

Synthesis and Characterization of Well-Defined Aluminum-Containing Heterobimetallic Selenides[†]

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A series of novel aluminum heterobimetallic selenides were reported. The reaction of $\text{LAl}(\text{SeH})_2$ (**1**) with $\text{LiN}(\text{SiMe}_3)_2$ resulted in the formation of $[\text{LAl}(\text{SeLi})_2(\text{THF})_2]$ (**2**) ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$). Compound **2** reacted with Me_2GeCl_2 , Ph_2GeCl_2 , Cp_2TiCl_2 , and Cp_2ZrCl_2 , respectively, to produce $\text{LAl}(\mu\text{-Se})_2\text{GeMe}_2$ (**3**), $\text{LAl}(\mu\text{-Se})_2\text{GePh}_2$ (**4**), $\text{LAl}(\mu\text{-Se})_2\text{TiCp}_2$ (**5**), and $\text{LAl}(\mu\text{-Se})_2\text{ZrCp}_2$ (**6**) in moderate yields. Compounds **2–6** were characterized by elemental analysis, NMR, and electron impact-MS. The X-ray single-crystal structure of **3** is reported and confirms the spirocyclic arrangement of the aluminum atom within the six-membered AlN_2C_3 and four-membered AlSe_2Ge rings.

Introduction

Heterobimetallic chalcogen compounds have attracted much interest because of inherent fundamental chemistry in addition to their potential applications.¹ Aluminum is the most abundant metal in the earth's crust, and many aluminum-containing heterobimetallic oxides have been synthesized and characterized.² In recent years, a few heterobimetallic sulfides have also been reported.³ However, there is still no structurally characterized aluminum heterobimetallic selenide known, for the reasons of limited synthetic methods and the compounds' thermodynamic instability. Because of its potential for biomedical,⁴ catalytic,⁵ and conducting⁶ applications and as a precursor for a chemical vapor deposition⁷

application, the synthesis of aluminum heterobimetallic selenides is an interesting subject. In 2000, $[\text{LAl}(\text{SeH})_2]$ (**1**) ($\text{L} = \text{HC}(\text{CMeNAr})_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) was reported by our group.⁸ This unusual species led us to explore a successful route to the synthesis of heterobimetallic selenides by metathesis of the SeH protons with metal atoms. Although heterobimetallic sulfides have been successfully prepared,^{3a} it is much more difficult to synthesize the corresponding selenide compounds for the reason of the weak metal–selenium bonds, which often lead to the cleavage of the

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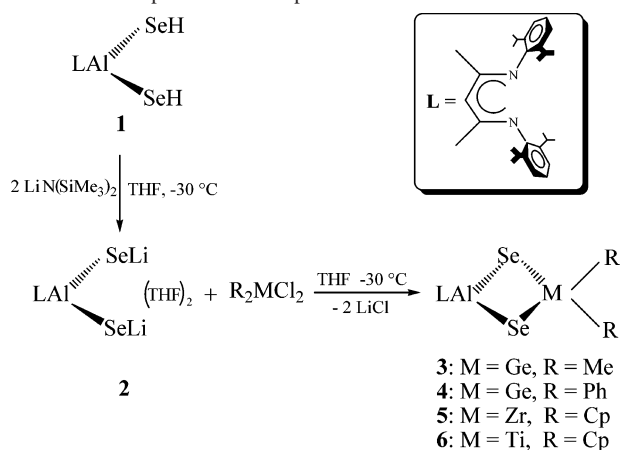
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Scheme 1. Preparation of Compounds 2–6



M–Se (M = metal) bond. The successful synthesis of the compound $[\text{LAl}(\text{SeLi})_2(\text{THF})_2]$ (**2**)⁹ (L = $\text{HC}(\text{CMe})\text{N}(\text{Ar})_2$, Ar = 2,6-*i*-Pr₂C₆H₃) opened the door to effectively prepare aluminum-containing heterobimetallic selenides. From the starting material **2**, we prepared a number of stable aluminum heterobimetallic selenides of composition $\text{LAl}(\mu\text{-Se})_2\text{GeMe}_2$ (**3**), $\text{LAl}(\mu\text{-Se})_2\text{GePh}_2$ (**4**), $\text{LAl}(\mu\text{-Se})_2\text{TiCp}_2$ (**5**), and $\text{LAl}(\mu\text{-Se})_2\text{ZrCp}_2$ (**6**) in high yield (Scheme 1). These systems include main-group metals as well as transition metals. They are well-defined, and **3** is the first structurally characterized organoaluminum heterobimetallic selenide to date.

