Journal of Organometallic Chemistry, 301 (1986) 15–25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SILYL-NITROGEN COMPOUNDS

I. REACTIONS OF DILITHIUM BIS(TRIMETHYLSILYL)HYDRAZINE WITH GROUP IV HALIDES

SHAM KUMAR VASISHT*, MOHINI SOOD, NIRUPMA SOOD and GURSHARAN SINGH
Department of Chemistry, Panjab University, Chandigarh-160014 (India)

(Received July 17th, 1985)

Summary

Dilithium 1,2-bis(trimethylsilyl)hydrazine (**1**) reacts with CCl_4, Me_3SiCCl_3 and CBr_4 to form predominantly bis(trimethylsilyl)aminocarbonimidic dichloride, bis(trimethylsilyl)aminoisocyanide and bis(trimethylsilyl)diazene, whereas similar reactions with $HCCl_3$, HCI_3, H_2CCl_2, H_2CI_2, $C_2H_4Cl_2$ or $C_2H_2Cl_4$ lead to increasing amounts of bis(trimethylsilyl)hydrazine. In addition to the hydrazone, $(Me_3Si)_2N{-}N{=}CH(Cl)$, the reaction of **1** with $CHCl_3$ forms a small amount of triazasilacyclopentane, $(Me_3Si)_2N{-}N{=}\overline{CN(NHSiMe_3)SiMe_2NHN}SiMe_3$. In contrast, Me_2SnCl_2 reacts with **1** to give tetraazadistannacyclohexane $[Me_2Sn(NSiMe_3)_2]_2$, whereas $SnCl_4$, $SnCl_2$ and $PbCl_2$ act mainly as oxidants and Me_2SiCl_2 forms polymers. Another product of the reaction of **1** with $SnCl_2$ or $PbCl_2$ is $LiN(SiMe_3)_2$ originating perhaps from $LiNH(SiMe_3)$ or $[LiNN(SiMe_3)_2]_2$.

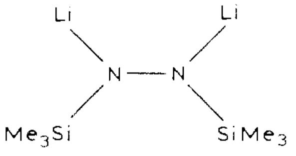
Introduction

Besides the synthesis and thermal stability of a variety of silylated alkalimetal tetrazenines [1] and diazanides [2,3], some reactions of lithium tris(trimethylsilyl)hydrazide [4] and tris(trimethylgermyl)hydrazine [5] have been reported. As part of our study on silyl-nitrogen compounds [6], we report here the reactions of Group IV halides with dilithium 1,2-bis(trimethylsilyl)hydrazine, $Li_2N_2(SiMe_3)_2$, undertaken with the aim of synthesizing nonmetallic hydrazines, hydrazones and redox reaction products.

Results and discussion

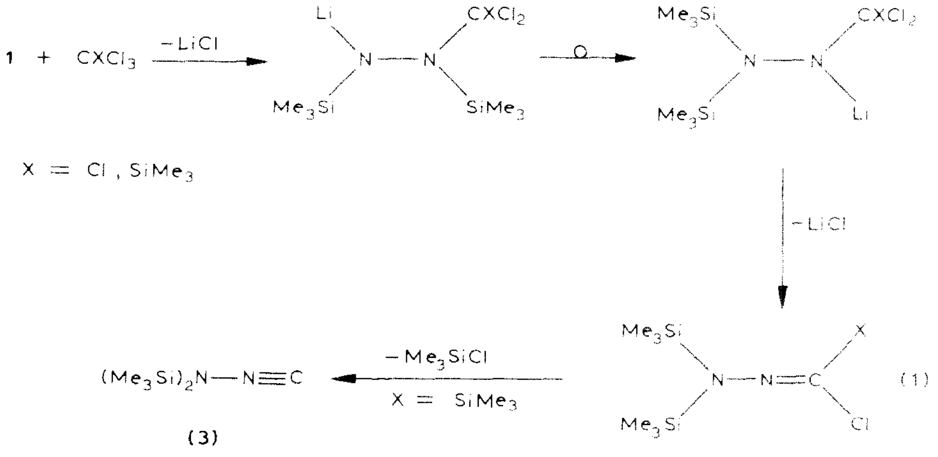
An isomeric mixture of bis(trimethylsilyl)hydrazine provides dilithium 1,2-bis(trimethylsilyl)hydrazine (**1**), [2]. An important feature of its reaction with CCl_4 or

0022-328X/86/$03.50



(1)

Me_3SiCCl_3 ($CXCl_3$) involves substitution followed by isomerization due to an anionic rearrangement [9] (eq. 1). Besides a 75% yield of bis(trimethylsilyl)amino-



(2, X = Cl)

carbonimidic dichloride $(Me_3Si)_2N{-}N{=}CCl_2$ (**2**) [7], the reaction mixture also contained small amounts of bis(trimethylsilyl)amine, $(Me_3Si)_2NH$ (BSA), and tris(trimethylsilyl)hydrazine, $(Me_3Si)_3N_2H$ (TrSH), which are attributed to the free radical decomposition of the intermediate bis(trimethylsilyl)diazene, $Me_3SiN{=}NSiMe_3$ (BSD), [8] originating from a redox side reaction of **1** with CCl_4 (cf. eq. 2).

