Oxidative Addition of Diethylchalcogenanes to Lapperts Germylene and Stannylene

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Keywords: Germylene, Stannylene, Dichalcogenanes, Main Group Chemistry

Oxidative addition of diethyldichalcogenanes Et_2E_2 ($\text{E} = \text{S}, \text{Se}, \text{Te}$) to bis[bis(trimethylsilyl)amido]germylene and -stannylene $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{M} = \text{Ge}, \text{Sn}$) proceed with formation of the corresponding bis(ethylchalcogenato)germanes

$(\text{Me}_3\text{Si})_2\text{N})_2\text{Ge}(\text{EEt})_2$ ($\text{E} = \text{S}$ **1**, Se **2**, Te **3**) and -stannanes $(\text{Me}_3\text{Si})_2\text{N})_2\text{Sn}(\text{EEt})_2$ ($\text{E} = \text{S}$ **4**, Se **5**, Te **6**). The solid structures of **1** - **6** were determined by single crystal X-ray diffraction.

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Introduction

In recent years, the heavier analogues of carbenes R_2C , i.e., silylenes R_2Si , germynes R_2Ge , stannynes R_2Sn , and plumbylenes R_2Pb have received increasing interest.^[1] These divalent species, in which the group 14 element adopts the formal oxidation state +II and whose stability increases with increasing number of the group 14 element, typically have singlet ground states due to the somewhat larger energy gap between the *ns* and *np* orbitals of the heavier group 14 elements ($n = 3, 4, 5, 6$) compared to carbon ($n = 2$). As a consequence, two electrons are located in a low lying s-orbital (electron lone-pair) while the higher-lying p-orbital is empty.^[2] As a consequence of this specific electronic situation, the heavier analogues of carbenes can simultaneously react as Lewis acid and as Lewis base. In particular silylenes and germynes have evolved from exotic reaction intermediates to important reagents in organic chemistry and they were shown to activate a large variety of small molecules.^[3]

Due to our general interest in the synthesis, structure and reactivity of complexes containing a direct group 14/16 and group 15/16 bond, which are also promising *single source precursors* for the generation of the corresponding binary materials,^[4] we recently started our studies on the synthesis of Ge/Sn-chalcogenide complexes.^[5] SnSe has only recently received particular interest due to its very promising thermoelectric properties.^[6] Reactions of germynes R_2Ge with chalcogenes typically occur with formation of complexes containing chalcogen-bridges,^[7] terminal $\text{Ge}=\text{E}$ bonds^[8] or polychalcogenides.^[9] Comparable findings were reported for analogous reactions of stannynes R_2Sn .^[10] In addition, reactions of R_2M with dichalcogenanes R_2E_2 are known to proceed with insertion into the E-E bond of the

formation of complexes of the type $\text{R}_2\text{M}(\text{ER}')_2$ ($\text{M} = \text{Ge}, \text{Sn}$, $\text{E} = \text{S}, \text{Se}, \text{Te}$).^[10a,11] Moreover, insertion reactions of monovalent tin (RSnSnR), antimony (RSb), bismuth (RBi) and zinc complexes (R_2Zn_2) in the E-E bond of R_2E_2 were recently reported.^[12]

We recently reported on reactions of the cyclic bis(amino)germylene $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}$ with dialkyldichalcogenanes R_2E_2 ($\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{Me}, \text{Et}$), which proceeded with formation of the expected germanium dichalcogenides $\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2\text{Ge}(\text{ER})_2$ as well as of the unexpected digermanes $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2\text{Ge}(\text{ER})]_2$, respectively.^[13] In order to further investigate this unexpected reaction behavior, we expanded our studies on analogous reactions of the acyclic bis[bis(trimethylsilyl)amido]germylene $(\text{Me}_3\text{Si})_2\text{N})_2\text{Ge}$ as well as on the corresponding bis[bis(trimethylsilyl)amido]stannylene $(\text{Me}_3\text{Si})_2\text{N})_2\text{Sn}$.^[14]

Results and Discussion

The reactions of $[(\text{Me}_3\text{Si})_2\text{N})_2\text{Ge}]$ with Et_2E_2 ($\text{E} = \text{S}, \text{Se}, \text{Te}$) in hexane at ambient temperature led to the quantitative formation of $[(\text{Me}_3\text{Si})_2\text{N})_2\text{Ge}(\text{EEt})_2$ ($\text{E} = \text{S}$ **1**, Se **2**, Te **3**).

Scheme 1. Synthesis of **1** - **3**.

