Synthesis and Characterization of Tris(trimethylsilyl)methylaluminum Chalcogenides $[RAl(\mu_3\text{-}E)]_4$ ($R = (Me_3Si)_3C$; E = Se, Te) and 1-Azaallylgallium Chalcogenides $[R'Ga(\mu_2\text{-}E)]_2$ ($R' = (Me_3Si)_2C(Ph)C(Me_3Si)N$; E = S, Se, Te)

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Received December 8, 2000

Tris(trimethylsilyl)methylaluminum dihydride, $(Me_3Si)_3CAlH_2{\cdot}THF$ (**1**), has been prepared by the reaction of $RLi{\cdot}2THF$ ($R = (Me_3Si)_3C$) with $H_3Al{\cdot}NMe_3$. The reaction of **1** with elemental Se or Te in toluene afforded the novel organoaluminum chalcogenide heterocubane $[RAl(\mu_3\text{-}E)]_4$ (E = Se (**2**), Te (**3**)) in good yield. $[R'GaH(\mu\text{-}H)]_2$ (**4**) ($R' = (Me_3Si)_2C(Ph)C(Me_3Si)N$) was obtained by the reaction of $R'Li{\cdot}THF$ with $H_3Ga{\cdot}NMe_3$ and compounds **5**−**7** by the reaction of $[R'GaH(\mu\text{-}H)]_2$ with S (**5**) and $RGaCl_2$ with $(Me_3Si)_2E$ (E = Se (**6**), Te (**7**)). The structures of **6** and **7** have been established by X-ray crystallography. Compounds **6** and **7** have a dimeric structure featuring fused planar four-membered ring systems with a central Ga_2E_2 core. On the basis of ^1H and ^{29}Si NMR data of **6** and **7**, the trans and cis isomers could not be confirmed due to the formation of several species in solution.

Introduction

Previously we described the basic chemistry of tris(trimethylsilyl)methyl- and 1-azaallyl-substituted aluminum and gallium compounds.[1] After the successful attempt to synthesize organoaluminum sulfur heterocubanes[2] and dimeric 1-azaallylaluminum chalcogenides,[3] we developed the chemistry of RMH_2 ($R = (Me_3Si)_3C$ or $(Me_3Si)_2C(Ph)C(Me_3Si)N$; M = Al, Ga) to get the corresponding organoaluminum chalcogenide (Se, Te) heterocubanes and the dimeric organogallium chalcogenides.

Organometallic cage compounds of aluminum and gallium with bonds to group 15 elements of composition $[RMER']_x$ (M = Al, Ga; E = N, P; R, R′ = H, alkyl, aryl) have been prepared over the last four decades,[4] especially to study their potential use as precursors for group 13−15 materials. In comparison to that, only a few fully characterized cage compounds of composition $[RME]_x$ (M = Al, Ga, In; E = S, Se, Te; R = alkyl, aryl, allyl) have been reported for group 13 and 16 elements.[5] These compounds have been preferentially prepared by (1) protolysis of R_3M or $RAlMe_2$ with H_2E, (2) reaction of $RMCl_2$ with $(Me_3Si)_2E$, or (3) treatment of R_3M or $RAlH_2$ with elemental chalcogenides.

Herein, we report on the synthesis of organometallic dihydrides (M = Al, Ga) containing the tris(trimethylsilyl)methyl and 1-azaallyl ligands and their facile reaction with S, Se, and Te to give heterocubanes as well as dimeric organogallium chalcogenides.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under a dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products toward air and moisture. A Braun Labmaster 130

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10.1021/om0010520 CCC: $20.00
Publication on Web 04/17/2001

drybox 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. Chemicals were purchased from Aldrich Chemical Co. and used as received; $H_3Al{\cdot}NMe_3$,[6] $(Me_3Si)_3CLi{\cdot}2THF$,[7] $H_3Ga{\cdot}NMe_3$,[6] $[(Me_3Si)_2C(Ph)C(Me_3Si)N]Li{\cdot}THF$,[8] $(Me_3Si)_2Se$,[9] $(Me_3Si)_2Te$,[9] and $[(Me_3Si)_2C(Ph)C(Me_3Si)N]GaCl_2$[1d] were prepared as described in the literature. NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments. Chemical shifts are reported in parts per million with reference to tetramethylsilane as external standard. EI mass spectra were obtained on a Finnigan MAT 8230 or Varian MAT CH 5 instrument, and FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates or as KBr pellets in the range of 4000−400 cm^{-1} (abbreviations used: vs, very strong; s, strong; m, medium). Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes and are uncorrected.