Experimental Section

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone ketyl prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ¹H, ⁷Li, ¹³C, ²⁷Al, and ⁷⁷Se NMR spectra were recorded on Bruker AM 200, 300, and 500 spectrometers. Electron impact (EI) mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH5 instruments. Melting points were measured in sealed glass tubes and were not corrected.

Preparation of $[\text{LAl}(\text{SeLi})_2(\text{THF})_2]$ (2**).** Compounds $\text{LAl}(\text{SeH})_2$ (**1**) (3.64 g, 6 mmol) and $\text{LiN}(\text{SiMe}_3)_2$ (2.99 g, 12 mmol) were mixed as solids in a flask, and subsequently, cold THF (60 mL, 0 °C) was added. The reaction mixture was cooled to –30 °C and maintained at this temperature for 15 min under vigorous stirring. After filtration, the solid was dried in vacuo and **2** was obtained as a pale yellow powder. Yield: 3.53 g (77.4%); mp, >400 °C (dec). ¹H NMR (300.13 MHz, CDCl₃, 25 °C, TMS): δ 7.10–7.00 (m, 6 H, Ar-*H*), 5.10 (s, 1 H, γ-*H*), 3.87 (sept, ³J_{H-H} = 6.8 Hz, 4 H, CHMe₂), 3.40 (m, 8 H, O(CH₂CH₂)₂), 1.68 (m, 8 H, O(CH₂CH₂)₂), 1.54 (s, 6 H, Me), 1.22 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂), 1.02 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂). ¹³C NMR (125.77 MHz, CDCl₃, 25 °C, TMS): δ 168.15 (CN), 145.47, 142.89, 125.47, 123.64 (*p*-, *m*-, *o*-, and *i*-C of Ar), 98.67 (γ-CH), 68.04 (O(CH₂CH₂)₂), 28.10 (CH(CH₃)₂), 26.91 (O(CH₂CH₂)₂), 25.31 (CH(CH₃)₂), 24.56 (CH(CH₃)₂), 24.46 (CH₃). ⁷Li NMR (116.64 MHz, CDCl₃, 25 °C, LiCl, 1 M in D₂O): δ 1.26. ²⁷Al NMR (78.21 MHz, CDCl₃, 25 °C, AlCl₃,

1 M in D₂O): δ 116.27. Anal. Calcd for C₃₇H₅₇AlLi₂N₂O₂Se₂ (760.66): C, 58.42; H, 7.55; N, 3.68. Found: C, 58.51; H, 7.58; N, 3.73.

Preparation of $[\text{LAl}(\mu\text{-Se})_2\text{GeMe}_2]$ (3**).** A solution of Me_2GeCl_2 (0.17 g, 1 mmol) in THF (10 mL) was added dropwise to a suspension of **2** (0.76 g, 1 mmol) in THF (20 mL) at –30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo. The solid was extracted with toluene (30 mL), and the toluene was removed in vacuo. The residue was washed with cold *n*-hexane to yield solid **3**, which was isolated as a white powder. Yield: 0.60 g (85%); mp, 251 °C. EI-MS: *m/z* (%) 706 (33) [M⁺], 691 (100) [M⁺ – Me]. ¹H NMR (500.13 MHz, C₆D₆, 25 °C, TMS): δ 7.18–7.12 (m, 6 H, Ar-*H*), 4.84 (s, 1 H, γ-*H*), 3.50 (sept, ³J_{H-H} = 6.8 Hz, 4 H, CHMe₂), 1.60 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂), 1.55 (s, 6 H, Me), 1.12 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂), 0.67 (s, 6 H, Me-Ge). ¹³C NMR (125.77 MHz, C₆D₆, 25 °C, TMS): δ 170.50 (CN), 144.98, 139.50, 127.81, 124.76 (*p*-, *m*-, *o*-, and *i*-C of Ar), 98.43 (γ-*C*), 28.16 (CHMe₂), 25.94 (CHMe₂), 24.91 (CHMe₂), 24.10 (Me), 11.49 (Ge-Me). ²⁷Al NMR (78.21 MHz, CDCl₃, 25 °C, AlCl₃, 1 M in D₂O): δ 95.41. ⁷⁷Se NMR (95.37 MHz, C₆D₆, 25 °C, SeMe₂, 1 M in C₆D₆): –180.65. Anal. Calcd for C₃₁H₄₇AlGeN₂Se₂ (705.20): C, 52.53; H, 6.69; N, 3.96. Found: C, 53.86; H, 7.03; N, 4.06. The slight differences in the found and calculated analytical data are due to the extreme moisture sensitivity of the product.