The progress of the reactions could be easily followed since a color change from yellow to colorless (**1** and **2**) as well as red to yellow (**3**), respectively, occurred within a

minute.^[15] ^1H and ^{13}C NMR spectra of the resulting products only showed the expected resonances due to the Et and $\text{N}(\text{SiMe}_3)_2$ groups in the expected 1:1 molar ratios, indicating the insertion of the germylene into the E-E bond with subsequent formation of the corresponding germanes. This is in remarkable contrast to the reactions between Et_2E_2 and the cyclic germylene $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}$, in which the digermanes $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2\text{GeEET}]_2$, containing a direct Ge-Ge bond and the Ge atoms adopting the formal oxidation state +III, were unexpectedly formed in addition to the expected germanes $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}(\text{EET})_2$, in which the Ge atoms adopt the preferred formal oxidation state +IV.^[13] In addition, the ^{77}Se NMR and ^{127}Te NMR spectra of **2** and **3** also showed only a single resonance (table 1).

Table 1. NMR resonances of **1** - **6** [ppm].^[a]

	1	2	3	4	5	6
^1H	2.77(q) 1.20(t) 0.47(s)	2.77(q) 1.29(t) 0.49(s)	2.71(q) 1.45(t) 0.50(s)	2.82(q) 1.23(t) 0.42(s)	2.83(q) 1.31(t) 0.48(s)	2.76(q) 1.46(t) 0.45(s)
^{13}C	6.6 17.2 24.7	6.7 17.0 19.9	4.1 7.0 17.7	6.2 18.7 23.4	6.5 17.3 18.4	-0.6 6.8 19.0
^{77}Se	-	124.7	-	-	39.7	-
^{119}Sn	-	-	-	699.2	699.2	699.2
^{127}Te	-	-	162.3	-	-	-15.5

[a] NMR spectra were recorded in C_6D_6 .

Single crystals of **1** - **3** were obtained upon storage of solutions of **1** - **3** in hexane at -30°C for 12h. **1** and **2** are isostructural and crystallize in the triclinic space group $P-1$ with two independent molecules in the asymmetric unit. **3** crystallizes in the monoclinic space group $C2/c$ with the molecule placed on a two-fold axis.

Figure 1. Solid state structure of **1**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels; H atoms and second orientation of disordered parts omitted for clarity.

The average Ge-E bond lengths (av. 2.2335(5) Å **1**; 2.3707(4) Å **2**; 2.5803(2) Å **3**) agree perfectly with calculated Ge-E single bond lengths (E = S 2.24 Å; Se 2.37 Å; Te 2.57 Å)^[16] and experimentally observed values of the corresponding chalcogenide-bridged dimers $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}-\mu\text{-E}\}_2$ (av. Ge-E 2.2266(13) Å (S), 2.3678(4) Å (Se), 2.595(2) Å (Te)).^[17] Moreover, the chalcogenide-bridged dimers $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2\text{Ge}-\mu\text{-E}]_2$, which were obtained from the reaction of the cyclic bis(amino)germylene $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}$ with elemental chalcogens, show almost identical Ge-E bond lengths of 2.226(3) Å (S), 2.363(3) Å (Se), and 2.592(5) Å (Te), respectively.^[18] In contrast, slightly elongated Ge-E bond

which were obtained from the reaction of the cyclic bis(amino)germylene $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}$ with elemental chalcogens, show almost identical Ge-E bond lengths of 2.226(3) Å (S), 2.363(3) Å (Se), and 2.592(5) Å (Te), respectively.^[18]

Figure 2. Solid state structure of **2**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, isotropically refined atoms shown as spheres, H atoms and second orientation of disordered parts omitted for clarity. Orientation of the molecules does not resemble their orientation in the asymmetric unit.

Figure 3. Solid state structure of **3**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels, H atoms omitted for clarity. Light colored part of the molecule generated by 2-fold symmetry.

The average Ge-E bond lengths (av. 2.2335(5) Å **1**; 2.3707(4) Å **2**; 2.5803(2) Å **3**) agree perfectly with calculated Ge-E single bond lengths (E = S 2.24 Å; Se 2.37 Å; Te 2.57 Å)^[16] and experimentally observed values of the corresponding chalcogenide-bridged dimers $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}-\mu\text{-E}\}_2$ (av. Ge-E 2.2266(13) Å (S), 2.3678(4) Å (Se), 2.595(2) Å (Te)).^[17] Moreover, the chalcogenide-bridged dimers $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2\text{Ge}-\mu\text{-E}]_2$, which were obtained from the reaction of the cyclic bis(amino)germylene $[\text{Me}_2\text{Si}(\text{N}t\text{-Bu})_2]\text{Ge}$ with elemental chalcogens, show almost identical Ge-E bond lengths of 2.226(3) Å (S), 2.363(3) Å (Se), and 2.592(5) Å (Te), respectively.^[18] In contrast, slightly elongated Ge-E bond

