white needles identified as *N*-trimethyl-*B*-trifluoroborazine, m.p. 86–88° (lit.[28] 90.5°).

Reaction of boron trichloride with heptamethyldisilazane (1/1 *mole ratio*)

Boron trichloride (6.01 g, 51.32 mmoles) was condensed onto a stirred solution of heptamethyldisilazane (9.01 g, 51.35 mmoles) in 150 ml dry pentane cooled to −78°, when a white precipitate was formed. After 16 h the suspension was pumped for 48 h via a liquid-air-cooled trap to condense out pentane together with any trimethylsilyl chloride and unreacted boron trichloride. Hydrolysis of the pentane condensate and subsequent analysis of the hydrolysate indicated that 0.05 g (0.40 mmoles) of boron trichloride had not reacted with the disilazane and 0.39 g (3.6 mmoles) of trimethylsilyl chloride had been evolved. Approximately 100 ml of pentane were condensed back onto the adduct and the suspension held at −46° for 30 h, recooled to −78° and the solvent and evolved trimethylsilyl chloride then condensed out into a liquid-air-cooled trap. Analysis of the hydrolysed pentane condensate indicated the evolution of a further 0.52 g (4.8 mmoles) of trimethylsilyl chloride. The process was repeated for suspensions in 100 ml pentane at various higher temperatures and the results are tabulated below.

Reaction conditions	Me_3SiCl evolved
4 days at −78°	3.6 mmoles
7 days at −78° plus 30 h at −46°	4.8
6 days at −78° plus 50 h at −23°	11.6
5 days at −78° plus 175 h at 0°	32.5
Total	52.5

Complete reaction according to the equation:

$$(Me_3Si)_2NMe + BCl_3 \rightarrow Me_3SiNMeBCl_2 + Me_3SiCl$$

requires the evolution of 50.9 mmoles of trimethylsilyl chloride.

Finally the reaction product was held at 0° and pumped via a trap cooled to −78° when 5.0 g (27.2 mmoles, 53%) of the compound $Me_3SiNMeBCl_2$ was obtained as a white solid which melted at −38° to a clear colourless liquid. (Found: B, 5.9; Cl, 39.0; N, 7.1. $C_4H_{12}BCl_2NSi$ calcd.: B, 5.9; Cl, 38.6; N, 7.6%].

Thermal decomposition of the compound $Me_3SiNMeBCl_2$. An ampoule containing a sample of the compound $Me_3SiNMeBCl_2$, which had stood at room temperature for 2 months, was connected to an evacuated trap cooled in liquid air to condense out pure trimethylsilyl chloride. The involatile residue in the ampoule consisted of white, needle-shaped crystals of *N*-trimethyl-*B*-trichloroborazine. (Found: B, 13.9; Cl, 46.8. $C_3H_9B_3Cl_3N_3$ calcd.: B, 14.4; Cl, 47.1%.)

Reaction of boron tribromide with heptamethyldisilazane (1/1 *mole ratio*)

Boron tribromide (14.65 g, 58.46 mmoles) was allowed to react with a solution of heptamethyldisilazane (10.26 g, 58.46 mmoles) in 150 ml dry pentane cooled to −78° to give a suspension of white solid. The pentane, unreacted boron tribromide and trimethylsilyl bromide were condensed off into an evacuated liquid-air-cooled trap from the suspension held at −78° over a 4-day period. Analysis of the hydrolysed pentane condensate indicated that 0.16 g (0.65 mmoles) of boron tribromide had not reacted and that 1.62 g (10.62 mmoles) of trimethylsilyl bromide had been evolved. Pentane (approximately 100 ml) was then condensed back onto the adduct and the rate of trimethylsilyl bromide evolution at various temperatures was determined as described above for the adduct with boron trichloride. The results are tabulated below.

Reaction conditions	Me_3SiBr evolved
4 days at −78°	10.60 mmoles
7 days at −78° plus 28 h at −46°	14.24
8 days at −78° plus 40 h at −23°	22.74
11 days at −78° plus 9 h at 0°	17.99
Total	65.57

Total reaction according to the equation:

$$(Me_3Si)_2NMe+BBr_3 \rightarrow Me_3SiNMeBBr_2+Me_3SiBr$$

requires the evolution of 57.81 mmoles of trimethylsilyl bromide. Thus the reaction has already gone beyond this stage by about 10%.

