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Ylenes in the $M^{II}\rightarrow Si^{IV}$ (M = Si, Ge, Sn) Coordination Mode

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Dedicated to Professor Daniel Kost on the occasion of his 70th birthday

Abstract: The reaction of the methimazolyl (mt, i.e., 2-mercapto-1-methylimidazolide) substituted silane $Si(mt)_4$ with $SnCl_2$ and $GeCl_2$ in dioxane affords the paddlewheel-shaped complexes $[ClSi(\mu\text{-}mt)_4MCl]$ (M = Sn (**1**) and Ge (**2**), respectively). These compounds represent the first crystallographically characterized hexacoordinate silicon complexes comprising a Sn or Ge atom in the Si coordination sphere. An attempt to synthesize the related silicon compound **3** $[ClSi(\mu\text{-}mt)_4SiCl]$ instead afforded the trisilane $[ClSi(\mu\text{-}mt)_4Si{-}SiCl_3]$ (**3a**), which provides the first crystallographic evidence for the feasibility of oligosilanes with adjacent hexacoordinate Si atoms. One of the hexacoordinate Si atoms of **3a** features the unprecedented $(Si_2S_4)Si$ skeleton. Natural bonding orbital (NBO) analyses of compounds **1**, **2**, **3a** (and the target compound **3**) revealed characteristics of $M^{II}\rightarrow Si^{IV}$ (for **2** and **3**) or $M^{I}\rightarrow Si^{IV}$ (for **3a**) dative bonding in the systems with M = Si and Ge, whereas compound **1** exhibits a covalent $Sn^{III}{-}Si^{III}$ bond.

Keywords: coordination compounds · intermetallic bonding · main group elements · oligosilanes · silylenes · Mössbauer spectroscopy

Introduction

Silicon in oxidation state +IV represents a relatively small and hard Lewis acid and is therefore mostly bound to hard Lewis bases (i.e., in the coordination sphere of F and O atoms) and other second-row atoms (N, C).[1] In addition to the thermodynamically very stable Si–F and Si–O bonds (and the relatively stable Si–N bonds), Si–C bonds are kinetically quite inert (but can be activated by Si-hypercoordination).[2] In sharp contrast, bonds between silicon and heavier donor atoms such as Br, I, and S atoms are usually significantly less stable (both thermodynamically and kinetically). Thus, Si–Br and Si–I bonds show a pronounced tendency to ionic dissociation,[3] and the construction of penta- or hexacoordinate silicon coordination spheres comprising the very soft donors of the heavier Group 16 and 17 elements remains challenging. Tacke et al. presented a rare example with I and S atoms attached to a pentacoordinate silicon atom,[4] and only recently this group reported pentacoordinate Si complexes which comprise four Se atoms or even a Te atom attached to the silicon atom.[5] In spite of these promising pioneering results, the investigation of heavier Group 14 lone pair donors (germylenes and stannylenes) in the Si coordination sphere remains an open task.[6] Although the heavier ylenes $GeCl_2$ and $SnCl_2$ are isolable, and the portfolio of isolable silylenes did enjoy a notable growth in recent years,[7] only carbenes were reported as Group 14 ylene ligands in the coordination sphere of hypercoordinate Si atoms so far.[8]

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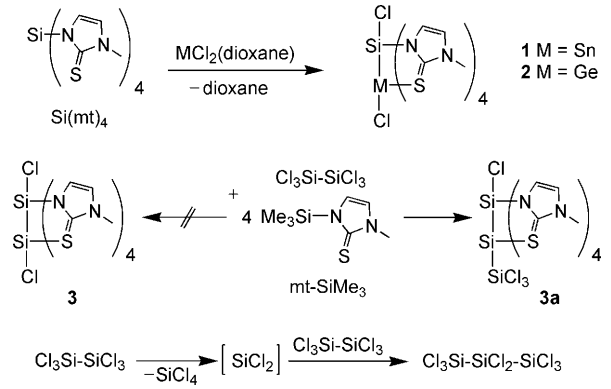
Results and Discussion

