

Syntheses and Structures of the Arylaluminum Chalcogenides (ArAlE)₂ (Ar = 2-(NEt₂CH₂)-6-MeC₆H₃, E = Se; Ar = 2,6-(NEt₂CH₂)₂C₆H₃, E = Se, Te)[†]

Chunming Cui, Herbert W. Roesky,* Mathias Noltemeyer, and Hans-Georg Schmidt

Institute of Inorganic Chemistry, University of Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

Received March 7, 2000

Two intramolecular stabilized arylaluminum dihydrides, {2-(NEt₂CH₂)-6-MeC₆H₃}AlH₂ (**1**) and {2,6-(NEt₂CH₂)₂C₆H₃}AlH₂ (**2**), were prepared by reducing the corresponding dichlorides with an excess of LiAlH₄ in diethyl ether. Reactions of **1** and **2** with elemental selenium afforded the dimeric arylaluminum selenides [{2-(NEt₂CH₂)-6-MeC₆H₃}AlSe]₂ (**3**) and [{2,6-(NEt₂CH₂)₂C₆H₃}AlSe]₂ (**4**). Reaction of **2** with metallic tellurium gave the dimeric arylaluminum telluride [{2,6-(NEt₂CH₂)₂C₆H₃}AlTe]₂ (**5**). The possible reaction pathway is discussed, and molecular structures determined by single-crystal X-ray analyses are presented for **3** and **5**.

Introduction

Heavier group 13 element chalcogenides are potential single-source precursors for group 13–16 materials.¹ The synthesis and characterization of this class of compounds have been one of the interesting research fields in recent years. Although numerous publications have discussed a variety of aluminum compounds containing heavier group 16 elements,² only a handful of the compounds with the formula (RAIE)_n (R = organic group, E = Se, Te)³ are known because of the lack of a general synthetic route. We recently reported that organoaluminum dihydrides are possible precursors for compounds of the formula (RAIE)_n.⁴ As an extension of the utilization of this route, we are now interested in employing bulky bidentate and tridentate ligand systems to generate monomeric RAIE moieties by intramolecular stabilization.

Aryl ligands of the type 2,6-(R₂NCH₂)₂C₆H₃ and 2-(R₂NCH₂)C₆H₄ (R = Me, Et, *i*-Pr, or other organic group) with one or two donor sidearms have been widely used in late transition chemistry,⁵ and some group 13 and 14 element compounds with this type of ligand have also been reported.⁶

These ligands can effectively control the geometry of a metal center and prevent association, as has been demonstrated by the synthesis of monomeric aluminum and gallium hydrides using the tridentate 2,6-(Me₂NCH₂)₂C₆H₃ ligand.^{7,8} However group 13 element chalcogenides with this type of ligand have not yet been reported. The only related compound is dimeric (Mes*AlS)₂ (Mes* = 2,4,6-(*t*-Bu)₃C₆H₂).⁹ Herein we report the first examples of arylaluminum selenides and a telluride of the general formula (ArAlE)_n.

Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents were dried by standard methods. Chemicals were purchased from Aldrich or Fluka and used as received. 2,6-(Et₂NCH₂)₂C₆H₃Br and its lithium salt were prepared as described in the literature.⁵

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. A Bruker AM 200 spectrometer was used to record the ¹H NMR (200.13 MHz) and ¹³C NMR (125.76 MHz) spectra. EI mass spectra were obtained on a Finnigan MAT 8230 instrument. Melting points were measured in sealed glass capillaries and were not corrected.

Synthesis of 2-(Et₂NCH₂)-6-MeC₆H₃Br (a). 2-(Et₂NCH₂)-6-MeC₆H₃-Br was obtained as a byproduct from the synthesis of 2,6-(Et₂NCH₂)₂-C₆H₃Br in ca. 10% yield. Bp: 76 °C/0.05 Torr. ¹H NMR (C₆D₆): δ 0.78 (t, Et), 2.23 (Et), 2.60 (Me), 3.45 (CH₂), 6.8–7.25 (m, Ph).

Synthesis of {2-(Et₂NCH₂)-6-MeC₆H₃}AlH₂ (1). A solution of {2-(Et₂NCH₂)-6-MeC₆H₃}Li prepared from **a** (0.76 g, 3 mmol) and BuLi (3 mL in hexane, 3 mmol) in diethyl ether (20 mL) was added to a solution of AlCl₃ (0.40 g, 3 mmol) in diethyl ether (10 mL) at –78 °C. The mixture was allowed to warm to room temperature and then

[†] Dedicated to Professor Richard Neidlein on the occasion of his 70th birthday.

