

Reactions of Dimethyl[tris(trimethylsilyl)methyl]metalanes of Aluminum and Gallium with H₂S and Elemental Chalcogens – Crystal Structures of [RAl(μ-S)]₂ · 2 THF, [RGa(μ₃-S)]₄, [{RAl(μ₃-S)}₃MeAl(μ₃-S)], [RAlMe(μ-SeMe)]₂, and [RGaMe(μ-TeMe)]₂ [R = C(SiMe₃)₃]

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The reaction of the trialkylalane (Me₃Si)₃CAI Me₂ × THF (**1**) with H₂S in toluene at room temperature results in the formation of the dimeric sulfido compound [(Me₃Si)₃CAI(μ-S)]₂ × 2 THF (**3**), while the reaction of the homologous gallane (Me₃Si)₃CGa Me₂ (**2**) with H₂S under similar conditions affords the heterocubane [(Me₃Si)₃CGa(μ₃-S)]₄ (**4**). Heating of compound **3** in vacuo gives a mixture of the symmetrically substituted [(Me₃Si)₃CAI(μ₃-S)]₄ (**5**) and the unsymmetrically substituted heterocubane [{(Me₃Si)₃CAI(μ₃-S)}₃MeAl(μ₃-S)] (**6**). Reaction of the trialkylmetalanes **1** and **2** with elemental selenium in refluxing toluene results in the formation of the corresponding selenolates [(Me₃Si)₃CMMe-

(μ-SeMe)]₂ (**7**, M = Al; **8**, M = Ga). The compounds exhibit a high thermal stability and can not be converted to the corresponding selenides [(Me₃Si)₃CM(μ₃-Se)]_n (M = Al, Ga) upon heating. In contrast, the trialkylalane **1** does not react with tellurium metal in refluxing toluene at all, while the trialkylgallane **2** affords the tellurolate [(Me₃Si)₃CGaMe(μ-TeMe)]₂ (**9**) under similar conditions. Compounds **3–9** have been characterized by ¹H- and ²⁹Si-NMR, mass, and IR spectroscopy. Furthermore, the molecular structures of compounds **3** · C₆H₆, **4** · 1.5 C₆H₆, **6**, **7** · C₆H₆ and **9** have been determined by X-ray crystallography.

Introduction

Organometallic cage compounds of aluminum and gallium with bonds to group 15 elements with composition [RMER']_x (M = Al, Ga; E = N, P; R, R' = H, alkyl, aryl) have been intensively studied over the last two decades^[1] especially due to their potential use as precursors of group 13–15 materials. In contrast, only a few of fully characterized cage compounds [RME]_x (R = alkyl, aryl; M = Al, Ga; E = S, Se, Te) of groups 13 and 16 have been reported.^[2] This is surprising, since materials with compositions ME and M₂E₃ (M = Ga, In; E = S, Se) have interesting electronic and optoelectronic properties and could possibly find applications for nonlinear optics,^[3] photovoltaics,^[4] and electronic devices.^[5] Moreover, the cubic phase of gallium sulfide prepared from the single source precursor [tBuGa(μ₃-S)]₄ has been shown to passivate GaAs^[6] and was used to realize a new class of GaAs transistors.^[7] Syntheses of mixed-metal chalcogenides such as CuInE₂ (E = S, Se) from single-source precursors^[8] have also been successful and their efficiency as photovoltaic cells is documented.^[9]

The few examples of structurally characterized 13–16 cage compounds [RME]_x^[2] have been preferentially prepared by a) protolysis of R₃M with H₂E, b) reaction of RMCl₂ with E(SiMe₃)₂, c) oxidation of RM with elemental

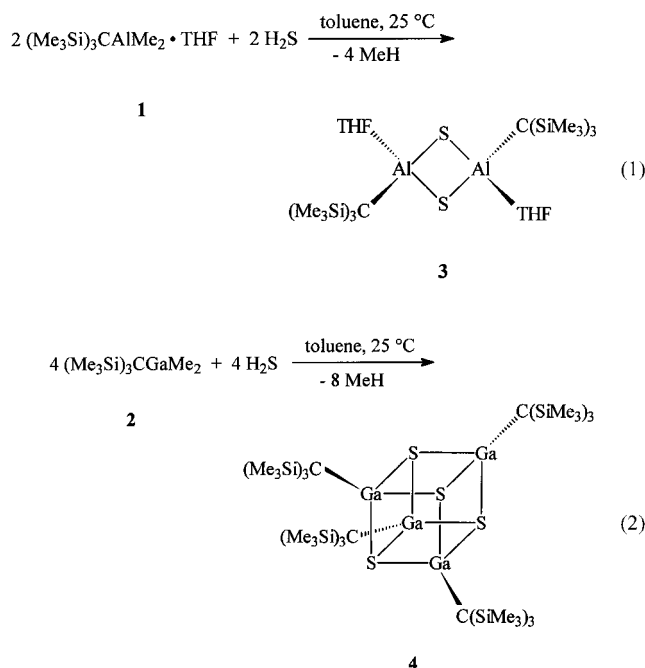
chalcogens, and d) reaction of R₃M with elemental chalcogens. The last mentioned process occurs via the corresponding chalcogenates [R₂M(μ-ER)]₂ as the first insertion products, which could be trapped in a few cases.^{[9b][9c]} The compounds are of particular interest as selective reagents in organic synthesis, e.g. [tBu₂AlER]_x (R = alkyl; E = S, Se, Te) for the conversion of aldehydes to thiol-, selenol-, and tellurol esters.^[10]

We have recently reported on hydrolysis studies of the trialkylmetalanes (Me₃Si)₃CAI Me₂ · THF (**1**) and (Me₃Si)₃CGa Me₂ (**2**) leading to the isolation and structural characterization of some unusual alkylaluminum- and -gallium-hydroxo(oxo) compounds.^[11] In continuation of our systematic studies on group 13–16 chemistry, we now report on the synthesis and characterization of some new alkylaluminum- and -gallium chalcogen compounds with the bulky tris(trimethylsilyl)methyl (“trisyl”) ligand.

