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Synthesis and Characterization of Novel Titanium, Germanium, and Tin Silazane Complexes Bearing a Cyclohexasilazanetriido Ligand

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Novel heterometallic silazane complexes were synthesized by the reaction of 1-lithio-2,2,4,4,6,6-hexamethylcyclotrisilazane Li(HMCTS)H_2 with the tetrachloride salts of titanium and germanium as well as by the reaction of 1,1,3,3,5,5-hexamethylcyclotrisilazane H_3(HMCTS) with tin tetrachloride and excess triethylamine. The products [H_3(DMCHS)TiCl] (**1**), [H_3(DMCHS)GeCl] (**2**), and [H_3(DMCHS)SnCl] (**3**) {H_3(DMCHS) = 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethylcyclohexasilazane-1,5,9-triido} were characterized by ^{1}H-, ^{13}C-, ^{14}N-, and ^{29}Si NMR spectroscopy, elemental analyses and single-crystal X-ray structure analyses. The complexes have a surprising and interesting structure, that of a new dodecamethylcyclohexasilazane system with the Ti, Ge, or Sn atom in the center. These metal atoms are coordinated by one chlorine atom and three nitrogen atoms. The metal centers are part of three six-membered hetero-silazane rings.
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Introduction

Silazanes offer promising ligand properties in reactions with metal chlorides because of their reactive N–H and Si–N bonds.[1–3] Especially, the cyclic silazane 1,1,3,3,5,5-hexamethylcyclotrisilazane H_3(HMCTS) shows striking reactivity patterns. In addition to substitution reactions, isomerizations of the cyclotrisilazane system into cyclodisilazanes and ring coupling reactions were observed, which led to an assortment of structurally diverse compounds.[4–10]

Silazanes are widely used as precursors for silicon-based non-oxide ceramic materials with outstanding thermal, mechanical, and chemical properties, which make them uniquely applicable under extreme conditions.[11–13] Furthermore, silazane derivatives of Ti, Zr, Fe, B, Al, and Ge are used for the synthesis of multinary ceramics. The incorporation of these elements provides access to new classes of ceramic materials and to the development of new applications. For example, the integration of boron can improve the thermal stability of silicon-based ceramic materials up to 2000 °C because of the suppression of recrystallization processes.[14] The incorporation of iron leads to magnetic ceramics.[15] The germanium(II) precursor, Ge[N$(SiMe_3)_2]_2$, has been employed to obtain germanium nanocrystals by thermal decomposition of the complex.[16]

These developments encouraged us to examine reactions between H_3(HMCTS) and $TiCl_4$, $GeCl_4$, and $SnCl_4$ in order to combine the interesting chemistry of cyclic silzanes and the synthesis of metal-atom-containing Si–C–N molecules. In this paper, we report the ring-isomerization of H_3(HMCTS) with formation of novel Ti-, Ge-, and Sn-centered tricyclic silazane frameworks.

Results and Discussion

1-Lithio-2,2,4,4,6,6-hexamethylcyclotrisilzane [Li(HMCTS)H_2] was prepared by treating a toluene solution of H_3(HMCTS) with an equimolar amount of a solution of *n*-butyllithium in hexane. The subsequent reaction of Li(HMCTS)H_2 with $TiCl_4$ or $GeCl_4$ in a molar ratio of 2:1 should produce Ti- or Ge-containing silazane compounds and LiCl as by-product (Scheme 1, route A). Surprisingly, the ^{29}Si NMR spectra of the products exhibit only one resonance signal. This fact and also the result of the elemental analyses were not in accord with any structures derived from simple substitutions or ring contractions of the cyclotrisilazane system. Fortunately, we were able to obtain crystals of both products, and the nature of the new complexes **1** and **2** could easily be clarified by crystal structure analysis (Scheme 1, route B).