- (1) For a review, see: Barron, A. R. *Adv. Mater. Opt. Electron.* **1995**, *5*, 245.
- (2) For leading references, see, for example: (a) Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; p 167. (b) Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995**, *14*, 3869. (c) Barron, A. R. *Comments Inorg. Chem.* **1993**, *14*, 123.
- (3) (a) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem.* **1993**, *105*, 1828; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 172. (b) Harlan, C. J.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479.
- (4) (a) Cui, C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **1999**, *18*, 5120. (b) Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **2000**, *112*, 1885; *Angew. Chem. Int. Ed.* **2000**, *39*, 1815.
- (5) For example: (a) van Beek, J. A. M.; van Koten, G.; Dekker, G. P. C. M.; Wissing, E. J. *Organomet. Chem.* **1990**, *394*, 659. (b) van Beek, J. A. M.; van Koten, G.; Ramp, M. J.; Coenjaarts, N. C.; Grove, D. M.; Goubitz, K.; Zoutberg, M. C.; Stam, C. H.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 3059. (c) van de Kuil, L. A.; Luitjes, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsens, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468.

- (6) For example: (a) Müller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493. (b) Dam, M. A.; Akkerman, O. S.; Bickelhaupt, F.; Veldman, N.; Spek, A. L. *Main Group Metal Chem.* **1995**, *18*, 633. (c) Probst, R.; Leis, C.; Gamper, S.; Herdtweck, E.; Zybille, C.; Auner, N. *Angew. Chem.* **1991**, *103*, 1155; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1132. (d) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Gorbelen, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400.
- (7) Cowley, A. H.; Gabbai, F. P.; Atwood, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 1559.
- (8) Contreras, L.; Cowley, A. H.; Gabbai, F. P.; Jones, R. A.; Carrano, C. J.; Bond, M. R. *J. Organomet. Chem.* **1995**, *489*, C1.
- (9) Wehmschulte, R. F.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1998**, 335.

stirred overnight. After filtration, the filtrate was added to a suspension of LiAlH_4 (0.30 g, 8 mmol) in diethyl ether (10 mL) at room temperature. The mixture was stirred at room temperature for 15 h. All volatiles were removed in vacuo, and the residue was extracted with *n*-hexane (50 mL). The extract was concentrated to incipient crystallization at -30°C to give white crystals of **1** (0.40 g, 65%). Mp: $92-93^\circ\text{C}$. ^1H NMR (C_6D_6): δ 0.62 (t, 6 H, $J = 7.3$ Hz, Et), 2.35 (q, 4 H, $J = 6.2$ Hz, Et), 2.57 (s, 3 H, Me), 4.60 (br s, 2 H, AlH_2), 7.02–7.23 (m, 3 H, Ph). ^{13}C NMR (C_6D_6): δ 8.75 (Et), 25.7 (Me), 45.8 (Et), 61.1 (CH_2), 121.1, 127.8, 128.3, 144.2, 146.5 (Ph), 149.3 (AlC). EI-MS: m/e 204 ($\text{M}^+ - \text{H}$). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{AlN}$: C, 70.24; H, 9.76; N, 6.83. Found: C, 69.47; H, 9.80; N, 6.72.

Synthesis of $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlH}_2$ (2**).** $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{-AlH}_2$ was prepared similarly to **1**. $2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Br}$ (3.26 g, 10 mmol), BuLi (10 mL in *n*-hexane, 10 mmol), AlCl_3 (1.33 g, 10 mmol), and LiAlH_4 (0.85 g, 22.5 mmol) were used. The crude product was crystallized from toluene/pentane (1/1) to give white crystals (1.8 g, 65.2%). Mp: $65-67^\circ\text{C}$. ^1H NMR (C_6D_6): δ 0.90 (t, 12 H, $J = 7.2$ Hz, Et), 2.75 (q, 8 H, $J = 7.1$ Hz, Et), 3.42 (s, 4 H, CH_2), 4.4 (br s, 2 H, AlH_2), 6.90 (d, 2 H, $J = 7.3$ Hz, Ph), 7.31 (t, 1 H, $J = 7.2$ Hz, Ph). ^{13}C NMR (C_6D_6): δ 9.27 (Et), 46.3 (Et), 60.0 (CH_2), 122.2, 128.3, 146.0 (Ph), 150.1 (AlC). EI-MS: m/e 275 ($\text{M}^+ - \text{H}$). Anal. Calcd for $\text{C}_{16}\text{H}_{29}\text{AlN}_2$: C, 69.53; H, 10.57; N, 10.13. Found: C, 69.35; H, 10.54; N, 9.88.