Results and Discussion

Reaction of (Me₃Si)₃CAI Me₂ · THF (**1**) with H₂S in toluene at room temperature yielded the dimeric trisylaluminum sulfido compound [(Me₃Si)₃CAI(μ-S)]₂ · 2 THF (**3**) (Eq. 1), presumably via an unstable hydridosulfido intermediate, i.e. [(Me₃Si)₃CAI Me(μ-SH)]₂ · 2 THF. The softer Lewis base

H₂S seems to be unable under the given reaction conditions to replace the harder Lewis base THF at the hard Lewis acidic aluminum center. Under similar conditions the trialkylgallane (Me₃Si)₃CGaMe₂ (**2**) gave the tetrameric compound [(Me₃Si)₃CGa(μ₃-S)]₄ (**4**) (Eq. 2).^[12] The hydridosulfido intermediate could not be trapped, in contrast to the reaction of *t*Bu₃Ga with H₂S, which allows the isolation of the thermal stable hydridosulfido product [*t*Bu₂Ga(μ-SH)]₂.^[9a]

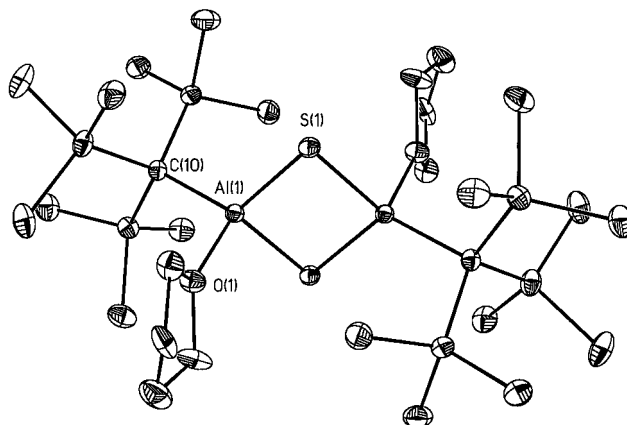


Compounds **3** and **4** have been fully characterized by ¹H- and ²⁹Si-NMR, mass, and IR spectroscopy as well as elemental analyses. In addition, recrystallization from benzene gave single crystals of **3** · C₆H₆ and **4** · 1.5 C₆H₆ suitable for X-ray diffraction analyses.

Figure 1 shows the molecular structure of compound **3**, which crystallizes with half of a molecule in the asymmetric unit in the orthorhombic space group Pbca. The planar Al₂S₂ core is elongated in the direction of the S–S axis (Al–S–Al 81.2°, S–Al–S 98.8°) comparable to the recently reported sulfide [Mes*Al(μ-S)]₂ · 2 Me₂SO (Mes* = 2,4,6-*t*Bu₃C₆H₂) (Al–S–Al 83.5°, S–Al–S 95.9°, average) with a nonplanar Al₂S₂ ring.^[13] Both aluminum centers show distorted tetrahedral coordination by two bridging sulfur atoms, one THF molecule and one trisyl group. The Al–S (224.8 pm) and Al–C (202.9 pm) distances in **3** · C₆H₆ are in good agreement with those observed for [Mes*Al(μ-S)]₂ · 2 Me₂SO (Al–S 225.1 pm, Al–C 202.2 pm).^[13] The Al–O distance in **3** · C₆H₆ (195.3 pm) is slightly shorter than that in the starting material **1** (196.8 pm)^[11] due to electron-withdrawing properties of the sulfur atoms.

The molecular structure of the tetrameric compound [(Me₃Si)₃CGa(μ₃-S)]₄ (**4**), which crystallizes in the trigonal space group *P* $\bar{3}$ *c*1 with four tetramers and six benzene molecules in each unit cell, is depicted in Figure 2. The core of compound **4** consists of a distorted cube with Ga and S

Figure 1. Crystal structure of [(Me₃Si)₃CAl(μ-S)]₂ · 2 THF (**3**), with anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity.^[a]



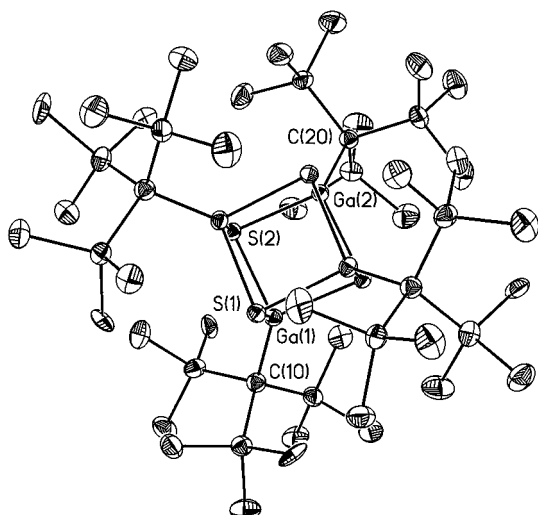
^[a] Selected bond lengths [pm] and angles [°]: Al(1)–C(10) 202.9(2), Al(1)–O(1) 195.29(17), Al(1)–S(1) 224.83(9), Al(1)–S(1A) 223.47(9); C(10)–Al(1)–O(1) 107.17(8), C(10)–Al(1)–S(1) 120.97(7), C(10)–Al(1)–S(1A) 121.21(7), O(1)–Al(1)–S(1) 103.27(6), O(1)–Al(1)–S(1A) 102.87(6), S(1)–Al(1)–S(1A) 98.79(3), Al(1)–S(1)–Al(1A) 81.21(3).

atoms at alternating corners. The pseudotetrahedral coordination sphere at each gallium atom is completed by a trisyl group. The average Ga–S distances (237.8 pm) are in the range of those observed for [*t*BuGa(μ₃-S)]₄ (235.9 pm),^[2a] [Me₂EtCGa(μ₃-S)]₄ (235.6 pm),^[2f] [(Cp(CO)₂Fe)Ga(μ₃-S)]₄ (237.5 pm)^[2g] and [tmpGa(μ₃-S)]₄ (tmp = 2,2,6,6-tetramethylpiperidyl) (235.6 pm).^[2h] The deviation from a perfect cube in **4** (average: Ga–S–Ga 86.4°, S–Ga–S 93.5°) is somewhat smaller than in [*t*BuGa(μ₃-S)]₄ (average: Ga–S–Ga 82.1°, S–Ga–S 97.3°),^[2a] [Me₂EtCGa(μ₃-S)]₄ (average: Ga–S–Ga 82.2°, S–Ga–S 97.2°),^[2f] [(Cp(CO)₂-Fe)Ga(μ₃-S)]₄ (average: Ga–S–Ga 84.1°, S–Ga–S 95.6°),^[2g] and [tmpGa(μ₃-S)]₄ (average: Ga–S–Ga 84.2°, S–Ga–S 95.5°).^[2h] The average Ga–C distance (202.0 pm) is a little shorter than the Ga–C_{trisyl} distance in (Me₃Si)₃CGaMe₂ · THF (204.6 pm)^[11] due to the higher effective positive charge of the gallium atoms caused by the electronegative sulfur atoms.

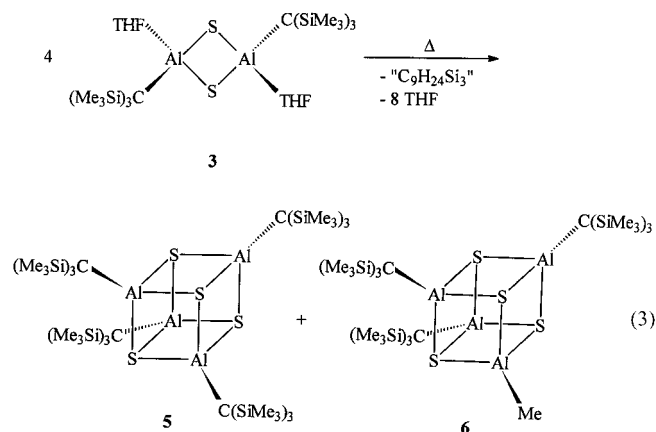
The cubane **4** exhibits high thermal stability and can be easily purified by sublimation in vacuo (180 °C, 10^{–2} mbar). A topological reorganization of the polyhedral core as reported for the formation of [*t*BuGaS]_x (x = 6, 7, 8) by thermolysis of [*t*BuGa(μ₃-S)]₄^[14] has not been observed for **4**.