Preparation of $(Me_3Si)_3CAlH_2{\cdot}THF$ (1). A solution of $H_3Al{\cdot}NMe_3$ in toluene (20 mL), prepared from $LiAlH_4$ (0.91 g, 24 mmol) and Me_3NHCl (1.91 g, 20 mmol), was added at −78 °C to a solution of $(Me_3Si)_3CLi{\cdot}2THF$ (5.74 g, 15 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature and stirred for 15 h. After filtration the solvent was removed in vacuo to yield compound **1** (4.26 g, 12.9 mmol, 86%) as a colorless solid.

Preparation of $[(Me_3Si)_3CAl(\mu_3\text{-}Se)]_4$ (2). To a suspension of selenium (0.95 g, 12.0 mmol) in toluene (10 mL) was added in excess at room temperature a solution of $(Me_3Si)_3CAlH_2{\cdot}THF$ (2.20 g, 6.6 mmol) in toluene (10 mL). After 15 h of stirring at room temperature, the solution was heated to 100 °C and stirred for an additional 1.5 h. Filtration and removal of the solvent afforded compound **2** (1.96 g, 1.5 mmol, 88%) as a yellow solid. Mp: 288 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.68 (s, $SiCH_3$, 27 H). ^{13}C NMR (125.76 MHz, C_6D_6): δ 3.4 ($CSiMe_3$), 6.4 ($SiCH_3$). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −0.37 ($SiMe_3$). MS: *m/e* 1335 (M^+ − Me, 10), 661 ($M^+/2$ − Me, 38), 323 ($M^+/4$ − Me, 68), 201 ($(Me_3Si)_3C^+$ − 2Me, 100). IR (KBr): 1261 (vs), 1169 (m), 1075 (s), 1036 (vs), 855 (vs), 790 (vs), 750 (m), 727 (m), 664 (vs), 614 (m), 481 (m), 386 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{108}Al_4Se_4Si_{12}$ (1350.09): C, 35.59; H, 8.06; Al, 7.99. Found: C, 35.8; H, 7.9; Al, 8.0.

Preparation of $[(Me_3Si)_3CAl(\mu_3\text{-}Te)]_4$ (3). A solution of $(Me_3Si)_3CAlH_2{\cdot}THF$ (2.20 g, 6.6 mmol) in toluene (10 mL) was slowly added at room temperature to a suspension of tellurium (1.54 g, 12.1 mmol) in toluene (10 mL) in excess. The mixture was stirred for 15 h at room temperature and then heated to 100 °C for 2 h. Filtration and concentration to ca. 5 mL afforded after crystallization pure **3** (2.12 g, 1.4 mmol, 83%) as yellow-green crystals. Mp: 294 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.72 (s, $SiCH_3$, 27 H). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −0.31 ($SiMe_3$). MS: *m/e* 1531 (M^+ − Me, 4), 757 ($M^+/2$ − Me, 25), 373 ($M^+/4$ − Me, 73), 201 ($(Me_3Si)_3C^+$ − 2Me, 100). Anal. Calcd for $C_{40}H_{108}Al_4Si_{12}Te_4$ (1544.65): C, 31.10; H, 7.05; Al, 6.99. Found: C, 30.9; H, 6.6; Al, 7.1.

Preparation of $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}H)]_2$ (4) in Situ. To a solution of $(Me_3Si)_2C(Ph)C(Me_3Si)NLi{\cdot}THF$ (2.05 g, 5.0 mmol) in toluene (20 mL) was slowly added at −78 °C a solution of $H_3Ga{\cdot}NMe_3$ (0.65 g, 5.0 mmol) in toluene (20 mL). The mixture was warmed to room temperature and stirred for 15 h to afford **4** as an intermediate.