Synthesis of $\{2\text{-(Et}_2\text{NCH}_2)\text{-6-MeC}_6\text{H}_3\}\text{AlSe}_2$ (3**).** To a mixture of **1** (0.25 g, 1.22 mmol) and selenium (0.10 g, 1.26 mmol) was added toluene (20 mL) at room temperature. The mixture was stirred at 80°C for 10 h and filtered to remove small amounts of precipitate. The filtrate was concentrated and stored at -20°C for 2 d to give colorless crystals of $3\cdot\text{C}_7\text{H}_8$, which easily lost solvent under vacuum to give **3** as a white solid (0.27 g, 78.2%). Mp: $220-222^\circ\text{C}$. ^1H NMR (C_6D_6): δ 0.85 (t, 6 H, Et), 2.72 (q, 4 H, Et), 2.94 (s, 3 H, Me), 3.43 (s, 2 H, CH_2), 7.00–7.30 (m, 3 H, Ph). ^{13}C NMR (C_6D_6): δ 9.01 (Et), 25.1 (Me), 46.6 (Et), 58.9 (CH_2), 121.6, 128.7, 129.3, 142.8, 146.2 (Ph), 147.7 (AlC). EI-MS: m/e 566 (M^+). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{AlNSe}$: C, 51.06; H, 6.38; N, 4.96. Found: C, 50.74; H, 6.32; N, 5.03.

Synthesis of $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlSe}_2$ (4**).** $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlSe}_2$ was prepared similarly to **3**. Compound **2** (0.33 g, 1.2 mmol) and selenium (0.10 g, 1.2 mmol) were used for the preparation. Crystallization from hot toluene (10 mL) gave colorless crystals of **4** (0.28 g, 66%). Mp: $160-162^\circ\text{C}$. ^1H NMR (CDCl_3): δ 1.08 (t, 12 H, $J = 7.2$ Hz, Et), 2.97 (q, 8 H, $J = 7.1$ Hz, Et), 3.96 (s, 4 H, CH_2), 7.2 (m, 3 H, Ph). ^{13}C NMR (CDCl_3): δ 11.06 (Et), 47.29 (Et), 59.70 (CH_2), 124.2, 128.7, 145.5 (Ph), 145.8 (AlPh). EI-MS: m/e 708 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{AlN}_2\text{Se}$: C, 54.38; H, 7.70; N, 7.93. Found: C, 54.19; H, 7.73; N, 7.89.

Synthesis of $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlTe}_2$ (5**).** A suspension of **2** (0.28 g, 1.04 mmol) and tellurium (0.13 g, 1.04 mmol) in toluene (20 mL) was refluxed for 8 h. After filtration to remove small amounts of precipitate, the filtrate was concentrated and stored at room temperature for 1 week to give large plates of **5** suitable for single-crystal X-ray analysis (0.33 g, 79%). Mp: $233-235^\circ\text{C}$. ^1H NMR (CDCl_3): δ 1.20 (t, 12 H, $J = 7.1$ Hz, Et), 3.03 (q, 8 H, $J = 7.2$ Hz, Et), 3.96 (s, 4 H, CH_2), 7.23 (m, 3 H, Ph). ^{13}C NMR (CDCl_3): δ 11.3 (Et), 47.4 (Et), 59.1 (CH_2), 124.1, 128.6, 145.3 (Ph), 144.6 (AlC). EI-MS: m/e 804 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{AlN}_2\text{Te}$: C, 47.85; H, 6.78; N, 6.97. Found: C, 48.63; H, 6.79; N, 6.97.

X-ray Structure Determinations and Refinements. Data for the crystal structures of **3** and **5** were collected on a Stoe-Siemens four-circle diffractometer using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-96)¹⁰ and refined against F^2 using SHELXL-97.¹¹ All heavy atoms were refined anisotropically. Hydrogen atoms were included by using a riding model with each U_{iso} related to the U_{iso} of the parent atom. Crystal data, data collection details, and solution and refinement procedures are summarized in Table 1.