lengths were reported for $[\text{C}_6\text{H}_{11}\text{NC}(\text{Me})\text{NC}_6\text{H}_{11}]_2\text{Ge}[\text{SeC}_6\text{H}_5]_2$ (2.4744(17) Å)^[19] and for a telluragermete containing sterically demanding substituents.^[20] Compared to the starting germylene $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$ (1.876(5) Å),^[21] **1** - **3** show slightly shorter Ge-N bond distances (av. value 1.8490(11) Å **1**; 1.8578(19) Å **2**; 1.8595(12) Å **3**), which most likely result from the decreased radius of Ge(IV) compared to Ge(II). The N-Ge-N bond angle in **1** - **3** steadily decrease with increasing atomic number of the chalcogen atom (113.30(5)° **1**; 112.72(9)° **2**; 109.62(8)° **3**), most likely resulting from the decreasing electronegativity of the chalcogen atoms, but are all widened compared to the germylene $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$ (107.1(2)°). In contrast, the average E-Ge-E bond angles in **1** - **3** (105.06(2)° **1**; 104.60(2)° **2**; 105.87(2)° **3**) are almost identical.

Table 2. Selected bond lengths [Å] and angles [°] of bis(ethylchalcogenato)germanes $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}(\text{EEt})_2$ (E = S **1**, Se **2**, Te **3**).

	1	2	3
Ge-N	1.8457(11)	1.8573(17)	1.8595(12)
	1.8500(10)	1.8582(18)	
	1.8500(11)	1.8573(18)	
	1.8502(11)	1.8585(19)	
Ge-E	2.2287(4)	2.3667(3)	2.5803(2)
	2.2359(5)	2.3720(4)	
	2.2287(4)	2.3613(3)	
	2.2408(4)	2.3828(4)	
N-Ge-N	113.30(5)	112.22(8)	109.62(8)
	113.30(5)	113.21(9)	
N-Ge-E	112.31(4)	107.14(5)	102.12(4)
	106.67(3)	112.32(6)	119.00(4)
	106.52(4)	111.63(6)	
	111.90(4)	107.29(5)	
E-Ge-E	109.96(4)	109.72(6)	
	112.20(4)	113.10(6)	
	110.55(4)	111.95(6)	
	106.22(4)	105.28(6)	
E-Ge-E	105.967(14)	106.125(12)	105.866(11)
	104.142(15)	103.072(13)	

[a] NMR spectra were recorded in C_6D_6 .

We also expanded our systematic studies on reactions of the analogous bis[bis(trimethylsilyl)amido]stannylene, which is monomeric in gas phase and solid state.^[22] $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ reacts with Et_2E_2 (E = S, Se, Te) in hexane at ambient temperature with insertion of the stannylene into the E-E bond and subsequent formation of the expected stannanes $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}(\text{EEt})_2$ (E = S **4**, Se **5**, Te **6**). Again, the progress of the reactions could be monitored by

the color change of the solutions (yellow to colorless **4**, **5**; red to yellow **6**), which occurred within a minute.^[15] The ^1H , ^{13}C as well as ^{77}Se , ^{119}Sn and ^{127}Te NMR spectra of **4** - **6**, which were also formed in almost quantitative yields, only showed a single resonance (table 1).

Scheme 2. Synthesis of **4** - **6**.

Single crystals of **4** - **6** were obtained upon storage of freshly prepared solutions of **4** - **6** in hexane at -30 °C for 12h. **4** and **5** are isostructural to **1** and **2**. **6** crystallizes in the monoclinic space group $P2_1/c$.

Figure 4. Solid state structure of **4**. Non-H-atoms shown as thermal ellipsoids at 50% probability levels for clarity.

Figure 5. Solid state structure of **5**, thermal ellipsoids are shown at 50% probability levels, H atom omitted for clarity. Orientation of the molecules does not resemble their orientation in the asymmetric unit.

The average Sn-E bond lengths increase with increasing atomic number of the chalcogen atom (av. 2.4032(4) Å **4**; 2.5250(5) Å **5**; 2.7480(5) Å **6**). These values are slightly

shorter than the calculated Sn-E single bond lengths (E = S 2.43 Å; Se 2.56 Å; Te 2.76 Å),^[16] but agree very well with the experimental values (CSD) for Sn-S and Sn-Se single bonds.^[23] Structurally characterized compounds containing terminal Sn-E single bond such as 2,6-Mes₂-C₆H₃TeSnMe₃ (2.7484(4) Å),^[24] 2,6-(Me₂N)₂-C₆H₃Sn(TePh)₂ (av. 2.7425(5) Å),^[10a] also show comparable Sn-Te bond lengths. In addition, the Sn-E bond lengths in the chalcogenide-bridged dimers {[Me₃Si)₂N]₂Sn-μ-E}₂ (E = S 2.416(6) Å; Se 2.541(1) Å; Te 2.754(1) Å),^[25] [Me₂Si(Nt-Bu)₂Sn-μ-E]₂ (E = Se 2.536(3) Å; Te 2.741(3) Å),^[18] and *t*-Bu₂Sn-μ-E)₂ (E = S 2.431(4), 2.422(4) Å; Se 2.551(2) Å; Te 2.756(1) Å)^[26] are nearly identical.