Our recently discovered route of loading the Si coordination sphere with a Pd^{II} or Pt^{II} atom as lone-pair donor,[9] achieved with the aid of the (N,S)-ambidentate buttressing ligand methimazolide (2-mercapto-1-methylimidazolide, mt), proved capable of forcing stannylenes and germylenes into the Si coordination sphere (Scheme 1). From 1,4-dioxane, the resulting complexes crystallized as solvates of the composition $[ClSi(\mu\text{-}mt)_4MCl]\cdot 3(dioxane)$ (M = Sn, Ge), and their molecular structures were elucidated by X-ray diffraction analyses (Figure 1).[10]



Scheme 1. Syntheses of paddlewheel compounds **1** and **2** comprising Sn–Si and Ge–Si bonds, respectively, and the related trisilane **3a**.

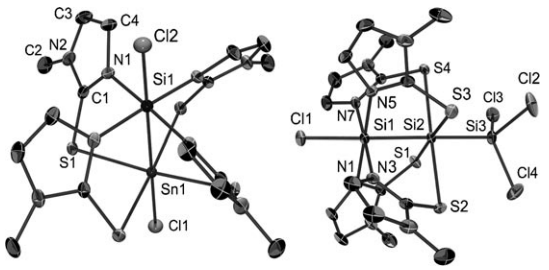


Figure 1. ORTEP diagrams (30% probability ellipsoids) of **1** in the crystal structure of $[ClSi(\mu\text{-}mt)_4SnCl]\cdot 3(dioxane)$ (left) and **3a** in **3a**·(toluene) (right).[10] Hydrogen atoms and solvent molecules are omitted. The molecular shape of **2** (not depicted) is similar to that of **1**. Selected bond lengths [Å] for **1**: Sn1–Cl1 2.370(1), Sn1–S1 2.664(1), Sn1–Si1 2.598(1), Si1–Cl2 2.158(1), Si1–N1 1.912(1); **2**: Ge1–Cl1 2.235(1), Ge1–S1 2.522(1), Ge1–Si1 2.474(1), Si1–Cl2 2.164(2), Si1–N1 1.892(2). Selected bond lengths [Å] and angles [°] for **3a**: Si1–Cl1 2.209(1), Si1–Si2 2.387(1), Si2–Si3 2.349(1), Si2–S1 2.479(1), Si2–S2 2.410(1), Si2–S3 2.377(1), Si2–S4 2.441(1), Si1–N1 1.910(2), Si1–N3 1.918(2), Si1–N5 1.914(2), Si1–N7 1.899(2); Cl1-Si1-Si2 178.52(4), Si1-Si2-Si3 173.09(3), S1-Si2-S3 177.98(3), S2-Si2-S4 178.52(3), N1-Si1-N5 178.9(1), N3-Si1-N7 178.7(1).

In general, their molecular architectures are related to those of the previously reported paddlewheel-shaped complexes $[ClSi(\mu\text{-}mt)_4MCl]$ (M = Pd, Pt), which we have called metallasilatranes because of their *metalla*-to-*sila*-site *trans*-*an*nular dative bond.[9] The Si–Sn and Si–Ge bond lengths (Figure 1), which are only slightly longer than those of $Ph_3Sn(SiMe_2)SnPh_3$ (2.57 Å)[11a] and $Me_3SiGePh_3$ (2.38 Å),[11b] respectively, are in the same range as the Si–M bonds of their analogues for M = Pd (2.569(1) Å) and Pt (2.469(2) Å). A remarkable difference is manifested in the pronounced tilt angle of the opposing methimazolide moieties (**1**: 73.5(1)°, **2**: 74.3(1)°), whereas in the above-mentioned Pd and Pt compounds these angles range between 50° and 55°. For compound **1**, this pronounced tilt results in a notable out-of-plane position of Sn with respect to the S_4 square (0.158(1) Å), whereas the Si atom remains closer within the N_4 square. For compound **2**, the out-of-plane position of Ge is less pronounced because of the shorter Si–Ge bond. Another notable difference between **1** and **2** and their related Group 10 transition-metal analogues is the presence of significantly longer M–S bonds to the main group atoms (Sn1–S1 2.664(1), Ge1–S1 2.522(1) Å; Pd–S and Pt–S ca. 2.33 Å), whereas the Sn–Cl (2.370(1) Å) or Ge–Cl bonds (2.235(1) Å) are notably shorter than the Pd–Cl or Pt–Cl bonds in the related systems (where they range between 2.60 and 2.79 Å). This pronounced formation of two short bonds (Si–M and M–Cl) already hints at retention of the initial divalency of $SnCl_2$ and $GeCl_2$ in **1** and **2**, which will be elucidated in the following.

