



## Silyl stabilized azanes: Reactions of mono- and dilithium bis(trimethylsilyl)hydrazide with dichloro- and tetrachlorostannane

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1,4-Bis(trimethylsilyl)-1,2,4,5-tetraza-3,

6-Distannacyclohexane

Stannimine

### ABSTRACT

SnCl<sub>4</sub> acts primarily as an oxidant and oxidizes monolithium bis(trimethylsilyl) hydrazide **1** to mainly bis(trimethylsilyl)amine, BSA and tris(trimethylsilyl)hydrazine, TrSH and itself get reduced to SnCl<sub>2</sub>. Similarly, reaction of SnCl<sub>4</sub> with dilithiumbis(trimethylsilyl) hydrazide **2**, oxidizes it to lithium tris(trimethylsilyl)hydrazide, Li-TrSH. Reaction of dichlorostannane (reduction of oxidation state of tin from +4 to +2) with **1** gives a simple substitution reaction and give a pale yellow solid, 1,4-bis(trimethylsilyl)-1,2,4,5-tetraza-3,6-distannacyclohexane, **3b**. Whereas, in reaction of **2** with SnCl<sub>2</sub> intermediate stannimine [(Me<sub>3</sub>Si)<sub>2</sub>N=N=Sn], tetramerizes and further loses tetrakis(trimethylsilyl)tetrazeno, TST to give a cubane compound [(Me<sub>3</sub>Si)N-Sn]<sub>4</sub>, **4**.

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### 1. Introduction

The synthesis and study of heterocycles containing main-group elements have played a pivotal role in the development of inorganic chemistry. Current research continues to uncover fascinating new ring systems which pose intriguing questions with respect to their bonding or which exhibit unexpected reactivity. Some noteworthy examples include 6π-electron gallium-based systems and pseudo aromatic cyclic silylenes [1,2], novel cyclic tellurium imides [3] and interesting aluminum–nitrogen heterocycles [4] among others [5–8]. In addition to the studies on bonding and reactivity, a further reason for studying inorganic rings is their potential use as precursors to polymers and solid-state materials. The use of inorganic rings to construct solid-state materials with novel properties has also been successfully developed. For example, materials with interesting electronic, magnetic and conductive properties have been prepared from sulfur–nitrogen or selenium–nitrogen heterocycles [9,10]. Further, inorganic rings have attracted considerable attention as precursors to ceramics *via* thermolysis: examples include the use of aluminum–nitrogen or gallium–arsenic heterocycles to prepare AlN and GaAs, respectively [11,12].

Heterocubanes are also a part of inorganic heterocycles. With the synthesis of cubane came the realization that other cubic struc-

tures previously thought impossible might be possible after all. Especially tantalizing were heterocubanes, single molecules arrayed in a simple unit cell pattern. Such chemical species have lattice energies on the order of ionic salts but with superior mobility, especially in the gas phase. This ability to store energy has made heterocubanes prime targets for both high energy density materials (HEDMs) [13] and metal-oxide chemical vapor deposition (MOCVD) [14]. GaS, GaSe, and various indium heterocubanes have been used industrially to cleanly produce both cubic and hexagonal surfaces for metal–insulator–semiconductor field-effect transistor (MISFET) applications [14,15]. Because of such interesting applications, the cubane is an important observed structural motif in solid-state inorganic chemistry. We envisaged that compounds **1** and **2** could act as potential precursors for the synthesis of various inorganic non-alternating heterocycles as we can incorporate a diazane moiety into a ring by using these compounds. The present paper deals with the outcome of such studies.

### 2. Experimental

All experiments were performed in dried glassware under purified nitrogen using standard inert atmosphere and vacuum line techniques. Bis(trimethylsilyl)hydrazine [16,17], monolithiumbis(trimethylsilyl)hydrazide [18–20], dilithiumbis(trimethylsilyl)hydrazide [18–20] and *n*-butyllithium [21] were prepared as reported in the literature. Special care was taken in the preparation of monolithiumbis(trimethylsilyl)hydrazide as it tends to slowly

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disproportionate to dilithiumbis(trimethylsilyl)hydrazide and bis(trimethylsilyl)hydrazine [19]. Therefore it is prepared in *n*-hexane and at low temperature and the salt was dried as soon as it is formed to rule out the possibility of disproportionation. Trimethylsilylchloride (Aldrich), dichlorostannane (Aldrich), and tetrachlorostannane (Aldrich) were used as such. Diethyl ether and tetrahydrofuran were dried over sodium benzophenoneketyl and *n*-hexane was kept over sodium wire and distilled under nitrogen prior to use. All NMR spectra were obtained on a Jeol AL 300 MHz (FT NMR) apparatus using tetramethylsilane ( $^1\text{H}$ ,  $^{29}\text{Si}$ , 0 ppm), deuteriochloroform ( $^{13}\text{C}$ , 77.1 ppm) and tetramethyltin ( $^{119}\text{Sn}$ , 0 ppm) as reference standards. The mass spectra on a Jeol Mstation JMS 700 or a Varian MAT CH7 spectrometer. The mass spectrum data are reported in mass to charge units ( $m/z$ ) followed by their relative intensities and fractions lost in parentheses.

