

Synthesis of Organoaluminum Chalcogenides $[\text{RAl}(\mu\text{-E})]_2$ ($\text{R} = \text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2$, $\text{E} = \text{Se}, \text{Te}$) from Aluminum Dihydride $[\text{RAlH}(\mu\text{-H})]_2^\dagger$

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1-Azaallylaluminum dihydride $[\text{RAlH}(\mu\text{-H})]_2$ (**1**) ($\text{R} = \text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2$) has been prepared in nearly quantitative yield from the reduction of RAlBr_2 with an excess of LiAlH_4 in diethyl ether. Reaction of **1** with elemental Se or Te in toluene afforded the novel organoaluminum chalcogenide $[\text{RAl}(\mu\text{-E})]_2$ ($\text{E} = \text{Se}$ (**2**); Te (**3**)) in good yield. The structures of compounds **1**, **2**, and **3** in the solid state have been characterized by X-ray diffraction analyses. Compounds **2** and **3** have a dimeric structure featuring three novel fused planar four-membered ring systems with a central Al_2E_2 core. Based on ^1H and ^{29}Si NMR data and crystal structural analysis of **2** and **3**, an equilibrium of the trans and cis isomers in solution is proposed for the two compounds due to the relative orientation of the two chelating rings of the bidentate R ligands.

Introduction

Previously we described the basic chemistry of 1-azaallyl aluminum compounds.¹ It seems that this very bulky chelating ligand R ($\text{R} = \text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2$) has unique steric and electronic properties, therefore leading to the isolation of the first dimeric aluminum difluoride $[\text{RAlF}(\mu\text{-F})]_2$. Consequently we developed the chemistry of the RAl moiety to synthesize RAlH_2 and to examine its reaction with the heavier group 16 elements (Se, Te). It is well-known that aluminum chalcogenides with a cubane structure can be prepared by the reaction of the appropriate aluminum alkyls with either H_2Se or elemental Se and Te and moreover by the reaction of $(\text{Cp}^*\text{Al})_4$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with elemental Se and Te.² However, so far, the former route involving elemental chalcogens (Se, Te) and Al(III) alkyls can only be employed using (*t*-Bu)₃Al and $(\text{Me}_2\text{EtC})_3\text{Al}$.³ In other cases, elemental Se or Te can insert only into one of the aluminum–carbon bonds, under forcing conditions; the final products are a mixture of organic-substituted chalcogenides.⁴ Overall there are only a few fully characterized organometallic compounds with the for-

mula $(\text{R}'\text{AlE})_n$ ($\text{R}' = \text{organic group}$; $\text{E} = \text{Se}, \text{Te}$), namely, the structurally characterized aluminum–selenium (tellurium) cage compounds $(\text{Cp}^*\text{AlE})_4$ ($\text{E} = \text{Se}$ or Te)² and $(\text{Me}_2\text{EtCAlSe})_4$.^{3b} Although the reaction of aluminum hydride $\text{Me}_3\text{N}\cdot\text{AlH}_3$ or $(\text{Mes}^*\text{AlH}_2)_2$ ($\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$) with organochalcogenides has been reported,⁵ the reactions of organoaluminum dihydrides with elemental Se and Te have not been investigated. Therefore this reaction would be an alternative route to generate organoaluminum chalcogenides of formula $(\text{R}'\text{AlE})_n$. Herein we report the synthesis and structure of 1-azaallylaluminum dihydride and its facile reaction with elemental Se and Te to give dimeric organoaluminum chalcogenides in good yields.

Experimental Section

All operations were carried out under purified N_2 atmosphere by using Schlenk techniques. Solvents were purified and dried by distillation from K or LiAlH_4 under N_2 prior to use. RAlBr_2 was prepared according to the published procedure.¹ Elemental selenium and tellurium were purchased from Aldrich and used as received.

^1H NMR (250.130 MHz), ^{13}C NMR (100.600 MHz), ^{29}Si NMR (79.460 MHz), and ^{27}Al NMR (65.170 MHz) spectra were recorded on a Bruker AM 200 or a Bruker AM 250 spectrometer. The chemical shifts were externally referenced to SiMe_4 or AlCl_3 (^{27}Al). EI (70 eV) mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. 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 were not corrected.

