(10) L. I. Elding and Ö. Gröning, to be submitted for publication.
(11) L. Ciavatta and M. Grimaldi, *J. Inorg. Nucl. Chem.*, **30**, 197 (1968).
(12) L. I. Elding and A. B. Gröning, *Chem. Scr.*, **11**, 8 (1977).
(13) L. I. Elding, *Proc. Int. Conf. Coord. Chem., 17th*, 39 (1976).
(14) L. I. Elding, *Inorg. Chim. Acta*, **28**, 255 (1978).
(15) I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).
(16) S. J. Lokken and D. S. Martin, *Inorg. Chem.*, **2**, 562 (1963).
(17) We have performed preliminary *T*-jump experiments, which indicate that the half-life for the acid hydrolysis of the trans chloride of Zeise's anion is approximately $5 \times 10^{-5}$ s.
(18) D. S. Martin, *Inorg. Chim. Acta, Rev.*, 87 (1967).
(19) Yu. N. Kukushkin and Yu. E. Vyazmenskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **15**, 1713 (1970).
(20) M. I. Gelfman and V. V. Kolin, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **16**, 403 (1971).
(21) R. Melanson, J. Hubert, and F. D. Rochon, *Acta Crystallogr., Sect. B*, **32**, 1914 (1976).
(22) J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Crystallogr., Sect. B*, **27**, 366 (1971).
(23) Yu. N. Kukushkin, M. A. Kuzmina, and N. V. Spevak, *Radiokhimiya*, **15**, 716 (1973).
(24) M. A. Tucker, C. B. Colvin, and D. S. Martin, *Inorg. Chem.*, **3**, 1373 (1964).
(25) L. I. Elding, *Acta Chem. Scand.*, **24**, 2557 (1970).
(26) Yu. N. Kukushkin and V. V. Kirillov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **17**, 1351 (1972); **18**, 756 (1973).
(27) L. I. Elding and A. B. Gröning, submitted for publication in *Inorg. Chim. Acta*.
(28) L. I. Elding, unpublished results.
(29) R. Romeo, S. Lanza, and M. Tobe, *Inorg. Chem.*, **16**, 785 (1977).

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Contribution from the Paul M. Gross Chemical Laboratory,
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# Structural Isomerization of (Bis(trimethylsilyl)amino)phosphine Oxides

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The reactions of lithium bis(trimethylsilyl)amide with phosphoryl chlorides $ClP(O)X_2$ (X = F, Cl, Ph) result in the formation of the N-silylated phosphinimines $Me_3SiN{=}PX_2OSiMe_3$ rather than the isomeric phosphine oxides $(Me_3Si)_2NP(O)X_2$. Stereochemical arguments and $^{13}C$ NMR data provide support for the assignment of the imine structure.

## Introduction

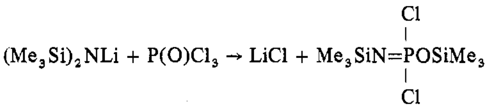
The reactions of lithium bis(trimethylsilyl)amide with simple phosphorus halides have been the subject of several recent investigations and, in some cases, conflicting results have appeared. For example, although $PF_3$ and $P(S)F_3$ react with $LiN(SiMe_3)_2$ to produce the expected products $(Me_3Si)_2NPF_2$[1,2] and $(Me_3Si)_2NP(S)F_2$,[2] $PF_5$ affords $(Me_3Si)_2NPF_2NSiMe_3$ if the reaction is carried out in ether[3] or $LiN(PF_4)_2$ if hexane is used as the solvent.[2] Even more inconsistent are the facts that Glemser et al.[4] report (bis(trimethylsilyl)amino)difluorophosphine oxide (**1**) as the product of the reaction (eq 1) of $P(O)F_3$ with $LiN(SiMe_3)_2$ in ether solution, while Fluck[5] has observed silicon–nitrogen bond cleavage under essentially the same conditions (eq 2).