Carbon tetrabromide behaves primarily as an oxidant to form BSD in a reaction with **1** at −78°C:

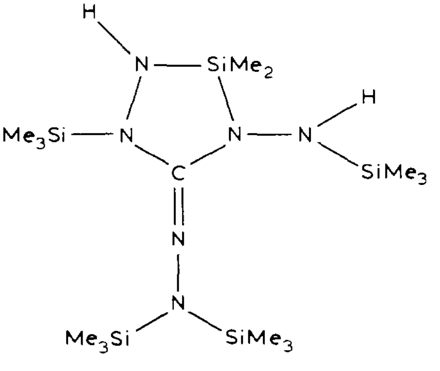
$$\mathbf{1} + CBr_4 \rightarrow Me_3SiN{=}NSiMe_3 + LiBr + LiCBr_3 \qquad (2)$$

Pure BSD could not be isolated by this method because it reacted further with $(Me_3Si)_2N{-}N{=}CBr_2$ (detected in the early stages but disappeared due to subsequent reactions), Me_3SiCBr_3 (formed from $LiCBr_3 + Me_3SiBr$) and CBr_4 to form $(Me_3Si)_2N{-}N{\equiv}C$, Me_3SiBr and N_2, in each step [4]. The reaction products at room temperature indicate almost 30% BSD thermolysis (BSA, TrSH and tetrasilylhydrazine, TSH) with the remainder undergoing the above reactions.

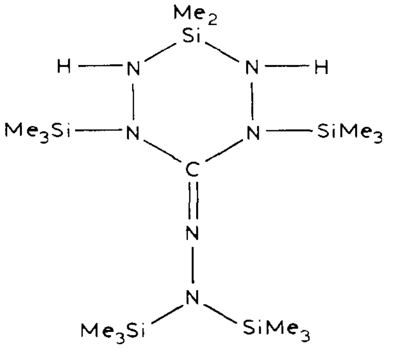
Compound **1** acts as a strong base and abstracts protons from weak acids like chloroform, iodoform, dichloromethane, diiodomethane, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane to form BSH and LiRX (X = halogen). Also **1** undergoes a redox reaction similar to eq. 2 to give BSD. Additionally, chloroform causes substitution followed by isomerization and elimination to provide *N*,*N*-bis(trimethylsilyl)chloroformylhydrazone (**4**).

$$\mathbf{1} + HCCl_3 \rightarrow \underset{(\mathbf{4})}{(Me_3Si)_2N{-}N{=}CH(Cl)} + 2LiCl \qquad (3)$$

Another product of the reaction of **1** and $HCCl_3$ is a white crystalline solid $C_{15}H_{44}N_6Si_5$ which appears to be either, 1-trimethylsilyl-3-dimethyl-4-silylamino-5-*exo*-[*N*,*N*-bis(trimethylsilyl)hydrazido]-1,2,4-triaza-3-silacyclopentane (**5a**) or 1,5-bis(trimethylsilyl)-3-dimethyl-6-*exo*-[*N*,*N*-bis(trimethylsilyl)hydrazido]-1,2,4,5-tetraaza-3-silacyclohexane (**5b**).



(5a)



(5b)

The mass spectrum of **5** shows the molecular ion with a relatively higher intensity (22%, 70 eV) at m/e 448, and the observed isotopic patttern (Fig. 1) agrees with that calculated for $C_{15}H_{44}N_6Si_5$ (see Experimental). Besides prominent fragments at 433 $(M-\text{Me})^+$, 346 $(M-\text{NNHSiMe}_3)^+$ and 274 $[M-\text{NN(SiMe}_3)_2{}^+]$ valuable metastable transitions for establishing fragmentation pathways have also been observed.

$$448 \xrightarrow[\text{calcd. } 418.5]{m^* = 419} 433$$

$$448 \xrightarrow[\text{calcd. } 267.2]{m^* = 267} 346$$

$$448 \xrightarrow[\text{calcd. } 167.6]{m^* = 167} 274$$

Fragmentation patterns and modes of decomposition, however, fail to distinguish between structures **5a** and **5b**.

The ^1H NMR spectra of **5** in benzene, Et_2O and CCl_4 are similar and consist of five signals with an integrated ratio of 18/18/6/1/1. The ^1H NMR spectrum in C_6H_6 shows the highest field signal at δ 0.130 ppm in line with the expectation for $(Me_3Si)_2N$ and a signal at 0.330 ppm due to Me_2Si protons. A singlet at δ 0.286 ppm for the remaining Me_3SiN protons supports structure **5b** because two separate signals could have been expected for Me_3SiN and Me_3SiNH protons in **5a**. On the other hand, the differently placed NH protons with singlets at 4.1 and 6.4 ppm favour **5a**. This is also supported by the IR spectrum with two separate bands at 3410 and 3365 cm^{-1} for ν(NH). In view of the above observations, structure **5a** is more likely.

Compound **5** undergoes easy stannylation with Me_3SnNEt_2 to form $C_{21}H_{60}N_6Si_5Sn_2$ with a probable structure of, 1-trimethylsilyl-2-trimethylstannyl-3-dimethyl-4-trimethylsilyltrimethylstannylamine-5-*exo*-[*N*,*N*-bis(trimethylsilyl)hydrazido]-1,2,4-triaza-3-silacyclopentane, $(Me_3Si)_2N-N{=}CN(NSiMe_3SnMe_3)SiMe_2\text{-}NSnMe_3NSiMe_3$. Its ^1H NMR spectrum in benzene shows the absence of NH protons.

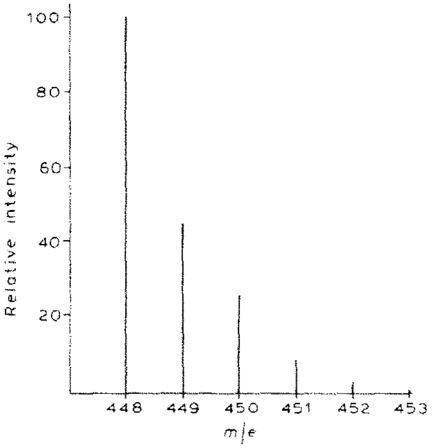


Fig. 1. Observed isotopic pattern of molecular ion in $C_{15}H_{44}N_6Si_5$.