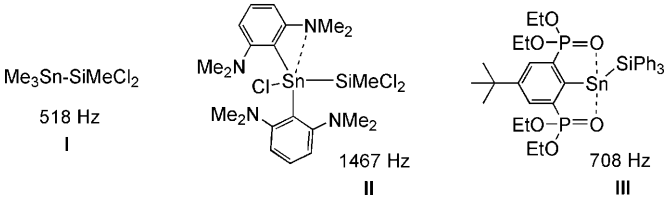
The synthesis of a disilane analogue **3** would have provided an extension of this series for systematic comparison of the development of coordination properties of the heavier congeners of carbon (i.e., from Si via Ge to Sn). The reaction of mt-$SiMe_3$[12] with hexachlorodisilane, however, failed to produce complex **3**. Instead, a trisilane **3a** containing the $[ClSi(\mu\text{-}mt)_4MR]$ (M = Si, R = $SiCl_3$) building pattern was obtained as a crystalline compound (Figure 1).[10] Although we cannot tell whether trisilane formation took place prior to or after formation of Si–N bonds, that is, under release of dichlorosilylene or methimazolyl-substituted silylenes, respectively, the well-known disproportionation of hexachlorodisilane[13] provides a plausible explanation for the generation of this Si_3 skeleton (Scheme 1 bottom). Whereas compound **3a** accounts for the trisilane formed, ^{29}Si NMR signals characteristic of $Cl_2Si(mt)_2$ and $ClSi(mt)_3$[9] were detected in the toluene mother liquor at $\delta = -42.6$ and -51.0 ppm, thus pointing at the formation of monosilanes and the consumption of further mt-$SiMe_3$. Nonetheless, compound **3a** serves our purpose in the expected fashion as it provides a cage architecture related to those of **1** and **2**. Furthermore, it provides the first example of a structurally characterized oligosilane bearing two neighboring hexacoordinate Si atoms,[14] and it represents the first crystallographically evidenced hexacoordinate Si compound where the coordination sphere comprises more than two chalcogen atoms heavier than oxygen.[15] As found for **1** and **2**, the effect of merely limited Si1–M bond lengthening upon Si1 hexacoordination is encountered in **3a**: the Si1–Si2 bond is only 0.04 Å longer than the Si2–Si3 bond.

The solid-state ^{29}Si NMR shifts of **1**, **2**, and **3a**[16] (ca. -170 ppm for the silicon atom in the ClN_4SiM (M = Sn, Ge,

Si) coordination mode, Table 1), are typical for hexacoordinate Si atoms, although shifted to lower field relative to the related paddlewheel complexes with a ClN_4SiPd (-183 ppm) and ClN_4SiPt (-218 ppm) pattern.[9] Furthermore, trisilane **3a** exhibits a resonance at $\delta = -2.7$ ppm, characteristic of tetracoordinate Si atoms (-$SiCl_3$), and a resonance at $\delta = -107.2$ ppm, which is at the "low-field boundary" of hexacoordinate Si atoms. ^{29}Si NMR shifts like the latter were reported for systems with less shielded Si atoms as result of alkyl substituents and five-membered chelate rings.[17] The ^{29}Si NMR shifts (for details see the Supporting Information) of **1**, **2**, and **3a** could be reproduced by quantum-chemical calculations (see Table 1), which thus confirm the accordance of the spectra of the gross products with the molecular structures determined from single crystals. Whereas for Si2 in **3a** the ^{29}Si NMR shift hints at special bonding properties, the ^{119}Sn NMR shift ($\delta = -190$ ppm) and the $^1J_{Si,Sn}$ coupling (4074 and 3894 Hz for ^{119}Sn and ^{117}Sn, respectively) serve that purpose for **1**. (Note: The computational analysis of the NMR data of **1** also predicts a coupling of notable magnitude $^1J(^{29}Si,^{119}Sn) = 3131$ Hz). For stannylsilanes such as **I** (Scheme 2), $^1J_{Si,Sn}$ coupling constants of approximately 500 Hz were reported.[18] The presence of lone-pair donors at the Sn atoms was already found to enhance this coupling, for example, in Sn^{IV} compounds such as **II**, and Sn^{II} compounds such as **III**, although the 5s-level of the latter should exert particular influence on the lone pair rather than on the covalent bonds.[19] The extraordinarily pronounced coupling in **1**, attributed to the hitherto unprecedented existence of a σ-bond between hexacoordinate Si and Sn atoms, hints at pronounced s-orbital contributions to the Si–Sn bond. The noticeably down-field shifted ^{119}Sn resonance with respect to other hexacoordinate Sn compounds (with a coordination sphere composed of third-row element atoms, for example, $[SnCl_6]^{2-}$ $\delta = -732$ ppm, (κ^2-*S*,*S*'-$Ph_2PS_2)_2SnCl_2$ $\delta = -796$ ppm, (κ^2-*S*,*S*'-$Et_2NCS_2)_2Sn(SC_6H_{11})_2$ $\delta = -649$ ppm),[20] confirms poor shielding of a nucleus at this special coordination site once again, as the same was found for the related Si atom in **3a**.