Interestingly, the mass spectrum of **3** shows, in addition to the signals for characteristic fragment ions of the dimeric sulfide, at elevated temperatures (above 200 °C) signals with higher masses (e.g. *m/z* 1147, 929), indicating formation of larger aggregates. These observations encouraged us to examine the thermolysis of **3** on a preparative scale. Heating of [(Me₃Si)₃CAl(μ-S)]₂ · 2 THF (**3**) in vacuo (220 °C, 10^{–2} mbar) for 30 minutes gave, after workup, a yellowish solid which was identified by ¹H- and ²⁹Si-NMR, and mass spectroscopy as a mixture of the tetrameric organoaluminum sulfides [(Me₃Si)₃CAl(μ₃-S)]₄ (**5**) and [(Me₃Si)₃CAl(μ₃-S)]₃MeAl(μ₃-S)] (**6**) (≈ 30:70) (Eq. 3). To our knowledge

Figure 2. Crystal structure of $[(\text{Me}_3\text{Si})_3\text{CGa}(\mu_3\text{-S})_4]$ (**4**), with anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity^[a]



^[a] Selected bond lengths [pm] and angles [°]: Ga(1)–C(10) 202.0(4), Ga(1)–S(1) 237.90(10), Ga(1)–S(2) 237.91(11), Ga(1)–S(2A) 237.63(11), Ga(2)–C(20) 201.9(6), Ga(2)–S(2) 237.74(10), C(10)–Ga(1)–S(1) 122.56(10), C(10)–Ga(1)–S(2) 122.31(11), C(10)–Ga(1)–S(2A) 123.45(11), S(1)–Ga(1)–S(2) 93.46(4), S(1)–Ga(1)–S(2A) 93.53(4), S(2)–Ga(1)–S(2A) 93.41(4), C(20)–Ga(2)–S(2) 122.80(3), S(2)–Ga(2)–S(2A) 93.43(3), Ga(1)–S(1)–Ga(1A) 86.37(4), Ga(1)–S(2)–Ga(1A) 86.43(3), Ga(1)–S(2)–Ga(2) 86.44(3), Ga(1A)–S(2)–Ga(2) 86.51(4).



such a fragmentation of the trisyl group under chemical conditions is unprecedented.

However, we were neither able to separate this mixture by fractional crystallization or sublimation nor to obtain pure compounds by variation of the reaction conditions. The recrystallization of the mixture from toluene at room temperature results in the formation of single crystals of both compounds, which differ in their shape (**5** rods, **6** blocks). Unfortunately, only the single crystals of compound **6** were suitable for X-ray diffraction analysis.

Figure 3 shows the molecular structure of the unsymmetrically substituted cubane $\{[(\text{Me}_3\text{Si})_3\text{CAL}(\mu_3\text{-S})_3]\text{MeAL}(\mu_3\text{-S})\}$ (**6**), which crystallizes in the triclinic space group *P*1̄. The distorted central Al_4S_4 heterocubane core (Al–S–Al 83.5°, S–Al–S 96.1°, average) is comparable with that ob-

served for the symmetrically substituted cubane $[\text{Me}_2\text{EtCAL}(\mu_3\text{-S})_4]$ (Al–S–Al 82.2°, S–Al–S 97.3°, average),^[2f] which is the only other example of a structurally characterized Al–S cubane. Due to the lower symmetry of the molecule caused by the different substituents at the aluminum atoms in **6**, the bond lengths and angles of the core are in a wider range than those of $[\text{Me}_2\text{EtCAL}(\mu_3\text{-S})_4]$.^[2f] For the Al coordinated by the methyl group the Al–S bonds are relatively similar (230.3–230.7 pm), while for the Al atoms coordinated by the trisyl ligands one long Al–S distance (235.5–235.8 pm), one distance in a middle range (233.7–234.2 pm) and one comparatively short distance (231.0–231.5 pm) are observed. In total, the Al–S distances (average: 232.8 pm) are close to those observed for $[\text{Me}_2\text{EtCAL}(\mu_3\text{-S})_4]$ (average: 231.3 pm)^[2f] but are distinctly longer than those of the starting material **3** (224.8 pm) and the recently reported dimeric organoaluminum sulfide $[\text{Mes}^*\text{Al}(\mu\text{-S})_2]$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$) (221.0 pm)^[13] due to the higher coordination number of the sulfur atoms. On the other hand the nearly equal Al–C_{trisyl} distances (average: 197.7 pm) are little shorter than those in the starting material **3** (average: 202.9 pm).

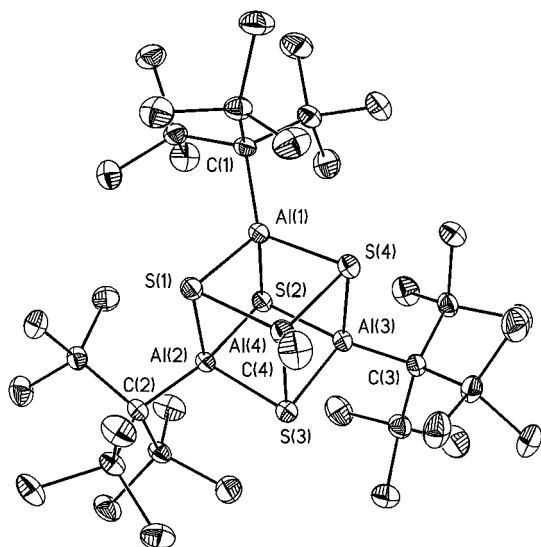
As mentioned above, a second method for the preparation of group 13–16 cage compounds is the reaction of trialkylmetalanes with elemental chalcogens. Because of the very high toxicity of H_2Se and H_2Te we tried to prepare the corresponding selenides and tellurides following this route.

Reactions of $(\text{Me}_3\text{Si})_3\text{CALMe}_2 \cdot \text{THF}$ (**1**) and $(\text{Me}_3\text{Si})_3\text{CGaMe}_2$ (**2**) with elemental selenium in a 1:1 ratio in refluxing toluene resulted in the formation of the corresponding selenolates $[(\text{Me}_3\text{Si})_3\text{CMMe}(\mu\text{-SeMe})_2]$ (**7**; M = Al, **8**; M = Ga) in good yields (Eqs. 4, 5).