Preparation of $[\text{LAl}(\mu\text{-Se})_2\text{GePh}_2]$ (4**).** Preparation was made like that of **3** from Ph_2GeCl_2 (0.30 g, 1 mmol) and **2** (0.76 g, 1 mmol). Product **4** was isolated as white powder. Yield: 0.75 g (90%); mp, 230 °C. EI-MS: *m/z* (%) 830 (93) [M⁺], 753 (100) [M⁺ – Ph]. ¹H NMR (500.13 MHz, C₆D₆, 25 °C, TMS): δ 7.65–7.64 (dd, 2 H, GePh), 7.38–7.37 (dd, 4 H, GePh), 7.15–7.12 (m, 6 H, Ar-*H*), 7.03–6.98 (m, 4 H, GePh), 4.85 (s, 1 H, γ-*H*), 3.49 (sept, ³J_{H-H} = 6.8 Hz, 4 H, CHMe₂), 1.55 (s, 6 H, Me), 1.42 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂), 0.95 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂). ¹³C NMR (125.77 MHz, C₆D₆, 25 °C, TMS): δ 170.86 (CN), 144.88, 139.45, 128.97, 124.90 (*p*-, *m*-, *o*-, and *i*-C of Ar), 140.25, 134.01, 133.75, 129.89 (*p*-, *m*-, *o*-, and *i*-C of SePh), 98.63 (γ-*C*), 29.27 (CHMe₂), 25.58 (CHMe₂), 25.45 (CHMe₂), 24.09 (Me). ²⁷Al NMR (78.21 MHz, C₆D₆, 25 °C, AlCl₃, 1 M in D₂O): δ 94.61. No satisfactory analytical data was obtained due to the extreme moisture sensitivity of the product.

Preparation of $[\text{LAl}(\mu\text{-Se})_2\text{TiCp}_2]$ (5**).** A solution of Cp_2TiCl_2 (0.25 g, 1 mmol) in THF (10 mL) was added dropwise to a suspension of **2** (0.76 g, 1 mmol) in THF (20 mL) at –30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo. The solid was extracted with toluene (30 mL), and the toluene was removed in vacuo; **5** was isolated as a red powder. Yield: 0.72 g (92%); mp, 290 °C (dec). EI-MS: *m/z* (%) 780 (15) [M⁺], 715 (100) [M⁺ – Cp]. ¹H NMR (200.13 MHz, C₆D₆, 25 °C, TMS): δ 7.39–7.38 (m, 6 H, Ar-*H*), 5.85 (s, 10 H, Cp-*H*), 4.77 (s, 1 H, γ-*H*), 3.60 (sept, ³J_{H-H} = 6.8 Hz, 4 H, CHMe₂), 1.95 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂), 1.58 (s, 6 H, Me), 1.08 (d, ³J_{H-H} = 6.8 Hz, 12 H, CHMe₂). ¹³C NMR (50.33 MHz, CDCl₃, 25 °C, TMS): δ 169.2 (CN), 145.5, 139.9, 127.3, 124.4 (*p*-, *m*-, *o*-, and *i*-C of Ar), 118.1 (Cp-*C*), 94.8 (γ-*C*), 28.9 (CHMe₂), 25.9 (CHMe₂), 25.4 (CHMe₂), 24.7 (Me). ²⁷Al NMR (78.21 MHz, CDCl₃, 25 °C, AlCl₃, 1 M in D₂O): δ 112.54. ⁷⁷Se NMR (95.43 MHz, CDCl₃, 25 °C, SeMe₂, 1 M in CDCl₃): 318.90. Anal. Calcd for C₃₉H₅₁AlN₂Se₂Ti (780.63): C, 60.01; H, 6.59; N, 3.59. Found: C, 59.05; H, 6.35; N, 3.59.

Preparation of $[\text{LAl}(\mu\text{-Se})_2\text{ZrCp}_2]$ (6**).** Preparation was made like that of **5** from Cp_2ZrCl_2 (0.29 g, 1 mmol) and **2** (0.76 g, 1 mmol). Product **6** was isolated as an orange powder. Yield: 0.73 g (88%); mp, 340 °C (dec.). EI-MS: *m/z* (%) 824 (89) [M⁺], 759 (100) [M⁺

(9) $[\text{LAl}(\text{SeLi})_2(\text{THF})_2]$ is the molecular formula of compound **2**. It probably has an oligomer $[\text{LAl}(\text{SeLi})_2(\text{THF})_2]_n$ composition.