$[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{AlH}(\mu\text{-H})]_2$ (**1**). A solution of RAlBr_2 (5.22 g, 10 mmol) in diethyl ether (30 mL) was added

[†] Dedicated to Professor Ulrich Müller on the occasion of his 60th birthday.

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Table 1. Summary of Crystallographic Data for Compounds 1, 2, and 3

	1	2	3
formula	C ₃₄ H ₆₈ Al ₂ N ₂ Si ₆	C ₃₄ H ₆₄ Al ₂ N ₂ Se ₂ Si ₆	C ₃₄ H ₆₄ Al ₂ N ₂ Si ₆ Te ₂
fw	727.40	881.29	978.57
temp (K)	153(2)	150(2)	213(2)
cryst syst	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.014(2)	8.7959(10)	9.0522(15)
<i>b</i> (Å)	9.1980(13)	11.6070(15)	11.666(2)
<i>c</i> (Å)	18.175(3)	23.153(4)	23.149(7)
α (deg)	90	100.984(10)	99.55(3)
β (deg)	106.760(15)	92.014(13)	91.415(14)
γ (deg)	90	91.248(9)	92.158(12)
<i>V</i> (Å ³)	2243.3(6)	2318.1(6)	2407.8(9)
<i>Z</i>	2	2	2
<i>d</i> (calcd) (Mg/m ³)	1.077	1.263	1.350
abs coeff (mm ⁻¹)	0.249	1.813	1.421
<i>F</i> (000)	792	920	992
cryst size (mm)	0.90 × 0.70 × 0.40	1.00 × 0.70 × 0.60	0.60 × 0.40 × 0.20
θ range (deg)	3.67–22.52	3.51–25.04	3.51–25.05
limiting indices	–15 ≤ <i>h</i> ≤ 15 –8 ≤ <i>k</i> ≤ 9 –18 ≤ <i>l</i> ≤ 19	–10 ≤ <i>h</i> ≤ 10 –13 ≤ <i>k</i> ≤ 13 –24 ≤ <i>l</i> ≤ 27	–10 ≤ <i>h</i> ≤ 10 –13 ≤ <i>k</i> ≤ 13 –10 ≤ <i>l</i> ≤ 27
no. of reflns collected	3590	9658	8518
no. of indep reflns	2912 (<i>R</i> _{int} = 0.0449)	8160 (<i>R</i> _{int} = 0.0323)	8518 (<i>R</i> _{int} = 0.0000)
no. of data/restraints/params	2911/0/216	8160/0/433	8518/0/435
GOF/ <i>F</i> ²	1.038	1.047	1.032
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0289 <i>wR</i> 2 = 0.0733	<i>R</i> 1 = 0.0363 <i>wR</i> 2 = 0.0946	<i>R</i> 1 = 0.0431 <i>wR</i> 2 = 0.1050
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0310 <i>wR</i> 2 = 0.0757	<i>R</i> 1 = 0.0422 <i>wR</i> 2 = 0.1018	<i>R</i> 1 = 0.0587 <i>wR</i> 2 = 0.1190
largest diff peak/hole (e Å ⁻³)	0.246/–0.193	0.630/–0.590	1.024/–0.837

to a suspension of LiAlH₄ (1.14 g, 30 mmol) in diethyl ether (10 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum, and the residue was extracted with toluene (30 mL). The extract was concentrated and then stored at –30 °C overnight to give white crystals (3.4 g, 94%). Mp: 82 °C. Anal. Calcd for C₃₄H₆₈Al₂N₂Si₆: C, 56.09; H, 9.42; N, 3.85. Found: C, 56.14; H, 9.56; N, 3.89. ¹H NMR (C₆D₆): δ –0.40 (s, 9 H, NSiMe₃), 0.25 (s, 18 H, SiMe₃), 4.72 (s, 2 H, AlH), 6.9–7.0 (3 H, Ph), 7.3 (d, 2 H, Ph). ¹H NMR (toluene-*d*₈, 295 K): δ –0.03 (s, 9 H, NSiMe₃), 0.22 (s, 18 H, SiMe₃), 4.61 (s, 2 H, AlH), 7.01, 7.20–7.30 (m, 5 H, Ph). ¹H NMR (toluene-*d*₈, 233 K): δ 0.04 (s, 9 H, NSiMe₃), 0.35 (s, 18 H, SiMe₃), 4.75 (s, 2 H, AlH), 7.06, 7.20–7.30 (m, 5 H, Ph). ¹H NMR (toluene-*d*₈, 193 K): δ 0.13 (s, 9 H, NSiMe₃), 0.48 (s br, 18 H, SiMe₃), 4.80 (s br, 2 H, AlH), 7.07, 7.27 (s br, 5 H, Ph). ¹³C NMR (C₆D₆): δ 0.34 (NSiMe₃), 2.74 (SiMe₃), 48.8 (br s, CSi₂), 127.0, 128.2, 130.6 (s, Ph), 142.9 (s, *ipso*-C), 209.8 (s, CN). ²⁹Si NMR (C₆D₆): δ 3.59 (s, CSi₂), 5.69 (s, NSiMe₃). ²⁷Al NMR (toluene-*d*₈, 296 K): δ 131.6 (*ν*_{1/2} = 2100 Hz).