Both complexes **1** and **2** exhibit the same cyclohexasilazane ring system with the titanium or germanium atom in the center of the ring system. When the reaction conditions were varied and H_3(HMCTS), titanium tetrachloride, and excess triethylamine were used, the same titanium complex **1** formed, with only a small difference in the yield. Furthermore, the reaction pathway was almost unaffected by the type of solvent used. The reaction of Li(HMCTS)H_2 with tin tetrachloride in a ratio of 2:1 yields the substitution product dichlorobis(2,2,4,4,6,6-hexamethylcyclotrisilazano)stannane, as we reported recently (Scheme 2, route A),[17] but a complex analogous to **1** or **2** was not found. Complex

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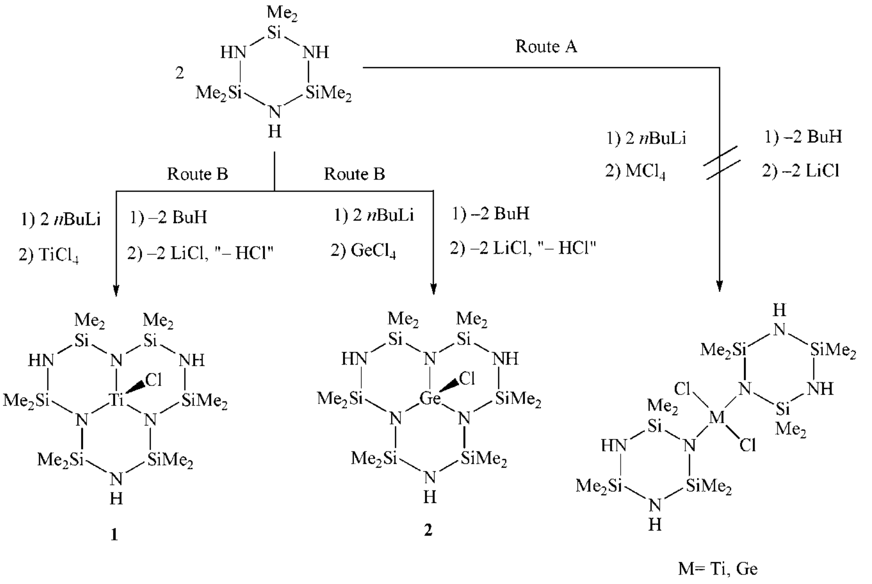
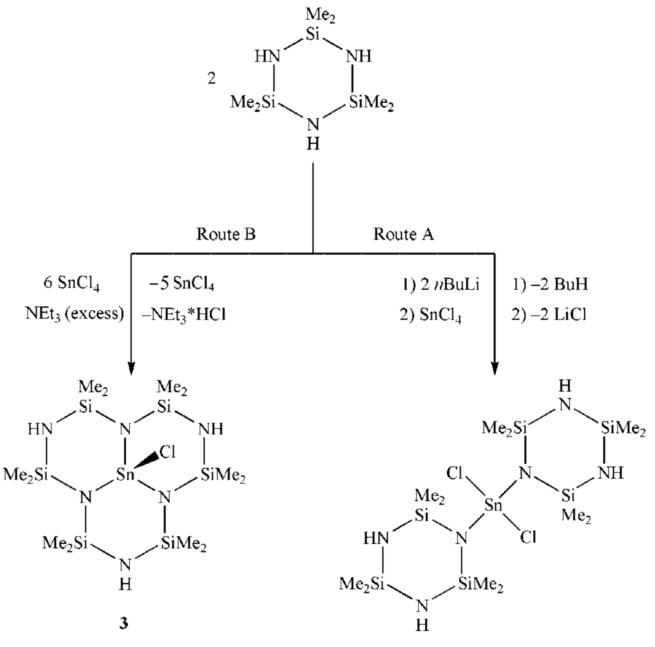


Scheme 1. Synthesis of titanium and germanium cyclohexasilazane complexes by reaction of lithiated H_3(HMCTS) with $TiCl_4$ and $GeCl_4$.

3, which exhibits the same molecular structure as **1** and **2**, was synthesized by reacting H_3(HMCTS) with 3 equiv. $SnCl_4$ and excess triethylamine (Scheme 2, route B).