### 2.1. $[\text{Me}_3\text{Si}(\text{H})\text{N}-\text{N}-\text{Sn}]_2$ , **3**

Monolithium bis(trimethylsilyl)hydrazide (6.67 g, 36.6 mmol) dissolved in 30 ml THF, was cooled to  $-20^\circ\text{C}$  and  $\text{SnCl}_2$  (3.47 g, 18.3 mmol), dissolved in 15 ml THF, was added dropwise with constant stirring. On addition the color of the solution turned yellow to orange and then to brown. After complete addition, the reaction mixture was allowed to come to room temperature slowly overnight. The color of the mixture turned yellow again. The reaction mixture was evacuated to remove THF and other volatile impurities. The residue was then treated with 30 ml *n*-hexane. The mixture was filtered to obtain white residue of LiCl (1.53 g, 36.0 mmol) and a yellow filtrate.  $^1\text{H}$  NMR of the filtrate showed one main signal at  $\delta$  0.10 ppm and small signals at  $\delta$  0.34, 0.25 and 0.22 ppm. The filtrate was evacuated to remove *n*-hexane. Fractional distillation at  $100^\circ\text{C}/10^{-3}$  torr provided small amount of BSH. The yellow solid left after evacuation, was crystallized from hexane in liquid  $\text{N}_2$ /acetone slurry. It was analyzed and found to be **3**.

### 2.2. $[(\text{Me}_3\text{Si})\text{N}-\text{Sn}]_4$ , **4**

Dilithium bis(trimethylsilyl)hydrazide (5.17 g, 27.5 mmol), dissolved in 30 ml THF, was cooled to  $-40^\circ\text{C}$  and  $\text{SnCl}_2$  (5.22 g, 27.5 mmol), dissolved in 20 ml THF, was added to it dropwise with constant stirring. On addition the color of the solution changed from yellow to brick red to dark red. After complete addition the reaction mixture was slowly allowed to come to room temperature overnight. The color of the solution again turned to yellow.  $^1\text{H}$  NMR of the clear solution showed one main signal at  $\delta$  0.22 ppm and some small signals at  $\delta$  0.07, 0.11, 22.0 and 0.37 ppm. Evacuated the reaction mixture thoroughly to remove THF and other volatile impurities. Thick gelatinous solid was taken in 35 ml *n*-hexane and filtered to get white solid of LiCl (2.274 g, 53.5 mmol) and a yellow filtrate.  $^1\text{H}$  NMR of the filtrate in *n*-hexane showed one main signal at  $\delta$  0.21 ppm and two small signals at  $\delta$  0.09 and 0.34 ppm. The filtrate was cooled at  $-80^\circ\text{C}$  in liquid  $\text{N}_2$ /acetone slurry to get pale yellow crystalline solid. Repeated crystallization provided pale yellow crystals of pure compound of **4**.

### 2.3. $[(\text{Me}_3\text{Si})_3\text{N}_2\text{Li}]$ , **5**

Dilithium bis(trimethylsilyl)hydrazine (6.87 g, 36.7 mmol), suspended in 40 ml *n*-hexane, was cooled to  $-20^\circ\text{C}$  and  $\text{SnCl}_4$  (4.84 g, 18.3 mmol), dissolved in 20 ml *n*-hexane, was added to it dropwise with constant stirring. After complete addition, the reaction mixture was allowed to come to room temperature slowly overnight.  $^1\text{H}$  NMR of the reaction mixture showed two prominent signals at  $\delta$  0.12 and 0.41 ppm due to TrSH and  $\text{Me}_3\text{SiCl}$ , respectively. The solution was filtered to obtain white solid (mixture of LiCl

and  $\text{SnCl}_2$ ) and a pale yellow filtrate. The pale yellow filtrate on cooling at  $-80^\circ\text{C}$  in liquid  $\text{N}_2$ /acetone slurry gave colorless crystalline solid. Recrystallization provided colorless crystals of **5**.