[{N(SiMe₃)C(Ph)C(SiMe₃)₂Al(μ-Se)]₂ (2). To a mixture of **1** (0.64 g, 0.89 mmol) and selenium (0.14 g, 1.79 mmol) was added toluene (15 mL) at room temperature. After the mixture was heated to 80 °C and stirred for 8 h, it was filtered. The filtrate was concentrated (3 mL), and *n*-hexane (5 mL) was added. Cooling of the solution to –30 °C overnight afforded colorless crystals, which were collected by filtration and dried (0.56 g, 71.3%). Mp: 247 °C (dec). Anal. Calcd for C₃₄H₆₄Al₂N₂Se₂Si₆: C, 46.34; H, 7.32; N, 3.18. Found: C, 45.92; H, 7.23; N, 3.26. ¹H NMR (C₆D₆): δ 0.28 (d, 18 H, NSiMe₃), 0.48 (br s, 36 H, SiMe₃), 6.82–6.90 (m, 6 H, Ph), 7.35 (m, 4 H, Ph). ¹H NMR (toluene-*d*₈, 295 K): δ 0.25 (d, 18 H, NSiMe₃), 0.44 (d, 36 H, SiMe₃), 7.01, 7.30–7.50 (m, 10 H, Ph). ¹H NMR (toluene-*d*₈, 233 K): δ 0.27 (d, 18 H, NSiMe₃), 0.50 (br s, 36 H, SiMe₃), 7.06, 7.30–7.50 (m, 10 H, Ph). ¹H NMR (toluene-*d*₈, 193 K): δ 0.29 (s, 18 H, NSiMe₃), 0.55 (s, 36 H, SiMe₃), 7.08, 7.35 (br s, 10 H, Ph). ²⁹Si NMR (C₆D₆): δ –2.5, –2.2 (s, SiMe₃), 7.9, 8.4 (s, NSiMe₃). MS (EI): *m/z* 882 (M⁺, 100), 867 (M⁺ – Me, 4), 441 (M⁺/2, 5).

[{N(SiMe₃)C(Ph)C(SiMe₃)₂Al(μ-Te)]₂ (3). A mixture of **1** (0.56 g, 0.78 mmol) and tellurium (0.20 g, 1.56 mmol) in

toluene (15 mL) was heated to 80 °C for 8 h and then refluxed for 4 h. After filtration, the solvent was evaporated to dryness, and the green residue was crystallized from benzene/pentane (2:1) to give greenish crystals (0.60 g, 78.6%). Mp: 176 °C (dec). Anal. Calcd for C₃₄H₆₄Al₂N₂Si₆Te₂: C, 41.70; H, 6.59; N, 2.86. Found: C, 40.96; H, 6.72; N, 3.10. ¹H NMR (C₆D₆): δ 0.34 (d, 18 H, NSiMe₃), 0.48 (d, 36 H, SiMe₃), 6.82–7.00 (m, 6 H, Ph), 7.30–7.40 (m, 4 H, Ph). ²⁹Si NMR (C₆D₆): δ –2.7, –2.4 (s, SiMe₃), 8.6, 9.1 (s, NSiMe₃). MS (EI): *m/z* 976 (M⁺, 100), 488 (M⁺/2, 10).

X-ray Structural Determinations and Refinements for 1, 2, and 3. Data for crystal structures of compounds **1**, **2**, and **3** were collected on a Stoe-Siemens four-circle diffractometer using Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods (SHELXS-96)⁶ and refined against *F*² using SHELXL-97.⁷ 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 atoms. A summary of cell parameters, data collection, and structure solutions is given in Table 1.