Figure 6. Solid state structure of **6**, thermal ellipsoids are shown at 50% probability levels, isotropically refined atoms shown as spheres, H atoms and second orientation of disordered parts omitted for clarity.

The Sn-N bond distances (av. value 2.0422(10) Å **4**; 2.045(2) Å **5**; 2.063(4) Å **6**) are shorter than those of the stannylene [(Me₃Si)₂N]₂Sn (2.092(6) Å)^[21] as was expected due to the smaller radius of Sn(IV) compared to Sn(II). In contrast to the analogous germanes **1** - **3**, the N-Sn-N bond angle in **4** - **6** are almost the same (113.30(4)° **4**; 112.60(10)° **5**; 112.75(14)° **6**). Again, they are significantly widened compared to [(Me₃Si)₂N]₂Sn (104.7(2)°). The average E-Sn-E bond angles slightly increase (104.81(2)° **4**; 104.82(2)° **5**; 108.51(2)° **6**) with increasing atomic number of the chalcogen atom.

In sharp contrast to the reaction of the cyclic germylene Me₂Si(Nt-Bu)₂Ge,^[13] both bis[bis(trimethylsilyl)amido]germylene (Me₃Si)₂N)₂Ge and -stannylene (Me₃Si)₂N)₂Sn only react with E₂Ph₂ with oxidative addition and formation of the corresponding germanes and stannanes (Me₃Si)₂N)₂M(EPh)₂ (M = Ge, Sn, E = S, Se, Te). This reaction behavior was expected since both compounds adopt monomeric structures in solution. As a consequence, the digermene formation as observed in the analogous reaction of Me₂Si(Nt-Bu)₂Ge most likely points to the formation of an at least weakly bonded dimer in solution, which consequently undergoes 2+2 cycloaddition reactions.

Table 3. Selected bond lengths [Å] and angles [°] of bis(ethylchalcogenato)stannanes [(Me₃Si)₂N]₂Sn(EEt)₂ (E = S **4**, Se **5**, Te **6**).

	4	5	6
Sn-N	2.0399(10)	2.045(2)	2.069(3)
	2.0410(10)	2.048(2)	2.056(4)
	2.0432(10)	2.043(2)	
	2.0448(10)	2.044(2)	
Sn-E	2.4019(3)	2.5182(4)	2.7356(5)
	2.4070(4)	2.5307(4)	2.7643(5)
	2.3970(3)	2.5226(4)	
	2.4070(3)	2.5286(5)	
N-Sn-N	113.02(4)	113.33(10)	112.75(14)
	113.60(4)	111.86(9)	
N-Sn-E	111.30(3)	108.33(7)	107.69(10)
	108.19(3)	113.62(7)	110.01(9)
	108.18(3)	112.66(7)	113.31(10)
	110.69(3)	104.69(7)	104.49(10)
	108.44(3)	108.36(6)	
	112.96(3)	111.61(7)	
	111.51(3)	110.38(6)	
	105.52(3)	108.67(6)	
E-Sn-E	105.187(12)	103.848(14)	108.507(17)
	104.439(12)	105.790(13)	

Conclusions

Oxidative addition reactions of diethyldichalcogenanes Et₂E₂ (E = S, Se, Te) with bis[bis(trimethylsilyl)-amido]germylene and -stannylene M[N(SiMe₃)₂]₂ (M = Ge, Sn) yield the corresponding bis(diethylchalcogenato)-germanes and stannanes **1** - **6**. In contrast to analogous reactions of Me₂Si(Nt-Bu)₂Ge, no formation of digermanes was observed. **1** - **6** were characterized by heteronuclear NMR and IR spectroscopy and their solid state structures of **1** - **6** were determined by single crystal X-ray diffraction.

