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[13] Satisfactory elemental analysis. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C, residual C$_6$H$_6$): The spectrum indicates a 2:1 molar mixture of isomers A and B. Isomer A: δ(Cp) = 4.58(s), 4.61(s), 4.76(s), 4.77(d, J = 1.5 Hz) and isomer B: δ(Cp) = 4.61(s), 4.70(s), 4.79(d, J = 1.5 Hz) and 4.86(s). A variable-temperature ^{1}H NMR study in C$_6$D$_5$CD$_3$ shows that isomer A is the predominant species below −30 °C (δ(Cp) = 4.39, 4.53, 4.63 and 4.71), and that rapid exchange of the four Cp rings at 90 °C gives rise to a singlet at δ = 4.77. ^{13}C NMR (67.80 MHz, C$_6$D$_6$): δ(Cp) = 91.71, 92.07, 92.72, 93.15. IR(toluene): $\tilde{v}$[cm^{-1}] = 2028vs, 1983vs, 1969vs, 1950vs, 1942vs, 1899s, 1882sh s, 1874vs (CO).

[14] Crystal data for 1: M_r = 1012.66, triclinic, space group P$\bar{1}$, a = 12.074(1), b = 12.880(3), c = 14.451(5) Å, α = 73.05(2), β = 73.21(1), γ = 78.67(1)°, V = 2042.5(9) Å^3, Z = 2, ϱ = 1.646 Mg m^{-3}, $F(000)$ = 1020, λ(Mo$_{K\alpha}$) = 0.71073 Å, μ = 13.65 cm^{-1}, T = 27 °C, crystal dimensions: 0.1 × 0.2 × 0.15 mm. Enraf-Nonius CAD4 diffractometer. ω-2θ scan mode. Of 6208 reflections measured, 3221 (I > 3$\sigma(I)$) were used in refinement. The crystal used for unit cell determination and data collection was coated with epoxy glue to prevent decomposition in air. Twenty-five strong reflections were used for accurate determination of the unit cell parameters. The measured intensities were processed for Lorentz-polarization effects and decay, and corrected for absorption [20]. The structure was solved by direct methods (MULTAN). All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically with a distance of 0.95 Å to the carbon atoms and were allowed to "ride" with B = 1.3. A THF solvent molecule was found at a general position in the unit cell and was disordered. The positional parameters for the THF ring were fixed, while their displacement parameters were refined as carbon atoms. Residual peaks in the final difference map account mainly for peaks around the THF molecule. Computations were performed by using the MolEN [21] package on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated [22]. Final R = 0.048, (R_w = 0.057). Further details of the crystal structure investigation are available from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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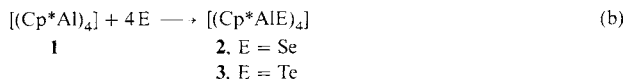
A Simple Synthesis of [(Cp*Al)$_4$] and Its Conversion to the Heterocubanes [(Cp*AlSe)$_4$] and [(Cp*AlTe)$_4$] (Cp* = η^5-C$_5$(CH$_3$)$_5$)**

By Stephan Schulz, Herbert W. Roesky,* Hans Joachim Koch, George M. Sheldrick, Dietmar Stalke, and Annja Kuhn

Dedicated to Professor Harry Eméleus
on the occasion of his 90th birthday

Aluminum occurs preferably in the oxidation state III in its compounds. In addition, there are several compounds with aluminum in the oxidation state II[1 − 3] and only a few containing aluminum in the oxidation state I.[4 − 6] One of these is the [(Cp*Al)$_4$] tetrahedron (1) synthesized by Schnöckel et al. from AlCl and [MgCp$_2^*$] (Cp* = η^5-C$_5$(CH$_3$)$_5$) in 1991.[4] The synthesis of the starting material AlCl from HCl and Al at 1200 K is rather difficult.[7] We report here on a simple alternative synthetic route to 1 as well as the first reactions of this compound.

Freshly prepared [Cp*AlCl$_2$][8] is allowed to react with a small excess of potassium in toluene under reflux [Eq. (a)]. After filtration of all the insoluble material from the hot solution, 1 is obtained in form of yellow crystals in a yield of 20 %.