Results and Discussion

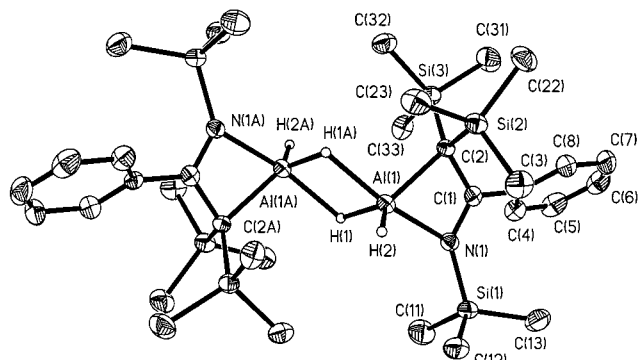
Synthesis and Molecular Structure of [RAIH(μ-H)]₂ (1). Reaction of RAlBr₂ with an excess of LiAlH₄ in diethyl ether afforded [RAIH(μ-H)]₂ (**1**) in nearly quantitative yield. **1** was characterized by ¹H, ¹³C, and ²⁹Si NMR, elemental analysis, and X-ray structural analysis. Single crystals of **1** were grown from *n*-hexane at 0 °C. The selected bond distances and angles are listed in Table 2. **1** adopts a dimeric structure in the solid state (Figure 1); as a consequence, the whole structure features three fused four-membered rings with asymmetric 1-azaallyl ligands in trans configuration. Each aluminum atom is 5-fold coordinated, and the geometry of the Al atoms can be described as trigonal

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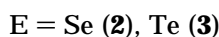
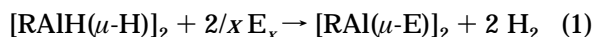
Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 1

Al(1)–H(1) 1.603	Al(1)–N(1) 2.026(2)	Al(1)–H(2) 1.509
Al(1)–H(1A) 1.966	Al(1)–C(1) 2.418(2)	Al(1)–C(2) 2.058(2)
C(1)–C(2) 1.495(2)	C(1)–N(1) 1.301(2)	Al(1)–Al(1A) 2.8154(11)
H(1)–Al(1)–H(1A) 76.3	H(1A)–Al(1)–N(1) 165.6	H(1)–Al(1)–N(1) 100.1
H(1)–Al(1)–H(2) 117.2	N(1)–Al(1)–C(2) 70.39	

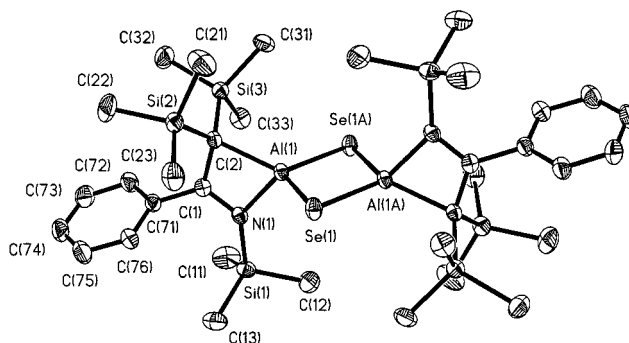
**Figure 1.** Molecular structure of **1** in the crystal. H atoms except those in central core have been omitted for clarity.

bipyramidal with the axis going through H(1A)–Al(1)–N(1) (165.6°). The two bridging Al–H bonds at the same aluminum atom differ in length by 0.363 Å due to the asymmetry of the bulky ligand, which is in sharp contrast to compound (Mes*AlH₂)₂, where the two bridging Al–H bonds are nearly equal.⁸ The terminal Al–H bonds (1.509 Å) are comparable to that (1.52(2) Å) in compound [HAl(NMe₂)₃][–],⁹ while the two shorter bridging Al–H bonds (1.603 Å) are shorter than those observed in compounds [Me₂Al(μ-H)]₂ (1.68(2) Å)¹⁰ and [*o*-(Me₂NCH₂)C₆H₄]AlH(μ-H)]₂ (1.688 Å).¹¹ The two other bridging Al–H separations (1.966 Å) of **1** are much longer than the sum of the covalent radii of Al and H (1.67 Å) and the longest observed in organoaluminum dihydrides, indicating only weak bonding interaction between the two monomers. The ¹H NMR spectra (C₆D₆ and toluene-*d*₈) at room temperature show only one sharp signal for AlH protons, and the ²⁷Al NMR resonance (δ 131.6 ppm) indicates that a 4-fold coordinated aluminum center is present in solution. Therefore a monomeric structure of **1** in solution is proposed. At low temperature (193, 233 K) the signal for AlH only broadens as the other singlets in the spectra, and there is no observation of a dynamic process, indicating that the monomeric structure is maintained at these temperatures.