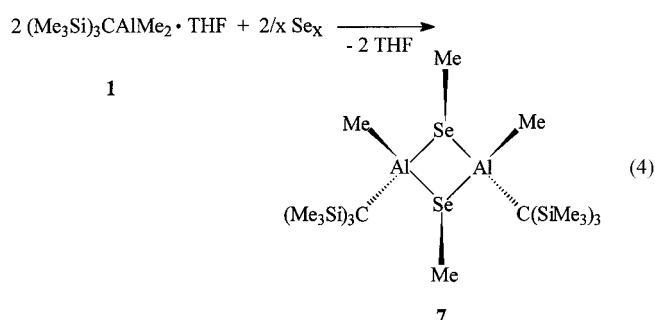
In both cases, the selenium reacted within 2 h, and the color of the reaction mixture changes from colorless through green to yellow. Compounds **7** and **8** are colorless, air- and moisture-sensitive, and extremely malodorous solids, which were fully characterized by ^1H - and ^{29}Si -NMR, mass, and IR spectroscopy as well as by elemental analyses (see Experimental Section). Additionally, recrystallization from benzene afforded single crystals of **7** · C_6H_6 suitable for X-ray diffraction analysis.

Figure 4 shows the crystal structure of the aluminum selenolate **7**, which crystallizes in the orthorhombic space group *Ibam* with eight dimers and eight benzene molecules in the unit cell. The central core of **7** is characterized by a distorted four-membered Al_2Se_2 ring (Al–Se–Al 86.2°, Se–Al–Se 84.0°, average) tilted towards the methyl groups at both aluminum and selenium in a *cis* conformation [angle between the planes defined by Al(1)/Se(1)/Se(2) and Al(1A)/Se(1)/Se(2) 133.6°]. In contrast, the ring of the only other structurally characterized dimeric aluminum selenolate $[\text{Mes}_2\text{Al}(\mu\text{-SeMe})_2]$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$)^[15] is planar and nearly undistorted (Al–Se–Al 89.4°, Se–Al–Se 90.6°, average) with the methyl substituents on the selenium in the *trans* conformation. This different behaviour can be explained by minimization of steric crowding caused by the bulky trisyl ligands. The Al–Se distances in **7** (average:

Figure 3. Crystal structure of $[(\text{Me}_3\text{Si})_3\text{CAl}(\mu_3\text{-S})]_3\text{MeAl}(\mu_3\text{-S})]$ (**6**), with anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity.^[a]



^[a] Selected bond lengths [pm] and angles [°]: Al(1)–C(1) 197.8(2), Al(1)–S(1) 231.49(11), Al(1)–S(2) 235.49(10), Al(1)–S(4) 233.70(14), Al(2)–C(2) 197.5(2), Al(2)–S(1) 234.22(10), Al(2)–S(2) 235.75(10), Al(2)–S(3) 231.00(13), Al(3)–C(3) 197.8(2), Al(3)–S(2) 235.65(14), Al(3)–S(3) 233.90(10), Al(3)–S(4) 231.20(10), Al(4)–C(4) 192.7(3), Al(4)–S(1) 230.52(13), Al(4)–S(3) 230.68(10), Al(4)–S(4) 230.28(11), C(1)–Al(1)–S(1) 117.38(7), C(1)–Al(1)–S(2) 127.59(8), C(1)–Al(1)–S(4) 118.83(7), S(1)–Al(1)–S(2) 95.08(4), S(1)–Al(1)–S(4) 97.01(4), S(2)–Al(1)–S(4) 94.31(4), C(2)–Al(2)–S(1) 118.57(7), C(2)–Al(2)–S(2) 127.75(7), C(2)–Al(2)–S(3) 117.76(7), S(1)–Al(2)–S(2) 94.29(4), S(1)–Al(2)–S(3) 97.13(4), S(2)–Al(2)–S(3) 94.64(4), C(3)–Al(3)–S(2) 128.78(8), C(3)–Al(3)–S(3) 118.95(8), C(3)–Al(3)–S(4) 116.20(7), S(2)–Al(3)–S(3) 93.91(4), S(2)–Al(3)–S(4) 94.93(4), S(3)–Al(3)–S(4) 97.36(4), C(4)–Al(4)–S(1) 119.76(10), C(4)–Al(4)–S(3) 118.93(10), C(4)–Al(4)–S(4) 118.60(10), S(1)–Al(4)–S(3) 98.27(4), S(1)–Al(4)–S(4) 98.26(5), S(3)–Al(4)–S(4) 98.54(4), Al(1)–S(1)–Al(2) 85.61(4), Al(1)–S(1)–Al(4) 82.18(4), Al(2)–S(1)–Al(4) 81.61(4), Al(1)–S(2)–Al(2) 84.37(4), Al(1)–S(2)–Al(3) 84.33(4), Al(2)–S(2)–Al(3) 84.61(4), Al(2)–S(3)–Al(3) 86.07(4), Al(2)–S(3)–Al(4) 82.27(4), Al(3)–S(3)–Al(4) 81.40(4), Al(1)–S(4)–Al(3) 85.73(4), Al(1)–S(4)–Al(4) 81.75(4), Al(3)–S(4)–Al(4) 82.07(4).



253.5 pm) are slightly longer than those in $[\text{Me}_2\text{Al}(\mu\text{-SeMe})]_2$ (251.9 pm)^[15] and in the heterocubane $[\text{Cp}^*\text{Al}(\mu_3\text{-Se})]_4$ (247.7 pm),^[2e] while the Al–C_{trisyl} (200.0 pm) and Al–C_{methyl} distances (196.6 pm) are somewhat shorter than those in the starting material (Me₃Si)₃CAlMe₂ · THF (**1**) (203.0 pm and 197.4 pm, respectively)^[11] due to the elec-

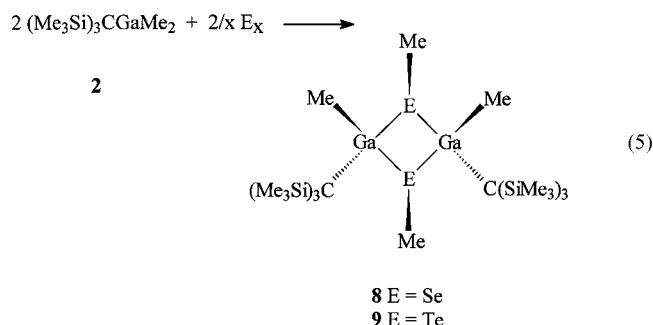
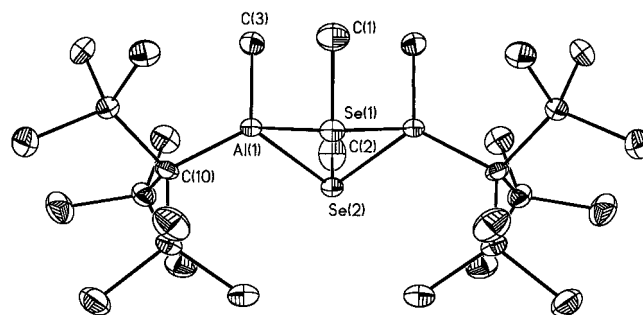