Table 1. X-ray Crystallographic Data for Compounds **3** and **5**

	0.5 $3\cdot\text{C}_7\text{H}_8$	0.5 5
formula	$\text{C}_{19}\text{H}_{26}\text{AlNSe}$	$\text{C}_{16}\text{H}_{27}\text{AlN}_2\text{Te}$
fw	374.35	401.98
temp (K)	133(2)	203(2)
cryst syst, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.498(3), 11.556(2), 14.256(3)	10.542(2), 11.726(3), 14.580(4)
α , β , γ (deg)	90, 114.03(3), 90	90, 105.04(2), 90
<i>V</i> (Å ³), <i>Z</i>	1880.4(7), 4	1740.8(7), 4
<i>d</i> _{calcd} (Mg/m ³)	1.187	1.534
abs coeff (mm ⁻¹)	2.041	1.753
<i>F</i> (000)	776	808
cryst size (mm)	1.00 × 0.80 × 0.70	0.60 × 0.60 × 0.20
θ range (deg)	2.36–27.50	3.52–25.01
limiting indices	$-16 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 18$	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$
no. of reflns collected	4301	9371
no. of indep reflns (<i>R</i> _{int})	4301 (0.0000)	3066 (0.0479)
no. of data/restraints/params	4296/0/203	3066/0/185
<i>GOF</i> / <i>F</i> ²	1.117	1.111
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]: <i>R</i> 1, <i>wR</i> 2	0.0435, 0.1016	0.0282, 0.0759
<i>R</i> indices (all data): <i>R</i> 1, <i>wR</i> 2	0.0627, 0.1147	0.0289, 0.0768
largest diff peak/hole (e Å ⁻³)	0.880/−0.563	0.984/−1.234

Results and Discussion

Aluminum dihydrides can be easily prepared by the reduction of the corresponding dihalides.^{6d,8} The reactions of $2\text{-(Et}_2\text{NCH}_2)\text{-6-MeC}_6\text{H}_3\text{Li}$ and $2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Li}$ with equal amounts of AlCl_3 yielded the aluminum dichlorides, and reductions with excess amounts of LiAlH_4 in diethyl ether afforded the intramolecular stabilized arylaluminum dihydrides $2\text{-(Et}_2\text{NCH}_2)\text{-6-MeC}_6\text{H}_3\text{AlH}_2$ (**1**) and $2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{AlH}_2$ (**2**), respectively, in modest yields (Scheme 1). The dichlorides were not isolated and characterized but were directly reduced in situ to yield **1** and **2**. The similar aluminum dichlorides $2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{AlCl}_2$ and $2\text{-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{AlCl}_2$, prepared in an analogous way, have been reported.^{6d,8} Dihydrides **1** and **2** were characterized by ^1H NMR, ^{13}C NMR, and EI-MS spectroscopy as well as elemental analyses. The EI mass spectra of **1** and **2** each give the highest peak corresponding to the $[\text{M}^+ - \text{H}]$ fragment, indicating that both compounds are monomeric in the gas phase. The ^1H NMR spectra of **1** and **2** each show a broad hydride resonance, which is characteristic for aluminum hydrides. Compound **2** might also be monomeric in the solid state, as was reported for $2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{AlH}_2$.⁸