Scheme 2. Formation of the tin cyclohexasilazane complex **3** by reaction of H_3(HMCTS) with $SnCl_4$ and Et_3N.

The formation of **3** deserves specific attention because of the different starting material molar ratios from those used in the reactions of Li(HMCTS)H_2 with $TiCl_4$ and $GeCl_4$. The NMR spectroscopic data of **1**, **2**, and **3** are presented in Table 1.

Table 1. ^1H, ^{13}C, ^{14}N, ^{29}Si, ^{49} Ti, and ^{119}Sn NMR spectroscopic data for the new complexes **1**, **2**, and **3**.

Compound	^1H Si–Me	N–H	^{13}C	^{14}N M–N	N–H	^{29}Si	^{49}Ti, ^{73}Ge or ^{119}Sn
1	0.20, 0.26	0.56	1.9, 4.5	–85	–343	–7.0	–137
2	0.28, 0.35	0.61	2.5, 5.3	–83	–349	–3.8	not obtained
3	0.21, 0.33	0.58	3.3, 4.6	–71	–350	–3.9	–169

The ^{29}Si NMR spectra of the heterometallic complexes exhibit one resonance signal each, which is located at –7 ppm for **1** and at ca. –4 ppm for **2** and **3**. Therefore, the chemical shifts are nearly identical with that of H_3(HMCTS) [$\delta(^{29}Si)$ = –4.3 ppm].

Time-dependent ^{29}Si NMR studies of the reaction between H_3(HMCTS) and $TiCl_4$ provided valuable data from which a possible reaction pathway can be proposed, although the overall reaction mechanism is not clear so far. The ^{29}Si resonance of the silazane starting material quickly disappears after the start of the reaction, and new resonance signals ranging from 10 to 15 ppm arise in the spectra. They can be assigned to silicon atoms of $(Si–N)_2$ rings[17] and indicate cyclodisilazanes as intermediates in the formation of the dodecamethylcyclohexasilazane ring, which is found in complexes **1**–**3**. During the reaction, the intensities of the resonance signals between 10 and 15 ppm decrease, and simultaneously, the ^{29}Si resonance of the titanium complex **1** appears at δ = –7 ppm.

Compound **1** has a ^{49}Ti NMR signal at δ = –137 ppm, and compound **3** a ^{119}Sn resonance at δ = –169 ppm, but no ^{73}Ge signal was measured for compound **2** because of the quadrupolar momentum of this nucleus and the unsymmetrical substitution pattern of the germanium atom in **2**. The methyl moieties at each silicon atom are diastereotopic as indicated by two signals for the methyl groups in both the ^{1}H- and ^{13}C NMR spectra of complexes **1**–**3**. The ^{14}N NMR spectra exhibit a broad resonance signal at around –350 ppm, which results from the nitrogen atoms bearing one hydrogen atom. The location of this signal is similar to that of the chemical shift of the silazane starting material [$\delta(^{14}N)$ = –360 ppm]. Additionally, a sharp signal is detected between –85 and –70 ppm, which indicates the deprotonated nitrogen atom that is bonded to the titanium, germanium, and tin atoms.

Crystals suitable for X-ray diffraction analysis were easily obtained in the case of compound **1** by crystallization from hexane. The reaction of $GeCl_4$ with Li(HMCTS)H_2 primarily gave a clear, colorless oil. However, storage of this oil at –20 °C for several days produced white crystals. In case of the tin complex **3**, crystals were obtained by sublimation (T = 120 °C, p = 5 Torr) of the crude product. The molecular structures of compounds **1**, **2**, and **3** are illustrated in Figures 1, 2, and 3, respectively. Crystal data collection parameters and structure refinement details are given in the Experimental Section (Table 2).