^1H NMR (200.13 MHz, C_6D_6): δ 0.09 (s, $NSiCH_3$, 9H), 0.23 (s, $SiCH_3$ 18 H), 5.81 (br s, HGa, 2 H), 6.80−6.98 (m, Ph, 3H), 7.38 (d, Ph, 2H). ^{13}C NMR (125.76 MHz, C_6D_6): δ 0.83 ($NSiCH_3$), 2.23 ($SiCH_3$), 68.71 (CSi_2), 126.14, 128.45, 130.04 (Ph), 132.21 (*ipso*-C), 192.53 (CN). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −3.42 ($SiCH_3$), 4.34 ($NSiCH_3$).

Preparation of $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}S)]_2$ (5). A solution of **4** (3.25 g, 4.0 mmol) in toluene (20 mL) was slowly added at room temperature to a suspension of sulfur (0.42 g, 13.0 mmol). The mixture was stirred for 15 h at room temperature and then heated to 80 °C for 2 h. After filtration and concentration to 10 mL, the solution was stored at 0 °C. Compound **5** was obtained by cyrstallization as colorless crystals (2.43 g, 2.6 mmol, 65%). Mp: 184 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.29, 0.31 (s, $NSiCH_3$, 9 H), 0.38, 0.39 (s, $SiCH_3$, 18 H), 6.80−6.98 (m, Ph, 3 H), 7.21 (d, Ph, 2H). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −0.34, −0.98 ($SiCH_3$), 6.53, 7.07 ($NSiCH_3$). MS: *m/e* 872 (M^+, 40), 285 ($M^+/2$ − Ph − $SiMe_3$, 82), 73 (Me_3Si^+, 100). Anal. Calcd for $C_{34}H_{64}Ga_2N_2S_2Si_6$ (872.97): C, 46.78; H, 7.39; N, 3.21. Found: C, 46.0; H, 7.0; N, 3.4.

Preparation of $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}Se)]_2$ (6). $(Me_3Si)_2Se$ (0.24 g, 1.0 mmol) was added at room temperature to a solution of $(Me_3Si)_2C(Ph)C(Me_3Si)NGaCl_2$ (0.50 g, 1.0 mmol) in toluene (20 mL). After the solution was stirred for 2 h, the solvent was removed in vacuo and the brown residue was crystallized from toluene (2 mL) to give **6** (0.89 g, 0.9 mmol, 88%) as colorless crystals. Mp: 202 °C. ^1H NMR (200.13 MHz, C_6D_6): δ 0.30, 0.32 (s, $NSiCH_3$, 9 H), 0.45, 0.46 (s, $SiCH_3$, 18 H), 6.82−7.00 (m, Ph, 3 H), 7.25 (d, Ph, 2H). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −0.57, −1.28 ($SiCH_3$), 7.60, 9.73 ($NSiCH_3$). MS: *m/e* 966 (M^+, 42), 73 (Me_3Si^+, 100). IR (KBr): 1249 (vs), 1069 (s), 1026 (m), 948 (m), 875 (s), 845 (vs), 765 (s), 656 (m), 514 (m) cm^{-1}. Anal. Calcd for $C_{34}H_{64}Ga_2N_2Se_2Si_6$ (966.05): C, 42.24; H, 6.67; N, 2.90. Found: C, 42.2; H, 6.7; N, 3.0.