### 2.4. X-ray crystallography

X-ray structure analyses were done on Stoe IPDS. Crystals suitable for single crystal diffraction studies were grown by cooling a saturated solution at  $-80^\circ\text{C}$  in liquid  $\text{N}_2$ /acetone slurry. A plate like single crystal with dimension  $0.39 \times 0.27 \times 0.18$  mm was mounted along the largest dimension and used for data collection. Single crystal X-ray diffraction data were collected at measurement temperature of 200 K using an image plate detector system (Stoe IPDS) with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal to image distance was set to 60 mm and  $\varphi$ -increment of  $1.2^\circ$  per exposure. The data were collected by dynamic area detection mode. The data were corrected for Lorentz and polarization factors and an analytical absorption correction was also applied. All other relevant information about the data collection is presented in Table 1.

The structure was solved by Direct Methods using SHELX-97 [22] package and also refined using the same one. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically by initially fixing their geometrical positions using the AFIX options in SHELX-97. A weighting scheme of the form  $1/[\sigma^2(F_o^2) + (0.0405P)^2]$  was used. The refinement converged to a final  $R$  value of 0.0331 ( $wR_2$  0.0711) for 3659 reflections [ $I > 2\sigma(I)$ ]. The final difference Fourier map was featureless. All other information regarding the refinement is also recorded in Table 1.

## 3. Results and discussion

Monolithium bis(trimethylsilyl)hydrazide (**1**) reacts with dichlorostannane in a redox reaction to form BSD, which on thermolysis [23] provides BSA and TrSH at room temperature. Formation of BSD is confirmed from  $^1\text{H}$  NMR recorded at different time intervals during the course of the reaction. In  $^1\text{H}$  NMR the signal

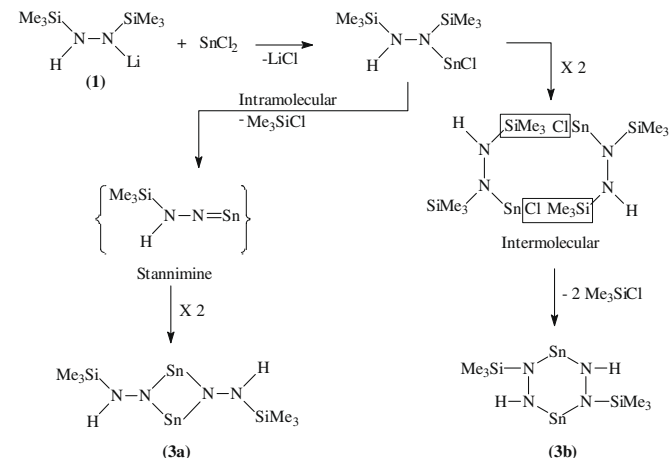
**Table 1**  
Crystal data and Structure refinement for **4**.

Empirical formula	$\text{C}_{12}\text{H}_{36}\text{N}_4\text{Si}_4\text{Sn}_4 \cdot 0.5(\text{C}_7\text{H}_8)$
Formula weight	869.69
Temperature	200 K
Diffraction method used	Stoe IPDS
Radiation used, wavelength	Mo $K\alpha$ , 0.71073 $\text{ \AA}$
Crystal system, space group	monoclinic, Cc (No. 9)
Unit cell dimensions	$a = 26.1398(14) \text{ \AA}$ $\alpha = 90^\circ$ $b = 12.0793(8) \text{ \AA}$ $\beta = 110.262(6)^\circ$ $c = 21.8990(12) \text{ \AA}$ $\gamma = 90^\circ$
Volume	$6486.7(7) \text{ \AA}^3$
Z, Calculated density	8, 1.781 $\text{g/cm}^3$
Absorption coefficient	$3.202 \text{ mm}^{-1}$
$F(000)$	3336
Crystal size	$0.39 \times 0.27 \times 0.18 \text{ mm}^3$
Theta range for data collection	$2.9\text{--}28^\circ$
Index ranges	$-34 \leq h \leq 34$ , $-15 \leq k \leq 15$ , $-28 \leq l \leq 28$
Reflections collected	27635
Independent reflections	14647 [ $R_{\text{int}} = 0.049$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	14647/0/496
Goodness-of-fit on $F^2$	0.83
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0405P)^2]$ , $P = F_o^2 + 2 * F_c^2$
Data to parameter ratio	29.53:1
Final $R$ indices, 3659 reflections	$R_1 = 0.0331$ , $wR_2 = 0.0711$
$[I > 2\sigma(I)]$	
$R$ indices (all data)	$R_1 = 0.0670$ , $wR_2 = 0.0799$
Largest difference in peak and hole	0.63 and $-0.70 \text{ e \AA}^{-3}$

at  $\delta$  0.21 ppm assigned to the methyl protons of  $(\text{Me}_3\text{Si})\text{N}$  group of BSD slowly disappears as the reaction progresses. However, the main reaction product is a pale yellow solid  $[(\text{Me}_3\text{Si})(\text{H})\text{N}-\text{Sn})_2$ , **3** which is formed by a substitution reaction followed by elimination. The yellow solid **3** can have two possible configurations 1,3-bis(trimethylsilylamino)-1,3-diaza-2,4-distannacyclobutane, **3a** or 1,4-bis(trimethylsilyl)-1,2,4,5-tetraza-3,6-distannacyclohexane, **3b**.