– Cp]. ^1H NMR (200.13 MHz, CDCl_3 , 25 °C, TMS): δ 7.35–7.23 (m, 6 H, Ar–H), 5.88 (s, 10 H, Cp–H), 5.05 (s, 1 H, γ -H), 3.40 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4 H, CHMe_2), 1.90 (s, 6 H, Me), 1.68 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2), 1.17 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H, CHMe_2). ^{13}C NMR (50.33 MHz, CDCl_3 , 25 °C, TMS): δ 170.11 (CN), 145.51, 139.62, 127.39, 124.46 (*p*-, *m*-, *o*-, and *i*-C of Ar), 114.33 (Cp–C), 95.79 (γ -C), 28.83 (CHMe_2), 25.54 (CHMe_2), 25.49 (CHMe_2), 24.77 (Me). ^{27}Al NMR (78.21 MHz, CDCl_3 , 25 °C, AlCl_3 , 1 M in D_2O): δ 112.89. ^{77}Se NMR (95.39 MHz, CDCl_3 , 25 °C, SeMe_2 , 1 M in CDCl_3): 41.96. Anal. Calcd for $\text{C}_{39}\text{H}_{51}\text{AlN}_2\text{Se}_2\text{Zr}$ (823.97): C, 56.85; H, 6.24; N, 3.40. Found: C, 56.85; H, 6.14; N, 3.19.

Single-Crystal X-ray Structure Determination and Refinement. The crystallographic data for compound **3** was collected on a STOE IPDS II array detector system with a four-circle instrument. Graphite-monochromated Mo K radiation ($\lambda = 0.71073$ Å) was used. The structures were solved by direct methods (*SHELXS-90*)¹⁰ and refined against F^2 using *SHELXL-97*.¹¹ Hydrogen atoms were included in geometrically idealized positions and refined isotropically using the riding model with U_{iso} tied to the U_{iso} of the parent atoms.

Results and Discussion

Compound **2** was prepared by the reaction of **1** with 2 equiv of $\text{LiN}(\text{SiMe}_3)_2$ at low temperature. Compounds **3–6** were synthesized by adding dropwise solutions of Me_2GeCl_2 , Ph_2GeCl_2 , Cp_2TiCl_2 , and Cp_2ZrCl_2 in THF, respectively, to **2** suspended in THF at -30 °C. Compound **2** is sparingly soluble in THF at low temperature. However, after adding Me_2GeCl_2 , Ph_2GeCl_2 , Cp_2TiCl_2 , and Cp_2ZrCl_2 , respectively, the suspension became clear and the light yellow color very quickly turned colorless (for Me_2GeCl_2 and Ph_2GeCl_2), red (for Cp_2TiCl_2), and orange (for Cp_2ZrCl_2). This is an indication for the progress of the reaction. Compounds **3** and **4** are colorless solids, whereas **5** is red and **6** is orange in the solid state. All are well soluble in toluene, benzene, and especially in chloroform.

Compounds **2–6** were characterized by EI-MS spectrometry, elemental analysis, ^1H , ^{13}C , ^7Li , ^{27}Al , and ^{77}Se NMR investigations, and single-crystal X-ray diffraction studies. The ^1H NMR spectra of **2–6** exhibit one set of resonances for the ligand (L), respectively. The ^1H NMR spectrum of **2** exhibits resonances around δ 4.0 and 1.6, which were assigned to the THF molecules. From the ratio of integration between THF with the ligand, it can be assumed that there are two molecules of THF coordinated to the lithium atoms in one $\text{LAL}(\text{SeLi})_2$ unit. There is no high-field ($\delta < 0$ ppm) resonance in the ^1H NMR spectrum of **2**; it clearly shows the complete exchange of the protons in the starting material of $\text{LAl}(\text{SeH})_2$ (**1**) by lithium atoms. There is a resonance ($\delta = 1.26$ ppm) in the ^7Li NMR spectrum of **2**, which indicates the existence of lithium in compound **2**. The ^1H NMR spectrum of **3** exhibits a Ge–Me resonance at δ 0.66 ppm in a 6:1 ratio to that of the γ -H proton while **4** shows the Ge–Ph resonances in ranges (δ 7.03 to 6.98, 7.38–7.37, and 7.65–7.64) which are distinct from those of the Ar–H resonances (δ 7.15–7.12 ppm). Compounds **5** and **6** exhibit Cp resonances at δ 5.88 and 5.85 in a 10:1 ratio to that of

