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SILAZANES PLUS MCl_4-SUBSTITUTION *vs.* REARRANGEMENT REACTIONS

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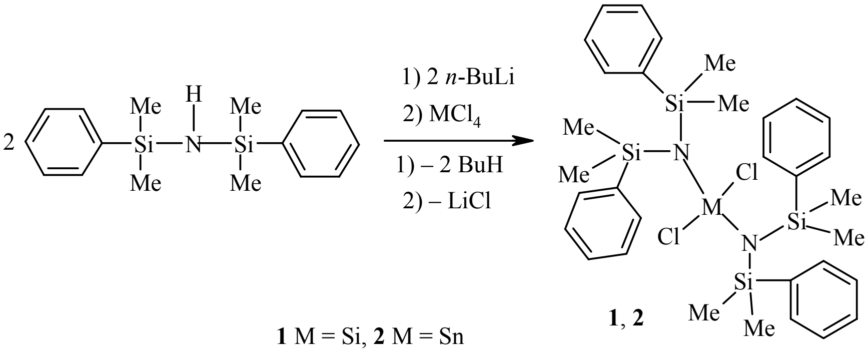
Novel silicon and tin compounds were synthesized by the reaction of lithium salts of 1,3-di-phenyl-1,1,3,3-tetramethyldisilazane H(DPTMDS) and 1,1,3,3,5,5-hexamethylcyclotrisilazane H_3(HMCTS) with $SiCl_4$ and $SnCl_4$, respectively. The reactions with H(DPTMDS) yield the substitution products $(DPTMDS)_2SiCl_2$ and $(DPTMDS)_2SnCl_2$. In contrast, the reactions with the cyclic silazane H_3(HMCTS) lead to a large variety of products due to the competition of substitution reactions and ring contractions. The resulting new compounds were characterized by elemental analyses, NMR spectroscopy, and single crystal X-ray structure analyses.

Keywords: 1,3-diphenyl-1,1,3,3-tetramethyldisilazane, 1,1,3,3,5,5-hexamethylcyclotrisilazane, rearrangement, substitution.

Silazanes offer promising ligand qualities in reactions with metal chlorides due to their reactive N–H and Si–N bonds. Disilazanes, e.g., 1,1,1,3,3,3-hexamethyldisilazane H(HMDS), as a main representative of this compound class, and their lithium salts were used to synthesize numerous metal complexes of the type $R_xM[N(SiMe_3)_2]_y$ (R = Cl, Br, alkyl) with unusually low coordination numbers which are favored by the sterically encumbering bis-(trimethylsilyl)amino moieties [1-5]. Cyclic silazanes, e.g., 1,1,3,3,5,5-hexamethylcyclotrisilazane H_3(HMCTS), exhibit striking reactivity patterns in analogous reactions. Besides substitution reactions, isomerizations of the cyclotrisilazane system into cyclodisilazanes and ring coupling reactions were observed, which led to an assortment of molecules with different skeletons [6-13].

In this article we emphasize this variability on the basis of the conversions of 1,3-diphenyl-1,1,3,3-tetramethyldisilazane H(DPTMDS) and H_3(HMCTS) with the tetrachlorides of silicon and tin, respectively.



1, **2**

1 M = Si, **2** M = Sn

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* Dedicated to Prof. Edmunds Lukevics on the occasion of his 70th birthday

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The lithium salt Li(DPTMDS) was prepared in the usual manner by treating a solution of the disilazane in toluene with an equimolar amount of an *n*-butyllithium solution in hexane. $SiCl_4$ as well as $SnCl_4$ reacted with this lithium salt in a molar ratio of 1:2 by exchange of two chlorine substituents for bis-(dimethylphenylsilyl)amino groups to form the substitution products $Cl_2Si[N(SiMe_2Ph)_2]_2$ (**1**) and $Cl_2Sn[N(SiMe_2Ph)_2]_2$ (**2**).

Crystals suitable for X-ray diffraction analysis were easily obtained in the case of Sn-compound **2**, but the reaction of $SiCl_4$ with Li(DPTMDS) yielded a clear colorless oil and attempts to crystallize compound **1** failed so far. The tin complex **2** crystallizes in the triclinic space group *P*-1 with 4 molecules in the unit cell. The asymmetric unit includes two independent molecules. One of them is presented in Fig. 1.

In both molecules the tin atom is almost tetrahedrally coordinated by the ligands. The corresponding bond lengths and angles of the two crystallographically independent molecules are only insignificantly different.

The Sn–N bonds in compound **2** are slightly shorter and the Si–N bonds in the same compound are slightly longer than those in the Sn(II) complex $Sn[N(SiMe_2Ph)_2]_2$, which measure 2.12-2.13 (Sn–N distances) and 1.72-1.73 Å (Si–N distances), respectively, reflecting the more electropositive character of Sn(IV) compared with Sn(II) [14].