$$(Me_3Si)_2NLi + P(O)F_3 \rightarrow LiF + \underset{\mathbf{1}}{(Me_3Si)_2NP(O)F_2} \qquad (1)$$

$$(Me_3Si)_2NLi + P(O)F_3 \rightarrow 2Me_3SiF + [F_2P(O)]_2NLi \qquad (2)$$

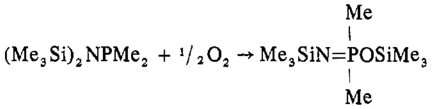
In still another study, Kling et al.[2] have obtained quantitative yields of $LiN[P(O)F_2]_2$ in hexane solution but mixtures of $LiN[P(O)F_2]_2$ and compound **1** in ether solution. However, these authors reported neither the yield of the phosphine oxide **1** nor its method of characterization.

Not only has there been difficulty in reproducing the synthesis of the (silylamino)phosphine oxide **1**, but the structural assignment of the compound may also be open to question. Thus, while the observation of two $Me_3Si$ signals in the $^1H$ NMR spectrum of **1** is attributed to hindered N–P bond rotation, a comparable spectrum obtained on the chlorine analogue[4] (eq 3) is cited as evidence for the rearranged phosphinimine structure **2**. A similar structural isomerization (eq 4) has been recently observed in our laboratory for the *P*-dimethyl compound.[6]



$$(Me_3Si)_2NLi + P(O)Cl_3 \rightarrow LiCl + Me_3SiN{=}\underset{Cl}{\overset{Cl}{P}}OSiMe_3 \qquad (3)$$

**2**



$$(Me_3Si)_2NPMe_2 + {}^1/_2O_2 \rightarrow Me_3SiN{=}\underset{Me}{\overset{Me}{P}}OSiMe_3 \qquad (4)$$

We report here an alternate synthetic route to compound **1** and an investigation of the generality of the phenomenon of $Me_3Si$ migration from nitrogen to oxygen in compounds of this type.

## Results and Discussion

In our hands, the reaction of $P(O)F_3$ with $LiN(SiMe_3)_2$ in ether solution produced only $Me_3SiF$ and a nonvolatile, white solid, presumed to be $LiN[P(O)F_2]_2$, as reported by Fluck.[5] No indication of the formation of **1** or any other liquid product was obtained. While this observation is not consistent with those of some other workers,[2,4] it may simply reflect the sensitivity of such reactions to small changes in reaction conditions as we have encountered previously.[6] Rather than attempt an exhaustive survey of this particular reaction, we chose to investigate other possible synthetic routes to compound **1**.

It was found to be impossible to prepare **1** by the direct oxidation (eq 5) of (bis(trimethylsilyl)amino)difluorophosphine. Even when heated at reflux in an atmosphere of oxygen for several hours, the phosphine resisted oxidation. By comparison, the less sterically hindered compound $Me_2NPF_2$ can be oxidized under considerably milder conditions.[7]

$$(Me_3Si)_2NPF_2 + O_2 \xrightarrow{155\ °C} \text{no reaction} \qquad (5)$$

Alternatively, when difluorophosphoryl chloride was allowed to react (eq 6) with an ether solution of $LiN(SiMe_3)_2$, the product obtained in 55% yield was a clear colorless liquid whose boiling point, infrared spectrum, and NMR ($^1H$ and $^{19}F$) spectra are identical with the data reported[4] for $(Me_3Si)_2NP(O)F_2$. This is taken as strong evidence that we have indeed prepared the same compound as the earlier workers.[4] The reaction (eq 6) is quite reproducible, giving high

$$(Me_3Si)_2NLi + ClP(O)F_2 \rightarrow LiCl + (Me_3Si)_2NP(O)F_2 \qquad (6)$$

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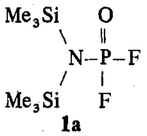
**Table I.** $^{13}C\{^1H\}$ NMR Data[a] for Some *N*-Trimethylsilylphosphinimines

| | NSiMe$_3$ | | OSiMe$_3$ | |
|---|---|---|---|---|
| | $\delta(^{13}C)$ | $^3J(^{31}P-^{13}C)$ | $\delta(^{13}C)$ | $^3J(^{31}P-^{13}C)$ |
| $Me_3SiNPF_2OSiMe_3$ | 2.27 | 4.76[b] | 0.41 | 1.95 |
| $Me_3SiNPF_2Ph$ | 2.79 | 4.52[c] | | |
| $Me_3SiNPCl_2OSiMe_3$ | 2.07 | 6.29 | 0.87 | 2.20 |
| $Me_3SiNPPh_2OSiMe_3$ | 3.80 | 3.48 | 1.60 | 1.47 |
| $Me_3SiNPMe_2OSiMe_3$[d] | 3.52 | 3.97 | 1.28 | 1.10 |