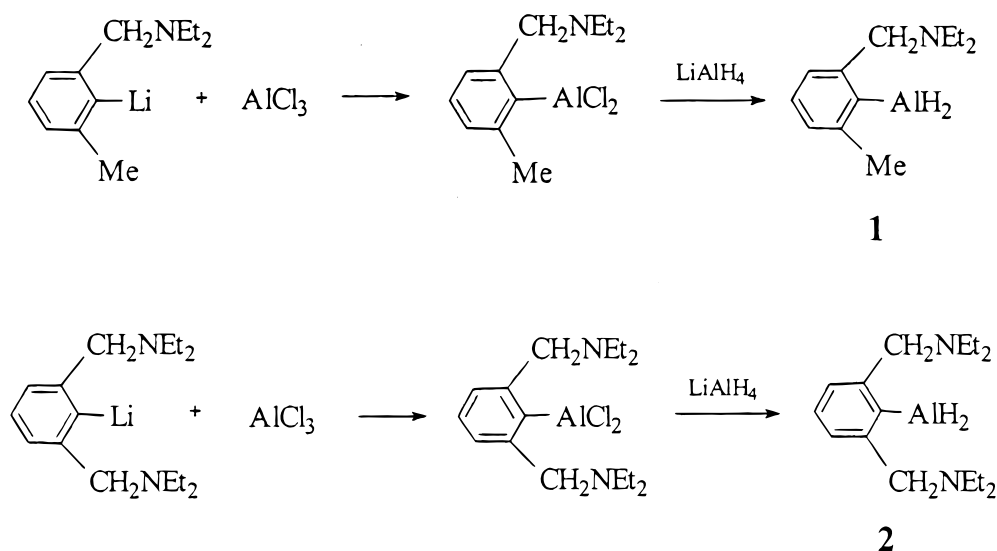
Reactions of **1** and **2** with selenium at 80°C respectively afforded the first examples of arylaluminum selenides $\{2\text{-(Et}_2\text{NCH}_2)\text{-6-MeC}_6\text{H}_3\}\text{AlSe}_2$ (**3**) and $\{2,6\text{-(Et}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlSe}_2$ (**4**) in good yields. We have briefly mentioned the mechanism of this type of reaction in our previous publication.^{4a} The isolation of an aluminum–SeH compound LAl(SeH)_2 ($\text{L} = \text{Ar'NC(Me)CHC(Me)NAr'}$, $\text{Ar}' = 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$)^{4b} suggests that this reaction proceeds through an aryl aluminum–SeH intermediate. It is proposed that the coordination of an Se_2 unit to the aluminum atom forms a hypervalent aluminum center¹² and that the activated Se_2 unit is concertedly reduced by the two hydride ligands to yield ArAl(SeH)_2 , which reacts immediately with another molecule of ArAlH_2 to eliminate hydrogen (Scheme 2). When 2 equiv of selenium is used for the reaction, only half of the selenium is consumed. This observation indicates that, in this case, the reaction of ArAl(SeH)_2 with ArAlH_2 is much faster. In contrast, when a very

(10) Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467.

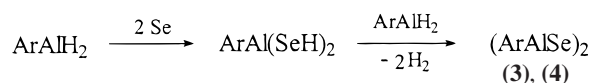
(11) Sheldrick, G. M. *SHELXL: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(12) Raston, C. L. *J. Organomet. Chem.* **1994**, 475, 15.

Scheme 1



Scheme 2



Ar = 2-(Et₂NCH₂)-6-MeC₆H₃ (3), 2,6-(Et₂NCH₂)₂C₆H₃ (4)

bulky chelating group L is used, the reaction of LAl(SeH)₂ with LiAlH₂ is markedly slowed due to the steric effect of the ligand. Unfortunately, we are unable to monitor this reaction because of its heterogeneous nature. Reaction of **2** with tellurium in refluxing toluene gave the arylaluminum telluride [{2,6-(Et₂NCH₂)₂C₆H₃}AlTe]₂ (**5**) in good yield. The mechanism might be similar to that for the reaction of the hydrides with selenium. Compounds **3** and **4** are inert to donor reagents such as phosphine, pyridine, and tmeda ((Me₂NCH₂)₂). They are only poorly soluble in toluene, THF, and DME and have a very limited solubility in CHCl₃.

The three compounds were fully characterized by multinuclear NMR spectroscopy, EI mass spectra, and elemental analyses. The MS spectra of **3–5** show the dimeric molecular ion peaks, and the NMR spectra exhibit the expected resonances. To elucidate the role of the NEt₂ donors, single-crystal X-ray determinations of compounds **3** and **5** were carried out. Single crystals suitable for X-ray crystal studies of **3** and **5** were obtained from toluene at -20 °C and at room temperature, respectively.

Compound **3** crystallizes as a dimer with a crystallographically required inversion center in the solid state (Figure 1). Selected bond lengths and angles are listed in Table 2. The NEt₂ arms are coordinated to the aluminum atoms with Al–N distances of 2.052(3) Å, which is in line with that of (Me₂NCH₂)₂C₆H₃AlCl₂.^{6b} The Se(1)–Al(1) and Se(1)–Al(1A) distances differ (by ca. 0.014 Å) probably because of different steric effects at the two sides of the aryl ligand. They are slightly longer than those of the dimeric compound [{N(SiMe₃)C(Ph)C(SiMe₃)₂}AlSe]₂ (average 2.35 Å).^{4a} The Al(1)–Se–Al(1A) internal angle is acute, with a value of 77.52°, which is nearly equal to that of [{N(SiMe₃)C(Ph)C(SiMe₃)₂}AlSe]₂.