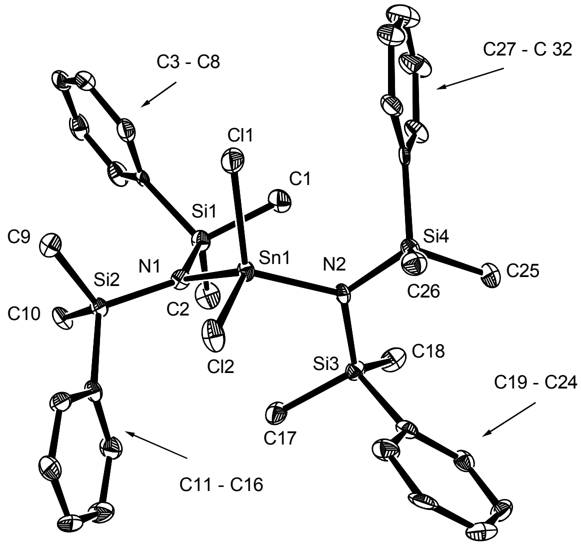
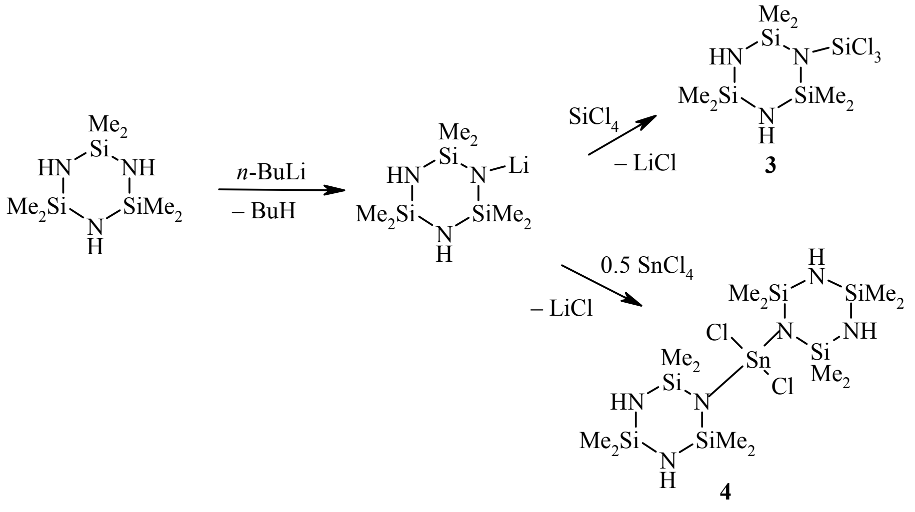


Fig. 1. ORTEP plot of one of two crystallographically independent molecules of compound **2** (thermal ellipsoids at 50% probability level).

The ^{29}Si solution NMR data of compounds **1** and **2** are well comparable, indicating the same molecular structure as observed in the solid state for **1**. The ^{29}Si resonances of the dimethylphenylsilyl moieties of compounds **1** (δ = -1.0) and **2** (δ = -1.6 ppm) are in the same region and slightly downfield shifted in comparison with the signal of the educt silazane (δ = -4.3 ppm). Additionally, a ^{29}Si resonance peak for compound **1** appears at 2.1 ppm, indicating the silicon atom in the center of the complex. In case of the tin complex **2** the ^{119}Sn resonance signal was observed at -130 ppm.

In contrast to H(DPTMDS), the cyclic silazane H_3(HMCTS) shows a completely different reactivity pattern regarding its reactions with $SiCl_4$ and $SnCl_4$. Simple substitution reactions take place when reacting LiH_2(HMCTS) with $SiCl_4$ in 1:1 ratio as well as with $SnCl_4$ in 2:1 ratio. The substitution products $Cl_3Si[(HMCTS)H_2]$ **3** and $Cl_2Sn[(HMCTS)H_2]_2$ **4** were isolated in good yields.

To the best of our knowledge, till now it was only reported that H_3(HMCTS) reacts with chlorosilanes [15, 16], with the exception of trialkylchlorosilanes [6], by cleavage of the (Si–N)$_3$ ring. In contrast, the reactions described above demonstrate that substitution products are accessible without Si_3N_3 ring cleavage. The molecular structures of compounds **3** and **4** are shown in Figs. 2 and 3.



Silazane **3** crystallizes in the monoclinic space group $P2_1/c$ with 4 molecules in the unit cell. Si–N bond lengths in cyclosilazane **3** are in the typical range (1.70-1.78 Å), and only the distance Si(1)–N(1) (1.67 Å) is significantly shorter. The shortening of this distance reflects the presence of electron-withdrawing chlorine substituents at Si(1). Thus, the silicon atom would become electron deficient, but this deficiency is alleviated by electron donation from N(1), resulting in a shorter Si–N bond.