Experimental Section

All manipulations were performed under Ar. Solvents were carefully dried with Na/K and degassed prior to use. [(Me₃Si)₂N]₂Ge and [(Me₃Si)₂N]₂Sn^[14] as well as Et₂Se₂ and Et₂Te₂^[27] were synthesized according literature procedures, whereas Et₂S₂ was commercially available and distilled before use. ¹H NMR, ¹³C{¹H}, ⁷⁷Se{¹H}, ¹¹⁹Sn{¹H}, and ¹²⁷Te{¹H} NMR spectra were recorded with a Bruker DMX 300 spectrometer and are referenced to internal C₆D₅H (¹H NMR: δ = 7.16 ppm; ¹³C NMR: δ = 128.0 ppm) and TMS (⁷⁷Se{¹H}, ¹¹⁹Sn{¹H}, and ¹²⁷Te{¹H}).^[28] IR spectra were recorded with an ALPHA-T FTIR-spectrometer equipped with a single-reflection ATR sampling module. Melting points were measured in sealed capillaries.

Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Essen.

General procedure for the synthesis of **1** - **3**.

0.5 mmol Et₂E₂ was added to a solution of 0.5 mmol [(Me₃Si)₂N]₂Ge in 20 mL of hexane and stirred for 1 h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C. Yellow crystals of **2a** and colorless crystals of **2b** and **2c** were formed within 12 h and isolated by filtration.

[(Me₃Si)₂N]₂Ge(SET)₂ 1: Yield (isolated crystals): 0.25 g (96%), M.p. 200 °C. Elemental analysis calcd (%) for C₁₆H₄₆GeN₂Si₄S₂ (515.65): C 37.27, H 8.99, N 5.43; found C 37.20, H 8.81, N 5.11. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 0.47 [s, 36H, Si(CH₃)₃], 1.20 [t, ³J_{HH} = 7.5 Hz, 6H, CH₂-CH₃], 2.77 [s, ³J_{HH} = 7.4 Hz, 4H, S-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 6.57 [Si(CH₃)₃], 17.18 [CH₂-CH₃], 24.74 [S-CH₂]. IR (ν, cm⁻¹): 2961, 1249, 1093, 1017, 839, 801, 761, 668, 622, 424 cm⁻¹.

[(Me₃Si)₂N]₂Ge(SeEt)₂ 2: Yield (isolated crystals): 0.28 g (93%), M.p. 197 °C. Elemental analysis calcd (%) for C₁₆H₄₆GeN₂Si₄Se₂ (605.45): C 31.53, H 7.61, N 6.40; found C 32.10, H 7.66, N 4.43. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 0.49 [s, 36H, Si(CH₃)₃], 1.29 [t, ³J_{HH} = 7.5 Hz, 6H, CH₂-CH₃], 2.77 [s, ³J_{HH} = 7.5 Hz, 4H, Se-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ = 6.70 [Si(CH₃)₃], 16.98 [CH₂-CH₃], 19.89 [Se-CH₂]. ⁷⁷Se NMR (57 MHz, C₆D₆, 298 K): δ = 124.7. IR (ν, cm⁻¹): 2959, 1249, 1224, 1017, 838, 798, 759, 734, 670, 621, 415 cm⁻¹.

[(Me₃Si)₂N]₂Ge(TeEt)₂ 3: Yield (isolated crystals): 0.32 g (90%), M.p. 153 °C. Elemental analysis calcd (%) for C₁₆H₄₆GeN₂Si₄Te₂ (706.73): C 27.19, H 6.56, N 3.96; found C 28.08, H 6.75, N 4.57. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 0.50 [s, 36H, Si(CH₃)₃], 1.45 [t, ³J_{HH} = 7.7 Hz, 6H, CH₂-CH₃], 2.71 [s, ³J_{HH} = 7.7 Hz, 4H, Te-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ = 4.05 [Te-CH₂], 6.97 [Si(CH₃)₃], 17.74 [CH₂-CH₃]. ¹²⁷Te NMR (95 MHz, C₆D₆, 298 K): δ = 162.3. IR (ν, cm⁻¹): 2961, 1246, 1186, 1028, 794, 721, 687, 667, 549, 506, 414 cm⁻¹.

General procedure for the synthesis of **4** - **6**.

0.5 mmol Et₂E₂ was added to a solution of 0.5 mmol [(Me₃Si)₂N]₂Sn in 20 mL of hexane and stirred for 1 h at ambient temperature. The solution was concentrated to 5 mL and stored at -30 °C. Yellow crystals of **4** and colorless crystals of **5** and **6** were formed within 12 h and isolated by filtration.