Compound **5** crystallizes in the monoclinic *P*2₁/*c* space group as a centrosymmetric dimer (Figure 2). Selected bond lengths and angles are listed in Table 3. The most interesting structural feature is that only one arm of the two NEt₂ sites of the aryl

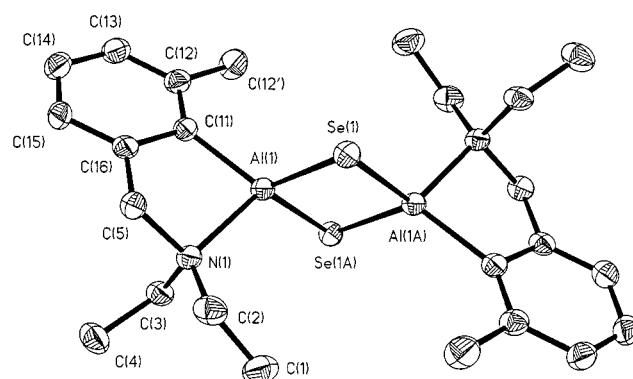


Figure 1. Molecular structure of **3** in the crystal. The solvent C₇H₈ and hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**

Se(1)–Al(1A)	2.352(7)	Al(1)–C(11)	1.960(3)
Se(1)–Al(1)	2.366(4)	Al(1)–N(1)	2.052(3)
Al(1A)–Se(1)–Al(1)	77.52(4)	N(1)–Al(1)–Al(1A)	126.9(9)
C(11)–Al(1)–N(1)	86.79(12)	Se(1A)–Al(1)–Al(1A)	51.45(3)
C(11)–Al(1)–Se(1A)	122.99(11)	Se(1)–Al(1)–Al(1A)	51.03(3)
N(1)–Al(1)–Se(1A)	115.58(8)	Se(1A)–Al(1)–Se(1)	102.48(4)
C(11)–Al(1)–Se(1)	119.58	C(11)–Al(1)–Al(1A)	146.00(11)
N(1)–Al(1)–Se(1)	108.70		

ligand is coordinated to an aluminum atom and the other arm is in a dangling position. However, the ¹H and ¹³C NMR spectra show only one set of signals for the Et₂NCH₂ group; it is assumed that, in solution, a rapid exchange of coordination and dissociation of the two NEt₂ groups takes place. Unfortunately, due to the low solubility of these compounds, we were not able to perform low-temperature NMR studies. Similar behavior has already been observed for the dimeric gallium compound (2,6-(NMe₂CH₂)₂C₆H₃GaPSiPh₃)₂.¹³ Compound **5** is the third structurally characterized organoaluminum telluride with the formula (RAITe)_n; the others are (Cp*AlTe)₄ (Cp* = C₅Me₅) and [{N(SiMe₃)C(Ph)C(SiMe₃)₂}AlTe]₂ reported by our group.^{3a,4a} The Te(1)–Al(1) (2.589 Å) and Te(1)–Al(1A) (2.582 Å) distances are only marginally different from each other. They are shorter

(13) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Ruiz, J.; Atwood, J. L.; Bott, S. G. *Angew. Chem.* **1990**, 102, 1169; *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1150.

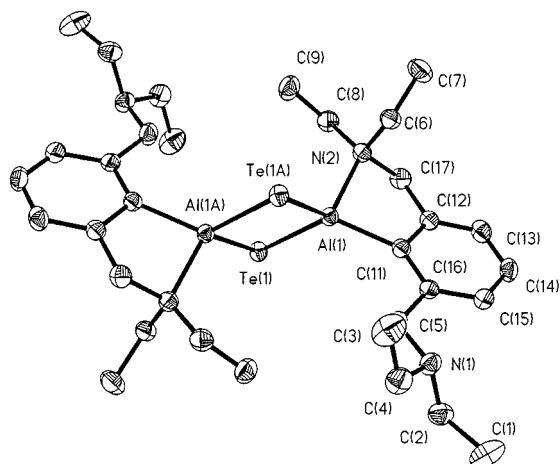


Figure 2. Molecular structure of **5** in the crystal. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