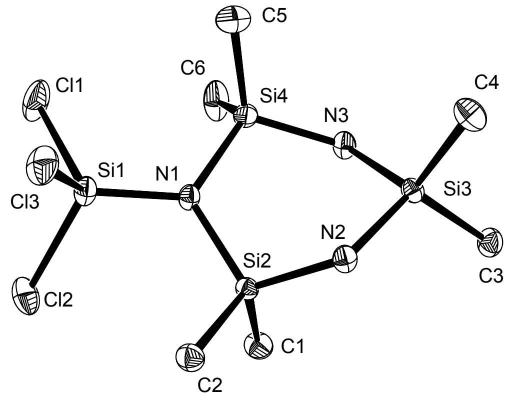


Fig. 2. ORTEP plot of compound **3** displaying thermal ellipsoids at the 50% probability level.

Silazane derivative **4** crystallizes in the monoclinic space group $C2/c$ with 4 molecules in the unit cell. The Sn atom in compound **4** is situated on a two-fold axis of rotation. Thus, the asymmetric unit consists of 0.5 molecules of compound **4**. In both complexes the atoms Si(1) and Sn(1) exhibit a distorted tetrahedral coordination sphere.

The ^{29}Si NMR spectra of compounds **3** and **4** exhibit two resonance signals located between -5 and 0 ppm in an intensity ratio 2:1. Therefore, these signals are assigned to the two chemically different silicon atoms of the Si_3N_3 ring. Additionally, a ^{29}Si resonance peak at -30.9 ppm was found in the spectrum of cyclosilazane **3**, indicating the silicon atom of the trichlorosilyl moiety. In the case of compound **4** the ^{119}Sn resonance was measured at -128 ppm.

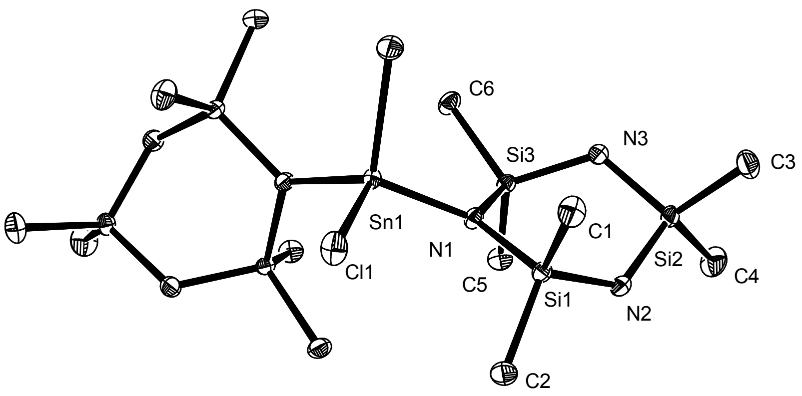
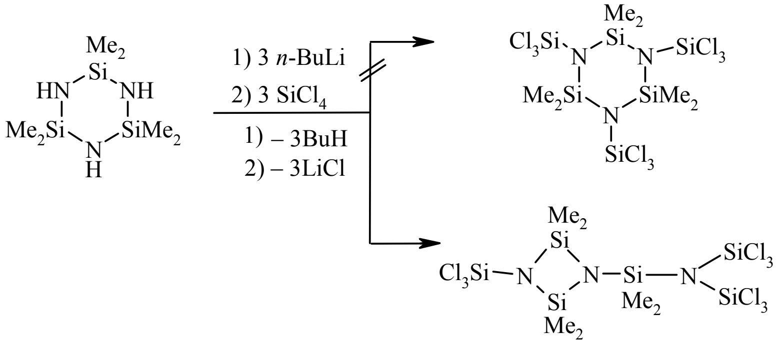


Fig. 3. ORTEP plot of **4** displaying thermal ellipsoids at the 50% probability level.

Variations in the molar ratios of the educts yielded cyclodisilazanes instead. The reaction of Li_3(HMCTS) with $SiCl_4$ in a molar ratio of 1:3 leads to the formation of cyclodisilazane **5** but not to tris(trichlorosilyl)hexamethylcyclotrisilazane.



5

The production of cyclodisilazane **5** can be explained on the basis of an anionic rearrangement accompanied by ring contraction. Detailed studies [17–19] have shown that isomerizations of the cyclotrisilazane system depend on both the extent of lithiation as well as the type of additional substituents. Also thermal effects are important. The crystal structure of the cyclodisilazane molecule **5** is presented in Fig. 4.

Cyclodisilazane **5** crystallizes in the monoclinic space group $P2_1$ with two molecules in the unit cell. The electronic situation in the molecule is reflected by the Si–N bond lengths. The electron-withdrawing character of the trichlorosilyl moieties results in the unusually short Si(4)–N(3) distance (1.66 Å) as well as long Si(1)–N(1) distance (1.82 Å) in comparison with the other Si–N bond lengths in cyclodisilazane **5**.