$$4[Cp^*AlCl_2] + 8 K \longrightarrow [(Cp^*Al)_4] + 8 KCl \qquad (a)$$

$$\mathbf{1}$$
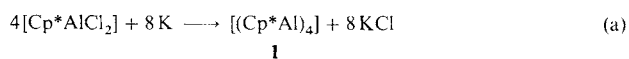
Compound 1 is extremely thermally stable and decomposes at 205 °C turning to a brown solid.[9] Only one signal with 100 % intensity for monomeric Cp*Al (M = 162 gmol^{-1}) occurs in the mass spectrum. We were not able to detect the molecular ion in the mass spectrum by field ionization (FI) methods. Compound 1 is only slightly air- and moisture-sensitive. Exposure of the crystalline material to air or even water for about 20 min leads to a white amorphous layer, presumably consisting of aluminum oxo and/or aluminum hydroxo compounds. This chemical inertness is a result of the steric shielding of the Al$_4$ tetrahedron by interlocked Cp* rings.[10] Because of the poor solubility of 1 NMR investigations in C$_6$D$_6$ were performed in the temperature range + 40 to + 78 °C. In the ^{1}H NMR spectrum a singlet appears for the methyl protons at δ = 1.89 and two signals occur in the ^{13}C NMR spectrum for the methyl-C and for the ring-C atoms at δ = 11.35 and 114.21, respectively. The ^{27}Al NMR spectrum shows, in contrast to the previously published results,[11] only one signal at δ = −78.3,[12] whose position does not change on raising or lowering the temperature. We were not able to detect a second signal that should appear above 30 °C (at δ = −145) corresponding to monomeric Cp*Al.[13, 14] In addition to finding a facile access to [(Cp*Al)$_4$] 1, we were also interested in the reactivity of this compound. It should undergo redox reactions in which the aluminum proceeds from the oxidation state I to its preferred oxidation state III. Hitherto, apart from reactions with AlCl, no reactions of aluminum(I) compounds have been described. We report here for the first time about reactions of 1 with elements from group 16. These reactions lead to the

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formation of the Al–Se and Al–Te heterocubanes, **2** and **3**, respectively. Moreover, **3** is the second organometallic

[(Cp*AlSe)₄] **2**

[(Cp*AlTe)₄] **3**

Al–Te compound characterized by X-ray crystallography.[23] Compounds of the type RAlE (E = Se, Te) are isolobal with those of the type RAlXR (X = N, P, As); the latter have been thoroughly investigated during the last few years, since they are potential precursors for industrially interesting AlX materials. In our opinion the compounds RAlE and AlE also have very promising material properties.

When a solution of **1** in toluene is treated with an excess of Se or Te [see Eq. (b)], yellow-green solutions are obtained

$$[(Cp^*Al)_4] + 4E \longrightarrow [(Cp^*AlE)_4] \qquad (b)$$

$$\begin{array}{ll} \textbf{1} & \textbf{2}, E = Se \\ & \textbf{3}, E = Te \end{array}$$

following the removal of the insoluble material by filtration. From these solutions **2** can be obtained in the form of colorless, octahedral crystals and **3** in the form of pale green shiny octahedral crystals by slow evaporation of the solvent.

Both compounds are extremely sensitive to air and moisture. Thus, they decompose with an accompanying change in color (red (**2**) or black (**3**)) and concomitant formation of H₂Se and H₂Te, respectively. Compound **2** decomposes at 244 °C and **3** does not melt until 350 °C.

Crystals of **2** are obtained from a THF solution of **2** by very slow evaporation of the solvent. Figure 1 shows the molecular structure of **2**. Suitable crystals for a single-crystal
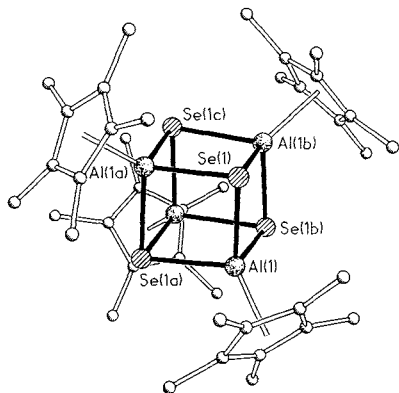

Fig. 1. Crystal structure of **2**. Selected bond lengths [pm] and angles [ ]: Al(1)-Se(1) 249.70(10), Al(1)-Se(1a) 246.16(10), Al(1)-Se(1b) 247.13(10); Al(1b)-Se(1)-Al(1a) 85.38(4), Al(1b)-Se(1)-Al(1) 84.62(3), Al(1)-Se(1)-Al(1a) 85.57(4), Se(1b)-Al(1)-Se(1) 94.39(4), Se(1b)-Al(1)-Se(1a) 95.28(4), Se(1a)-Al(1)-Se(1) 94.16(4).