The spectrum shows singlets at 0.124, 0.274, 0.300 and 0.34 ppm with the relative ratio at 3/3/3/1. The signal at 0.300 ppm is assigned to stannyl protons.

The reaction of **1** with iodoform is slower but similar to that with $CHCl_3$ except that it shows the formation of a small amount of $(Me_3Si)_2N-N{\equiv}C$ which may involve the intermediate formation of $(Me_3Si)_2N-N{=}C(H)I$. Diiodomethane reacts with **1** to give a 40% yield of *N*,*N*-bis(trimethylsilyl)formylhydrazone $(Me_3Si)_2N-N{=}CH_2$ [4b], whereas, CH_2Cl_2 behaves differently forming BSH, BSD and $LiN(SiMe_3)_2$.

1,2-Dichloroethane and 1,1,2,2-tetrachloroethane react with **1** to give high yields (70 and 100%, respectively) of BSH. The reactions are very fast and appear to occur by a free radical mechanism.

The reaction of dichlorodimethylstannane with **1** generates a set of two products

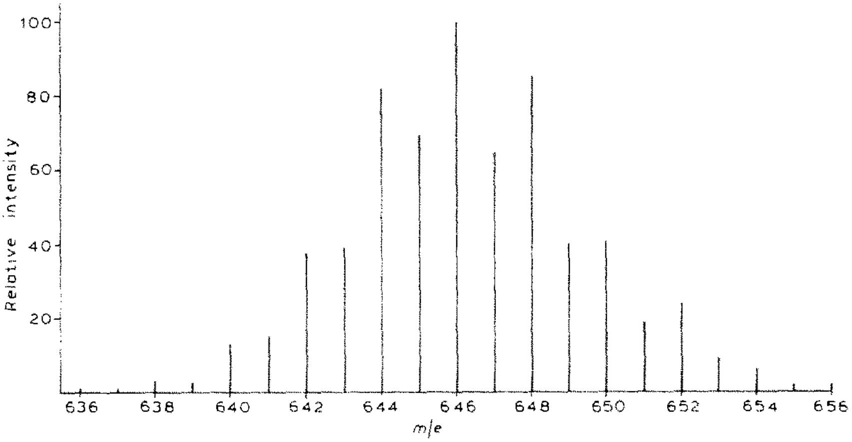
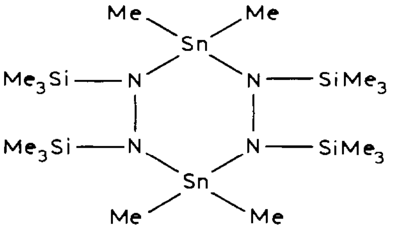


Fig. 2. Observed isotopic pattern of molecular ion in $C_{16}H_{48}N_4Si_4Sn_2$.

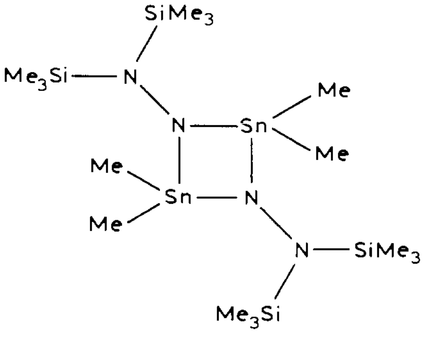
(eq. 4). The white crystalline compound $C_{16}H_{48}N_4Si_4Sn_2$ (**6**) has two possible

$$\mathbf{1} + Me_2SnCl_2 \begin{cases} \xrightarrow{80\%} \tfrac{1}{2}\left[Me_2Sn(NSiMe_3)_2\right]_2 \\ \qquad\quad (\mathbf{6}) \\ \xrightarrow{20\%} (Me_2SnCl)Me_3SiN\text{-}NSiMe_3(Me_2SnCl) \\ \qquad\qquad\qquad (\mathbf{7}) \end{cases} \qquad (4)$$

configurations: 1,2,4,5-tetrakis(trimethylsilyl)-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-distannacyclohexane (**6a**) or 1,3-bis[bis(trimethylsilyl)amino]-2,2,4,4-tetramethyl-1,3-diaza-2,4-distannacyclobutane (**6b**).



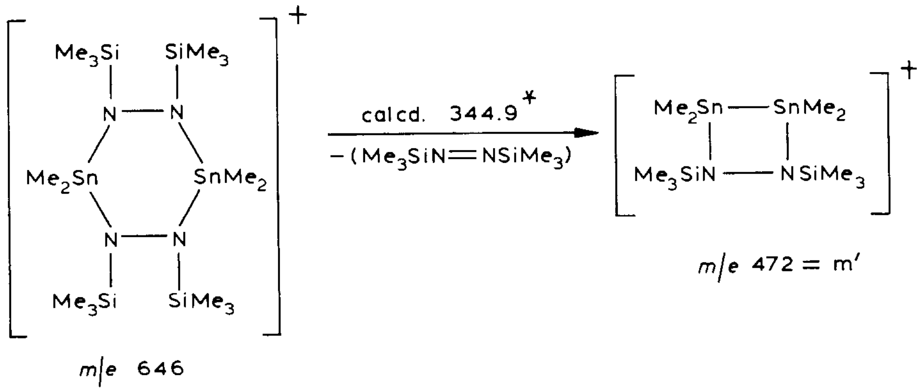
(6a)



(6b)

Simple elimination of LiCl followed by an anionic rearrangement [9] leading to $(Me_3Si)_2N\text{-}N(Me_2SnCl)Li$ can cause further intramolecular loss of LiCl to form a transitory stannimine $[(Me_3Si)_2N\text{-}N{=}SnMe_2]$, which dimerises immediately to give **6b**. On the other hand, intermolecular loss of LiCl will give rise to **6a**.