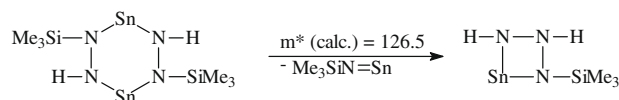
**3a** could be formed by simple elimination of  $\text{LiCl}$  leading to the formation of  $[(\text{Me}_3\text{Si})\text{HN}-\text{N}(\text{Me}_3\text{Si})(\text{SnCl})]$  which further undergoes intramolecular loss of  $\text{Me}_3\text{SiCl}$  to form intermediate stannimine  $[(\text{Me}_3\text{Si})\text{HN}-\text{N}=\text{Sn}]$ . It immediately dimerises to give **3a**. On the other hand, elimination of  $\text{LiCl}$  followed by intermolecular loss of  $\text{Me}_3\text{SiCl}$  will provide **3b** (see equation).

$^1\text{H}$  NMR of **3** in benzene (toluene) shows one signal at  $\delta$  0.23 (0.21) ppm for the methyl protons of  $(\text{Me}_3\text{Si})\text{N}$  groups.  $^{13}\text{C}$  NMR in benzene (toluene) also shows a singlet at  $\delta$   $-0.12$  ( $-0.67$ ) ppm and  $^{29}\text{Si}$  NMR in  $d^8$ -toluene shows a signal at  $\delta$  4.06 due to  $(\text{Me}_3\text{Si})\text{N}$  group.  $^{119}\text{Sn}$  NMR indicates a signal at  $\delta$  786 ppm (N–Sn–N group). This value is much lower than that for compounds with four coordinated tin(IV) hydrazine derivatives [24].



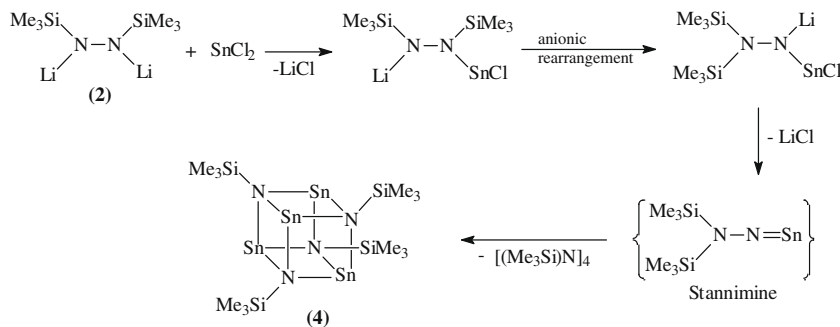
well within the range observed for tin(II) compounds [25–28]. In the bis(amino)stannylenes, the relative energies of electrons in Sn–N  $\sigma$  bonds is lower and therefore, the energy difference between the ground states and the relevant excited states is larger, which causes a smaller contribution to the paramagnetic shielding term in the tin amides than in the organostannylenes where  $^{119}\text{Sn}$  chemical shift values are in the range of 2000–2500 ppm [29].

Its mass spectral analysis shows a molecular ion peak with relative low intensity at  $m/z$  444. Other significant fragments are observed at  $m/z$  429, 414, 371, 356, 283, 268 indicating the loss of radicals like  $\text{Me}$ ,  $2\text{Me}$ ,  $\text{Me}_3\text{Si}$ ,  $(\text{Me}_3\text{Si})\text{NH}$ ,  $(\text{Me}_3\text{Si})_2\text{NH}$  and  $(\text{Me}_3\text{Si})\text{HN}-\text{NH}(\text{SiMe}_3)$ . An important fragment is observed at  $m/z$  237 corresponding to the loss of radical  $(\text{Me}_3\text{SiN}=\text{Sn})$  from the molecular ion. This is also supported by a metastable peak at  $m/z$  126 which provides evidence for the loss of molecule of  $(\text{Me}_3\text{SiN}=\text{Sn})$  due to the initial ionization at the largely polar Sn–N bond.