X-ray structural analysis of **3** can be obtained from toluene by slow evaporation of the solvent over a week. Figure 2 shows the molecular structure of **3**, which is isostructural to **2**. Both compounds are tetrameric; the parent skeleton comprises an Al–E heterocubane (E = Se, Te). The Al–Se bond lengths present in **2** vary from 246.2 to 249.7 pm. The Al–Se bond lengths thus lie in the range of those found in [Ph₃PSe·AlCl₃][15] and in [CH₃Se{Al(CH₃)₃}₃]⁻.[16] The Al–Te bonds in **3** range from 268.8 to 275.0 pm and are thus slightly longer than those in Al₇Te₁₀ (263.7–266.2 pm for the bonds from the three-coordinate Te atoms).[17] Since the

atomic distances lie in a relatively narrow range and also the bond angles at Al and Se and Te, respectively, deviate very little from the ideal 90° angle (average Se-Al-Se: 94.61°, Te-Al-Te: 95.06°, Al-Se-Al: 85.19°, Al-Te-Al: 84.68°), **2** and **3** form almost ideal cubes. In both compounds, each Al atom is additionally coordinated to an η^5-Cp* ligand[18] (Al-Cp*(center) [pm]: 194.9 in **2** and 196.5 in **3**; 201.5 in [(Cp*Al)₄]).
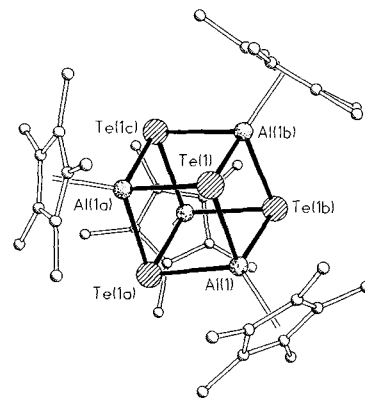

Fig. 2. Crystal structure of **3**. Selected bond lengths [pm] and angles [ ]: Al(1)-Te(1) 275.00(9), Al(1)-Te(1a) 268.83(9), Al(1)-Te(1b) 269.17(9); Al(1b)-Te(1)-Al(1a) 84.86(2), Al(1b)-Te(1)-Al(1) 83.68(2), Al(1)-Te(1)-Al(1a) 85.51(2), Te(1b)-Al(1)-Te(1) 94.84(2), Te(1b)-Al(1)-Te(1a) 96.29(2), Te(1a)-Al(1)-Te(1) 94.06(2).

Noteworthy is the analogous construction of these Al heterocubanes to the [RAlNR′]₄ compounds described by Veith[19] in a review on cage molecules. These compounds exhibit a cubic Al₄N₄ framework. The facile formation of this organometallic Al–Te compound under very mild reaction conditions in good yield is quite surprising. It illustates again the strong desire of aluminum in the oxidation state ι (as occurs in **1**) to attain the more stable oxidation state ιιι. The new facile synthesis of **1** accompanied by the high reactivity of **1** in solution should allow the access to other interesting Al compounds.

Experimental Procedure

373, 350, 272. MS (EI): *m/z* 1025 (*M*⁺ − Cp*, 2%), 580 (*M/2*⁺, 25), 135 (Cp*, 100). Correct elemental analysis.

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[9] The physical and chemical properties of 1 described by Schnöckel et al. are slightly different from those found by us.

[10] A single-crystal X-ray structure analysis at −120 °C confirms the existence of 1. Crystal data: $C_{40}H_{60}Al_4$, M_r = 648.85, triclinic, space group $P\bar{1}$, a = 10.759(4), b = 10.913(3), c = 18.027(5) Å, α = 82.94, β = 81.82, γ = 66.88, V = 2116.6(12) Å³, Z = 2.

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[12] The measurements were carried out at +40, +70, and +78 °C.

[13] If the NMR sample tube is left open for 1 h, and then the sample is remeasured at +70 °C, two additional signals at δ = −9.3 and −148.2 appear in the ²⁷Al NMR spectrum. The latter signal is consistent with the values postulated for monomeric Cp*Al.

[14] Because of the poor solubility of 1, it is not possible to carry out a molar mass determination.