Figure 4. Crystal structure of $[(\text{Me}_3\text{Si})_3\text{CAlMe}(\mu\text{-SeMe})]_2$ (**7**), with anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity.^[a]



^[a] Selected bond lengths [pm] and angles [°]: Al(1)–C(3) 196.6(6), Al(1)–C(10) 200.0(3), Al(1)–Se(1) 252.71(11), Al(1)–Se(2) 254.35(10), Se(1)–C(1) 196.8(5), Se(2)–C(2) 196.1(5); C(3)–Al(1)–C(10) 118.46(13), C(3)–Al(1)–Se(1) 107.28(11), C(3)–Al(1)–Se(2) 107.89(11), C(10)–Al(1)–Se(1) 117.21(9), C(10)–Al(1)–Se(2) 116.65(9), Se(1)–Al(1)–Se(2) 84.01(3), Al(1)–Se(1)–Al(1A) 86.48(5), Al(1)–Se(1)–C(1) 103.70(12), Al(1A)–Se(1)–C(1) 103.71(12), Al(1)–Se(2)–Al(1A) 85.79(5), Al(1)–Se(2)–C(2) 106.68(13), Al(1A)–Se(2)–C(2) 106.68(13).

tron-withdrawing properties of the two selenium atoms coordinated at each aluminum atom.

The metal selenolates **7** and **8** show high thermal stabilities, and can be sublimed in vacuo (180–200 °C, 10^{–2} mbar) without decomposition. Their EI mass spectra show no signs for the formation of the corresponding metal selenides. In contrast, the selenolates $[\text{tBu}_2\text{M}(\mu\text{-Se-tBu})]_2$ (M = Al, Ga) give the corresponding tetrameric metal selenides $[\text{tBuM}(\mu_3\text{-Se})]_4$ (M = Al, Ga) upon heating.^{[2b][2c]}

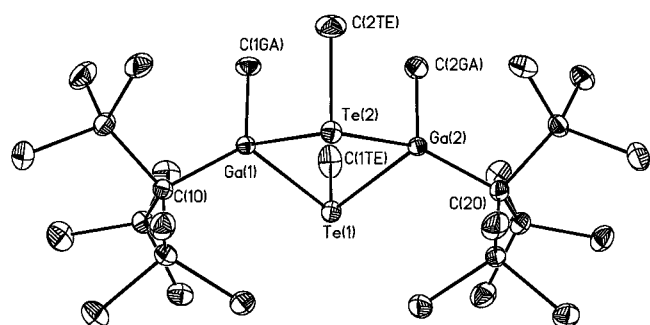
A different behaviour was observed for the reaction of the trialkylmetalanes **1** and **2** with elemental tellurium. While the reaction of the trialkylgallane **2** with tellurium powder in refluxing toluene results in the formation of the corresponding telluroalumane $[(\text{Me}_3\text{Si})_3\text{CGaMe}(\mu\text{-TeMe})]_2$ (**9**) in good yield within 3 h (Eq. 5), the trialkylalane **1** does not react with tellurium metal at all. Even after refluxing in toluene with a fivefold excess of tellurium for two days compound **1** and tellurium have been recovered nearly quantitatively.

The gallium telluroalumane **9** is a greenish, very air- and moisture-sensitive, malodorous solid which was fully characterized by ¹H- and ²⁹Si-NMR, mass, and IR spectroscopy as well as by elemental analysis (see Experimental Section). Additionally, recrystallization from toluene at

room temperature gave single crystals suitable for X-ray diffraction analysis.

The molecular structure of the gallium telluroate **9**, which crystallizes in the monoclinic space group $C2/c$, is depicted in Figure 5. The distorted central four-membered Ga_2Te_2 ring ($\text{Ga}-\text{Te}-\text{Ga}$ 85.5° , $\text{Te}-\text{Ga}-\text{Te}$ 87.5° , average) has a conformation [angle between the planes defined by $\text{Ga}(1)/\text{Te}(1)/\text{Te}(2)$ and $\text{Ga}(2)/\text{Te}(1)/\text{Te}(2)$ 139.9°] similar to the aluminum selenolate **7** and the two other structurally characterized dimeric organogallium telluroates $[(t\text{-BuCH}_2)_2\text{Ga}(\mu\text{-TePh})_2]$ ($\text{Ga}-\text{Te}-\text{Ga}$ 83.8° , $\text{Te}-\text{Ga}-\text{Te}$ 92.0° , angle between $\text{Ga}1/\text{Te}1/\text{Te}2$ and $\text{Ga}2/\text{Te}1/\text{Te}2$ 148°)^[16] and $[(\text{PhCH}_2)_2\text{Ga}(\mu\text{-Te-}t\text{Bu})_2]$ ($\text{Ga}-\text{Te}-\text{Ga}$ 81.8° , $\text{Te}-\text{Ga}-\text{Te}$ 92.0° , angle between $\text{Ga}1/\text{Te}1/\text{Te}2$ and $\text{Ga}2/\text{Te}1/\text{Te}2$ 141°),^[17] but in these molecules the substituents on the Te are in the *trans* position relative to the ring. The $\text{Ga}-\text{Te}$ distances in **9** (average: 274.6 pm) are in the range of those observed for $[(t\text{BuCH}_2)_2\text{Ga}(\mu\text{-TePh})_2]$ (average: 275.5 pm)^[16] and $[(\text{PhCH}_2)_2\text{Ga}(\mu\text{-Te-}t\text{Bu})_2]$ (average: 269.3 pm)^[17] but are distinctly longer than the sum of the covalence radii of Ga and Te (262 pm).^[18] The $\text{Ga}-\text{C}_{\text{trisyl}}$ (202.5 pm) and $\text{Ga}-\text{C}_{\text{methyl}}$ distances (198.3 pm) are slightly shorter than those observed for $(\text{Me}_3\text{Si})_3\text{CGaMe}_2 \cdot \text{THF}$ (204.6 and 197.9 pm, respectively).^[11]

Figure 5. Crystal structure of $[(\text{Me}_3\text{Si})_3\text{CGaMe}(\mu\text{-TeMe})_2]$ (**9**), with anisotropic displacement parameters depicting 50% probability. Hydrogen atoms have been omitted for clarity.^[a]