The single-crystal X-ray structure analysis of **1** shows that the titanium complex crystallizes in two different modifications (trigonal $P31c$; hexagonal $P6_3$) with two molecules in each unit cell. Both modifications exhibit analogous molecular conformations and similar cell dimensions. The corresponding bond lengths and angles of **1** in the two modifications are identical within the range of standard error. The titanium atom is coordinated by three nitrogen atoms and one chlorine substituent. Thus, the coordination sphere exhibits a tetrahedral geometry (Figure 1). The angles N1–Ti–N1* [109.6(1)°] and N1–Ti–Cl [109.3(1)°] in **1** ($P6_3$) perfectly match this coordination pattern. Si–N bond lengths in **1** are in the typical range 1.72–1.75 Å. In both modifications, the Ti–Cl bond is situated on a threefold axis of rotation. Therefore, the asymmetric unit consists of one third of a molecule of **1**.

The germanium complex **2** crystallizes in the same trigonal space group $P31c$ as found for one modification of **1** with two molecules in the unit cell. The germanium atom in **2** has a slightly distorted tetrahedral coordination sphere with a N1–Ge–N1* angle of 111.6(1)° and a N1–Ge–Cl angle of 107.3(1)° (Figure 2).

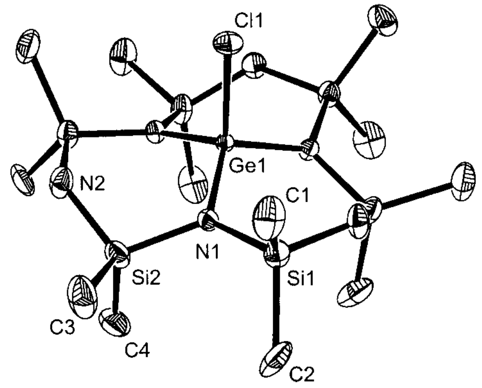


Figure 2. ORTEP plot of one molecule of **2** (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: **2**: Ge–N1 1.823(4), Ge–Cl 2.192(2), Si1–N1 1.735(4), Si2–N1 1.761(5), Si1–N2 1.720(5), Si2–N2 1.722(5), N1–Ge–N1* 111.6(1), N1–Ge–Cl 107.3(1), N1–Si1–N2 105.0(2), N1–Si2–N2 107.4(2), Si1–N1–Si2 122.0(3), Si1–N2–Si2 125.8(3).

The tin complex **3** crystallizes in the hexagonal space group $P6_3$ with two molecules in the unit cell and is isomorphic with one modification of **1**. The tin atom in the center of the complex is almost tetrahedrally coordinated by the ligands, with bond angles of 110.1° and 108.8° for N1–Sn–N1* and N1–Sn–Cl, respectively (Figure 3). Despite the different metal atoms, the corresponding bond lengths and angles in **2** and **3** are similar to those in **1** with only minor differences that can arise as a result of the different atomic radii of Ti, Ge, and Sn.

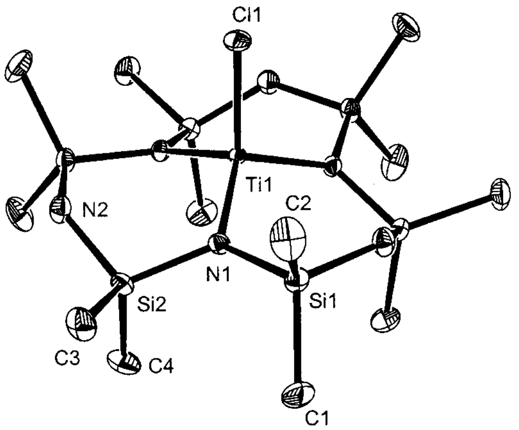


Figure 1. ORTEP plot of one molecule of **1** in space group $P6_3$ (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: **1** ($P6_3$): Ti–N1 1.899(1), Ti–Cl 2.276(1), Si1–N1 1.740(1), Si2–N1 1.751(1), Si2–N2 1.717(1), N1–Ti–N1* 109.6(1), N1–Ti–Cl 109.3(1), N1–Si1–N2 105.8(1), N1–Si2–N2 107.4(1), Si1–N1–Si2 123.0(1), Si1–N2–Si2 127.7(1).