Synthesis and Structure of [RAl(μ-E)]₂ (E = Se (2), Te (3)). The reaction of **1** with selenium or metallic tellurium proceeded smoothly in toluene at elevated temperature to afford dimeric aluminum selenide (**2**) or telluride (**3**) in good yield (eq 1).



This reaction type obviously represents a new and facile route to organoaluminum chalcogenides. The detailed reaction pathway is currently unknown. The reaction

**Figure 2.** Molecular structure of **2** in the crystal. H atoms have been omitted for clarity.

may be comparable to those of group 13 alkyls with elemental Se and Te, where products [R'₂M(μ-ER')]₂ (R' = alkyl, M = Al, Ga) can be isolated.^{4d} In a similar way, this reaction presumably involves a hydroselenolate (hydrotelluroate) intermediate,^{4c} followed by elimination of hydrogen. The related reactions of the cleavage of element–element bonds of group 16 using an aluminum hydride include the reactions of diorganodiselenides or -ditellurides with *i*-Bu₂AlH¹² or Me₃N·AlH₃.^{5a} Compounds **2** and **3**, which are very air and moisture sensitive, but thermally quite stable as indicated by their high melting points and EI mass spectra, in which 100% M⁺ was observed for both compounds, have been characterized by ¹H and ²⁹Si NMR spectroscopy, elemental analysis, and EI mass spectra. The structures of the two compounds have been determined by X-ray diffraction analyses as well, and one of those is shown in Figure 2 (**2** and **3** are isostructural) with the atom-labeling scheme. The selected bond lengths and angles for **2** and **3** are given in Table 3. Crystals of X-ray diffraction quality of **2** (colorless) or **3** (greenish) were obtained from toluene/*n*-hexane solution at –20 °C or benzene/*n*-hexane at 6 °C, respectively. **2** and **3** crystallize in the triclinic unit cell *P* $\bar{1}$ group. The two, essentially equal molecules in the unit cell, only marginally different in bond lengths and angles, are crystallographically centrosymmetric (Figure 2 shows only one molecule of **2**). The structure of **2** consists of three fused four-membered rings with a central Al(1)–Se(1)–Al(1A)–Se(1A) core (the mean deviation of the plane Δ = 0.000, the sum of the internal angles = 360.01°, the central core of the other molecule in the unit cell is represented by Al(2)–Se(2)–Al(2A)–Se(2A)), nearly perpendicular to the two other rings (the angles between two adjacent planes in the two different molecules are 92.7° and 91.8°, respectively). The Al–Se distances (2.3424–2.3563 Å) are shorter than those in cubane compounds (Cp*AlSe)₄ (2.462–2.497 Å) and (Me₂-EtCAlSe)₄ (2.444–2.481 Å) due to the lower coordination number of Se (two) atoms in **2**. The Al–Al separations

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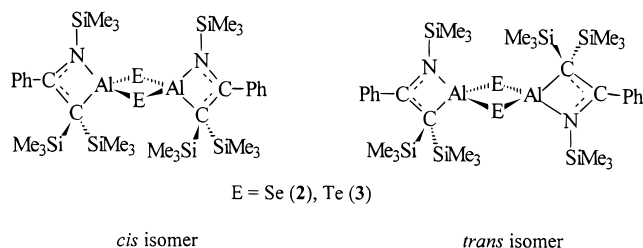
Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 2 and 3