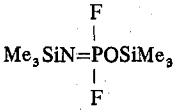
[a] Chemical shifts in ppm relative to $Me_4Si$; coupling constants in Hz; solvent is $CDCl_3$. [b] $^4J_{FC} = 0.80$ Hz. [c] $^4J_{FC} = 1.27$ Hz. [d] Data taken from ref 6.

yields, provided that the $P(O)F_2Cl$ is carefully distilled to remove any dissolved HCl.

The question still remaining concerns the structural assignment (**1a** or **1b**) of this reaction product with the critical point being the interpretation for the observation of nonequivalent $Me_3Si$ groups in the $^1H$ NMR spectrum. Glemser et al.[4] have attributed this nonequivalence to hindered N–P bond rotation in the aminophosphine oxide (**1a**) but recent studies of the dynamic stereochemistry of phosphorus–nitrogen compounds conflict sharply with such an explanation. The rotational barriers in (bis(trimethylsilyl)amino)phosphines, $(Me_3Si)_2NPX_2$ (X = Me, F, Cl, $CF_3$), are not extraordinary and, even in the highest extreme (X = $CF_3$), $Me_3Si$ nonequivalence is not observed in the ambient temperature spectrum.[1] Moreover, Jennings and co-workers[8] have shown that oxidation of an aminophosphine results in a lowering of the N–P rotational barrier. The combination of these stereochemical observations leads us, therefore, to assign the phosphinimine structure **1b** to the compound. This structure results simply from a $Me_3Si$ migration from nitrogen to oxygen, a process that has been observed previously in silyl-substituted amides,[9] anilides,[10] sulfinic amides,[11] and phosphoramidates.[12]



**1a**

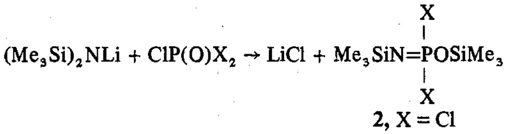


$$Me_3SiN{=}\overset{\displaystyle F}{\underset{\displaystyle F}{P}}OSiMe_3$$

**1b**

A second, and perhaps more compelling, line of evidence for the structural isomerization (**1a** → **1b**) consists of the $^{13}C$ NMR data (Table I) obtained for **1b** and related compounds. The spectra of **1b** and the model compound $Me_3SiN{=}PF_2Ph$[3] both contain a doublet of triplets in the $Me_3Si$ region indicating that the $Me_3SiN{=}PF_2$ moiety is a structural feature in both molecules. In fact, the observation of a substantial P—N—Si—C coupling appears to be a general feature of N-silylated phosphinimines.[13] The less pronounced doublet in the $^{13}C$ NMR spectrum of **1b** is then reasonably assigned to the $OSiMe_3$ moiety. Similar $^{13}C$ NMR data have recently been reported for other systems containing the Si—N=P—O—Si linkage.[14]

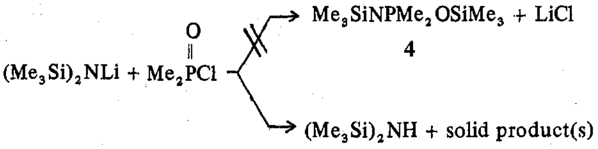
The reactions of $LiN(SiMe_3)_2$ with other phosphoryl chlorides (eq 7) have been carried out as part of this study



$$(Me_3Si)_2NLi + ClP(O)X_2 \rightarrow LiCl + Me_3SiN{=}\overset{\displaystyle X}{\underset{\displaystyle X}{P}}OSiMe_3 \qquad (7)$$