[(Me₃Si)₂N]₂Sn(SET)₂ 4: Yield (isolated crystals): 0.26 g (95%), M.p. 182 °C. Elemental analysis calcd (%) for C₁₆H₄₆SnN₂Si₄S₂ (561.73): C 34.21, H 8.25, N 4.99; found C 69.08, H 7.70, N 10.67. ¹H NMR (300 MHz, C₆D₆, 298 K): δ 0.42 [s, 36H, Si(CH₃)₃], 1.23 [t, ³J_{H,H} = 7.6 Hz, ⁴J_{SnH} = 1.8 Hz, 6H, CH₂-CH₃], 2.83 [q, ³J_{HH} = 7.7 Hz, ³J_{H17SnH} = 21.3 Hz, ³J_{H19SnH} = 22.4 Hz, 4H, Se-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 6.23 [s, ²J_{SnC} = 27.9 Hz, Si(CH₃)₃], 18.73 [s, ³J_{SnC} = 20.3 Hz, CH₂-CH₃], 23.36 [s, ²J_{SnC} = 10.4 Hz, S-CH₂]. ¹¹⁹Sn NMR (110 MHz, C₆D₆, 298 K): δ = 699.2. IR (ν, cm⁻¹): 2961, 1249, 1017, 839, 766, 668, 620, 505, 422 cm⁻¹.

[(Me₃Si)₂N]₂Sn(SeEt)₂ 5: Yield (isolated crystals): 0.31 g (95%), M.p. 175 °C. Elemental analysis calcd (%) for C₁₆H₄₆SnN₂Si₄Se₂ (655.53): C 29.32, H 7.07, N 4.27; found C 29.51, H 7.73, N 4.20. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 0.48 [s, 36H, Si(CH₃)₃], 1.31 [t, ³J_{HH} = 7.5 Hz, ⁴J_{SnH} = 1.9 Hz, 6H, CH₂-CH₃], 2.83 [q, ³J_{HH} = 7.5 Hz, ³J_{H17SnH} = 22.5 Hz, ³J_{H19SnH} = 23.8 Hz, 4H, Se-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ = 6.45 [s, ²J_{SnC} = 27.9 Hz, Si(CH₃)₃], 17.25 [s, ³J_{SnC} = 10.3 Hz, CH₂-CH₃], 18.35 [s, ²J_{SnC} = 17.4 Hz, Se-CH₂]. ⁷⁷Se NMR (57 MHz, C₆D₆, 298 K): δ = 39.7. ¹¹⁹Sn NMR (110 MHz, C₆D₆, 298 K): δ = 699.2. IR (ν, cm⁻¹): 2960, 1249, 1017, 798, 723, 670, 508, 420 cm⁻¹.

[(Me₃Si)₂N]₂Sn(TeEt)₂ 6: Yield (isolated crystals): 0.35 g (92%), M.p. 163 °C. Elemental analysis calcd (%) for C₁₆H₄₆SnN₂Si₄Te₂

(752.81): C 34.21, H 8.25, N 4.99; found C 33.88, H 8.55, N 5.24. ¹H NMR (300 MHz, C₆D₆, 298 K): δ = 0.45 [s, 36H, Si(CH₃)₃], 1.46 [t, ³J_{HH} = 7.4 Hz, ⁴J_{SnH} = 2.2 Hz, 6H, CH₂-CH₃], 2.76 [q, ³J_{HH} = 7.4 Hz, ³J_{H17SnH} = 24.7 Hz, ³J_{H19SnH} = 26.0 Hz, 4H, Te-CH₂]. ¹³C NMR (75 MHz, C₆D₆, 298 K): δ = -0.62 [s, ²J_{SnC} = 8.5 Hz, Te-CH₂], 6.83 [s, ²J_{SnC} = 28.1 Hz, Si(CH₃)₃], 18.95 [s, ³J_{SnC} = 13.1 Hz, CH₂-CH₃]. ¹¹⁹Sn NMR (110 MHz, C₆D₆, 298 K): δ = 699.2. ¹²⁷Te NMR (95 MHz, C₆D₆, 298 K): δ = -15.5. IR (ν, cm⁻¹): 2961, 1246, 1150, 780, 721, 687, 553, 515, 414 cm⁻¹.

Single crystal X-ray diffraction. Crystallographic data of **1** - **6**, which were collected on a Bruker AXS SMART diffractometer (MoKα radiation, λ = 0.71073 Å) at 100(1) K (**1**), 180(1) K (**2**), 100(1) K (**3**), 100(1) K (**4**), 180(1) K (**5**), and 200(1) K (**6**), are summarized in Table S1 (SI). The solid-state structures of **1** - **6** are shown in Figures 1 - 6, bond lengths and angles of **1** - **6** are summarized in tables 2 and 3. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97).^[29,30] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The -E-CH₂-CH₃ groups of **1**, **2**, **5** and **6** were disordered over two positions and not all of the carbon atoms could be refined anisotropically. The anisotropic displacement parameters of these groups in **4** also suggest disorder, however in this case it could not be resolved. The crystallographic data of **1** - **6** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1035552 (**1**), CCDC-1035550 (**2**), CCDC-1035551 (**3**), CCDC-1035553 (**4**), CCDC-1035555 (**5**) and CCDC-1035554 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): A CIF file giving X-ray crystallographic data of **1** - **6** as well as ¹H, ¹³C, ⁷⁷Se ¹¹⁹Sn and ¹²⁷Te NMR spectra of **1** - **6**.