[RAl(μ -Se)] ₂ (2)		
Al(1)–Se(1) 2.3424(8)	Al(1)–Se(1A) 2.3527(9)	Al(1)–N(1) 1.948(2)
Al(1)–C(2) 2.051(3)	Al(1)–Al(1A) 2.9412(16)	N(1)–C(1) 1.308(3)
C(1)–C(2) 1.491(4)	Al(2)–Se(2) 2.3469(8)	Al(2)–Se(2A) 2.356(3)
Al(2)–N(2) 1.953(2)	Al(2)–C(4) 2.052(3)	Al(2)–Al(2A) 2.9473(15)
Se(1)–Al(1)–Se(1A) 102.42(2)	Al(1)–Se(1)–Al(1A) 77.58(3)	N(1)–Al(1)–C(2) 72.01(10)
Se(2)–Al(2)–Se(2A) 102.39(3)	Al(2)–Se(2)–Al(2A) 77.61(3)	C(2)–Al(1)–Se(1) 123.17(8)
[RAl(μ -Te)] ₂ (3)		
Al(1)–Te(1) 2.5619(12)	Al(1)–Te(1A) 2.5768(14)	Al(2)–Te(2) 2.5753(12)
Al(2)–Te(2A) 2.5765(14)	Al(1)–N(1) 1.946(3)	Al(1)–C(2) 2.064(4)
N(1)–C(1) 1.319(5)	C(1)–C(2) 1.484(6)	N(1)–Al(1)–C(2) 71.80(15)
N(1)–Al(1)–Te(1) 110.03(11)	Te(1)–Al(1)–Te(1A) 103.12(4)	Al(1)–Te(1)–Al(1A) 76.88(4)
C(2)–Al(1)–Te(1) 123.06(12)	Te(2)–Al(2)–Te(2A) 102.79(4)	Al(2)–Te(2)–Al(2A) 77.21(4)

(2.9412(16), 2.9473(15) Å) are slightly longer than that in the starting material **1** (2.8154(11) Å) due to longer Al–Se bonds than the bridging Al–H bonds even though the aluminum atoms in the latter is 5-fold coordinated. The internal angles at Al (102.42(3)°, 102.39(3)°) are more open than at Se (77.58(3)°, 77.61(3)°) due to acute angles N–Al–C (72.01(10)°, 71.74(10)°), which are only slightly more open than those in the 5-fold coordinated aluminum atoms of **1**. **2** crystallizes as a trans isomer with the backbone of the ligands in trans configuration.

Compound **3** is the second example of a monoorganoaluminum telluride to be fully structurally characterized. The only previous example is the tetrameric (Cp*AlTe)₄ reported by our group, which has an Al₄Te₄ cubane structure with Al–Te distances in the range from 2.688 to 2.750 Å. The longer Al–Te bond lengths in that compound are due to the higher coordination number of Te (three). The short Al–Te distances (2.5619–2.5768 Å) in **3** are similar to those observed in the compound [(SiMe₃)₂HC₂Al]₂Te (2.549 Å).¹⁴ It is noteworthy that the internal angles at Al and at Te in **3** are quite similar to those at Al and at Se in **2**, respectively, despite the longer Al–Te bond lengths compared to the Al–Se bonds (the central cores of the two different molecules in the unit cell of **3** are represented by Al(1)–Te(1)–Al(1A)–Te(1A) and Al(2)–Te(2)–Al(2A)–Te(2A), respectively; see Table 3).

Both ¹H and ²⁹Si NMR spectra indicate the existence of an equilibrium of two isomers of **2** and **3**, respectively, in C₆D₆ solution, which is probably caused by the relative orientation of the ligand chelating rings. The variable-temperature (193–295 K) ¹H NMR spectra of **2** indicate that the conversion of the two isomers in toluene-*d*₈ becomes slow at 193 K, as indicated by the fact that only one singlet for NSiMe₃ and SiMe₃ can be

Scheme 1

observed at this temperature. Due to the ligand backbone, which is arranged nearly perpendicular to the central core, two possible isomers (trans and cis) are given in Scheme 1. The ratio of the two isomers (1:2) for both **2** and **3** at room temperature is estimated by using the ¹H NMR spectra. Because of the flexibility of the ligand R, the M–C bond cleavage mechanism has been proposed to explain the dynamic processes of compounds (CIMR)₂ (M = Sn, Pb)¹⁴ and [RAIF(μ -F)]₂.¹ In a similar manner, the Al–C bond dissociation/association process might also be responsible for the conversion of the two isomers in solution.

Conclusion

The reaction of RAlH₂ with elemental Se and Te has been shown to be an efficient and facile route to synthesize organoaluminum chalcogenides. Due to the chelating and bulky nature of R, low aggregation products (RAlE)₂ were obtained. We will further explore the reactivities of the two dimeric compounds.

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Supporting Information Available: Tables of crystal data and refinement details, bond lengths, bond angles, and thermal parameters for **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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