Mass spectral analysis of **6** shows a molecular ion peak at m/e 646 and the isotopic pattern (Fig. 2) agrees almost quantitatively with that calculated for $C_{16}H_{48}N_4Si_4Sn_2$ (see Experimental). In contrast to tetraazadisilacyclohexanes [10], the loss of silylnitrene $Me_3Si\text{-}\ddot{N}$: from the molecular ion is not observed in **6**. The first prominent fragment at 472 $(M - Me_3SiN{=}NSiMe_3)^+$ supported by the appropriate metastable ion at $m^\star = 345$ is the loss of the neutral molecule BSD:



This is understandable considering the initial ionization at the largely polar Sn–N bond. The molecular ion *m/e* 472 = M^+ shows successive loss of up to 3 Me radicals before losing the important fragments silylnitrene $\text{Me}_3\text{Si–}\dot{\text{N}}\text{:}$ at 385 ($M^+ - \text{Me}_3\text{SiN}$) and BSD at 298 ($M^+ - \text{Me}_3\text{SiN=NSiMe}_3$). The mass spectral analysis favours structure **6a** with the tetraazadistannacyclohexane configuration.

The ^{1}H NMR spectrum in benzene (ether) shows a silyl signal at δ 0.203 (0.140) ppm and a stannyl signal at 0.397 (0.440) ppm with an integrated ratio of 3/1.

The hydrazine $\text{(Me}_2\text{SnCl)(Me}_3\text{Si)N–N(SiMe}_3\text{)(Me}_2\text{SnCl)}$ (7) shows a different ^{1}H NMR spectrum in benzene (ether) with a silyl singlet at 0.183 (0.089) ppm and a stannyl singlet at 0.465 (0.483) ppm with a relative ratio of 3/2.

In contrast to this, SnCl_4 acts primarily as an oxidant (eq. 5, 6). The reaction of **1**

$$\mathbf{1} + \text{SnCl}_4 \rightarrow \text{Me}_3\text{SiN=NSiMe}_3 + 2\text{LiCl} + \text{SnCl}_2 \tag{5}$$

$$\text{Me}_3\text{SiN=NSiMe}_3 + \text{SnCl}_4 \rightarrow 2\text{Me}_3\text{SiCl} + \text{N}_2 + \text{SnCl}_2 \tag{6}$$

with Me_2SiCl_2 is complicated by a variety of products which are highly viscous and polymeric in nature. There appears to be a small yield of tetraazadisilacyclohexane $[\text{Me}_2\text{Si(NSiMe}_3)_2]_2$ contaminated with some other silyl-nitrogen derivatives. This has been tentatively derived from ^{1}H NMR spectra, wherein signals with a relative ratio of 1/3 are observed at δ 0.473 (0.533) and 0.233 (0.263) ppm in benzene (CCl_4) due to Me_2Si and Me_3Si protons, respectively.

Stannous chloride reacts with **1** predominantly in a redox reaction to form BSD which thermolyses to give BSA, TrSH and TSH [8]. Also, small amounts of lithium bis(trimethylsilyl)amide are formed due to a free radical reaction. This is supported by the reaction of **1** with PbCl_2, wherein, besides BSA, TrSH, TSH and BSH, a significant amount of $\text{LiN(SiMe}_3)_2$ (> 25% yield) is obtained as a white sublimate whose ^{1}H NMR spectra in Et_2O, benzene and CCl_4 show a singlet at 0.047, 0.128 and 0.043 ppm, respectively. However, its ^{1}H NMR spectrum in THF shows two broad signals at δ −0.113 and 0.03 ppm (very small). On treatment with Me_3SiCl this compound forms mainly $\text{(Me}_3\text{Si)}_3\text{N}$ and a small amount of $\text{HN(SiMe}_3)_2$ indicative of contamination of $\text{LiN(SiMe}_3)_2$ with $\text{LiNH(SiMe}_3)$. It appears that **1** undergoes free radical decomposition into $\text{Li(Me}_3\text{Si)N}^{\cdot}$ which interacts with the solvent to form $\text{LiNH(SiMe}_3)$. It then undergoes disproportionation (eq. 7).

$$2\text{LiNH(SiMe}_3) \rightarrow \text{LiN(SiMe}_3)_2 + \text{LiNH}_2 \tag{7}$$

$\text{LiN(SiMe}_3)_2$ can also arise as a decomposition product from the radical $\text{Li}\dot{\text{N}}\text{N(SiMe}_3)_2$ via tetraazanide [16]:

$$\begin{array}{l} [\text{LiN}_2\text{(SiMe}_3)_2]_2 \rightleftharpoons [\text{(Me}_3\text{Si)}_2\text{N–NLi–NLi–N(SiMe}_3)_2] \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad \text{(Me}_3\text{Si)}_2\text{NLi} + \text{N}_2 + \text{LiN(SiMe}_3)_2 \end{array} \tag{8}$$

Experimental

General comments

All investigations were carried out under vacuum and in the absence of air and moisture. All glassware was flame-dried also under vacuum. Bis(trimethylsilyl)hydrazine [11], butyllithium [12], dilithium bis(trimethylsilyl)hydrazine [2], dichlorodimethylstannane [13] and trimethylsilyltrichloromethane [14] were prepared as reported in the literature. Diethyl ether and tetrahydrofuran were dried over sodium benzophenoneketyl and the hydrocarbons were kept over sodium wire. Carbon halides and hydrohalides were rigorously dried. ^{1}H NMR spectra were recorded on a Varian EM-390 apparatus, IR spectra on a Perkin–Elmer 621 spectrometer and the mass spectrum on a Varian MAT CH7.