Other important fragments are observed at  $m/z$  222 ( $\text{Me}_3\text{SiN}_2\text{HSn}^+$ ), 208 ( $\text{Me}_3\text{SiNHSn}^+$ ), 134 ( $\text{NSn}^+$ ) and 73 ( $\text{Me}_3\text{Si}^+$ ). The mass spectral analysis appears to support the configuration of **3b** as 1,4-bis(trimethylsilyl)-1,2,4,5-tetraza-3,6-distannacyclohexane. Various attempts to grow good crystals of the product were unsuccessful and the unequivocal nature of the molecular structure could not be ascertained.

Dilithium bis(trimethylsilyl)hydrazide (**2**) reacts with dichlorostannane leading to the simple elimination of  $\text{LiCl}$  followed by anionic rearrangement [30] leading to the formation of  $[(\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{Li})(\text{SnCl})]$ . It further undergoes intramolecular loss of  $\text{LiCl}$  to form intermediate stannimine  $[(\text{Me}_3\text{Si})_2\text{N}-\text{N}=\text{Sn}]$ , which tetramerizes and further loses tetrakis(trimethylsilyl)tetrazene,  $[(\text{Me}_3\text{Si})\text{N}]_4$ , TST to give  $[(\text{Me}_3\text{Si})\text{N}-\text{Sn}]_4$ , **4**.



The literature reports that  $^{119}\text{Sn}$  nuclear shielding decreases with the decrease in the coordination number of tin and this value falls

Its  $^1\text{H}$  NMR in toluene (hexane) shows one signal at  $\delta$  0.25 (0.20) ppm for the methyl protons of  $(\text{Me}_3\text{Si})\text{N}$  group.  $^{13}\text{C}$  NMR in toluene shows a singlet at  $\delta$   $-0.38$  ppm for  $(\text{Me}_3\text{Si})\text{N}$  group.  $^{29}\text{Si}$  NMR in

toluene shows a triplet at  $\delta$  4.19 due to  $(\text{Me}_3\text{Si})\text{N}$  group.  $^{119}\text{Sn}$  NMR indicates a singlet at  $\delta$  783.49 ppm for the Sn–N groups which falls in the range observed for two coordinated tin(II) amino derivatives [25–28]. In addition to that the coupling of three  $^{14}\text{N}$  nuclei ( $I = 1$ ) around each  $^{119}\text{Sn}$  atom split the  $^{119}\text{Sn}$  signal into a septet with a coupling constant of  $^1J$  ( $^{14}\text{N}$ ,  $^{119}\text{Sn}$ ) = 101.7 Hz and  $^2J$  ( $^{17}\text{Sn}$ ,  $^{119}\text{Sn}$ ) = 59 Hz.

It is evident from the  $^{119}\text{Sn}$  chemical shifts of transition metal complexes of bis(amino)stannylenes [31], that the engagement of the lone pair of electrons at the tin atom in M–Sn bonds does not induce a dramatic shift of the  $^{119}\text{Sn}$  NMR signal. Thus, paramagnetic effects as the result of  $B_0$  induced charge circulation involving the formally unoccupied Sn- $p_z$  orbital arises mainly from the lone pair of electrons at the tin atom. This explains that the dimerization of stannylenes causes a marked increase in  $^{119}\text{Sn}$  nuclear shielding since the Sn- $p_z$  orbital is now used in donor–acceptor interaction [25].

Mass spectrum of **4** shows molecular ion peak at  $m/z$  824 and the observed isotopic pattern agrees quantitatively with that calculated for  $\text{C}_{12}\text{H}_{36}\text{N}_4\text{Si}_4\text{Sn}_4$ . The molecular ion shows the loss of Me,  $\text{SiMe}_3$  and  $\text{SiMe}_4$  at  $m/z$  809, 751 and 736 before losing stannimine  $(\text{Me}_3\text{Si})\text{HNN}=\text{Sn}$  at  $m/z$  602. This loss is supported by a metastable peak at  $m/z$  440. The molecular ion  $M'$  ( $m/z = 602$ ) shows fragment at  $m/z$  572 for the loss of 2Me. The other prominent peak is observed at  $m/z$  453 indicating the loss of  $(\text{Me}_3\text{Si}-\text{SiMe}_3)$ , which is supported by a metastable peak at  $m/z$  339. Other significant fragments are observed at  $m/z$  397 [ $\text{Sn}_2(\text{SiMe}_3)_3(\text{Me}_2)$ ], 221 ( $\text{Me}_3\text{SiNNSn}$ ), 192 ( $\text{Me}_3\text{SiSn}$ ), 147 ( $\text{Me}_3\text{Si}-\text{SiMe}_3$ ), 119 (Sn), 100 ( $\text{Me}_3\text{SiN}_2$ ), 86 ( $\text{Me}_3\text{SiN}$ ) and 73 ( $\text{Me}_3\text{Si}$ ). Base peak is observed at  $m/z$  147 corresponding to  $(\text{Me}_3\text{Si}-\text{SiMe}_3)$ . The mass spectrum appears to support the cubane structure, which is further supported by X-ray crystallography.