Finally the reaction product was held at 0° and pumped via a trap cooled to −78° and the condensate twice recrystallised from pentane at −78° to give 6.88 g (25.22 mmoles, 44%) of the compound $Me_3SiNMeBBr_2$ as a clear colourless liquid, m.p. −22°. (Found: B, 4.2; Br, 59.3; N, 5.2. $C_4H_{12}BBr_2NSi$ calcd.: B, 4.0; Br, 58.6; N, 5.1%.)

Thermal decomposition of the compound $Me_3SiNMeBBr_2$. A sample of the compound $Me_3SiNMeBBr_2$ which had stood at room temperature for several months was investigated in a manner analogous to that described above for the thermolysis of $Me_3SiNMeBCl_2$. The sole reaction products were trimethylsilyl bromide and white needle-shaped crystals of *N*-trimethyl-*B*-tribromoborazine, m.p. 143°. (Found: B, 8.7; Br, 64.3. $C_3H_9B_3Br_3N_3$ calcd.: B, 9.0; Br, 66.7%.)

Reaction of boron trifluoride with heptamethyldisilazane (1/2 *mole ratio*)

Boron trifluoride (1037 cc STP, 46.3 mmoles) was condensed onto heptamethyldisilazane (16.25 g, 92.6 mmoles) cooled to −78°. After all the halide had been absorbed the resultant white suspension was warmed to room temperature, allowed to stand for 1 week and then heated to 60° for 3 h to ensure that the reaction had gone to completion. Fractionation of the colourless liquid product yielded 8.02 g (87.0 mmoles, 94%) of trimethylsilyl fluoride, 6.59 g (37.6 mmoles) of unreacted heptamethyldisilazane contaminated with *N*-trimethyl-*B*-trifluoroborazine, and 2.64 g (11.3 mmoles, 25%) of the compound $(Me_3SiNMe)_2BF$ as a clear colourless liquid, m.p. −20°, b.p. 71.5°/9.5 mm. (Found: B, 4.3; N, 12.2. $C_8H_{24}BFN_2Si_2$ calcd.: B, 4.6; N, 12.0%.)

The yield of $(Me_3SiNMe)_2BF$ was not improved when the reacting ratio of heptamethyldisilazane to boron trifluoride was increased to 3.9/1 and the compound isolated by distillation employing a spinning band column.

Reaction of $Me_3SiNMeBCl_2$ *with heptamethyldisilazane* (1/1 *mole ratio*)

Onto 10.70 g (58.2 mmoles) of $Me_3SiNMeBCl_2$ held at −78° were condensed 10.17 g (58.0 mmoles) of heptamethyldisilazane and the mixture warmed slowly to room temperature. After eight days the clear liquid was connected to an evacuated, liquid-air-cooled trap to condense out 6.66 g (61.3 mmoles, 106%) of trimethylsilyl chloride. Two fractionations of the residue under reduced pressure gave the compound $(Me_3SiNMe)_2BCl$ as a clear colourless liquid, m.p. −24°, b.p. 48°/0.5 mm. (Found: B, 4.1; Cl, 14.4; N, 11.7. $C_8H_{24}BClN_2Si_2$ calcd.: B, 4.3; Cl, 14.1; N, 11.2%.) The compound decomposes slowly at room temperature with evolution of trimethylsilyl chloride, but appears to be stable at −78°.

Reaction of boron tribromide with heptamethyldisilazane (1/3 *mole ratio*)

Onto 21.7 g (123.6 mmoles) of heptamethyldisilazane cooled to −78° were condensed 10.3 g (41.2 mmoles) of boron tribromide and the suspension slowly warmed to 0°. After 12 h all the adduct had passed into solution and the clear liquid was warmed to room temperature and allowed to stand for 4 days. Fractionation at atmospheric and then at successively reduced pressures yielded 18.8 g (122.2 mmoles, 99%) of trimethylsilyl bromide, 3.4 g (19.4 mmoles) of unreacted heptamethyldisilazane and 4.4 g (13.7 mmoles, 33%) of the compound $(Me_3SiNMe)_3B$ as a clear colourless liquid, b.p. 55–57°/0.001 mm. (Found: B, 3.2; N, 13.4. $C_{12}H_{36}BN_3Si_3$ calcd.: B, 3.4; N, 13.2%.)