Te(1)–Al(1A)	2.581(8)	Al(1)–C(11)	1.976(3)
Te(1)–Al(1)	2.588(7)	Al(1)–N(2)	2.054(2)
Al(1A)–Te(1)–Al(1)	76.30(3)	C(11)–Al(1)–Te(1)	119.59(7)
C(11)–Al(1)–N(2)	86.74(9)	N(2)–Al(1)–Te(1)	109.22(6)
C(11)–Al(1)–Te(1A)	122.62(8)	Te(1A)–Al(1)–Te(1)	103.70(3)
N(2)–Al(1)–Te(1A)	113.80(6)		

than those of the cubic $(\text{Cp}^*\text{AlTe})_4$ derivative (2.688–2.750 Å) due to the low coordination number of the Te atom in compound **5**, and they are only slightly longer than those in $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{AlTe}]_2$ (2.562–2.577 Å). The Al(1)–C(11) distance (1.976(3) Å) is only slightly longer than that of compound **3** (1.960 Å), and both are in the range of those reported for $\{(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{AlCl}_2\cdot\text{THF}$ (1.987 Å) and dimeric $[\{(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}\text{AlCl}_2]_2$ (1.941 Å).⁶ The Te–Al–Te (103.70(3)°) and Al–Te–Al (76.30(3)°) angles are quite similar to those of dimeric $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{AlTe}]_2$ (103.12(4), 76.88(4)°) even though the Al_2Te_2 core binds to quite different ligands in the two compounds. In addition, the angles of the Al_2Te_2 unit are also nearly equal to those of Al_2Se_2 for compound **3** (102.48(4), 77.52(4)°) and $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{AlSe}]_2$ (averages 102.4, 77.6°) despite the longer Al–Te distances.

(Ph) $\{\text{C}(\text{SiMe}_3)_2\}\text{AlSe}]_2$ (averages 102.4, 77.6°) despite the longer Al–Te distances.

Conclusions and Remarks

The results of the syntheses for compounds **4** and **5** indicate that the dimeric form with one dangling NEt_2 group is energetically favored in comparison to the corresponding monomeric species with two chelating arrangements at the aluminum atom. Using the more bulky aryl ligand (2,6- $\{(t\text{-Bu})(\text{Me})\text{NCH}_2\}_2\text{C}_6\text{H}_3$), the dimeric form was also obtained (according to mass spectra). The ^1H NMR spectrum shows a broad singlet for the $t\text{-Bu}$ and Me groups, indicating that the bulky substituents at the nitrogen atoms are responsible for the slower exchange (coordination and dissociation) on the NMR time scale.¹⁴ The dimeric compounds **3–5** as well as $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)_2\}\text{AlE}]_2$ (E = Se, Te) are thermally quite stable systems. They do not dissociate in polar solvents (THF, DME), even under reflux conditions. In addition, strong donors such as pyridine, tmeda, or phosphine have no effect on the dissociation of the dimers. The utilization of the bulky bidentate ligand $\text{N}(\text{Ar}')\text{C}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ar}')$ ($\text{Ar}' = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) unexpectedly leads to the isolation of the first example of an aluminum–SeH compound. Inspired by this result, we are now exploring the possibility of synthesizing the donor-free compounds R_2AlEH (E = S, Se, Te; R = monodentate anion). The deprotonation of this class of compounds might give anionic $[\text{R}_2\text{AlE}]^-$ species, which may possess π -bonding character between aluminum and the chalcogen atom.¹⁵ This work is presently in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC000255D

(14) The compounds 2,6- $\{(t\text{-Bu})(\text{Me})\text{NCH}_2\}_2\text{C}_6\text{H}_3\text{AlH}_2$ (**b**) and $2,6\text{-}\{(t\text{-Bu})(\text{Me})\text{NCH}_2\}_2\text{C}_6\text{H}_3\text{AlSe}]_2$ (**c**) were prepared similarly to compounds **2** and **4**. Data for **b**: mp 91–92 °C; EI-MS m/e 303 ($\text{M}^+ - \text{H}$). Data for **c**: mp 322–323 °C; ^1H NMR (CDCl_3) δ 1.35 (s, 18 H, $t\text{-Bu}$), 2.57 (s, 6 H, Me), 4.04 (s, 4 H, CH_2), 7.21 (m, 3 H, Ph); ^{77}Se NMR (CDCl_3) δ –14.2, –13.8; EI-MS m/e 764 (M^+).

(15) Power, P. P. *Chem. Rev.* **1999**, 99, 3463.