^{1}H NMR of Me_3Si protons, δ (ppm) in benzene (Et_2O): $(Me_3Si)_2N_2H_2$, 0.117 (0.066); $(Me_3Si)HN{-}NH(SiMe_3)$, 0.041 (0.000); $(Me_3Si)_2N{-}N(SiMe_3)_2$, 0.225 (0.205); $(Me_3Si)_2N{-}NH(SiMe_3)$, 0.133 and 0.108 doublet 2/1 (0.095); $(Me_3Si)_2NH$, 0.087 (0.050); $LiN(SiMe_3)_2$, 0.128 (0.047); $Me_3SiN{=}NSiMe_3$, 0.260 (0.200); $(Me_3Si)_3N$, 0.047 (0.215); Me_3SiCl, 0.208 (0.400); Me_3SiBr, 0.334 (0.550); Me_2SnCl_2, 0.400 (0.520); Me_3SiCCl_3, 0.144 (0.360); $Me_3SiCHCl_2$ (CCl_4), 0.27 [15]; $Me_3SiCH_2Cl(CCl_4)$, 0.14 [15]; $(Me_3Si)_2N{-}N{=}CCl_2$, 0.135 (0.160); $(Me_3Si)_2N{-}N{=}CBr_2$, 0.140 (0.167); Me_3SiCBr_3, 0.193 (0.400); $(Me_3Si)_2N{-}N{\equiv}C$, 0.070 (0.255).

General procedure

Dilithium bis(trimethylsilyl)hydrazine (**1**) (40 mmol, 7.520 g) was suspended (dissolved) in 40–50 ml of Et_2O (THF) and cooled to −40 (to −78°C). The required amounts of carbon halides (80 mmol or as stated) and of silicon, tin or lead halides (40 mmol or as stated) were added dropwise (or in small quantities) and the reaction mixture was allowed to warm slowly to room temperature with stirring. It was filtered to isolate LiX (X = Cl, Br or I). The ^{1}H NMR spectrum of a part of the filtrate was studied. The main filtrate was carefully evacuated to remove the solvents (up to 60 Torr/room temperature) and then fractionated (sublimed) to isolate various products. These products were refractionated in an appropriate column or resublimed to isolate pure fractions which were characterised mostly by ^{1}H NMR (in the case of known compounds) and other methods which are indicated in each case. The yield of pure products, obtained in significant amounts, is based on the amount isolated, whereas that of unseparable mixtures or very small amounts of compounds is calculated from ^{1}H NMR integrated ratios after adding a known amount of cyclohexane or toluene.

Reaction with CCl_4

The reaction of **1** with CCl_4 in ether occurring at about −50°C gave a white solid LiCl (77 mmol) and a light greenish yellow solution changing to yellow at room temperature. Its fractional distillation provided bis(trimethylsilyl)hydrazine, (BSH) (2 mmol) at 55°C/10 Torr; $(Me_3Si)_2NH$ (BSA) (4 mmol) at 50°C/60 Torr and $(Me_3Si)_2NNH(SiMe_3)$, (TrSH) (1 mmol) and $(Me_3Si)_2N{-}N{=}CCl_2$ (30 mmol) together at 75–80°C/10 Torr. $(Me_3Si)_2N{-}N{=}CCl_2$ was purified by redistillation or crystallisation from n-pentane and characterised [4,7].

Reaction with Me_3SiCCl_3

An equimolar reaction with **1** in Et_2O at −78°C was slow and provided an almost quantitative yield of LiCl. The colourless filtrate was fractionated. The ^{1}H NMR spectrum of the fractions at 55–60°C/740 Torr and 95–100°C/740 Torr in CCl_4 indicate the presence of Me_3SiCl (17 mmol) and Me_3SiCH_2Cl (4 mmol), respectively. The ^{1}H NMR spectrum of the fraction at 50–60°C/50–10 Torr in Et_2O, CCl_4 and benzene indicated a mixture consisting of BSA (2 mmol), BSH (4 mmol), $Me_3SiCHCl_2$ (6 mmol) and Me_3SiCCl_3 (1 mmol). A fraction at 30–50°C/0.1 Torr consisted of $(Me_3Si)_2N–N{\equiv}C$ and TrSH (^{1}H NMR) from which the former (20 mmol) was distilled out at 35°C/0.1 Torr [4].

Reaction with CBr_4

The green coloured reaction mixture in Et_2O at −78°C showed the formation of BSD which could not be sublimed out in pure form at −30°C/10^{-3} Torr. The mixture at room temperature gave LiBr (70 mmol). An immediate ^{1}H NMR study of the filtrate in Et_2O (benzene) showed (besides others) signals due to Me_3SiCBr_3 at δ (ppm) 0.400 (0.193) [4]; $(Me_3Si)_2NN{=}CBr_2$ at 0.167 (0.140) [4] and $Me_3SiN{=}NSiMe_3$ at 0.200 (0.260) which soon disappear. Fractional distillation provided Me_3SiBr (26 mmol) at 80°C/740 Torr; BSH (4 mmol) and BSA (6 mmol) at the temperatures indicated above and TrSH (2 mmol), $(Me_3Si)_4N_2$ (TSH) (0.5 mmol) and $(Me_3Si)_2N–N{\equiv}C$ (12 mmol) together at 30–60°C/0.1 Torr from which the latter was isolated at 35°C/0.1 Torr [4].