Even when the reacting ratio of heptamethyldisilazane to boron tribromide was increased to 4.8/1, the yield of the compound $(Me_3SiNMe)_3B$ was not improved. In an experiment when the reacting ratio of BBr_3 to disilazane was 1/2 no $(Me_3SiNMe)_2BBr$ could be isolated and 2.87 molar equivalents of trimethylsilyl bromide were evolved.

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REFERENCES

1 A. B. Burg and E. S. Kuljian, *J. Amer. Chem. Soc.*, 72 (1950) 3103.
2 H. Nöth, *Z. Naturforschg.*, *B*, 16 (1961) 618.
3 H. Nöth and H. Vahrenkamp, *J. Organometal. Chem.*, 16 (1969) 357.
4 O. J. Scherer, *Organometal. Chem. Rev.*, *A*, 3 (1968) 281.
5 H. Nöth and M. J. Sprague, *J. Organometal. Chem.*, to be published.
6 R. L. Wells and A. L. Collins, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 201.
7 R. L. Wells and A. L. Collins, *Inorg. Chem.*, 5 (1966) 1327.
8 R. L. Wells and A. L. Collins, *Inorg. Chem.*, 7 (1968) 419.
9 M. Becke-Goehring and H. Krill, *Chem. Ber.*, 94 (1961) 1059.
10 H. Jenne and K. Niedenzu, *Inorg. Chem.*, 3 (1964) 68.
11 E. W. Abel, D. A. Armitage, R. P. Bush and G. R. Willey, *J. Chem. Soc.*, (1965) 62.
12 P. Geymayer, E. G. Rochow and U. Wannagat, *Angew. Chem.*, 76 (1964) 499; *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 633.
13 P. Geymayer and E. G. Rochow, *Monatsh. Chem.*, 97 (1966) 429.
14 P. Geymayer and E. G. Rochow, *Monatsh. Chem.*, 97 (1966) 437.
15 P. Geymayer and E. G. Rochow, *Int. Symp. Organosilicon Chem., Sci. Commun.*, Prague, 1965, p. 306; *Chem. Abstr.*, 65 (1966) 10605*h*.
16 A. Gahm, Staatsexamensarbeit, University of Munich, 1966.
17 H. Nöth und H. Vahrenkamp, *Chem. Ber.*, 99 (1966) 1049.
18 R. C. Osthoff and S. W. Kanter, *Inorg. Syn.*, 5 (1957) 58.
19 H. Nöth and H. Vahrenkamp, *J. Organometal. Chem.*, 11 (1968) 399.
20 W. Gerrard, E. F. Mooney and R. G. Rees, *J. Chem. Soc.*, (1964) 740.
21 H. Nöth and P. W. Fritz, *Z. Anorg. Allg. Chem.*, 322 (1963) 297.
22 K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, 82 (1960) 4223.
23 E. W. Abel, S. H. Dandegaonker, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, (1965) 62.
24 R. J. Brotherton, A. L. McCloskey, L. L. Petterson and H. Steinberg, *J. Amer. Chem. Soc.*, 82 (1960) 6242.
25 J. Goubeau, M. Rahtz and H. J. Becher, *Z. Anorg. Allg. Chem.*, 275 (1954) 161.
26 J. H. Smalley and S. F. Stafiej, *J. Amer. Chem. Soc.*, 81 (1959) 582.
27 D. T. Haworth and L. F. Hohnstedt, *J. Amer. Chem. Soc.*, 82 (1960) 3860.
28 K. Niedenzu, *Inorg. Chem.*, 1 (1962) 943.
29 K. H. Hermannsdörfer, E. Matejcikova and H. Nöth, *Chem. Ber.*, in press.