**2**, X = Cl
**3**, X = Ph

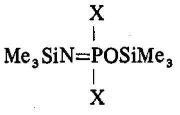
in order to assess the generality of the structural isomerization proposed for compound **1** and to substantiate the $^{13}C$ NMR spectral evidence. Our preparation of the chloro compound **2** confirms the results of Glemser et al.[4] while the diphenyl derivative **3** is reported here for the first time. Interestingly, the analogous dimethyl compound **4** could not be prepared by this procedure. When $LiN(SiMe_3)_2$ was treated with dimethylphosphoryl chloride (eq 8), the only liquid product



(8)

obtained after solvent removal was $(Me_3Si)_2NH$ indicating that the reaction proceeded with proton abstraction rather than chloride displacement by the amide anion. Other products from this reaction include an unidentified phosphorus-containing solid. The reactions of lithium silylamides with $Me_2PX_3$ (X = F, Cl) have also given anomalous results[13b] and the nature of the phosphorus products is under investigation. The dimethyl compound **4** is obtainable, however, from the direct oxidation of $(Me_3Si)_2NPMe_2$ (eq 4) as previously reported.[6]

All of these compounds (**1–4**) contain two $Me_3Si$ resonances in both the $^1H$ and $^{13}C$ NMR spectra with the *J*(PNSiC) coupling constant of ca. 3–6 Hz being especially characteristic of the $Me_3SiN{=}P$ moiety. Thus it is concluded that, for a wide variety of phosphorus substituents, *the compounds containing two Me$_3$Si groups exist as the phosphinimine isomers*,



$$Me_3SiN{=}\overset{\displaystyle X}{\underset{\displaystyle X}{P}}OSiMe_3$$

X = F, Cl, Me, Ph

and not as the phosphine oxides.

From the above, it should not be inferred that $Me_3Si$ migration to oxygen occurs in all (silylamino)phosphine oxides since a few such compounds have indeed been reported[15] and, in one instance, an oxide–imine equilibrium has been observed.[12] These are cases, however, in which the compound contains only one trimethylsilyl substituent. In view of the rearrangements described here, we suggest that structural assignments be made with caution particularly when only one silyl group and, correspondingly, one NMR signal is present. In such cases, $^{13}C$ NMR may be a valuable spectroscopic tool for structure elucidation.

## Experimental Section

**Materials and General Procedures.** The phosphorus oxyhalides, $P(O)X_3$ (X = F, Cl), were obtained from commercial sources and used without further purification. Lithium bis(trimethylsilyl)amide,[1,16] diphenylphosphoryl chloride,[17] and dimethylphosphoryl chloride[18] were prepared according to published procedures. Difluorophosphoryl chloride,[19] prepared by the reaction of $PCl_5$ with $F_2PO_2H$, was distilled through a low-temperature fractionation column at −78 °C and retained in a U-trap at −117 °C to remove HCl. Ethyl ether was distilled from calcium hydride prior to use. Solvents for NMR studies were dried over molecular sieves. Standard vacuum and inert atmosphere techniques were used in all experiments. Proton, $^{19}F$, and $^{13}C\{^1H\}$ NMR spectra were recorded, respectively, on JEOL MH-100, Varian A 56/60, and JEOL FX-60 spectrometers. Infrared spectra were obtained on a Perkin-Elmer 297 spectrophotometer. Elemental analyses were performed at Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