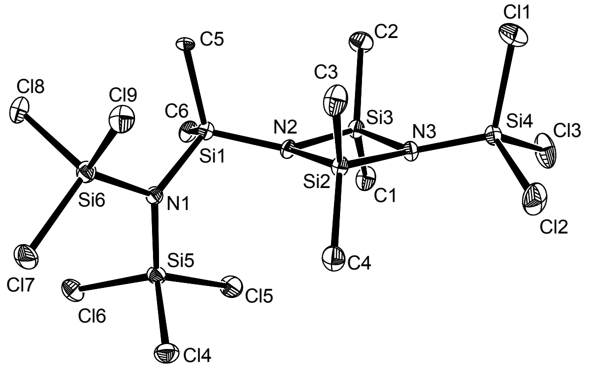
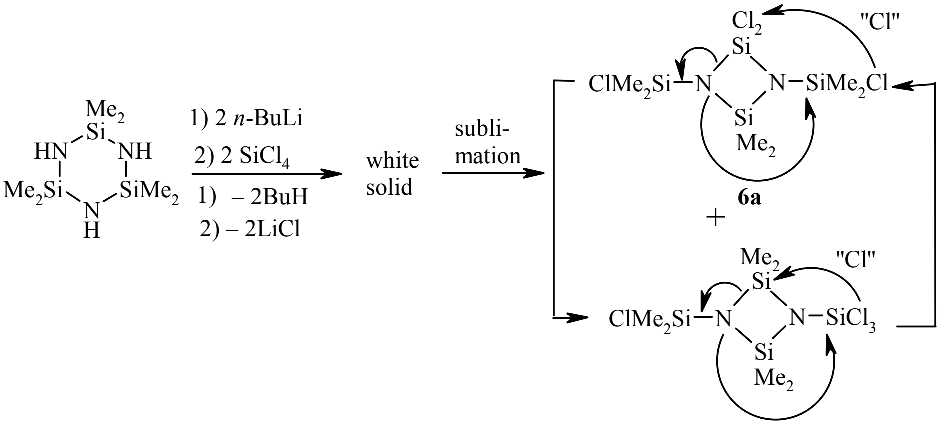


Fig. 4. ORTEP plot of **5** displaying thermal ellipsoids at the 50% probability level.

Cyclodisilazanes **6a**,**b**, which regarding their structure are related to 1,3-bis(chlorodimethylsilyl)-tetramethylcyclodisilazane described by Wannagat [20] and Breed [21], are obtained by the reaction of Li_2H(HMCTS) with $SiCl_4$ followed by sublimation of the primarily produced white solid.



6a + **6b**

In solution both isomers **6a**,**b** coexist (concentration ratio 7:3) according to ^{29}Si NMR spectroscopy. The X-ray diffraction analysis shows that both molecules can replace each other. They are a part of the sublimed crystals in the same concentration ratio as in solution. In comparison with compound **5**, the Si–N bond in the side chain of the Si_2N_2 ring has to be cleaved to form cyclodisilazanes **6a**,**b**. Whether the cleavage does take place during the reaction or only during the sublimation is not clear so far. The occurrence of unexpectedly substituted silicon atoms is also a remarkable fact. The structures of both isomeric cyclodisilazanes involve terminal chlorodimethylsilyl and trichlorosilyl groups as well as $SiCl_2$ and $SiMe_2$ groups in the Si_2N_2 ring. Thus, the overall reaction includes dismutations of Si–Cl and Si–N bonds. The fact that there is the same ratio of **6a**,**b** in solution as well as in the solid gives strong evidence that dismutations between both molecules do not occur in the final product and both isomers are already part of the primarily obtained white solid. The molecular structures of the cyclodisilazanes **6a**,**b** are presented in Fig. 5.

Cyclodisilazane **6** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. The Si(1)–N(1)–Si(1)* as well as N(1)–Si(1)–N(1)* bond angles, which measure 90.9(1) and 89.1(1)°, respectively, are almost ideal for the planar Si_2N_2 ring. These values reflect the more symmetrical substitution of the four-membered silazane ring in contrast to cyclodisilazane **5**, in which the corresponding bond angles exhibit larger variations from the ideal angle of 90°. Further details of molecules **6a**,**b** cannot be discussed due to their disorder.

In the ^{14}N NMR spectra of compounds **5** and **6a**,**b** as well as in those of compounds **1-4** (in comparison with those of H(DPTMDS) and H_3(HMCTS) with $\delta^{14}N \approx -360$ ppm), characteristic downfield shifts of the resonance signals of the deprotonated nitrogen atoms are found. Their resonances are measured in the region between -75 and -70 ppm. The ^{29}Si NMR spectra of compounds **5** and **6a**,**b** exhibit resonance signals in the region between 8 and 14 ppm, which are assigned to silicon atoms of $(Si–N)_2$ rings. They appear ca. 10-15 ppm downfield shifted from the signals of silicon atoms of the cyclotrisilazane ring, which are located between -5 and 0 ppm.

The lithium salts of H(DPTMDS) and H_3(HMCTS) vary in their reactivity patterns in reactions with $SiCl_4$ and $SnCl_4$. Whereas the reactions with Li(DPTMDS) yielded the expected substitution products, in the case of Li-salts of H_3(HMCTS) a competition resulted between substitution reactions and isomerizations at the cyclotrisilazane ring, which lead to different products. Compounds **1-6** represent valuable synthons for further reactions due to the reactive Si–Cl and Sn–Cl moieties, respectively.