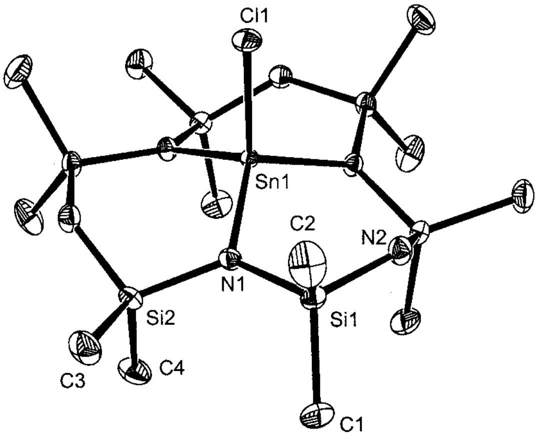


Figure 3. ORTEP plot of one molecule of **3** (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and angles [°]: **3**: Sn–N1 2.016(1), Sn–Cl 2.351(1), Si1–N1 1.731(1), Si2–N1 1.741(1), Si1–N2 1.720(1), Si2–N2 1.721(1), N1–Sn–N1* 110.1(1), N1–Sn–Cl 108.8(1), N1–Si1–N2 106.0(1), N1–Si2–N2 107.5(1), Si1–N1–Si2 127.9(1), Si1–N2–Si2 130.7(1).

Conclusions

For the first time, titanium, germanium, and tin complexes exhibiting a dodecamethylcyclohexasilazano ligand have been synthesized by reactions starting from H_3(HMCTS) and MCl_4 (M = Ti, Ge, Sn). In contrast to conversions of $TiCl_4$ and $GeCl_4$ with Li(HMCTS)H_2 to the new compounds **1** and **2**, respectively, the analogous reaction with $SnCl_4$ leads to the substitution product $Cl_2Sn[(HMCTS)H_2]_2$. However, the tin complex **3** that features the same molecular structure of **1** and **2** is obtained by using NEt_3/H_3(HMCTS) instead of Li(HMCTS)H_2 as starting materials. The formation of the novel cyclohexasilazane framework in **1**–**3** emphasizes the striking reactivity patterns of H_3(HMCTS) in reactions with metal chlorides to mark a new reaction pathway in addition to the well-known ring-contraction reactions and substitution reactions of the cyclotrisilazane system. The titanium and germanium complexes **1** and **2** are potentially good candidates to act as single-source precursors for ceramic materials of the quaternary SiCNTi and SiCNGe systems, respectively. All new compounds represent valuable synthons for further reactions because of their reactive M–Cl bonds. Further investigation of derivatization reactions of **1**–**3** and of the reaction mechanism of the overall formation reaction are to be undertaken now.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon by using a standard Schlenk line, a glovebox, and syringe techniques. H_3(HMCTS) was purchased from ABCR GmbH, and *n*BuLi, $SiCl_4$, $GeCl_4$, and $SnCl_4$ from Acros Organics. Toluene and hexane were distilled from over sodium/benzophenone and stored over sodium wire. NMR spectra were recorded at 400.13 MHz (^1H NMR), 100.62 MHz (^{13}C NMR), 28.91 MHz (^{14}N NMR), 79.49 MHz (^{29}Si NMR), 22.56 MHz (^{49}Ti NMR), and 149.21 MHz (^{119}Sn NMR) with a BRUKER DPX 400 instrument. Elemental analyses were performed on a Foss Heraeus CHN-O-Rapid apparatus. X-ray structure data were recorded with a Bruker-Nonius-X8-APEX2-CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å), 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. Merohedral twinning was found for **1** in both modifications as well as for **2** (about 50:50 ratio in each case). The crystal of **3** exhibited neither merohedral nor racemic twinning. Selected data for the structure determination and refinement are summarized in Table 2. CCDC-621166 (**1** *P*31*c*), CCDC-621165 (**1** *P*6$_3$), CCDC-621164 (**2**), and CCDC-621163 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Chlorido-2,2,4,4,6,6,8,8,10,10,12,12-dodecamethylcyclohexasilazane-1,5,9-triidotitanium (1): A solution of *n*-butyllithium (3.7 mL of a 2.5-M solution, 9.2 mmol) in hexane was slowly added to an ice-cooled solution of 1,1,3,3,5,5-hexamethylcyclotrisilazane (2.0 g, 9.1 mmol) in toluene (25 mL). The resulting clear, colorless solution was allowed to reach room temperature and was stirred for 1 h. A solution of $TiCl_4$ (0.86 g, 4.5 mmol) in toluene (25 mL) was then added dropwise to the resulting solution of 1-lithio-2,2,4,4,6,6-hexamethylcyclotrisilazane. This procedure led to a