Good single crystals of **4** have been grown by slowly cooling a saturated solution in *n*-hexane at  $-80^\circ\text{C}$  in liquid  $\text{N}_2$ /acetone slurry. A perspective ORTEP view of the molecules with atom numbering scheme is shown in Fig. 1. Details of data collection and structural refinement are given in Table 1. The molecule crystallizes in monoclinic crystal system (Cc space group) with two independent molecules in the asymmetric unit. The cuboid nature of the  $(\text{Sn}-\text{N})_4$  moiety is amply evident from figure and this is the first crystal structure of an inorganic cuboid entirely build up of tin and nitrogen atoms synthesized from the hydrazide salts. The cube is not perfect as can be observed from the selected bond lengths and bond angles shown in Table 2.

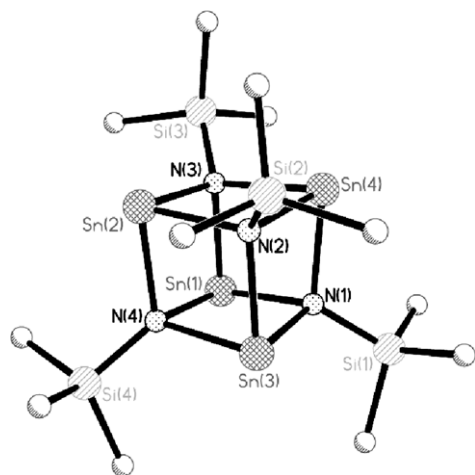


Fig. 1. A perspective view of one of the cuboid structures of **4** in the asymmetric unit. Hydrogen atoms are not shown for clarity.

Table 2  
Important bond lengths [Å] and angles [ $^\circ$ ] in **4**.

Sn1–N1	2.187(13)	Sn1–N3	2.195(18)
Si2–N2	1.776(17)	Sn1–N4	2.186(19)
Sn2–N2	2.188(14)	Sn2–N3	2.228(18)
Sn3–N4	2.276(19)	Si4–N4	1.714(18)
Sn4–N1	2.179(16)	Sn4–N2	2.197(15)
Sn4–N3	2.271(19)	Si1–N1	1.773(16)
Sn2–N3–Si3	120.5(10)	Sn4–N3–Si3	118.1(9)
Sn1–N3–Sn2	97.5(6)	Sn1–N3–Sn4	95.2(7)
Sn1–N3–Si3	124.2(11)	Sn2–N3–Sn4	94.7(7)
Sn3–N4–Si4	116.5(9)	Sn1–N4–Sn3	95.8(7)
Sn3–N1–Sn4	98.5(6)	Sn1–N1–Sn3	98.9(6)
Sn1–N1–Sn4	98.1(6)	Sn1–N1–Si1	119.2(9)
Sn2–N2–Sn3	98.2(6)	Sn4–N2–Si2	118.2(8)
N–Sn–N	81.1–83.7		

In one of the cuboid structures due to the distortion of the cube to a greater extent the Sn–Sn contacts are 3.299 Å (Sn4...Sn1) and 3.296 Å (Sn4...Sn3), respectively.

The Sn–N bond length at the edges of the cube has a considerable variation and it ranges from 2.139 to 2.276 Å. Similarly the angles vary from  $94.7^\circ$  to  $98.9^\circ$  around the Sn atoms. One of the bonds associated with the Sn–N being a coordinate bond is slightly longer than the other two bonds, the maximum difference being 0.137 Å. To avoid the eclipsing interactions of the methyl groups with Sn–N edges the methyl groups of the  $-\text{SiMe}_3$  moiety occupies a staggered position (for example, Sn3–N9–Si8–C18 =  $64.3^\circ$ ) as shown in Fig. 2. In the figure, C18, C27 and C29 carbon atoms are in between the three Sn atoms at the corners of the cube and this is true for all the four  $-\text{SiMe}_3$  groups attached to the corners of the cube.

It is interesting that there are 0.5 molecules of toluene per one cuboid moiety in the crystal lattice. These toluene molecules are incorporated into the lattice upon crystallization. The cuboid structure of **4** forms linear channels running through the *ac* plane and stabilize the lattice (Fig. 3). However there are no short contacts of hydrogen atoms with heteroatoms (or between the heavier atoms) observed in the lattice. The lattice structure is hence stabilized through van der Waal's interactions. The single crystal x-ray diffraction study of compound **4** produces a comparable result as reported by Veith et al. [32]. This group has synthesized the compound from the reaction of the cyclic diazastannylenes **1** with primary silylamines. Another research group of William Jr. have also synthesized the similar compound using stannylamine and  $\text{SnCl}_2$  [33].