TABLE 1. Data of Crystal Structure Determination and Refinement of Silazanes **2-6**

Compound	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{32}H_{44}Cl_2N_2Si_4Sn$	$C_6H_2N_3Si_4$	$C_{12}H_{40}Cl_2N_6Si_6Sn$	$C_6H_{18}Cl_9N_3Si_6$	$C_6H_{18}Cl_4N_2Si_4$
FW	758.64	352.96	626.63	619.82	372.38
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$C2/c$	$P2_1$	$P2_1/n$
a, Å	11.431(1)	8.677(1)	20.638(1)	9.352(1)	6.498(1)
b, Å	15.893(1)	11.879(1)	8.687(1)	12.014(1)	12.843(2)
c, Å	20.626(1)	16.736(1)	16.293(1)	11.296(1)	10.789(1)
α, °	78.5(1)	90	90	*90*	*90*
β, °	82.7(1)	100.9(1)	97.2(1)	*100.2(3)*	*102.3(1)*
γ, °	86.0(1)	90	90	*90*	*90*
V, $Å^3$	3637.7(3)	1693.9(2)	2898.2(3)	1248.92(12)	879.5(2)
Z	4	4	4	2	2
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{calc.}$, g·cm^{-3}	1.385	1.384	1.436	1.648	1.406
Crystal size, mm	0.20×0.08×0.04	0.25×0.11×0.04	0.55×0.30×018	0.41×0.32×0.10	0.22×0.10×0.06
T, K	93(2)	93(2)	93(2)	93(2)	93(2)
R_1 [I>2σ(I)]	0.0484	0.0279	0.0166	0.0293	0.0210
wR_2 [I>2σ(I)]	0.1050	0.0627	0.0407	0.0818	0.0590
R_1 (all data)	0.0905	0.0423	0.0201	0.0323	0.0251
wR_2 (all data)	0.1130	0.0658	0.0417	0.0828	0.0605
GOF	1.060	1.037	1.133	1.030	1.049

TABLE 2. Selected Bond Lengths and Angles in Silazanes **2-6**

Compound	Lengths	*l*, Å	Angles	δ, deg.
1	2	3	4	5
2	Sn(1)–N(1)	2.000(4)	N(1)–Sn(1)–N(2)	119.8(2)
	Sn(1)–N(2)	2.020(4)	N(1)–Sn(1)–Cl(1)	105.8(1)
	Sn(1)–Cl(1)	2.319(2)	N(2)–Sn(1)–Cl(1)	112.2(1)
	Sn(1)–Cl(2)	2.328(2)	N(1)–Sn(1)–Cl(2)	111.8(1)
	Si(1)–N(1)	1.764(5)	N(2)–Sn(1)–Cl(2)	105.8(1)
	Si(1)–C(1)	1.872(6)	N(1)–Si(1)–C(1)	112.6(3)
	Si(1)–C(2)	1.855(6)	N(1)–Si(1)–C(2)	109.8(2)
	Si(1)–C(3)	1.873(6)	C(2)–Si(1)–C(1)	106.5(3)
	Si(2)–N(1)	1.774(5)	N(1)–Si(1)–C(3)	110.5(2)
			C(2)–Si(1)–C(3)	110.4(3)
			C(1)–Si(1)–C(3)	106.8(3)
3	Si(1)–Cl(1)	2.034(1)	N(1)–Si(1)–Cl(1)	112.9(1)
	Si(1)–N(1)	1.672(2)	Si(1)–N(1)–Si(2)	120.4(1)
	Si(2)–N(1)	1.780(2)	N(1)–Si(2)–N(2)	109.1(1)
	Si(2)–N(2)	1.708(2)	N(2)–Si(3)–N(3)	101.0(1)
	Si(2)–C(1)	1.849(2)	N(1)–Si(2)–C(1)	106.9(1)
	Si(3)–N(2)	1.718(2)	N(2)–Si(2)–C(1)	112.4(1)
	Si(3)–N(3)	1.718(2)	N(2)–Si(3)–C(3)	114.9(1)
	Si(3)–C(3)	1.855(2)		
4	Sn(1)–N(1)	1.990(1)	Cl(1)–Sn(1)–Cl(1)*	101.7(1)
	Sn(1)–Cl(1)	2.336(2)	Cl(1)–Sn(1)–N(1)*	109.8(1)
	Si(1)–N(1)	1.758(1)	N(1)–Sn(1)–N(1)	117.6(1)
	Si(1)–N(2)	1.728(1)	N(1)–Si(1)–N(2)	106.1(1)
	Si(1)–C(1)	1.863(1)	N(1)–Si(1)–C(1)	109.0(1)
	Si(2)–N(2)	1.731(1)	N(2)–Si(1)–C(1)	111.1(1)
	Si(2)–C(3)	1.859(1)	Si(1)–N(2)–Si(2)	127.2(1)
			N(2)–Si(2)–C(3)	114.0(1)
5	Cl(1)–Si(4)	2.032(1)	N(1)–Si(1)–N(2)	107.7(1)
	Cl(4)–Si(5)	2.024(1)	N(1)–Si(1)–C(5)	110.3(1)
	Cl(7)–Si(6)	2.027(1)	Si(1)–N(1)–Si(5)	119.9(1)
	Si(1)–N(1)	1.818(1)	Si(5)–N(1)–Si(6)	119.1(1)
	Si(1)–N(2)	1.707(1)	N(1)–Si(5)–Cl(4)	113.4(1)
	Si(1)–C(5)	1.884(2)	N(2)–Si(1)–C(5)	109.4(1)
	Si(2)–N(2)	1.746(1)	Si(1)–N(2)–Si(2)	133.9(1)
	Si(2)–N(3)	1.763(1)	N(2)–Si(2)–N(3)	88.2(1)
	Si(2)–C(3)	1.844(2)	N(2)–Si(2)–C(3)	115.9(1)
	Si(4)–N(3)	1.661(1)	Si(2)–N(2)–Si(3)	92.2(1)
	Si(5)–N(1)	1.713(1)	Si(2)–N(2)–Si(4)	131.3(1)
			N(3)–Si(4)–Cl(1)	113.2(1)
6	Si(1)*–C(1)	1.841(7)	Si(1)–N(1)–Si(2)	133.3(1)
	Si(1)–Cl(1)	2.018(3)	Si(1)–N(1)–Si(1)*	90.9(1)
	Si(1)–N(1)	1.740(1)	N(1)–Si(1)–Cl(1)	114.4(1)
	Si(2)–N(1)	1.704(1)	N(1)–Si(1)–C(1)	116.0(3)
	Si(2)–C(3)	1.830(7)	N(1)–Si(1)–N(1)*	89.1(1)
	Si(2)*–Cl(3)	1.989(4)	N(1)*–Si(2)*–Cl(3)	109.9(2)
			N(1)–Si(2)–C(3)	108.8(3)