^[a] Selected bond lengths [pm] and angles $^\circ$: $\text{Ga}(1)-\text{C}(1\text{GA})$ 198.5(6), $\text{Ga}(1)-\text{C}(10)$ 202.6(6), $\text{Ga}(1)-\text{Te}(1)$ 274.34(8), $\text{Ga}(1)-\text{Te}(2)$ 274.39(7), $\text{Ga}(2)-\text{C}(2\text{GA})$ 198.1(6), $\text{Ga}(2)-\text{C}(20)$ 202.3(6), $\text{Ga}(2)-\text{Te}(1)$ 274.19(8), $\text{Ga}(2)-\text{Te}(2)$ 275.37(8), $\text{Te}(1)-\text{C}(1\text{TE})$ 215.4(7), $\text{Te}(2)-\text{C}(2\text{TE})$ 215.3(6); $\text{C}(1\text{GA})-\text{Ga}(1)-\text{C}(10)$ 120.8(3), $\text{C}(1\text{GA})-\text{Ga}(1)-\text{Te}(1)$ 104.93(19), $\text{C}(1\text{GA})-\text{Ga}(1)-\text{Te}(2)$ 104.34(19), $\text{C}(10)-\text{Ga}(1)-\text{Te}(1)$ 116.10(17), $\text{C}(10)-\text{Ga}(1)-\text{Te}(2)$ 117.64(16), $\text{Te}(1)-\text{Ga}(1)-\text{Te}(2)$ 87.58(2), $\text{C}(2\text{GA})-\text{Ga}(2)-\text{C}(20)$ 120.4(3), $\text{C}(2\text{GA})-\text{Ga}(2)-\text{Te}(1)$ 104.9(2), $\text{C}(2\text{GA})-\text{Ga}(2)-\text{Te}(2)$ 104.14(19), $\text{C}(20)-\text{Ga}(2)-\text{Te}(1)$ 116.41(16), $\text{C}(20)-\text{Ga}(2)-\text{Te}(2)$ 118.13(17), $\text{Te}(1)-\text{Ga}(2)-\text{Te}(2)$ 87.41(2), $\text{C}(1\text{TE})-\text{Te}(1)-\text{Ga}(1)$ 97.8(2), $\text{C}(1\text{TE})-\text{Te}(1)-\text{Ga}(2)$ 99.23(19), $\text{Ga}(1)-\text{Te}(1)-\text{Ga}(2)$ 85.57(2), $\text{C}(2\text{TE})-\text{Te}(2)-\text{Ga}(1)$ 98.76(18), $\text{C}(2\text{TE})-\text{Te}(2)-\text{Ga}(2)$ 99.7(2), $\text{Ga}(1)-\text{Te}(2)-\text{Ga}(2)$ 85.34(2).

In contrast to $[t\text{Bu}_2\text{Ga}(\mu\text{-Te-}t\text{Bu})_2]$, which has been converted to the corresponding tetrameric telluride $[t\text{BuGa}(\mu_3\text{-Te})_4]$ upon heating,^[2c] thermolysis of compound **9** results in the formation of an ochre colored powder which was identified by ^1H - and ^{29}Si -NMR spectroscopy as a complex mixture of unknown products.

Conclusions and Remarks

In summary we have shown that compounds $(\text{Me}_3\text{Si})_3\text{-AlMe}_2 \cdot \text{THF}$ (**1**) and $(\text{Me}_3\text{Si})_3\text{CGaMe}_2$ (**2**) are ideal starting materials for the preparation of various chalcogen-containing derivatives. Under the reaction conditions reported the $\text{Al}-\text{C}(\text{SiMe}_3)_3$ and the corresponding $\text{Ga}-\text{C}$ bond was not cleaved either using H_2S or the heavier elements of group 16, leading to products which could be recrystallized from organic solvents. The MOCVD experiments using the compounds described in this paper are still in progress. However, these results will be reported elsewhere.

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Experimental Section

General: All experiments were performed with standard Schlenk techniques under dry nitrogen atmosphere due to the extreme sensitivity of reactants and products toward air and moisture. A Braun MB 150-GI glovebox was used to store the compounds and to prepare the samples for spectroscopic characterizations. All solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. H_2S , Se metal, and Te metal were purchased from Aldrich Chemical Co., $(\text{Me}_3\text{Si})_3\text{AlMe}_2 \cdot \text{THF}$ and $(\text{Me}_3\text{Si})_3\text{-CGaMe}_2$ were prepared as described in the literature.^[11] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. It is well-known that the analysis for carbon in group 13 compounds is often low due to the generation of metal carbides.^[19] In compounds containing silicon, the content of carbon is decreased further by formation of silicon carbide. – NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments, and were externally referenced to tetramethylsilane in ppm with low-field shift positive. – FT-IR spectra were measured on a Bio-Rad FTS-7 as nujol mulls between KBr plates in the range of $4000-400\text{ cm}^{-1}$ (abbreviations used: vs, very strong; s, strong; m, medium) and EI mass spectra on Finnigan MAT 8230 or Varian MAT CH 5 instruments. The most intensive peak of each isotopic distribution is given. – Melting points were measured in sealed glass tubes and are not corrected.

Synthesis of $[(\text{Me}_3\text{Si})_3\text{Al}(\mu\text{-S})_2] \cdot 2\text{ THF}$ (3**):** Dry H_2S was bubbled slowly through a solution of 3.70 g of $(\text{Me}_3\text{Si})_3\text{AlMe}_2 \cdot \text{THF}$ (10.3 mmol) in toluene (100 ml) at room temperature for 45 minutes. The opaque reaction mixture was stirred at room temperature for 1 h and then filtered through celite. Removal of all volatiles in vacuo gave analytically pure compound **3**. Yield: 2.60 g (87%), colorless solid, m.p. 235°C . – ^1H NMR (200.13 MHz, C_6D_6): δ = 3.77 (m, 8 H, OCH_2CH_2), 1.33 (m, 8 H, OCH_2CH_2), 0.49 (s, 54 H, SiCH_3). – ^{29}Si NMR (49.69 MHz, C_6D_6): δ = -3.7. – MS (70 eV): m/z (%) 1147 (30) [$\{(\text{Me}_3\text{Si})_3\text{AlS}\}_4 - \text{Me}$], 929 (46) [$\{(\text{Me}_3\text{Si})_3\text{AlS}\}_4 - \text{C}(\text{SiMe}_3)_3$], 565 (50) [$\text{M}^+ - \text{Me} - 2\text{ THF}$], 275 (90) [$(\text{M}/2)^+ - \text{Me} - \text{THF}$], 201 (100) [$\text{C}(\text{SiMe}_3)_3 - 2\text{ Me}$]. – IR: $\tilde{\nu}$ = 1346 (m), 1253 (vs), 1095 (m), 1042 (m), 1012 (m), 989 (m), 917 (m), 848 (vs), 793 (s), 752 (m), 721 (m), 669 (s), 642 (m), 616 (m), 533 (m), 490 (m), 447 (s), 424 (m) cm^{-1} . – $\text{C}_{28}\text{H}_{70}\text{Al}_2\text{O}_2\text{S}_2\text{Si}_6$ (725.49): calcd. C 46.36, H 9.73; found: C 45.6, H 9.7.