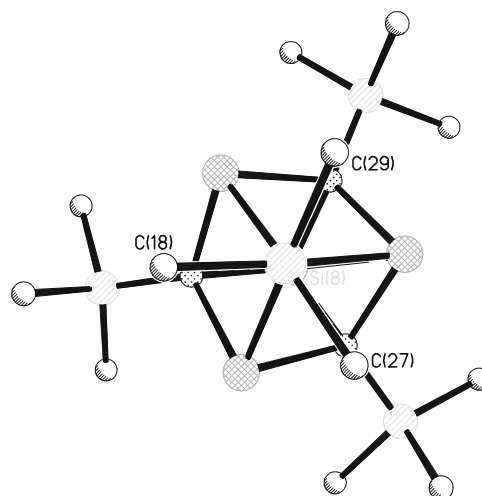


Fig. 2. A projection of the second molecule of **4** down Si8–N8 bond.

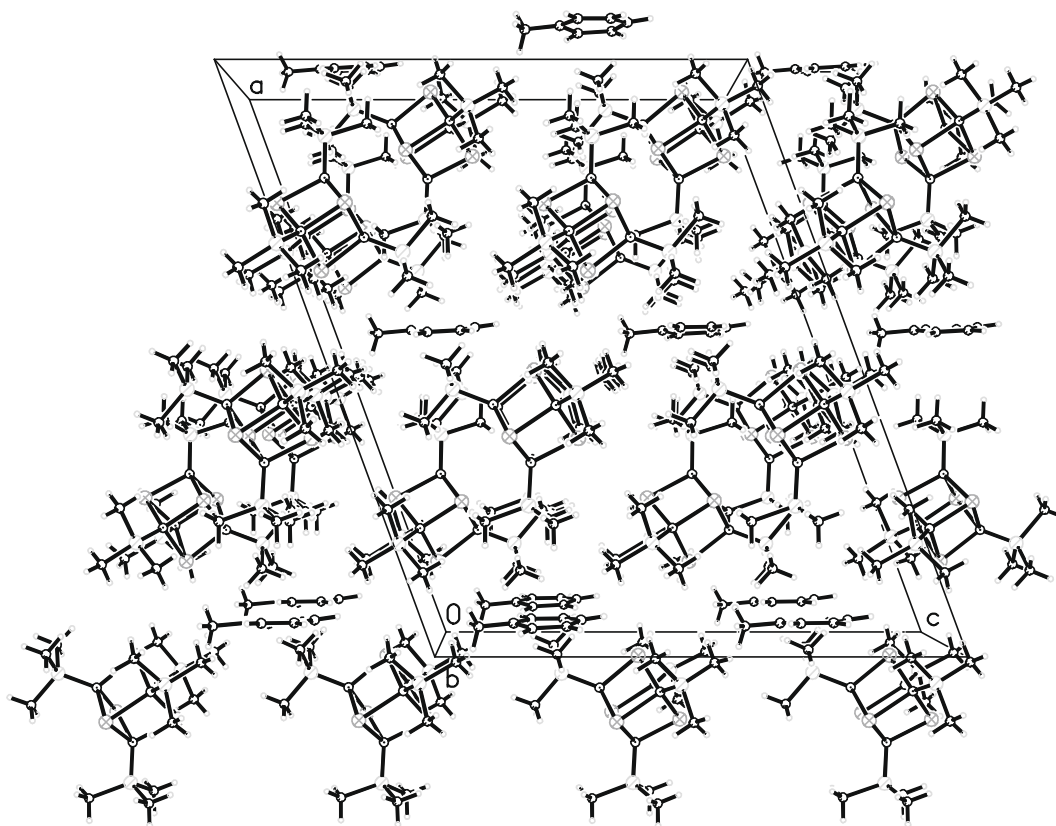
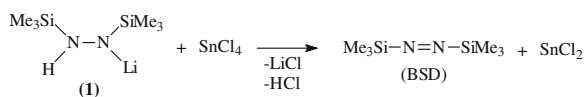


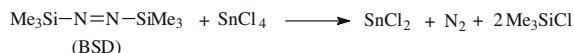
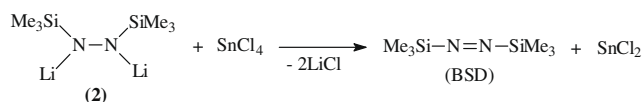
Fig. 3. Packing of the molecules of **4** viewed down the *ac* plane.