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* See Fig. 5.

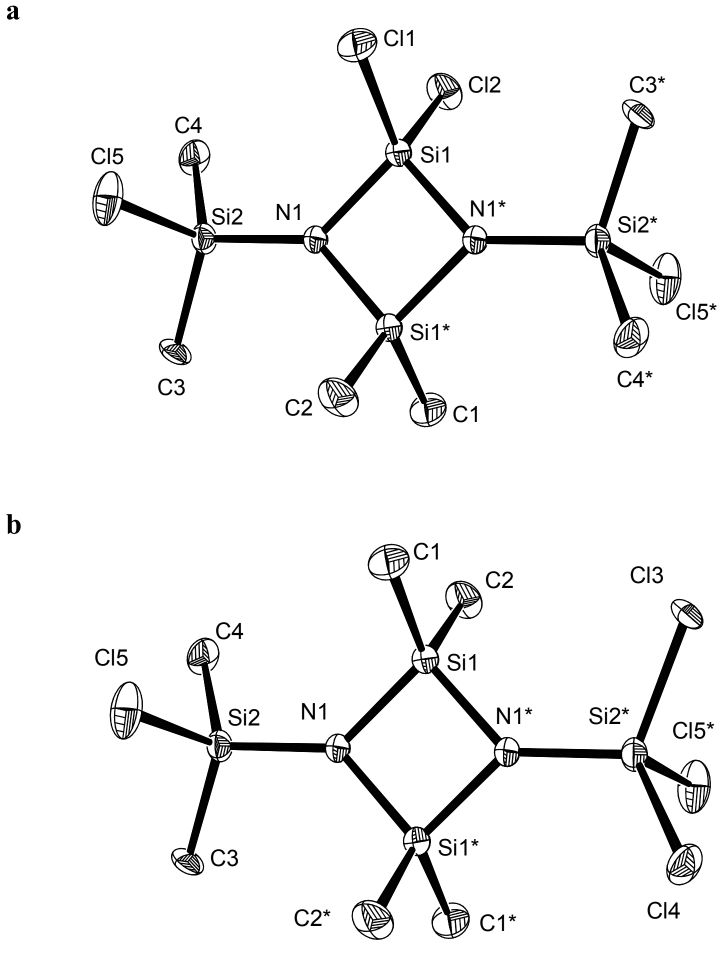

Fig. 5. ORTEP plot of **6a**,**b** displaying thermal ellipsoids at the 50% probability level.

EXPERIMENTAL

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line, glovebox and syringe techniques. H(DPTMDS) and H_3(HMCTS) were purchased from ABCR GmbH as well as *n*-BuLi, $SiCl_4$, and $SnCl_4$ from Acros Organics. Toluene and hexane were distilled from sodium/benzophenone and stored over sodium wire. NMR spectra were recorded at 400 (^1H), 100 (^{13}C), 29 (^{14}N), 79 (^{29}Si), and 149 MHz (^{119}Sn) on a Bruker DPX 400 instrument. Elemental analyses were performed on a Foss Heraeus CHN-O-Rapid apparatus. X-Ray structure data were recorded on a Bruker-Nonius-X8-APEX2-CCD diffractometer with Mo-Kα-radiation ($\lambda = 0.71073$ nm) and semi-empirical correction (SADABS) was applied. The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least-squares methods (refinement of F^2 against all reflections with SHELXS-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined isotropically. Selected data of structure determination and refinement are summarized in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-619442 (**2**), CCDC-619440 (**3**), CCDC-619441 (**4**), CCDC-619439 (**5**), and CCDC-619443 (**6**).