Preparation of $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}Te)]_2$ (7). To a solution of $(Me_3Si)_2C(Ph)C(Me_3Si)NGaCl_2$ (1.20 g, 12.5 mmol) in toluene (20 mL) was added at room temperature $(Me_3Si)_2Te$ (0.24 g, 1.0 mmol). The mixture was stirred for 3 h, and the solvent was removed in vacuo. The residue was crystallized from toluene (4 mL) to give **7** (2.23 g, 2.1 mmol, 82%) as colorless crystals. Mp: 221 °C. ^1H NMR (500.13 MHz, toluene-d_8, 300 K): δ 0.26 (s, $NSiCH_3$, 6 H), 0.33 (s, $NSiCH_3$, 9 H), 0.40 (s, $CSiCH_3$, 18 H), 0.41 (s, $CSiCH_3$, 3 H), 7.10−7.20 (m, Ph, 3H), 7.43 (m, Ph, 2 H). ^1H NMR (500.13 MHz, toluene-d_8, 253 K): δ 0.30 (s, $NSiCH_3$, 6 H), 0.35 (s, $NSiCH_3$, 9 H), 0.42 (s, $CSiCH_3$, 18 H), 0.44 (s, $CSiCH_3$, 3 H), 7.00−7.20 (m, Ph, 3 H), 7.42 (m, Ph, 2 H). ^1H NMR (500.13 MHz, toluene-d_8, 223 K): δ 0.32 (br s, $NSiCH_3$, 6 H), 0.35 (s, $NSiCH_3$, 9 H), 0.45, 0.46 (br s, $CSiCH_3$, 18 H), 7.00−7.40 (m, Ph, 5 H). ^1H NMR (500.13 MHz, toluene-d_8, 183 K): δ 0.38, 0.48 (br s, $NSiCH_3$, br s, $CSiCH_3$, 27 H), 7.10−7.40 (m, Ph, 5 H). The hydrogen atoms give the integration of the signals. ^{29}Si NMR (79.46 MHz, C_6D_6): δ −0.75, −1.15 ($SiCH_3$), 7.45, 8.36 ($NSiCH_3$). MS: *m/e* 1064 (M^+, 36), 73 (Me_3Si^+, 100). IR (KBr): 1600 (m), 1525 (st), 1249 (sst), 1069 (sst), 1026 (m), 1001 (m), 944 (st), 921 (m), 874 (st), 844 (sst), 762 (st), 706 (st), 674 (m), 655 (st), 610 (m), 599 (m), 511 (st), 442 (m) cm^{-1}. Anal. Calcd for $C_{34}H_{64}Ga_2N_2Si_6Te_2$ (1064.05): C, 38.38; H, 6.06; N, 2.63. Found: C, 38.1; H, 6.1; N, 2.7.

Crystal Structure Solution and Refinement for 6 and 7. Data for structures **6** and **7** were collected on a Stoe-Siemens-Huber four-circle diffractometer using Mo Kα radiation (λ = 0.710 73 Å). All structures were solved by direct methods (SHELXS-96)[10] and refined against F^2 using SHELXS-97.[11] 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. The structure parameters and refinement procedures are summarized in Table 1.

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Table 1. Crystal Data and Structure Refinement for 6 and 7

compound	**6**	**7**
empirical formula	$C_{34}H_{64}Ga_2N_2Se_2Si_6$	$C_{34}H_{64}Ga_2N_2Si_6Te_2$
fw	966.77	1064.05
temp (K)	200(2)	200(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	*Pbca*
a (Å)	15.440(2)	15.351(3)
b (Å)	13.1961(14)	13.300(2)
c (Å)	23.422(4)	24.029(5)
$\alpha = \beta = \gamma$ (deg)	90	90
vol (Å^3)	4772.2(12)	4905.8(15)
Z	4	4
density(calcd) (Mg/m^3)	1.346	1.441
abs coeff (mm^{-1})	2.829	2.434
F(000)	1984	2128
cryst size (mm^3)	0.60 × 0.40 × 0.10	1.00 × 0.80 × 0.20
θ range (deg)	3.52−22.52	3.64−25.12
index ranges	$-16 \le h \le +16$ $-1 \le k \le +14$ $-25 \le l \le +25$	$-18 \le h \le +18$ $-3 \le k \le +15$ $-28 \le l \le +28$
no. of reflns collected	3368	5498
no. of independent reflns	3116 [*R*(int) = 0.0272]	4326 [*R*(int) = 0.0333]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3112/0/217	4313/0/217
goodness of fit on F^2	1.088	1.034
final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0555$ $wR2 = 0.1375$	$R1 = 0.0822$ $wR2 = 0.2152$
R indices (all data)	$R1 = 0.0766$ $wR2 = 0.1639$	$R1 = 0.0931$ $wR2 = 0.2449$
largest diff peak and hole (e·Å^{-3})	+1.010 and −0.729	+1.933 and −1.440