Synthesis of $[(\text{Me}_3\text{Si})_3\text{CGa}(\mu_3\text{-S})_4]$ (4**):** Dry H_2S was bubbled slowly through a toluene solution (160 ml) of 4.00 g of $(\text{Me}_3\text{Si})_3\text{-CGaMe}_2$ (12.1 mmol) at room temperature for 45 minutes. After 2

h stirring at room temperature, the opaque solution was filtered through celite. Removal of all volatiles in vacuo and washing of the residue with pentane (20 ml) gave compound **4**. Yield: 3.7 g (92%); colorless, air- and moisture-sensitive solid; m.p. 316 °C. – ¹H NMR (200.13 MHz, C₆D₆): δ = 0.47 [C(SiCH₃)]. – ²⁹Si NMR (49.69 MHz, C₆D₆): δ = -1.0. – MS (70 eV): *m/z* (%) 1317 (1) [M⁺ – Me], 1101 (3) [M⁺ – C(SiMe₃)₃], 769 (5) [(3/4 M)⁺ – C(SiMe₃)₃], 666 (15) [(M/2)⁺], 651 (60) [(M/2)⁺ – Me], 317 (100) [(M/4)⁺ – Me], 201 (45) [C(SiMe₃)₃ – 2 Me]. – IR: ν̄ = 1288 (m), 1262 (s), 1250 (s), 1099 (m), 1019 (m), 980 (m), 854 (vs), 849 (vs), 785 (m), 726 (m), 673 (s), 663 (s), 630 (m), 616 (m), 556 (m) cm⁻¹. – C₄₀H₁₀₈Ga₄S₄Si₁₂ (1333.50): calcd. C 36.03, H 8.16; found C 36.3, H 8.7.

Synthesis of [(Me₃Si)₃Al(μ₃-S)]₄ (5**) and {[(Me₃Si)₃Al(μ₃-S)]₃MeAl(μ₃-S)} (**6**):** Compound **3** (2.00 g, 2.76 mmol) was heated in vacuo (10⁻² mbar) without solvent to 220 °C for 30 minutes. The slightly yellow residue was extracted with toluene (50 ml) and filtered through celite. Storage at -26 °C gave colorless crystals of a mixture of the compounds [(Me₃Si)₃Al(μ₃-S)]₄ (**5**) and {[(Me₃Si)₃Al(μ₃-S)]₃MeAl(μ₃-S)} (**6**) (1.10 g), which could not be separated by crystallization or sublimation. – ¹H NMR (200.13 MHz, C₆D₆): δ = 0.48 (s, SiCH₃ of **6**), 0.44 (s, SiCH₃ of **5**), 0.13 (s, AlCH₃ of **6**). – ²⁹Si NMR (49.69 MHz, C₆D₆): δ = -2.24 (**6**), -2.31 (**5**). – MS (70 eV): *m/z* (%) 1147 (25) [**5** – Me], 929 (90) [**6** – Me], 275 (85) [(5/4) – Me], 201 (100) [C(SiMe₃)₃ – 2 Me]. – IR (KBr, Nujol): ν̄ = 1496 (m), 1413 (m), 1341 (m), 1294 (m), 1260 (s), 1252 (s), 1096 (m), 1081 (m), 1030 (m), 1012 (m), 849 (vs), 837 (vs), 794 (s), 752 (m), 727 (m), 714 (m), 667 (vs), 644 (s), 619 (m), 577 (m) cm⁻¹.

Synthesis of [(Me₃Si)₃AlMe(μ-SeMe)]₂ (7**):** To a suspension of 0.44 g of gray selenium (5.54 mmol) in toluene (20 ml) was added

a solution of 2.00 g of (Me₃Si)₃AlMe₂ · THF (5.54 mmol) in toluene (30 ml) at room temperature. The reaction mixture was stirred for 15 h at room temperature, and then heated under reflux for 2 h. During this time the color changed from colorless through green to yellow, and the selenium was completely consumed. After filtration of the solution through celite and concentration to 15 ml, compound **7** crystallized as a colorless solid on cooling to -26 °C. Yield: 1.55 g (76%); colorless, air- and moisture-sensitive crystals; m.p. 278 °C. – ¹H NMR (200.13 MHz, C₆D₆): δ = 1.79 (s, 6 H, SeCH₃), 0.37 (s, 54 H, SiCH₃), -0.13 (s, 6 H, AlCH₃). – ²⁹Si NMR (49.69 MHz, C₆D₆): δ = -3.6. – MS (70 eV): *m/z* (%) 368 (1) [(M/2)⁺], 353 (15) [(M/2)⁺ – Me], 273 (100) [(M/2)⁺ – SeMe]. – IR: ν̄ = 1260 (s), 1248 (s), 1195 (m), 855 (vs), 789 (s), 721 (m), 671 (s), 613 (m), 603 (m) cm⁻¹. C₂₄H₆₆Al₂Se₂Si₆ (735.20): calcd. C 39.21, H 9.05; found: C 39.7, H 9.0.

Preparation of [(Me₃Si)₃CGaMe(μ-SeMe)]₂ (8**):** A solution of 2.00 g of (Me₃Si)₃CGaMe₂ (6.04 mmol) in toluene (30 ml) was slowly added to a suspension of 0.48 g of gray selenium (6.04 mmol) in toluene (20 ml) at room temperature. The reaction mixture was stirred at room temperature for 8 h and then heated under reflux for 2 h. During this time the color changed from colorless through green to yellow, and the selenium was consumed completely. After filtration of the opaque solution through celite and concentration to 25 ml compound **8** crystallized as a slightly yellow solid on cooling to -26 °C. Yield: 1.95 g (79%), slightly yellow air- and moisture-sensitive crystals, m.p. 256 °C. – ¹H NMR (200.13 MHz, C₆D₆): δ = 1.79 (s, 6 H, SeCH₃), 0.36 (s, 54 H, SiCH₃), 0.29 (s, 6 H, GaCH₃). – ²⁹Si NMR (49.69 MHz, C₆D₆): δ = -2.5. – MS (70 eV): *m/z* (%) 775 (7) [M⁺ – 3 Me], 760 (7) [M⁺ – 4 Me], 745 (10) [M⁺ – 5 Me], 395 (12) [(M/2)⁺ – Me], 365 (20) [(M/2)⁺ – 3 Me], 315 (50) [(M/2)⁺ – SeMe – Me], 201 (100) [C(SiMe₃)₃

Table 1. Crystallographic data for compounds **3** · C₆H₆, **4** · 1.5 C₆H₆, **6**, **7** · C₆H₆, and **9**