2-Lithio-1,1,3,3-tetramethyl-1,3-diphenyldisilazane. A 2.5 molar solution of *n*-butyllithium (2.9 ml, 7.25 mmol) in hexane was slowly added to an ice-cooled solution of 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (2 g, 7.00 mmol) in toluene (20 ml). The resulting clear colorless solution was allowed to reach room temperature and stirred for 1 h. For the reactions with $SiCl_4$ and $SnCl_4$, respectively the solution of this lithium salt of the disilazane was used as prepared.

Dichlorobis[bis(dimethylphenylsilyl)amino]silane (1). A solution of silicon(IV) chloride (0.59 g, 3.47 mmol) in toluene (10 ml) was added dropwise to the solution of 2-lithio-1,1,3,3-tetramethyl-1,3-diphenyldisilazane. This procedure leads to a slight warming of the reaction mixture. After 24-h stirring at room temperature the solvents were removed under reduced pressure. The residue was dissolved in hexane, LiCl was filtered off, and evaporation of the solvent yielded a clear colorless oil. Yield 1.89 g (81.6%). ^1H NMR spectrum, δ, ppm: 0.59 (24H, s, SiMe); 7.43 (12H, s, SiPh); 7.68 (8H, s, SiPh). ^{13}C NMR spectrum, δ, ppm: 1.1 (SiMe); 125.5, 128.3, 132.4, 139.8 (SiPh). ^{14}N NMR spectrum, δ, ppm: -75. ^{29}Si NMR spectrum, δ, ppm: -1.6, 2.1. Found, %: C 57.88; H 6.73; N 4.11. $C_{32}H_{44}Cl_2N_2Si_5$. Calculated, %: C 57.53; H 6.64; N 4.19.

Dichlorobis[bis(dimethylphenylsilyl)amino]stannane (2). The synthesis was carried out as described for compound 1 with a 2.5 molar solution of *n*-butyllithium (2.9 ml, 7.25 mmol) in hexane, 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (2 g, 7.00 mmol) in toluene (25 ml), and tin(IV) chloride (0.91 g, 3.49 mmol) in toluene (10 ml) as reagents. After removal of the solvents, dissolving the residue in hexane, filtration, and concentration of the filtrate, compound 2 formed pale yellow (almost colorless) crystals, which were filtered off and dried in vacuum. Yield 1.92 g (72.5%). ^1H NMR spectrum, δ, ppm: 0.62 (24H, s, SiMe), 7.61 (12H, s, SiPh), 7.84 (8H, s, SiPh). ^{13}C NMR spectrum, δ, ppm: 0.3 (SiMe); 127.8, 129.4, 133.1, 139.7 (SiPh). ^{14}N NMR spectrum, δ, ppm: -72. ^{119}Sn NMR spectrum, δ, ppm: -130. ^{29}Si NMR spectrum, δ, ppm: -1.0. Found, %: C 50.93; H 5.91; N 3.64. $C_{32}H_{44}Cl_2N_2Si_4Sn$. Calculated, %: C 50.66; H 5.85; N 3.69.

1-Lithio-2,2,4,4,6,6-hexamethylcyclotrisilazane. A 2.5 molar solution of *n*-butyllithium (3.7 ml, 9.25 mmol) in hexane was slowly added to an ice-cooled solution of 1,1,3,3,5,5-hexamethylcyclotrisilazane (2 g, 9.11 mmol) in toluene (20 ml). The resulting clear colorless solution was allowed to reach room temperature and stirred for 1 h. For further reactions this lithium salt of the cyclic silazane was used directly in solution. ^{29}Si NMR spectrum, δ, ppm: -6.6, -16.2.

Two- and three-fold lithiation of 1,1,3,3,5,5-hexamethylcyclotrisilazane. The bi- or trimolar amount of the standard butyllithium solution (7.4 ml, 18.5 mmol or 11.1 ml, 27.75 mmol) was added dropwise at 0 °C to a solution of 1,1,3,3,5,5-hexamethylcyclotrisilazane (2 g, 9.11 mmol) in toluene (25 ml). A white suspension formed, which was allowed to reach room temperature. The mixture was stirred for 1 h. Suspensions of multiple lithiated hexamethylcyclotrisilazane, obtained by this procedure, were used directly for further reactions with $SiCl_4$ and $SnCl_4$ without characterization because of the poor solubility of the lithium salts of the cyclic silazane in common organic solvents.

Reactions of lithiated hexamethylcyclotrisilazane with $SiCl_4$ and $SnCl_4$ (General procedure). A solution of MCl_4 (M = Si, Sn) in toluene was slowly added at 0°C to the solution of 1-lithio-2,2,4,4,6,6-hexamethylcyclotrisilazane or the suspension of the two- or three-fold lithiated hexamethylcyclotrisilazane in a hexane/toluene mixture. After 24 h of stirring, the solvents were removed in vacuum and the resulting residue was extracted with hexane to yield a clear solution. The products were obtained from this solution by slow evaporation of the solvent.