Tetrachlorostannane reacts with **1** at low temperature to give a blue colored reaction mixture. The blue color disappears slowly as the reaction mixture is allowed to come to room temperature over a period of time. Probably  $\text{SnCl}_4$  oxidizes **1** to form bis(trimethylsilyl)diazene, BSD as indicated in the  $^1\text{H}$  NMR.

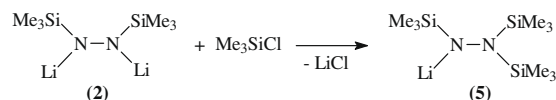


Bis(trimethylsilyl)diazene, BSD,  $\text{Me}_3\text{SiN}=\text{NSiMe}_3$  is a well-known compound which tends to thermolyses above  $-30^\circ\text{C}$  [23] or it may react further with the Lewis acid at low temperature. The decomposition products above  $-30^\circ\text{C}$  vary with the reaction conditions and catalytic effects of the Lewis and protic acids. The decomposition products of BSD are reported and they are TSH, BSA and TrSH.

On the other hand, dilithiumbis(trimethylsilyl)hydrazide **2** reacts with tetrachlorostannane in a redox manner to form BSD, which further reacts with  $\text{SnCl}_4$  to form  $\text{Me}_3\text{SiCl}$  and  $\text{N}_2$  is released.



This  $\text{Me}_3\text{SiCl}$  reacts with another molecule of **2** to give lithium tris(trimethylsilyl)hydrazide,  $[(\text{Me}_3\text{Si})_3\text{N}_2\text{Li}]$ , Li-TrSH, **5**.



Compound **5** is a white crystalline solid which catches fire on exposure to traces of air or moisture. Its  $^1\text{H}$  NMR in benzene shows two signals at  $\delta$  0.11 and 0.93 ppm in the intensity ratio 2:1 for  $(\text{Me}_3\text{Si})_2\text{N}$  and  $(\text{Me}_3\text{Si})\text{N}$  groups.  $^{13}\text{C}$  NMR in benzene shows two signals at  $\delta$  0.50 and 0.88.  $^{29}\text{Si}$  NMR ( $^1\text{H}$ -decoupled) in  $\text{CDCl}_3$  also shows two signals at  $\delta$  22.78 and 23.51 ppm due to  $(\text{Me}_3\text{Si})_2\text{N}$  and  $(\text{Me}_3\text{Si})\text{N}$  groups, respectively. Mass spectrum of the molecule shows a molecular ion peak at  $m/z$  248. Fragments corresponding to the loss of Me, 2Me, 3Me and  $\text{Me}_3\text{Si}$  are quite significant. Base peak in the spectrum corresponds to  $(\text{Me}_3\text{Si}-\text{SiMe}_3)^+$  at  $m/z$  147.

Synthesis and reactivity of compound **5** is already reported in the literature [34–37]. Compound **5** dissolves in *n*-hexane and slow cooling provided colorless crystals suitable for X-ray crystal structure determination. Crystal structure of this compound has already been undertaken by Metzler et al. [38].

#### 4. Summary

Tetrachlorostannane acts primarily as an oxidant and oxidizes **1** to mainly bis(trimethylsilyl)amine, BSA and tris(trimethylsilyl)hydrazine, TrSH and itself get reduced to  $\text{SnCl}_2$ . Similarly, reaction of  $\text{SnCl}_4$  with **2**, oxidizes it to lithium tris(trimethylsilyl)hydrazide, **5**. It crystallizes in triclinic space group ( $P\bar{1}$ ) with two molecules in the asymmetric unit.

Reaction of dichlorostannane (reduction of oxidation state of tin from +4 to +2) with **1** gives a simple substitution reaction and give a pale yellow solid, 1,4-bis(trimethylsilyl)-1,2,4,5-tetraza-3,6-distannacyclohexane, **3b**. Whereas, in reaction of **2** with  $\text{SnCl}_2$

intermediate stannimine [(Me<sub>3</sub>Si)<sub>2</sub>N–N=Sn], tetramerizes and further loses TST, [(Me<sub>3</sub>Si)N]<sub>4</sub> to give [(Me<sub>3</sub>Si)N–Sn]<sub>4</sub>, **4**. Good single crystals of **4** have been grown by slowly cooling a saturated solution in *n*-hexane at –80 °C in liquid N<sub>2</sub>/acetone slurry and its single crystal X-ray structure determination was carried out. The molecule crystallizes in monoclinic crystal system (Cc space group) with two independent molecules in the asymmetric unit. The structure shows a cuboid architecture in which four tin atoms and four nitrogen atoms share the corners. This is the first crystal structure of an inorganic cuboid entirely build up of tin and nitrogen atoms synthesized from the hydrazide salts.

### 5. Supplementary material

CCDC 715953 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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