Results and Discussion

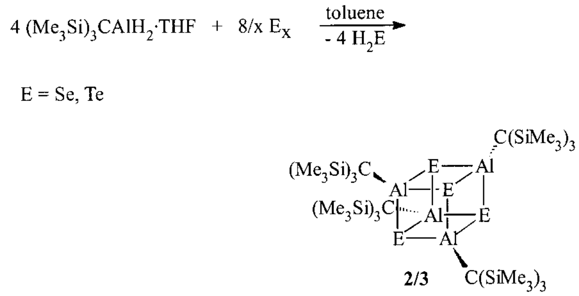
Synthesis of $(Me_3Si)_3CAlH_2{\cdot}THF$ (1). Eaborn et al. reported recently on the preparation of **1** using $Li(THF)_2Al_2H_5R_2$ (R = $(Me_3Si)_3C$) and Me_3SiCl.[12] Power et al. developed a new and easy synthetic route to organoaluminum hydrides by the reaction of $H_3Al{\cdot}NMe_3$ and RLi.[13] These results prompted us to generalize the concept realized with the derivatives having the tris(trimethylsilyl)methyl group. The reaction of $H_3Al{\cdot}NMe_3$ and $(Me_3Si)_3CLi{\cdot}2THF$ in toluene afforded **1** in high yield (eq 1). The physical data of **1** are in agreement with those reported in the literature.[12]

$$(Me_3Si)_3CLi\cdot 2\ THF + H_3Al\cdot NMe_3 \xrightarrow[\substack{-\ LiH\\ -\ THF/NMe_3}]{} \underset{\mathbf{1}}{(Me_3Si)_3CAlH_2\cdot THF} \quad (1)$$

Synthesis of $[(Me_3Si)_3CAl(\mu_3\text{-}E)]_4$ (E = Se (2), Te (3)). Recently our research group synthesized a mixture of compounds containing $[(Me_3Si)_3CAl(\mu_3\text{-}S)]_4$ and $[\{(Me_3Si)_3CAl(\mu_3\text{-}S)\}_3\{MeAl(\mu_3\text{-}S)\}]$.[2] Although Raston et al. reported on the preparation of aluminum and gallium selenides and tellurides,[14] it was not possible to obtain the corresponding cubanes with the heavier group 16 elements.

The reaction of **1** with an excess of elemental selenium or tellurium proceeded smoothly in toluene at elevated temperature to afford the aluminum selenide (**2**) and telluride (**3**) in good yield (eq 2).

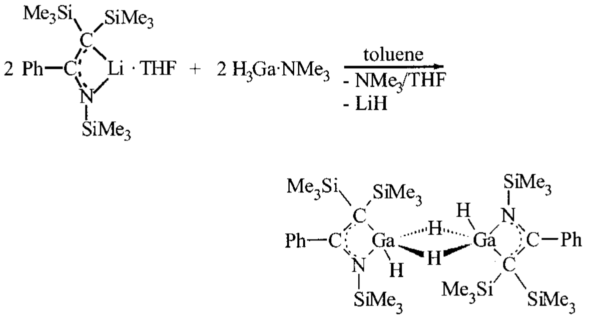
This reaction represents a new and facile route to organoaluminum chalcogenides. Compounds **2** and **3** have been characterized by ^{1}H and ^{29}Si NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analyses.



2/3

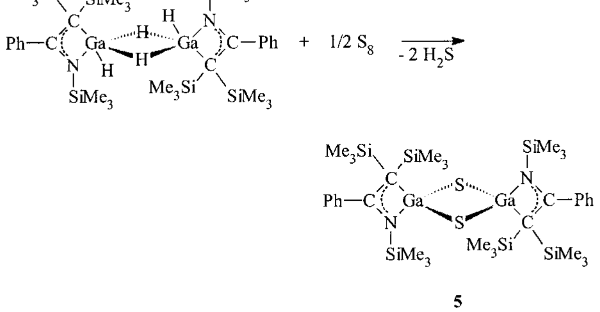
Synthesis of $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}H)]_2$ (4) and $[(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}E)]_2$ (E = S (5), Se (6), Te (7)). Our recent results highlight the synthesis of $RAlH_2$[3] as precursor for $[RAlE]_2$[3] and prompted us to generalize the concept realized with other group 13 metals.

The reaction of $H_3Ga{\cdot}NMe_3$ with $(Me_3Si)_2C(Ph)C(Me_3Si)NLi{\cdot}THF$ in toluene afforded **4** (eq 3). The ^{1}H NMR of the crude product in solution confirms the formulated composition of **4**. However, compound **4** was not isolated and purified and directly reacted in situ with sulfur.