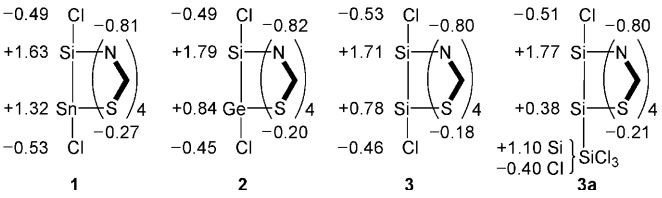
Table 1. ^{119}Sn and ^{29}Si NMR shifts (δ/ppm, relative to $SnMe_4$ and $SiMe_4$, respectively) of **1**, **2**, and **3a**, determined by CP/MAS NMR experiments (exp) and by quantum-chemical calculations (calcd).

	1 (^{119}Sn)	**1** (^{29}Si)	**2** (^{29}Si)	**3a** (^{29}Si)
exp	−190	−169.9	−168.5	−170.7, −107.2, −2.7
calcd	−157	−171.3	−168.7	−168.8, −100.8, −3.6



Scheme 2. Examples for compounds with a Sn–Si bond and their $^1J(^{29}Si,^{119}Sn)$ coupling constants.

For a closer examination of the Si–M (M = Sn, Ge, Si) bonding properties in **1**, **2**, **3**, and **3a**, an analysis with the natural bonding orbitals (NBO) model was performed (for details see the Supporting Information). Scheme 3 shows selected natural charges (NCs), and Tables 2 and 3 list selected NBO contributions.



Scheme 3. Natural charges (NCs) next to the respective atoms of **1**, **2**, **3**, and **3a**. For the N and S atoms of **3** and **3a**, the NCs are average values from four independent atoms each. The mt ligand is simplified for the sake of clarity.

Table 2. Occupancies and hybrids of the M–Si bond obtained by NBO analyses of **1**, **2**, **3**, and **3a** (M = Sn, Ge, Si, Si, respectively).

	Oc[a]/e	% Si	% M	Si Hybrid[b] % s/p/d	M Hybrid[b] % s/p/d
1	1.34	50.05	49.95	22/53/25	30/45/25
2	1.40	38.7	61.3	20/53/27	35/43/22
3	1.49	44.7	55.3	26/51/23	32/47/21
3a	1.50	40.7	59.3	23/52/25	34/45/21

[a] Electronic occupancy of the NBO. [b] Contributions to the electronic occupancy arise from s and p orbitals only, see Table 3.

Table 3. Electronic valence configurations obtained by NBO analyses of **1**, **2**, **3**, and **3a** (M = Sn, Ge, Si, Si, respectively).