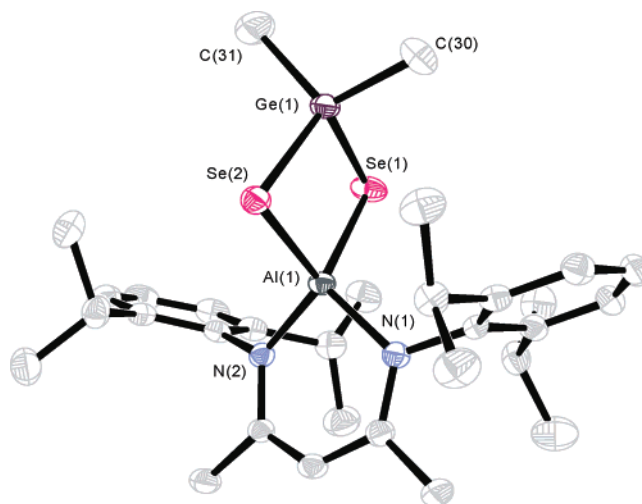


Figure 1. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)–N(1) 1.897(3), Al(1)–N(2) 1.880(3), Al(1)–Se(1) 2.356(1), Al(1)–Se(2) 2.367(1), Ge(1)–Se(1) 2.350(1), Ge(1)–Se(2) 2.350(1), Ge(1)–C(31) 1.942(3), Ge(1)–C(30) 1.943(3), Se(1)–Al(1)–Se(2) 99.16(3), N(1)–Al(1)–N(2) 98.03(11), Al(1)–Se(1)–Ge(1) 79.99(2), Al(1)–Se(2)–Ge(1) 79.75(2), Se(2)–Ge(1)–Se(1) 99.844(16), C(31)–Ge(1)–C(30) 111.10(17).

the γ -H proton, respectively. The EI mass spectra of **3–6** ($m/z = 706$, 830, 780, and 824) show the parent ions [M^+] with their isotopic patterns. The isotopic patterns of compounds **3–6** as determined by EI-MS spectrometry agree very well with the results of calculation, which also provide solid proof of the identities of these compounds (Figures S1–S8, see the Supporting Information).

The composition of **3** was assigned by single-crystal X-ray structural analysis. Colorless crystals of **3** were obtained from toluene at 4 °C. Compound **3** crystallizes in the monoclinic space group $P2_1/c$.¹² The molecular structure of **3** is shown in Figure 1. The characteristics of **3** are the $(\mu\text{-Se})_2$ bridges between the aluminum and germanium atoms, generating an unambiguous novel heterobimetallic selenide moiety. The Al–Se bond lengths (2.356 and 2.367 Å) are a little longer than those in **1** (2.331 and 2.340 Å)⁸ and just in the range of those in $\text{Al}(\mu\text{-Se})_2\text{Al}$ (2.352–2.394 Å).¹³ The replacement of the SeH protons by Ge has some influence on the Al–Se bond length because the partial negative charge on the Se atom in **3** has been transferred to the Se–Ge bond, which led to the lower electron density and an elongation of the Al–Se(H) bond. The Ge–Se bond lengths (2.350 Å) are also in accordance with those reported (2.357–2.370 Å).¹⁴ The AlSe_2Ge four-membered ring is essentially planar, with the sum of inner angles equal to about 360°. The angle at the

(12) Crystal data for **3**: $\text{C}_{31}\text{H}_{47}\text{AlGeN}_2\text{Se}_2$, $M_r = 705.20$, monoclinic, space group $P2_1/c$, $a = 11.9939(10)$ Å, $b = 17.4552(9)$ Å, $c = 16.0281(13)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 90.686(6)^\circ$, $V = 3355.3$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.396$ Mg m⁻³, $F(000) = 1440$, $R(\text{int}) = 0.0553$, goodness-of-fit on $F^2 = 0.963$; the R values are $R1 = 0.0301$ and $wR2 = 0.0667$ ($I > 2\sigma(I)$); the residual electron density is $0.459/-0.437$ e Å⁻³.

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aluminum center (99.16°) is almost equal to the angle at germanium (99.84°), and the angles at the two selenium centers are almost equal (79.99° and 79.75°) to each other.

Conclusion

In summary, we discovered a new strategy for the preparation of aluminum heterobimetallic selenides and prepared the first series of well-defined aluminum heterobimetallic selenides.

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Supporting Information Available: Figures S1–S8 (PDF), as well as CIF data for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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