Reaction with $CHCl_3$

Chloroform reacted with **1** in Et_2O at −40°C. The filtrate, after separation of LiCl (72 mmol), was fractionated to isolate BSH (24 mmol) and BSA (6 mmol) at the temperatures given above and $C_7H_{19}ClN_2Si_2$ (**4**) (5 mmol) at 80°C/6 Torr. Found: C, 36.95; H, 8.32; N, 12.21; Cl, 14.85. $C_7H_{19}ClN_2Si_2$ calcd.: C, 37.75; H, 8.54; N, 12.58; Cl, 15.95%. Important IR bands (thin film, cm^{-1}): 1575s (ν(C=N)), 990s (ν(N–N)), 945s ($\nu_{as}(Si_2N)$).

^{1}H NMR(CCl_4): δ (ppm) 0.160 (s, 18H, Me_3Si) and 7.10 (s, 1H, CH). (Et_2O) δ (ppm) 0.156 (s, 18H, Me_3Si) and 7.10 (s, 1H, CH). After distillation of the silylhydrazone **4**, the residue was heated to 80–120°C/10^{-2} Torr to give white crystals in a yellowish liquid which were cooled in a glass boat to −78°C. The product was recrystallised twice from n-hexane at low temperatures forming white crystals which were sublimed at 70°C/10^{-3} Torr and analysed as $C_{15}H_{44}N_6Si_5$ (**5**). Found: C, 39.86; H, 9.63; N, 18.81; $C_{15}H_{44}N_6Si_5$ calcd.: C, 40.16; H, 9.82; N, 18.75%. Important IR bands (Nujol mull, cm^{-1}): 3410m, 3365m (ν(NH)), 1600s (ν(C=N)), 1090sh, 1050s (ν(N–N)), 950sb ($\nu_{as}(Si_2N)$).

^{1}H NMR(CCl_4, Et_2O, C_6H_6, C_6D_6): δ (ppm) 0.058, 0.106, 0.130, 0.127 (s, 18H, $(Me_3Si)_2N$); 0.137, 0.160, 0.286, 0.315 (s, 18H, $2Me_3SiN$); 0.193, 0.207, 0.330, 0.355 (s, 6H, Me_2Si); 3.83, –, 4.1, 4.1 (s, 1H, NH); 6.17, 6.13, 6.4, 6.4 (s, 1H, NH).

Mass spectrum (70, 15eV). *m/e* (assignment; relative intensity 70, 15 eV, %): 448 (M^+; 22, 100), 447 ($M^+ - H$; 1.5, 0), 433 ($M^+ - Me$; 5, 4), 346 ($M^+ - Me_3SiN_2H$; 11, 8), 274 ($M^+ - Me_3SiNNSiMe_3$; 24, 11), 273 ($M^+ - 175$; 2, 1), 232 ($M^+ - 216$; 6, 10), 231 ($M^+ - 217$; 2, 3), 190 ($M^+ - 258$; 18, 57), 189 ($Me_3SiNNHSiMe_2NNH^+$; 6, 15), 175 ($Me_3SiNHNSiMe_2NH^+$; 65, 40), 98 ($HNSiMe_3^+$; 77, 41), 97 ($NSiMe_3^+$; 32, 10), 73 (Me_3Si^+; 100, 1). Metastable fragments at 419, 267 and 167 have been observed both at 70 and 15 eV.

$C_{15}H_{44}Si_5N_6$: Isotopic pattern (calcd.):

Mass	448	449	450	451	452	453	454	455
$I_{max} = 100$	100.000	45.142	26.197	7.888	2.458	0.531	0.108	0.012

$C_{15}H_{44}N_6Si_5$ (1 mmol) was dissolved in benzene (2 ml) and treated with Me_3Sn-NEt_2 (4 mmol) at room temperature. After 6 h stirring the reaction mixture was evacuated to remove Et_2NH, Me_3SnNEt_2 and benzene. Vacuum sublimation led to decomposition, therefore, the residue was crystallised from n-hexane to get $C_{21}H_{60}N_6Si_5Sn_2$. Found: C, 30.50; H, 7.60; N, 10.23. $C_{21}H_{60}N_6Si_5Sn_2$ calcd.: C, 32.58; H, 7.76; N, 10.86%.

^1H NMR (benzene): δ (ppm) 0.124 (s, 18H, $(Me_3Si)_2N$), 0.274 (s, 18H, $2Me_3SiN$), 0.340 (s, 6H, Me_2Si) and 0.300 (s, 18H, $2Me_3Sn$) with $J(^1H-^{117}Sn)$ and $J(^1H-^{119}Sn)$ satellites at 52.4 and 55.0 Hz.

Reaction with CHI_3

Equimolar amounts of **1** with CHI_3 in Et_2O or THF at room temperature (48 h) gave only 50% yield (40 mmol) of LiI. A dark yellow filtrate provided BSH (10 mmol), BSA (4 mmol) and $(Me_3Si)_2N-N{\equiv}C$ (3 mmol) at temperatures already mentioned and CHI_3 crystals (15 mmol) subliming at 50–60°C/1 Torr.