***P*,*P*-Difluoro-*P*-trimethylsiloxy-*N*-trimethylsilylphosphinimine (1b).** A solution of $LiN(SiMe_3)_2$ (107 mmol) in ether (100 mL) was prepared in a 250-mL, nitrogen-filled flask equipped with a magnetic stirrer. The flask was attached to a vacuum system, cooled to −78 °C and evacuated. Difluorophosphoryl chloride (97 mmol) was allowed to distill into the stirred suspension of $LiN(SiMe_3)_2$ at −78 °C giving a colorless solution. When the mixture was allowed to warm to room temperature a white solid formed. The mixture was stirred 1 h and the bulk of the solvent was removed under vacuum. The remaining volatile components were distilled through a U-trap at −45 °C. The contents of the trap were then fractionally distilled to afford **1b** as a colorless liquid (13.17 g, 55% yield, bp 29–30 °C (7 Torr)). The $^1$H NMR ($\delta$ 0.12, singlet; $\delta$ 0.38, doublet, $J_{PH} = 0.8$ Hz), $^{19}$F NMR (+71.7 ppm, doublet, $J_{PF} = 965$ Hz), and infrared spectral data are in excellent agreement with results reported[4] previously for (bis(trimethylsilyl)amino)difluorophosphine oxide (**1a**). Anal. Calcd for $C_6H_{18}F_2NOPSi_2$: C, 29.37; H, 7.39. Found: C, 29.55; H, 7.69.

**P,P-Dichloro-P-trimethylsiloxy-N-trimethylsilylphosphinimine (2).** Using the procedure described by Glemser,[4] the reaction of $P(O)Cl_3$ with $LiN(SiMe_3)_2$ afforded compound **2** as a colorless liquid (50% yield, bp 28–29 °C (0.1 Torr)) identified by its $^1$H NMR and infrared spectra.[4]

**P,P-Diphenyl-P-trimethylsiloxy-N-trimethylsilylphosphinimine (3).** Diphenylphosphoryl chloride (18.5 mL, 100 mmol) was added slowly to a stirred solution of $LiN(SiMe_3)_2$ (100 mmol) in ether (125 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 20 min. After filtration and solvent removal, distillation afforded **3** as a low-melting white solid (18.8 g, 52% yield, bp 103–104 °C (0.01 Torr), mp 37–39 °C). Infrared spectrum (KBr disk): 3100 (s), 2950 (m), 2900 (w), 1430 (m), 1290 (s), 1240 (s), 1180 (s), 1120 (m), 1100 (m), 950 (s), 850 (vs), 740 (m), 720 (m), 690 (s) cm$^{-1}$. The $^1$H NMR spectrum (20% $CH_2Cl_2$ solution) consisted of two $Me_3Si$ singlets ($\delta$ −0.02 and 0.21) and a phenyl multiplet centered at $\delta$ 7.5. Anal. Calcd for $C_{18}H_{28}NOPSi_2$: C, 59.79; H, 7.81. Found: C, 60.03; H, 7.53.

**Attempted Preparation of P,P-Dimethyl-P-trimethylsiloxy-N-trimethylsilylphosphinimine (4).** A solution of $Me_2P(O)Cl$ (13.9 g, 124 mmol) in benzene (60 mL) was added to a stirred solution of $LiN(SiMe_3)_2$ (124 mmol) in ether (200 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 30 min. Solid products (slightly yellow) were removed by filtration and washed with hexane. Distillation of the filtrate gave only solvents and $(Me_3Si)_2NH$ (15 g, 75% yield) which was identified by comparison of its IR and $^1$H NMR spectra to those of an authentic sample. Elemental analysis (C, 21.87; H, 5.74; P, 19.08) of the solid indicates that it contains phosphorus product(s), the nature of which is still under investigation.

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**Registry No.** **1b**, 66416-57-7; **2**, 41309-94-8; **3**, 66416-58-8; $Me_3SiNPF_2Ph$, 61701-83-5; $LiN(SiMe_3)_2$, 4039-32-1; $ClP(O)F_2$, 13769-75-0; $ClP(O)Ph_2$, 1499-21-4; $^{13}$C, 14762-74-4.