	Config Si[a]	s/p	Config M[a]	s/p
1	3s(0.75), 3p(1.54)	0.49	5s(1.16), 5p(1.46)	0.79
2	3s(0.69), 3p(1.44)	0.48	4s(1.33), 4p(1.75)	0.76
3	3s(0.77), 3p(1.45)	0.53	3s(1.13), 3p(1.98)	0.57
3a	3s(0.71), 3p(1.44)	0.49	3s(1.20), 3p(2.33)	0.52

[a] Occupancies of other non-core orbital levels are equal to or less than 0.06 e.

The relatively similar NCs of the ClN_4-coordinated Si atoms are typical for hexacoordinate Si atoms in the formal oxidation state +IV, for example, between those calculated for $HSiMeCl_2$(4-methylpyridine)$_2$ (+1.46)[21] and a Si compound with an $O_2N_2F_2Si$ skeleton (+2.27).[22] Compound **1**, however, reveals some distinct differences to the others (**2**, **3**, and **3a**). Whereas for **1** similar NCs were calculated, for Si and Sn (the one of Sn being slightly lower (0.31 e)), a clear divergence is found for **2** (0.95 e), **3** (0.92 e), and **3a** (1.39 e), in favor of the S_4-coordinated Group-14-element atom having the notably lower charge. In compound **1** the soft–soft Sn–S and Sn–Cl interactions can be considered as

one important contribution to the pronounced positive charge of the Sn atom, since the sum of these five donor atoms' NCs is 0.36 e more negative than in the related Ge compound **2**. The Sn–Si bond, however, also contributes to the positive NC at Sn as it appears as a rather covalent bond (concluded from the equal contributions to the constituting NBO) and renders the NC of the ClN_4-coordinated Si atom less positive than in **2**, **3**, and **3a**. The NC at the Sn site in **1** is notably less positive than, for example, the NC reported by Jurkschat et al. for pentacoordinate Sn^{IV} compounds (ca. +2.5),[23] and the one reported for Sn^{IV} in a structurally related $Pd^{II}\rightarrow Sn^{IV}$ system (+2.31).[24] Instead, it is close to the NC of +1.48 reported by Schoeller et al. for a bis(amidinate)Sn^{II} complex.[25]

The ^{119}Sn Mössbauer spectrum[26,27] of **1** (Figure 2) shows a single signal at an isomer shift of $\delta = 2.00(1)$ mm s^{-1}, subject to significant quadrupole splitting of 1.75(1) mm s^{-1}. The experimental line width of 0.83(1) mm s^{-1} is in the usual range observed for tin compounds. The isomer shift is between the values usually observed for Sn^{II} (around 4 mm s^{-1}) and Sn^{IV} (around 0 mm s^{-1}) compounds and thus points to Sn^{III}, similar to the mixed-valent complex $[\{(RSn^{IV})_2(\mu\text{-}S)_2\}_3Sn^{III}{}_2S_6]$,[28] the thiophenolato-bridged Sn^{III} complex $[LFeSnFeL]^{n+}$,[29] or to the Zintl phases A_3SnTe_3 (A = K, Rb, Cs).[30] The course of the isomer shift in **1** nicely fits into the shift systematic for various tin compounds given by Lippens.[31] The large quadrupole splitting parameter is in accord with the molecular structure of **1** and expresses the notable electric field gradient at the Sn site due to a strong deviation from cubic symmetry. Finally, we need to comment on the asymmetry of the spectrum. This is most likely due to the Gol'danskii–Karyagin effect, (anisotropy of atomic vibrations) similar to the case in $Ni_3Sn_2S_2$,[32] $[H_3Pt(SnCl_3)_5]\cdot 3(C_{10}H_8N_2)$,[33] and $EuRuSn_3$.[34]

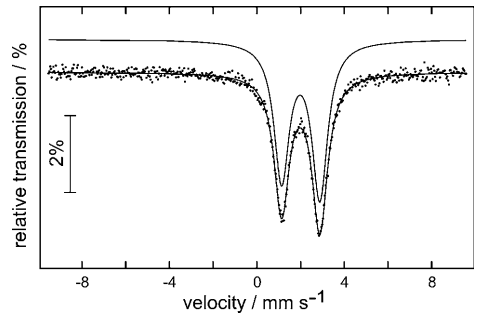
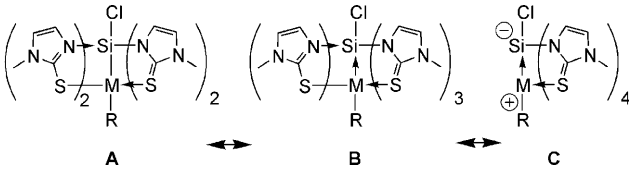


Figure 2. Experimental and simulated ^{119}Sn Mössbauer spectrum of **1**.