Reaction with CH_2Cl_2

CH_2Cl_2 reacted with **1** in Et_2O or THF at -30 to -40°C to form LiCl (65 mmol) in a mustard yellow solution which provided BSH (17 mmol), BSA (12 mmol), TrSH (4 mmol) and a small amount of TSH at temperatures already mentioned. A white sublimate obtained at 100–120°C/10^{-3} Torr (resublimable at 70–80°C/10^{-3} Torr) was characterised as discussed later for the reaction with $PbCl_2$.

Reaction with CH_2I_2

The reaction in Et_2O was slow at -40°C and led to LiI (70 mmol). The yellow filtrate was distilled to get BSH (3 mmol) and BSA (15 mmol) as mentioned above and a mixture of $(Me_3Si)_2N-N{=}CH_2$ [4] (15 mmol) and CH_2I_2 together at 60–70°C/10 Torr. The mixture consisted of two layers with the upper layer containing mainly $(Me_3Si)_2N-N{=}CH_2$ and the lower layer predominantly CH_2I_2. In order to obtain pure $(Me_3Si)_2N-N{=}CH_2$, equimolar amounts of reactants are recommended. ^1H NMR of $(Me_3Si)_2N-N{=}CH_2$ (CCl_4): δ (ppm) 0.177 (s, 18H, $2Me_3Si$); 6.56 (d, J(H–H) 12.0 Hz, 1H, CH); 7.0 (d, J(H–H) 12.0 Hz, 1H, CH) [4].

Reaction with $C_2H_4Cl_2$

This reaction in Et_2O at -40°C gave a low yield of LiCl (60 mmol) and the filtrate gave BSH (28 mmol), BSA (8 mmol) and TrSH (1 mmol) at the temperatures given above.

Reaction with $C_2H_2Cl_4$

The reaction of **1** with $C_2H_2Cl_4$ in Et_2O at -40°C gave almost a quantitative yield of BSH (36 mmol) with trace amounts of BSA and TrSH. The yield of LiCl was 96% (76.8 mmol).

Reaction with Me_2SnCl_2

Equivalent amounts (20 mmol) of **1** in 40 ml Et_2O and Me_2SnCl_2 in 30 ml Et_2O were taken in separate flasks of a V unit. The flasks were cooled to liquid nitrogen temperature and then evacuated to 10^{-3} Torr. The main stop cock was closed and the two were reacted in vacuo at -78°C and then allowed to come to room temperature and stirred for a further one hour. The mixture was toeplered and no N_2

gas was found to evolve. Lithium chloride (35 mmol) was removed to get a pale yellow filtrate showing ^1H NMR signals at δ 0.059, 0.094, 0.288 and 0.322 ppm. Ether was evacuated to get a solid residue which could not be purified by sublimation at 100°C/10^{-3} Torr because both the compounds sublimed together. Crystallisation from n-pentane at -78°C provided a white crystalline solid (m.p. 135°C and s.p. 100°C/10^{-3} Torr) $C_{16}H_{48}N_4Si_4Sn_2$. Found: C, 28.80; H, 6.92; N, 8.37. $C_{16}H_{48}N_4Si_4Sn_2$ calcd.: C, 29.72; H, 7.43; N, 8.67%.

^1H NMR (Et_2O, benzene): δ 0.142, 0.205 (s, 36H, $4Me_3Si$) and 0.440, 0.397 (s, 12H, $2Me_2Sn$).

Mass spectrum (70, 15 eV), *m/e* (assignment; relative intensity 70, 15 eV, %): 646 (M^+; 4, 100) 472 ($M^+ - Me_3SiN{=}NSiMe_3 = M'$; 8, 76) 457 ($M' -$ Me; 2, 6), 427 ($M' -$ 3Me; 1, 0), 385 ($M' - Me_3SiN$; 0.5, 4), 323 ($M' - Me_2Sn$; 1, 2), 313 ($M' - Me_5Si_2N_2$; 6, 27), 298 ($M' - 2Me_3SiN$; 1, 1), 248 ($M' - 224$; 1, 12), 239 ($M' - 233$; 1, 4), 190 ($M' - 258$; 3, 5), 174 ($2Me_3SiN^+$; 32, 91), 146 ($2Me_3Si^+$; 22, 40), 118 (Me_4Si^+; 3, 0), 73 (Me_3Si^+; 100, 0). A metastable fragment has been observed at 345 both in 70 and 15 eV.

$C_{16}H_{48}N_4Si_4Sn_2$: Isotopic pattern (calcd.)

Mass	634	635	636	637	638	639	640	641	642
$I_{max} = 100$	0.057	0.048	1.110	1.037	3.009	2.638	13.042	14.852	37.842
Mass	643	644	645	646	647	648	649	650	651
$I_{max} = 100$	40.131	82.266	69.133	100.000	64.886	85.416	39.864	40.590	18.581
Mass	652	653	654	655	656	657	658	659	660
$I_{max} = 100$	23.951	8.916	6.177	1.909	2.096	0.725	0.325	0.083	0.021

Repeated crystallisation of the mother liquor gave pure hydrazine $C_{10}H_{30}N_2Cl_2$-Si_2Sn_2 whose yield improved considerably in a 1/2 ratio of **1** with Me_2SnCl_2. Found: C, 20.48; H, 5.12; N, 4.86; Cl, 13.01. $C_{10}H_{30}N_2Cl_2Si_2Sn_2$ calcd.: C, 22.12; H, 5.53; N, 5.16; Cl, 13.09%. ^1H NMR (Et_2O, benzene): δ (ppm) 0.089, 0.183 (s, 18H, $2Me_3Si$) and 0.483, 0.465 (s, 12H, $2Me_2Sn$).