Table 2. Crystallographic data for complexes **1**, **2**, and **3**.

Compound	**1a**	**1b**	**2**	**3**
Empirical formula	$C_{12}H_{39}ClN_6Si_6Ti$	$C_{12}H_{39}ClN_6Si_6Ti$	$C_{12}H_{39}ClGeN_6Si_6$	$C_{12}H_{39}ClN_6Si_6Sn$
F_w	519.38	519.38	544.07	590.17
Crystal system	trigonal	hexagonal	trigonal	hexagonal
Space group	*P*31*c*	*P*6$_3$	*P*31*c*	*P*6$_3$
a [Å]	11.368(1)	11.343(1)	11.285(1)	11.475(1)
b [Å]	11.368(1)	11.343(1)	11.285(1)	11.475(1)
c [Å]	12.320(1)	12.205(1)	12.211(1)	12.257(1)
α [°]	90	90	90	90
β [°]	90	90	90	90
γ [°]	120	120	120	120
V [Å^3]	1378.8(1)	1360.0(1)	1346.8(2)	1397.8(1)
Z	2	2	2	2
λ [Å]	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-3}]	1.251	1.268	1.342	1.402
Crystal size [mm]	0.50 × 0.40 × 0.30	0.60 × 0.40 × 0.20	0.40 × 0.05 × 0.03	0.30 × 0.14 × 0.10
T [K]	203(2)	90(2)	93(2)	90(2)
Limiting indices	$-20 \le h \le 19$	$-11 \le h \le 17$	$-13 \le h \le 13$	$-24 \le h \le 24$
	$-20 \le k \le 19$	$-23 \le k \le 20$	$-13 \le k \le 12$	$-24 \le k \le 24$
	$-21 \le l \le 14$	$-25 \le l \le 25$	$-14 \le l \le 14$	$-24 \le l \le 25$
R(int)	0.0303	0.0405	0.0738	0.0300
Θ_{max} [°]/compl. [%]	39.23/99.6	47.99/99.9	25.00/100.0	48.99/100.0
Max. transmission	0.8223	0.8747	0.9560	0.8829
Min. transmission	0.7278	0.7458	0.5956	0.8022
Data/parameters	4778/81	8686/80	1601/81	9081/82
R_1/wR_2 [$I > 2\sigma(I)$]	0.0286/0.0702	0.0266/0.0518	0.0338/0.0653	0.0213/0.0447
R_1/wR_2 (all data)	0.0330/0.0722	0.0353/0.0546	0.0416/0.0679	0.0263/0.0458
GOF	1.024	1.039	1.054	1.041