Acknowledgement

Stephan Schulz gratefully acknowledges financial support by the Mercator Research Center Ruhr (MERCUR).

- [1] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479.
- [2] a) C. Boehme, G. Frenking, *J. Am. Chem. Soc.* **1996**, *118*, 2039. b) M. Z. Kassaei, S. Soleimani-Amiri, M. Ghambarian, F. Boazar, E. Motamedi, *Theochem.* **2008**, *849*, 37. c) A. Bundhun, P. Ramasami, H. F. Schaefer III, *J. Phys. Chem. A* **2009**, *113*, 8080.
- [3] a) N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251. b) O. Kühn, *Coord. Chem. Rev.* **2004**, *248*, 411. c) S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27*, 457. d) S. Yao, Y. Xiong, M. Driess, *Organometallics*, **2011**, *30*, 1748. e) B. Blom, M. Stoelzel, M. Driess, *Chem. Eur. J.* **2013**, *19*, 40.
- [4] a) S. Schulz, S. Heimann, J. Friedrich, M. Engenhorst, G. Schierning, W. Assenmacher, *Chem. Mater.* **2012**, *24*, 2228; b) S. Schulz, S. Heimann, K. Kaiser, O. Prymak, W. Assenmacher, J. T. Brüggemann, B. Mallik, A.-V. Mudring, *Inorg. Chem.* **2013**, *52*, 14326; c) G. Bendt, S. Schulz, S. Zastrow, K. Nielsch, *Chem. Vap. Deposition* **2013**, *19*, 235.
- [5] M. Bouška, L. Štrížík, L. Dostál, A. Růžička, A. Lyčka, L. Beneš, M. Vlček, Jan Příkryl, P. Knotek, T. Wágner, R. Jambor, *Chem. Eur. J.* **2013**, *19*, 1877.