### References and Notes

(1) R. H. Neilson, R. C.-Y. Lee, and A. H. Cowley, *Inorg. Chem.*, **16**, 1455 (1977).
(2) L. Kling, C. B. Colburn, and W. E. Hill, *J. Inorg. Nucl. Chem. Suppl.*, 5 (1976).
(3) P. Wisian-Neilson, R. H. Neilson, and A. H. Cowley, *Inorg. Chem.*, **16**, 1460 (1977).
(4) G. Czieslik, G. Flaskerud, R. Höfer, and O. Glemser, *Chem. Ber.*, **106**, 399 (1973).
(5) E. Fluck and E. Beuerle, *Z. Anorg. Allg. Chem.*, **412**, 65 (1975).
(6) J. C. Wilburn and R. H. Neilson, *Inorg. Chem.*, **16**, 2519 (1977).
(7) G. H. Sprenger and J. M. Shreeve, *J. Fluorine Chem.*, **4**, 201 (1974).
(8) J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2*, 1052 (1976).
(9) C. H. Yoder, W. C. Copenhafer, and B. DuBeshter, *J. Am. Chem. Soc.*, **96**, 4283 (1974).
(10) C. H. Yoder and A. D. Belber, *J. Organomet. Chem.*, **114**, 251 (1976).
(11) A. Blaschette, D. Rinne, and H. C. Marsmann, *Z. Anorg. Allg. Chem.*, **420**, 55 (1976).
(12) P. K. G. Hodgson, R. Katz, and G. Zon, *J. Organomet. Chem.*, **117**, C63 (1976).
(13) (a) W. Buchner and W. Wolfsberger, *Z. Naturforsch. B*, **29**, 328 (1974); (b) R. H. Neilson, unpublished results.
(14) R. Appel and J. Halstenberg, *Chem. Ber.*, **110**, 2374 (1977).
(15) See for example (a) R. Keat, *J. Chem. Soc. A*, 1795 (1970); (b) H. W. Roesky and H. H. Glere, *Z. Naturforsch., B*, **25**, 773 (1970); (c) C. Glidewell, *J. Organomet. Chem.*, **108**, 335 (1976).
(16) E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *Inorg. Synth.*, **8**, 19 (1966).
(17) E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 4296 (1965).
(18) K. A. Pollart and H. J. Harwood, *J. Org. Chem.*, **27**, 4444 (1962).
(19) H. Roesky, *Inorg. Synth.*, **15**, 194 (1974).

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# Preparation and Thermal Decomposition Reactions of Some *tert*-Butyldimethylsilyl-Substituted Aminoboranes[1]

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A number of (silylamino)boranes containing the bulky *tert*-butyldimethylsilyl group have been prepared by the reaction of the lithiated silylamines $t\text{-}BuMe_2SiN(R)Li$ (R = H, Me, $SiMe_3$) with various chloroboranes. The products are colorless liquids which in many cases decompose at or above room temperature to form borazines. The thermal stabilities of those compounds where R = $Me_3Si$ is high presumably because of the steric "protection" afforded the boron atom toward nucleophilic attack.

## Introduction

Although a large number of acyclic (silylamino)boranes have been synthesized since the initial report by Burg and Kulijian in 1950,[2] the vast majority have contained only methyl groups bonded to silicon. Thus, aside from a few compounds containing silyl,[2,3] triethylsilyl,[4,5] triphenylsilyl,[4] and various halogenated silyl groups,[6,7] relatively little is known about compounds containing the linkage $R_1(R_2)(R_3)Si\text{–}N\text{–}B$ ($R_1$, $R_2$, or $R_3 \neq$ Me).

Since a report by Corey[8] the *tert*-butyldimethylsilyl moiety has come into common use in organic synthesis as a "blocking group" for many alcohols and amines for which the trimethylsilyl group does not provide sufficient protection. The ability of this substituent to lower chemical reactivity is evidenced by the fact that the primary aminosilane $t\text{-}BuMe_2SiNH_2$ can be isolated at room temperature. This is in contrast to several less hindered primary and secondary aminosilanes (eq 1).[9]

$$2R_3SiN(H)R' \xrightarrow[<25\ ^\circ C]{-NH_2R'} (R_3Si)_2NR' \qquad (1)$$

$$R = H;\ R' = H, Me$$
$$R = Me;\ R' = H$$

The presence of large substituents in aminoboranes has occasionally led to the isolation of relatively rare four-[10–14] and eight-membered[15–17] ring systems instead of the more common borazine structure. For example, the thermal decomposition of [*tert*-butyl(trimethylsilyl)amino]dichloroborane resulted in