Compound	3 · C ₆ H ₆	4 · 1.5 C ₆ H ₆	6	7 · C ₆ H ₆	9
Empirical formula	C ₃₄ H ₇₆ Al ₂ O ₂ S ₂ Si ₆	C ₄₉ H ₁₁₇ Ga ₄ S ₄ Si ₁₂	C ₃₁ H ₈₄ Al ₄ Si ₉	C ₃₀ H ₇₂ Al ₂ Se ₂ Si ₆	C ₂₄ H ₆₆ Ga ₂ Si ₆ Te ₂
Molecular mass [g/mol]	803.60	1450.63	945.95	813.30	917.95
T (K)	133(2)	133(2)	203(2)	133(2)	133(2)
Crystal size [mm]	0.40 × 0.20 × 0.20	0.40 × 0.30 × 0.30	0.50 × 0.50 × 0.30	0.70 × 0.50 × 0.40	0.50 × 0.40 × 0.40
Crystal system	orthorhombic	trigonal	triclinic	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>P3c1</i>	<i>P1</i>	<i>Ibam</i>	<i>C2/c</i>
<i>a</i> [pm]	14.696(3)	15.570(2)	14.044(4)	17.518(4)	15.511(1)
<i>b</i> [pm]	13.416(4)	15.570(2)	14.201(5)	17.706(4)	9.224(1)
<i>c</i> [pm]	23.289(5)	34.958(7)	16.462(6)	28.756(6)	56.613(11)
<i>α</i> [°]	90	90	98.44(3)	90	90
<i>β</i> [°]	90	90	100.65(2)	90	96.00(1)
<i>γ</i> [°]	90	120	119.37(1)	90	90
<i>V</i> [10 ⁻³⁰ m ³]	4592(2)	7340(10)	2702(2)	8920(10)	8055(2)
<i>Z</i>	4	4	2	8	8
<i>d</i> _{calcd.} [g/cm ³]	1.162	1.313	1.163	1.211	1.514
<i>μ</i> (mm ⁻¹)	0.338	1.792	0.462	1.877	2.949
<i>F</i> (000)	1752	3068	1024	3440	3680
2θ range	4.5° ≤ 2θ ≤ 50.2°	4.7° ≤ 2θ ≤ 50.0°	7.1° ≤ 2θ ≤ 50.3°	7.1° ≤ 2θ ≤ 45.2°	4.3° ≤ 2θ ≤ 49.4°
Reflections collected	52394	87752	12402	3905	36639
Independent reflections	4080 (<i>R</i> _{int} = 0.0782)	4342 (<i>R</i> _{int} = 0.0566)	9396 (<i>R</i> _{int} = 0.0234)	3019 (<i>R</i> _{int} = 0.0260)	6868 (<i>R</i> _{int} = 0.0487)
Absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from ψ-scans	semiempirical from ψ-scans	semiempirical from equivalents
<i>R</i> ^[a] , <i>wR</i> ^[b] [<i>I</i> > 2σ(<i>I</i>)]	0.0426, 0.0750	0.0531, 0.0941	0.0342, 0.0820	0.0324, 0.0766	0.0466, 0.0848
<i>R</i> , <i>wR</i> 2 (all data)	0.0575, 0.0796	0.0751, 0.1034	0.0426, 0.0894	0.0419, 0.0833	0.0531, 0.0866
Goodness of fit <i>S</i> ^c	1.157	1.213	1.080	1.040	1.409
Parameters	233	325	461	323	330
Restraints	109	1023	0	691	0
Max./min. residual [10 ³⁰ e/m ³]	0.273/−0.205	0.937/−0.524	0.375/−0.309	0.556/−0.589	0.651/−0.94

[a] *R* = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|. – [b] *wR*2 = [Σ*w*(*F*_o² − *F*_c²)²]/[Σ*w*(*F*_o²)²]^{1/2}. [c] *S* = [Σ*w*(*F*_o² − *F*_c²)²]/(*n* − *p*)^{1/2}. *w*⁻¹ = σ²(*F*_o²) + (*aP*)² + *bP*, *P* = [*F*_o² + 2*F*_c²]/3.

– 2 Me]. – IR: $\tilde{\nu}$ = 1289 (m), 1260 (s), 1247 (s), 1201 (m), 857 (vs), 847 (vs), 784 (s), 753 (m), 722 (s), 672 (s), 659 (s), 625 (m), 616 (m), 549 (m), 539 (m) cm^{-1} . – $\text{C}_{24}\text{H}_{66}\text{Ga}_2\text{Se}_2\text{Si}_6$ (820.70): calcd. C 35.12, H 8.11; found: C 35.7, H 8.1.

Preparation of [(Me₃Si)₃CCGaMe(μ -TeMe)]₂ (9): To a suspension of 1.54 g of tellurium metal (12.1 mmol) in toluene (30 ml) was slowly added a solution of 2.00 g of **2** (6.04 mmol) in toluene (30 ml) at room temperature. The reaction mixture was stirred for 3 d at room temperature and then heated under reflux for 3 h. After filtration of the dark yellow mixture through celite and concentration to 35 ml compound **9** crystallized on cooling to –26 °C. Yield: 2.00 g (72%), slightly green crystals, air- and moisture-sensitive, m.p. 296 °C (dec.). – ¹H NMR (200.13 MHz, C₆D₆): δ = 1.62 (s, 6 H, TeCH₃), 0.50 (s, 6 H, GaCH₃), 0.37 (s, 54 H, SiCH₃). – ²⁹Si NMR (49.69 MHz, C₆D₆): δ = –2.3. MS (70 eV): m/z (%) 858 (3) [M⁺ – 4 Me], 445 (7) [(M/2)⁺ – Me], 315 (100) [(M/2)⁺ – TeMe], 201 (80) [C(SiMe₃)₃ – 2 Me]. – IR: $\tilde{\nu}$ = 1289 (m), 1260 (vs), 1248 (vs), 1217 (s), 1191 (m), 858 (vs), 783 (s), 722 (m), 673 (m), 667 (m), 624 (m), 615 (m), 541 (s), 532 (s) cm^{-1} . $\text{C}_{24}\text{H}_{66}\text{Ga}_2\text{Si}_6\text{Te}_2$ (917.97): calcd. C 31.40, H 7.25; found C 32.2, H 7.4.

Crystal-Structure Determinations: Single crystals of compounds **3** · C₆H₆, **4** · 1.5 C₆H₆ and **7** · C₆H₆, **6** and **9** were obtained by recrystallization from benzene and toluene at room temperature, respectively. Crystal data and structure refinement parameters are given in Table 1. Data for structures **3** · C₆H₆, **4** · 1.5 C₆H₆, and **9** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens SMART CCD area detector and for structures **6** and **7** · C₆H₆ on a Stoe-Siemens AED four-circle diffractometer. Mo-K α radiation (λ = 71.073 pm) was used in all cases. All structures were solved by direct methods (SHELXS-97)^[20] and refined against F^2 using SHELXL-97.^[21] All heavy atoms were refined anisotropically, hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom. For structure **9** an extinction correction was employed.

In structures **4** · 1.5 C₆H₆ and **7** some of the trisily ligands were disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters. The anisotropic displacement parameters of the Si atoms lying opposite to each other were constrained to be the same. Additionally the THF molecules in **3** · C₆H₆ and one benzene molecule in **7** · C₆H₆ were disordered. Again distance restraints and restraints for the anisotropic displacement parameters were used.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication numbers CCDC-102100, 102101, 102102, 102103, and 102104. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. +44 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

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