4

The reaction proceeds smoothly in toluene at elevated temperature to afford dimeric gallium sulfide **5** (eq 4).



5

The synthesis of the Se- and Te-containing analogues of **5** using **4** has not been successful so far. Therefore, we reacted $(Me_3Si)_2E$ and the gallium precursor as previously demonstrated in the preparation of the heterocubane $[Cp^*Ga(\mu\text{-}Te)]_4$.[5e]

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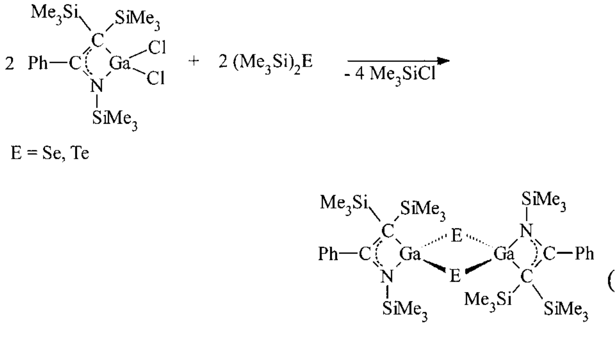
Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}Se)]_2$ (6)

Ga(1)−Se(1)	236.9(1)	Ga(1)−C(2)	207.2(6)
C(1)−C(2)	147.8(9)	Ga(1)···Ga(1′)	301.8(15)
Ga(1)−N(1)	207.3(5)	Ga(1)−Se(1′)	237.2(11)
Ga(1′)−Se(1)	237.2(11)	N(1)−C(1)	129.8(9)
Se(1)−Ga(1)−Se(1′)	100.9(3)	Ga(1)−Se(1)−Ga(1′)	79.1(3)
C(2)−Ga(1)−Se(1)	129.0(2)	C(2)−Ga(1)−N(1)	69.0(2)
C(2)−Ga(1)−Se(1′)	125.5(2)	N(1)−Ga(1)−Se(1)	114.2(2)
N(1)−C(1)−C(2)	115.4(6)	N(1)−Ga(1)−Se(1′)	113.2(15)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$(Me_3Si)_2C(Ph)C(Me_3Si)NGa(\mu\text{-}Te)]_2$ (7)

Ga(1)−Te(1)	257.0(9)	Ga(1)−C(2)	207.1(6)
C(1)−C(2)	149.4(9)	N(1)−C(1)	129.6(9)
Ga(1)−N(1)	206.9(6)	Ga(1′)−Te(1)	257.6(9)
Ga(1)−Te(1′)	257.6(9)		
Te(1)−Ga(1)−Te(1′)	101.6(3)	Ga(1)−Te(1)−Ga(1′)	78.4(3)
C(2)−Ga(1)−Te(1)	128.5(2)	C(2)−Ga(1)−N(1)	69.5(2)
C(2)−Ga(1)−Te(1′)	125.0(2)	N(1)−Ga(1)−Te(1)	113.2(2)
N(1)−C(1)−C(2)	115.4(6)	N(1)−Ga(1)−Te(1′)	113.9(2)

The reaction of $(Me_3Si)_2C(Ph)C(Me_3Si)NGaCl_2$ with $(Me_3Si)_2Se$ and $(Me_3Si)_2Te$ in toluene at room temperature afforded the dimeric gallium selenide (**6**) and telluride (**7**), respectively, in high yield (eq 5).



(5)

6/**7**

Compounds **6** and **7** have been characterized by X-ray crystal structure analysis. Crystal data for compounds **6** and **7** are summarized in Table 1. Selected bond distances and angles are collected in Tables 2 and 3. Single crystals for X-ray diffraction analysis were obtained by crystallization from toluene at 0 °C.

Compounds **6** and **7** are isostructural and crystallize in the orthorhombic space group *Pbca*. The molecular structures of **6** and **7** are shown representatively in Figures 1 and 2, respectively. Both molecules are centrosymmetric and consist of three fused four-membered rings with a central Ga_2Se_2 or Ga_2Te_2 core, respectively. The central Ga_2E_2 unit is nearly perpendicularly arranged with the two other chelating rings.