- [6] a) Hao Zhang and Dmitri V. Talapin, *Angew. Chem. Int. Ed.* **2014**, *53*, 9126; b) L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* **2014**, *508*, 373.
- [7] a) G. Pfister-Guillouzo, C. Guimon, *Phosphorus and Sulphur* **1985**, *23*, 197; b) P. B. Hitchcock, H. A. Jasim, M. F. Lappert, W.-P. Leung, A. K. Rai, R. E. Taylor, *Polyhedron* **1991**, *10*, 1203; c) D. Ellis, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1992**, 3397; d) I. Schranz, L. Grocholl, C. J. Carrow, L. Stahl, R. J. Staples, *J. Organomet. Chem.* **2008**, *693*, 1081; e) W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou, T. C. W. Mak, *Chem. Commun.* **1996**, 505.
- [8] a) M. Veith, S. Becker, V. Huch, *Angew. Chem., Int. Ed.* **1989**, *28* (), pp. 1237; b) N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, *J. Am. Chem. Soc.* **1993**, *115*, 8855; c) T. Matsumoto, N. Tokitoh, R. Okazaki, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2316; d) N. Tokitoh, T. Matsumoto, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 2337; e) W.-P. Leung, W.-H. Kwok, Z.-Y. Zhou, T.C.W. Mak, *Organometallics* **2000**, *19*, 296; f) R. K. Siwatch, D. Yadav, G. Mukherjee, G. Rajaraman, S. Nagendran, *Inorg. Chem.* **2014**, *53*, 5073. For review articles see also: a) M.C. Kuchta, G. Parkin, *Coord. Chem. Rev.* **1998**, *176*, 323; b) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625; R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877.
- [9] a) N. Tokitoh, T. Matsumoto, R. Okazaki, *Tetrahedron Lett.* **1992**, *33*, 2531. b) T. Matsumoto, N. Tokitoh, R. Okazaki, *Organometallics* **1995**, *14*, 1008.
- [10] a) P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, A. V. Protchenko, P. G. H. Uiterweerd, *J. Chem. Soc. Dalton Trans.* **2009**, 4578; b) M. Bouška, L. Dostal, A. Růžicka, L. Beneš, R. Jambor, *Chem. Eur. J.* **2011**, *17*, 450; c) M. Bouška, L. Dostal, F. de Proft, A. Růžicka, A. Lyčka, R. Jambor, *Chem. Eur. J.* **2011**, *17*, 455; d) M. Bouška, L. Dostál, Z. Padělková, A. Lyčka, S. Herres-Pawlis, K. Jurkschat, R. Jambor, *Angew. Chem. Int. Ed.* **2012**, *51*, 3478; e) E. Moos, T. Augenstein, D. Garnier, F. Breher, *Can. J. Chem.* **2014**, *92*, 574.
- [11] S. R. Foley, G. P. A. Yap and D. S. Richeson, *J. Chem. Soc., Dalton Trans.* **2000**, 1663.
- [12] a) M. Wagner, C. Dietz, M. Bouška, L. Dostál, Z. Padělková, R. Jambor and K. Jurkschat, *Organometallics*, **2013**, *32*, 4973; b) P. Šimon, R. Jambor, A. Růžicka, L. Dostál, *Organometallics* **2013**, *32*, 239; c) P. Šimon, R. Jambor, A. Růžicka, L. Dostál, *J. Organomet. Chem.* **2013**, *740*, 98; d) M. Bouška, M. Novák, L. Dostál, A. Růžicka, T. Mikysek, R. Metelka, R. Jambor, *Eur. J. Inorg. Chem.* **2014**, 310; e) S. Gondzik, S. Schulz, D. Bläser, C. Wölper, *J. Chem. Soc. Chem. Commun.* **2014**, *50*, 1189.
- [13] P. Steiniger, G. Bendt, D. Bläser, C. Wölper, S. Schulz, *J. Chem. Soc. Chem. Commun.* **2014**, *50*, 15461.
- [14] M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière, M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.* **1977**, 2004.
- [15] The colors of the starting reagents are as follows: $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ge}$ light yellow; $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ orange; Et_2S_2 colorless, Et_2Se_2 orange, Et_2Te_2 red.
- [16] P. Pyykkö, M. Atsumi, *Chem.-Eur. J.*, **2009**, *15*, 186.
- [17] a) G. L. Wegner, A. Jockisch, A. Schier, H. Schmidbaur, *Z. Naturforsch.* **2000**, *55B*, 347; b) P. B. Hitchcock, H. A. Jasim, M. F. Lappert, Wing-Por Leung, A. K. Rai, R. E. Taylor, *Polyhedron* **1991**, *10*, 1203.
- [18] M. Veith, M. Nötzel, L. Stahl, V. Huch, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1264.
- [19] S. R. Foley, G. P. A. Yap, D. S. Richeson, *J. Chem. Soc., Dalton Trans.*, **2000**, 1663.
- [20] T. Sasamori, T. Sasaki, N. Takeda, N. Tokitoh, *Organometallics* **2005**, *24*, 612.
- [21] R. W. Chorley, P. B. Hitchcock, M. F. Lappert, Wing-Por Leung, P. P. Power, M. M. Olmstead, *Inorg. Chim. Acta* **1992**, *198*, 203.
- [22] T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power, A. J. Thorne, *J. Chem. Soc. Dalton Trans.* **1986**, 1551.
- [23] CSD search for fragment Sn-S-C, $\text{cn}(\text{Sn}) = 4$, $\text{Cn}(\text{S}) = 2$, 726 bonds from 336 hits, 2.357 to 2.819 Å, mean 2.462(2) Å, median at 2.457 Å. CSD search for fragment Sn-Se-C, $\text{cn}(\text{Sn}) = 4$, $\text{Cn}(\text{Se}) = 2$, 41 bonds from 20 hits, 2.478 to 2.746 Å, mean 2.552(9) Å, median at 2.539 Å.
- [24] H. Poleschner, S. Ellrodt, M. Malischewski, J. Nakatsuji, C. Rohner, K. Seppelt, *Angew. Chem. Int. Ed.* **2012**, *51*, 419.
- [25] P. B. Hitchcock, E. Jang, M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1995**, 3179.
- [26] H. Puff, B. Breuer, W. Schuh, R. Sievers, R. Zimmer, *J. Organomet. Chem.* **1987**, *332*, 279.
- [27] Ming T. Chen, John W. George, *J. Organometal. Chem.* **1968**, *12*, 401-403.
- [28] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Magn. Reson. Chem.* **2002**, *40*, 489.
- [29] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
- [30] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **1997** (see also: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.).

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Georg Bendt, Silvia Lapsien, Phillip Steiniger, Dieter Bläser,
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DOI: 10.1002/zaac.201500023

URN: urn:nbn:de:hbz:464-20201125-104328-9

This is the **peer reviewed version** of the following article: *Z. Anorg. Allg. Chem.* 2015, 641, 797-902, which has been published in final form at:
<https://doi.org/10.1002/zaac.201500023>

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