Reaction with $SnCl_4$

A 1/1 or 1/2 ratio of **1** with $SnCl_4$ in Et_2O at -78°C in a V shaped unit gave an initial green colour (due to BSD) which soon vanished. The reaction mixture (1/2) gave a white residue of LiCl and $SnCl_2$. The ^1H NMR of the filtrate showed 2 predominant signals at δ 0.053 and 0.400 ppm due to BSA and Me_3SiCl, respectively. After careful removal of Et_2O at 35–40°C, Me_3SiCl (60 mmol) at 57°C/740 Torr and BSA (8 mmol) at 50°C/60 Torr were isolated. A small amount of BSH was also indicated in the residue.

Reaction with Me_2SiCl_2

A 1/1 or 1/2 ratio of **1** with Me_2SiCl_2 in Et_2O at -78°C did not show a green colour and both gave similar ^1H NMR spectra. In the 1/2 reaction ratio, the colourless solution, after removal of LiCl (75 mmol), gave BSH (1.5 mmol) at 55°C/10 Torr and 0.3 ml of a liquid distilling at 75°C/0.1 Torr. This liquid contained two compounds one of which seemed to be tetraazadisilacyclohexane $[Me_2Si(NSiMe_3)_2]_2$ with ^1H NMR in CCl_4 (benzene) showing singlets at δ 0.533 (0.473) and 0.263 (0.233) ppm with a relative ratio of 1/3. The compound could not be collected in a pure state. The main fraction (4.8 ml) was distilled at 115–120°C/0.1

Torr as a colourless, viscous liquid soluble in benzene, Et_2O or CCl_4. It contained a very large number of silyl proton signals between 0 to 0.3 ppm.

Reaction with $SnCl_2$

A 1/2 ratio of **1** with $SnCl_2$ in Et_2O was stirred for 48 h at room temperature to give 2.5 g of LiCl (calcd., 3.4 g) contaminated with tin and $SnCl_2$. The filtrate gave BSH (10 mmol), BSA (9 mmol) and TrSH (4.2 mmol) at the temperatures given above and a small amount of white sublimate at 80–100°C/10^{-3} Torr consisting of $LiN(SiMe_3)_2$ and $(Me_3Si)_4N_2$.

Reaction with $PbCl_2$

An equimolar reaction of **1** with $PbCl_2$, as above, gave an insoluble mixture of LiCl and greyish black Pb. The filtrate was fractionated to get BSH (1 mmol), BSA (2 mmol) and TrSH (2 mmol) as above and TSH (trace amounts) and $LiN(SiMe_3)_2$ subliming together at 80°C/10^{-3} Torr. The latter was purified by recrystallisation from n-hexane (12 mmol). Its ^1H NMR (Et_2O, benzene, CCl_4) showed singlets at δ 0.047, 0.128, and 0.043 ppm, respectively. The ^1H NMR spectrum in THF showed the main signal at -0.113 and a small signal at 0.030 ppm. The compound on treatment with Me_3SiCl formed $(Me_3Si)_3N$ and a small amount of $(Me_3Si)_2NH$ to indicate that the white sublimate is primarily $LiN(SiMe_3)_2$ with some impurity of $LiN(H)(SiMe_3)$.

Acknowledgements

We thank Dr. Gerd Fischer, Institüt für Anorganische Chemie der Universität, München-2, for some mass spectral work, elemental analyses and useful suggestions. Ms M.S. and Dr. G.S. thank CSIR, New Delhi for research followships.

References

1 N. Wiberg, H. Bayer, and S.K. Vasisht, Chem. Ber., 114 (1981) 2658.
2 N. Wiberg, E. Weinberg, and W.Ch. Joo, Chem. Ber., 107 (1974) 1764.
3 N. Wiberg, S.K. Vasisht, G. Fischer, and E. Weinberg, Chem. Ber., 109 (1976) 710.
4 (a) N. Wiberg, and G. Hübler, Z. Naturforsch. B, 31 (1976) 1317; 32 (1977) 1003; 33 (1978) 575; (b) G. Hübler, Doktor Arbeit, L.M. Universität, München, 1977.
5 N. Wiberg, S.K. Vasisht, and G. Fischer, Angew. Chem., 88 (1976) 257.
6 N. Wiberg, R. Meyers, S.K. Vasisht, and H. Bayer, Chem. Ber., 117 (1984) 2886.
7 N. Wiberg, and W. Uhlenbrock, Chem. Ber., 104 (1971) 3989.
8 N. Wiberg, and W. Uhlenbrock, J. Organomet. Chem., 70 (1974) 239, 249.
9 R. West, Adv. Organomet. Chem., 16 (1977) 1.
10 K.G. Das, P.S. Kulkarni, V. Kalyanaraman, and M.V. George, J. Org. Chem., 35 (1970) 2140.
11 U. Wannagat, and H. Niederprüm, Z. Anorg. Allg. Chem., 310 (1961) 32.
12 H. Gilman, J.A. Beel, C.G. Brannen, M.W. Bullock, G.E. Dunn, and L.S. Miller, J. Am. Chem. Soc., 71 (1949) 1499.
13 E.V. Van Berghe, and G.P. Van Der Kelen, J. Organomet. Chem., 6 (1966) 522.
14 W.R. Bamford, and B.C. Pant, J. Chem. Soc. C, (1967) 1470.
15 H. Sakurai, H. Yamamori, and M. Kumada, J. Org. Chem., 33 (1968) 1527.
16 N. Wiberg, W.CH. Joo, and E. Weinberg, J. Organomet. Chem., 73 (1974) 49.