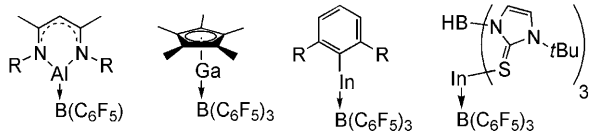
The Mössbauer spectra and NBO analysis support a bonding model for **1** that comprises contributions from the canonical formulas **A**, **B**, and **C** with particular emphasis on form **A** (Scheme 4). This model and the notable s contributions involved provide an explanation for the intense $^1J_{Si,Sn}$ coupling in **1**. In contrast, NBO analyses for **2**, **3**, and **3a** show that their Ge–Si and Si2–Si1 bonds are clearly described by NBOs with pronounced contributions from Ge or Si2 (ca. 60%), whereas the ClN_4-coordinated Si atom contributes to a lesser extent (ca. 40%), a situation which indicates a polar bond. Since Si and Ge have similar electronegativities, an explanation for this polar bonding situation is provided by the model of a M→Si donor–acceptor bond, as indicated by the canonical formulas **B** (ylene form) and **C** (yliumylidene form) in Scheme 4, whereas contributions of form **A** (ideal covalent M–Si bond) should play a less pronounced role. Contributions of forms **B** and **C**, thus assigning the formal oxidation states $Ge^{II}\rightarrow Si^{IV}$ (**2**), $Si^{II}\rightarrow Si^{IV}$ (**3**), $(Cl_3Si^{III})Si^{I}\rightarrow Si^{IV}$ (**3a**), are nicely reflected by the systematic decrease of the NCs from Si^{IV} (+1.71, +1.79) via Si^{III} (+1.10) via Ge^{II} (+0.84) and Si^{II} (+0.78) to Si^{I} (+0.38).



Scheme 4. Selected canonical formulas that might be considered as contributing to the bonding in **1**, **2**, **3**, and **3a**.

Conclusion

In addition to the first crystallographic evidence for complexes comprising a hexacoordinate Si atom adjacent to another hexacoordinate Group-14-element atom (Si, Ge, Sn), we presented the first Si compound with four S atoms in its octahedral coordination sphere. These novel compounds were shown to comprise covalent (M^{III}–Si^{III}) and dative ($M^{II}\rightarrow Si^{IV}$) bonding features in their Si–M bonds, with pronounced characteristics of type $M^{II}\rightarrow Si^{IV}$ for M = Si and Ge. Whereas examples for heavier main group elements (in lower oxidation state) acting as lone-pair donors towards a light element Lewis acid of the same main group are already known for Group 13 (Scheme 5),[35] compound **2** ($Ge^{II}\rightarrow Si^{IV}$ pattern) represents the first extension of the principle towards Group 14 elements.



Scheme 5. Selected examples for formal $E^{I}\rightarrow B^{III}$ dative bonding with E = a heavier Group 13 element (R = 2,6-diisopropylphenyl).[35]

Experimental Section

Synthesis of Si(mt)$_4$: The synthesis of Si(mt)$_4$ (as chloroform solvate) is described in reference [9]. The herein presented alternative approach delivers Si(mt)$_4$ free of solvent in good yield: A solution of $Me_3Si(mt)$[12] (7.50 g, 40.3 mmol) and $SiCl_4$ (1.75 g, 10.3 mmol) in *o*-dichlorobenzene (25 mL) was stirred at room temperature (for ca. 5 min) followed by heating to 140 °C (oil bath temperature) and stirring the mixture at this

temperature for 4 h, whereupon the mixture was allowed to adjust to room temperature. After 1 h the white precipitate of $Si(mt)_4$ was filtered off, washed with *o*-dichlorobenzene (4 mL), washed with *n*-pentane (12 mL), and dried in vacuum. Yield: 4.0 g (8.3 mmol, 82 %). ^{1}H, ^{13}C, and ^{29}Si NMR data correspond to those reported in reference [9]. C/H/N/S microanalysis calcd (%) for $C_{16}H_{20}N_8S_4Si$: C 39.98, H 4.19, N 23.31, S 26.68; found: C 39.79, H 4.13, N 22.91, 26.75.