1-Trichlorosilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane (**3**). The reaction of a 2.5 molar solution of *n*-butyllithium (3.7 ml, 9.25 mmol) in hexane, 1,1,3,3,5,5-hexamethylcyclotrisilazane (2 g, 9.11 mmol) in toluene (25 ml) and silicon(IV) chloride (1.54 g, 9.06 mmol) in toluene (15 ml) as educts yielded white needles of compound **4**. Yield 2.24 g (70.1%). ^1H NMR spectrum, δ, ppm: 0.14-0.25 (18H, m, SiMe); 0.36 (2H, s, NH). ^{13}C NMR spectrum, δ, ppm: 4.3, 4.8 (SiMe). ^{14}N NMR spectrum, δ, ppm: -74, -360. ^{29}Si NMR spectrum, δ, ppm: -30.9, -3.4, -1.9. Found, %: C 20.55; H 5.79; N 11.81. $C_6H_{20}Cl_3N_3Si_4$. Calculated, %: C 20.42; H 5.71; N 11.91.

Dichlorobis(hexamethylcyclotrisilazano)stannane (4). The synthesis was carried out with a 2.5 molar solution of *n*-butyllithium (3.7 ml, 9.25 mmol) in hexane, 1,1,3,3,5,5-hexamethylcyclotrisilazane (2 g, 9.11 mmol) in toluene (20 ml), and tin(IV) chloride (1.18 g, 4.53 mmol) in toluene (15 ml) as reagents. After working-up the mixture of the products a clear yellow solution was obtained. Slow evaporation of hexane produced crystals of the tin complex, which were filtered off and dried in vacuum. Yield 1.90 g (66.9%). ^{1}H NMR spectrum, δ, ppm: 0.10-0.22 (36H, m, SiMe); 0.36 (4H, s, NH). ^{13}C NMR spectrum, δ, ppm: 3.4, 4.6 (SiMe). ^{14}N NMR spectrum, δ, ppm: -72, -358. ^{29}Si NMR spectrum, δ, ppm: -1.0, -3.6. ^{119}Sn NMR spectrum, δ, ppm: -128. Found, %: C 22.93; H 6.38; N 13.52. $C_{12}H_{40}Cl_2N_6Si_6Sn$. Calculated, %: C 23.00; H 6.43; N 13.41.

1-Trichlorosilyl-3-bis(trichlorosilyl)aminodimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (5). The reaction of a 2.5 molar solution of *n*-butyllithium (5.5 ml, 13.75 mmol) in hexane, 1,1,3,3,5,5-hexamethylcyclotrisilazane (1 g, 4.56 mmol) in toluene (25 ml), and silicon(IV) chloride (2.32 g, 13.66 mmol) in toluene (25 ml) yielded white needles of the product, which were filtered off and dried in vacuum. Yield 2.04 g (42.3%). ^{1}H NMR spectrum, δ, ppm: 0.32 (12H, s, SiMe); 0.61 (6H, s, SiMe). ^{13}C NMR spectrum, δ, ppm: 3.8, 6.5 (SiMe). ^{14}N NMR spectrum, δ, ppm: -71. ^{29}Si NMR spectrum, δ, ppm: -32.1, -1.3, -0.1, 13.4. Found, %: C 11.43; H 2.82; N 6.94. $C_6H_{18}Cl_9N_3Si_6$. Calculated, %: C 11.63; H 2.92; N 6.78.

1,3-Bis(dimethylchlorosilyl)-2,2-dichloro-4,4-dimethylcyclodisilazane (6a) and 1-trichlorosilyl-3-chlorodimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (6b). The synthesis was carried out with a 2.5 molar solution of *n*-butyllithium (7.4 ml, 18.5 mmol) in hexane, 1,1,3,3,5,5-hexamethylcyclotrisilazane (2 g, 9.11 mmol) in toluene (25 ml), and silicon(IV) chloride (3.10 g, 18.25 mmol) in toluene (25 ml) as starting materials. After working up the reaction mixture a white solid was obtained as product. Subsequent sublimation at 100 C and 5 Torr gave white crystals of compound **6**. Yield 2.07 g (61.0%). ^{1}H NMR spectrum, δ, ppm: 0.38-0.41 (m, SiMe). ^{13}C NMR spectrum, δ, ppm: 2.8, 3.7, 3.9, 4.3 (SiMe). ^{14}N NMR spectrum, δ, ppm: -73. ^{29}Si NMR spectrum, δ, ppm: 11.0, 8.3, -4.1 (**6a**); 9.3, -2.2, -33.9 (**6b**). Found, %: C 19.46; H 4.95; N 7.41. $C_6H_{18}Cl_4N_2Si_4$ (372.38). Calculated, %: C 19.35; H 4.87; N 7.52.

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