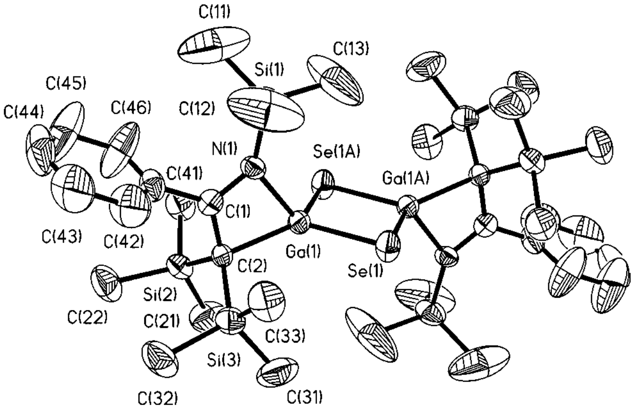


Figure 1. Molecular structure of **6** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

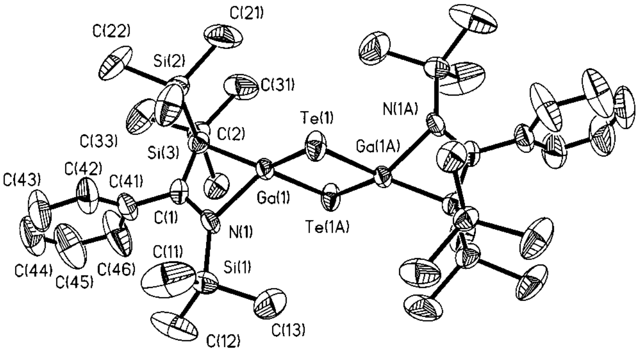


Figure 2. Molecular structure of **7** in the crystal (50% probability). Hydrogen atoms have been omitted for clarity.

The Ga−Se bond lengths in **6** (2.369(1) and 2.372(11) Å) are in good accordance with those in [$MesC_6H_7NGa(\mu\text{-}Se)]_2$ (2.378(12) and 2.387(13) Å)[15] and are shorter than the ones in [$(Me_3Si)_3CGa(\mu_3\text{-}Se)]_4$ (2.503(2), 2.497(2), 2.515(2), and 2.489(2) Å)[16] due to the different coordination numbers at the Se atoms. The angles at the Ga atoms (100.9(3)°) within the four-membered Ga_2Se_2 ring are larger than those at the Se atoms (79.1(3)°) due to the acute N−Ga−C angle (69.0(2)°). **6** was isolated as the trans isomer.

The corresponding telluride is one of the first monoorganogallium tellurides to be fully structurally characterized. The Ga−Te bond lengths in [$Cp^*Ga(\mu_3\text{-}Te)]_4$ range from 2.652(1) to 2.692(1) Å and are longer than those in compound **7** (2.570(9) and 2.576(9) Å) due to the increased coordination sphere at Te. The Ga−Te bond lengths in [$(Me_3Si)_2CHGa{-}Te{-}GaCH(SiMe_3)_2$] (2.552(4) Å)[17] are comparable to those in **7**. It is noteworthy that the angles at Ga and Te within the four-membered Ga_2Te_2 ring are quite similar to those at Ga and Se in **6**. Compound **7** was isolated also as the trans isomer.

Both the ^1H and ^{29}Si NMR spectra of **6** and **7**, respectively, at room temperature indicate the existence of various species in toluene-d_8 solution. The variable-temperature (183−300 K) ^1H NMR spectra of **7** show that the intensities of the $NSiMe_3$ and $CSiMe_3$ groups vary. Due to the fact that several signals were obtained (even at 183 K), we assume that in toluene-d_8 more than one species of **7** exists.

Conclusion

The reactions of $RAlH_2$ and $RGaH_2$, respectively, with elemental Se and Te and of $RGaCl_2$ with $(Me_3Si)_2Se$ or $(Me_3Si)_2Te$ have been shown to be efficient and facile routes for the synthesis of organoaluminum or organogallium chalcogenides. The nature of R is responsible

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for the formation of dimeric or tetrameric aggregates. We will further explore these organometallic chalcogenides as precursors for MOCVD experiments.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften.

Supporting Information Available: Tables of crystal data and refinement details, bond lengths, bond angles, and thermal parameters for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0010520