Synthesis of 1·3(dioxane): At 40 °C a colorless clear solution of $SnCl_2$·dioxane[36] (0.46 g, 1.65 mmol) in dioxane (20 mL) was added to a colorless clear solution of $Si(mt)_4$ (0.80 g, 1.7 mmol) in dioxane (40 mL), whereupon the color changed to light greenish-yellow. Upon storage at room temperature some cloudy precipitate formed, which was removed by filtration after one day. Upon further storage at room temperature (for six weeks) light yellow crystals of **1**·3(dioxane) formed, which were separated from the supernatant by decantation, washed with dioxane (2 mL), and briefly dried in vacuum. Yield: 0.52 g (0.56 mmol, 34 %). C/H/N/S microanalysis calcd (%) for $C_{28}H_{44}Cl_2N_8O_6S_4SiSn$: C 35.98, H 4.74, N 11.99, S 13.72; found: C 35.43, H 4.61, N 12.11, 13.56. For ^{29}Si CP/MAS NMR and ^{119}Sn MAS NMR data see Figure SI5, SI6, and SI9 in the Supporting Information.

Synthesis of 2·3(dioxane): At 40 °C a colorless clear solution of commercially available (Aldrich) $GeCl_2$·dioxane (0.15 g, 0.65 mmol) in dioxane (3 mL) was added to a colorless clear solution of $Si(mt)_4$ (0.30 g, 0.63 mmol) in dioxane (15 mL), whereupon the color changed only marginally to light yellow. Upon storage at room temperature some cloudy precipitate formed, which was removed by filtration after 6 h. Upon further storage at room temperature (for four days) light yellow (almost colorless) crystals of **2**·3(dioxane) formed, which were separated from the supernatant by decantation, washed with dioxane (2 mL), and only briefly dried in vacuum. Yield: 0.28 g (0.32 mmol, 51 %). C/H/N/S microanalysis indicates loss of dioxane from the crystals upon sample preparation: The original contents found (C 34.04, H 4.47, N 13.04, S 14.48) match the composition **2**·2.25(dioxane) when scaled by a factor of 1.07: found^{scaled} (%): C 36.44, H 4.78, N 13.95, S 15.49; calcd for $C_{25}H_{38}Cl_2N_8O_{4.5}S_4SiGe$: C 36.51, H 4.66, N 13.62, S 15.59. The scaling factor applied (1.07) appears reasonable for predominant loss of dioxane upon sample preparation, as it matches the expected mass loss {*M*[**2**·3(dioxane)]/*M*[**2**·2.25(dioxane)] = 888.53/822.45 = 1.08} very well. For ^{29}Si CP/MAS NMR spectroscopic data see Figure SI7 in the Supporting Information.

Synthesis of 3a·(toluene): To a solution of $Me_3Si(mt)$ (3.00 g, 16.1 mmol) in toluene (20 mL) at room temperature was added hexachlorodisilane (1.10 g, 4.09 mmol) under vigorous stirring. Within one day some white precipitate had formed on the wall of the Schlenk tube, which was separated by decantation. The clear solution thus obtained was stored at room temperature for three weeks to yield colorless crystals of **3a**·(toluene), which were separated by decantation, washed with toluene (3 mL), and briefly dried in vacuum. Yield: 0.80 g (1.04 mmol, 51 % taking into consideration that two molecules of $Cl_3SiSiCl_3$ are required for the formation of one molecule of **3a**, acoompanied by the formation of Me_3SiCl, $Cl_2Si(mt)_2$, $ClSi(mt)_3$). C/H/N/S microanalysis calcd (%) for $C_{23}H_{28}Cl_4N_8S_4Si_3$: C 35.84, H 3.66, N 14.54, S 16.64; found (%): C 35.88, H 3.72, N 14.73, 16.39. For ^{29}Si CP/MAS NMR spectroscopic data see Figure SI8 in the Supporting Information.

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