slight warming of the reaction mixture. After 24 h of stirring at room temperature, the color of the solution became yellow-orange. The solvents were removed under reduced pressure, and the residue was dissolved in hexane and filtered to give a clear yellow solution. After reducing the filtrate volume by evaporation of the solvent, yellow crystals were obtained, which were filtered off and dried in vacuo. Yield: 2.94 g (62%). $C_{12}H_{39}ClN_6Si_6Ti$ (519.38): calcd. C 27.74, H 7.57, N 16.18; found C 27.37, H 7.38, N 16.03. ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.20$ (s, 12 H, Si–Me), 0.26 (s, 12 H, Si–Me), 0.56 (s, 3 H, N–H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): $\delta = 1.9$ (Si–Me), 4.5 (Si–Me) ppm. ^{14}N NMR (28.91 MHz, $CDCl_3$, 25 °C): $\delta = -85$ (Ti–N), –343 (N–H) ppm. ^{29}Si NMR (79.49 MHz, $CDCl_3$, 25 °C): $\delta = -7.0$ ppm. ^{49}Ti NMR (22.56 MHz, $CDCl_3$, 25 °C): $\delta = -137$ ppm.

Chlorido-2,2,4,4,6,6,8,8,10,10,12,12-dodecamethylcyclohexasilazane-1,5,9-triidogermanium (2): The synthesis was carried out as described for **1** with a solution of *n*-butyllithium (5.5 mL of a 2.5-M solution, 13.8 mmol) in hexane, 1,1,3,3,5,5-hexamethylcyclotrisilazane (3.0 g, 13.7 mmol) in toluene (25 mL), and $GeCl_4$ (1.46 g, 6.8 mmol) in toluene (25 mL) as reagents. After removal of the solvents, dissolution of the residue in hexane, and filtration, the hexane was removed from the filtrate under vacuum to give a clear, colorless oil. Storage of the oil at –20 °C for several days led to the formation of white crystals, which were dried in vacuo. Yield: 2.56 g (69%). $C_{12}H_{39}ClGeN_6Si_6$ (544.05): calcd. C 26.49, H 7.22, N 15.45; found C 26.52, H 7.37, N 15.37. ^1H NMR (400.13 MHz, $CDCl_3$, 25 °C): $\delta = 0.28$ (s, 12 H, Si–Me), 0.35 (s, 12 H, Si–Me), 0.61 (s, 3 H, N–H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): $\delta = 2.5$ (Si–Me), 5.3 (Si–Me) ppm. ^{14}N NMR (28.91 MHz, $CDCl_3$, 25 °C): $\delta = -83$ (Ti–N), –349 (N–H) ppm. ^{29}Si NMR (79.49 MHz, $CDCl_3$, 25 °C): $\delta = -3.8$ ppm.

Chlorido-2,2,4,4,6,6,8,8,10,10,12,12-dodecamethylcyclohexasilazane-1,5,9-triidotin (3): At room temperature, a solution of $SnCl_4$ (7.04 g, 27.0 mmol) in toluene (20 mL) was added dropwise to a solution of 1,1,3,3,5,5-hexamethycyclotrisilazane (2.0 g, 9.1 mmol) and triethylamine (3.0 g, 29.7 mmol) in toluene (40 mL). The resulting yellow reaction mixture was stirred for 24 h. Precipitated $NEt_3{\cdot}HCl$ was filtered off, and the solvent as well as the excess triethylamine were removed from the filtrate under reduced pressure to give a brownish solid product. Subsequent sublimation (T = 120 °C, p = 5 Torr) yielded white crystals of compound **3**. Yield: 1.47 g (54.7%). $C_{12}H_{39}ClN_6Si_6Sn$ (590.17): calcd. C 24.42, H 6.66, N 14.24; found C 24.28, H 6.58, N 14.11. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.21$ (s, 12 H, Si–Me), 0.33 (s, 12 H, Si–Me), 0.58 (s, 3 H, N–H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 °C): $\delta = 3.3$ (Si–Me), 4.6 (Si–Me) ppm. ^{14}N NMR (28.91 MHz, $CDCl_3$, 25 °C): $\delta = -71$ (Ti–N), –350 (N–H) ppm. ^{29}Si NMR (79.49 MHz, $CDCl_3$, 25 °C): $\delta = -3.9$ ppm. ^{119}Sn NMR (149.21 MHz, $CDCl_3$, 25 °C): $\delta = -169$ ppm.

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