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[18] Crystal data of 2: $C_{10}H_{15}AlSe$, M_r = 241.16, tetragonal, space group $I\bar{4}$, a = b = 12.144(1), c = 14.373(2) Å, V = 2119.7(4) Å³, Z = 8, ρ_{calcd} = 1.511 Mgm⁻³, $F(000)$ = 976, λ = 0.71073 Å, $\mu(Mo_{K\alpha})$ = 0.397 mm⁻¹. The data were collected on a Stoe-Siemens-Huber diffractometer. Intensities of a rapidly cooled crystal with dimensions 0.6 × 0.5 × 0.4 mm in an oil drop [20] were collected at −120 °C by the $2\theta/\omega$ method in the range 8 ≤ 2θ ≤ 50. Of the 1403 reflections collected, 1367 were unique and these were corrected for absorption by using a semiempirical procedure; highest minimum and maximum of the final difference Fourier synthesis: 0.32 and −0.28 eÅ⁻³, respectively. $R1$ = 0.021, $wR2$ = 0.050 (all data). The absolute structure was determined to 0.00(14) by a refinement of the Flack parameter (H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876). Crystal data of 3: $C_{10}H_{15}AlTe$, M_r = 289.80, tetragonal, space group $I\bar{4}$, a = b = 12.430(2), c = 14.546(3) Å, V = 2247.4(7) Å³, Z = 8, ρ_{calcd} = 1.713 Mgm⁻³, $F(000)$ = 1120, λ = 0.71073 Å, $\mu(Mo_{K\alpha})$ = 0.397 mm⁻¹. The data were collected on a Stoe-Siemens-Huber diffractometer. Intensities of a rapidly cooled crystal with the dimensions 0.5 × 0.4 × 0.4 mm in an oil drop [20] were collected at −120 °C by the $2\theta/\omega$ method in the range 8 ≤ 2θ ≤ 55. Of the 2370 reflections collected, 2278 were unique and these were corrected for absorption by using a semiempirical procedure; highest minimum and maximum of the final difference Fourier synthesis: 0.39 and −0.44 eÅ⁻³, respectively. $R1$ = 0.017, $wR2$ = 0.042 (all data). The absolute structure was determined to 0.03(2) by a refinement of the Flack parameter (H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876). The values of $R1$ and $wR2$ were defined as $R1 = \Sigma||F_o| − |F_c||/[\Sigma|F_o|]$; $wR2 = \{[\Sigma w(F_o^2 − F_c^2)^2]/[\Sigma w(F_o^2)]\}^{1/2}$. The structures were solved by direct methods (SHELXS-90) [21] and refined by least-squares procedures (SHELXL-93) [22]. The hydrogen positions were refined according to a riding model in which the CH₃ groups were allowed to rotate about their local threefold axis. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallography Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), by quoting the full journal citation.

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A Molecular Heterometal Amide with High Molecular Dynamics: Does the Lithium Atom Orbit?**

By *Michael Veith,** Michael Zimmer,*
and *Stefan Müller-Becker*

Dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday

Whilst the motion of lithium atoms in solids, such as, for example, in solid Li₃N, has been thoroughly investigated and is generally accepted,[1] many indications, but little concrete evidence for such a motion in molecules exists, in spite of much effort (see e.g. ref. [2]). Here we report on our studies of the heterometal amide [Me₂Si(NSiMe₃)₂]₂InLi (1), an example of a class of molecular complexes that has still not been investigated in detail.[3] Compound 1 can easily be prepared according to Equation (a).

$$2\,Me_2Si(NSiMe_3)_2Li_2 + InCl_3 \longrightarrow 3\,LiCl + [Me_2Si(NSiMe_3)_2]_2InLi \quad (a)$$
$$\mathbf{1}$$
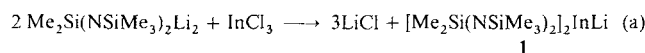
According to the X-ray crystal structure analysis,[4] (Fig. 1) the trivalent indium and the monovalent lithium atom in 1 are bound close together in a tricycle of four-membered rings (In ··· Li = 2.748(9) Å). The ¹H, ¹³C, ¹⁵N, and ²⁹Si NMR spectra of 1 at room temperature in toluene (see Experimental Procedure) are not consistent with the molecular structure represented in Figure 1. Thus, only one reso-
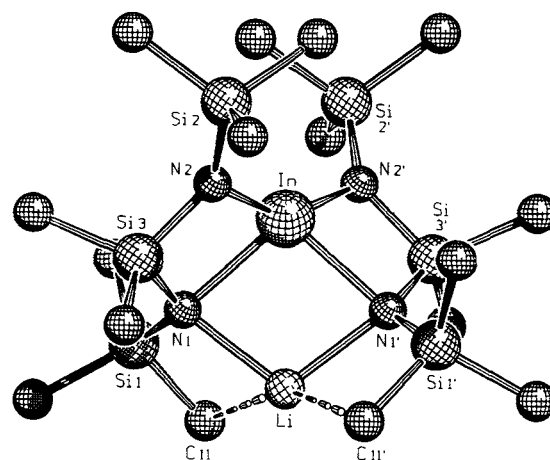

Fig. 1. Molecular structure of 1. Some important distances [Å] and angles [°]: N1−In 2.223(3), N2−In 2.055(3), N1−Li 2.064(6), N1−Si1 1.720(3), N1−Si3 1.737(3), N2−Si2 1.714(3), N2−Si3 1.717(3). Li ··· C11 2.635(7); N1-In-N1′ 95.2(1), N2-In-N2′ 148.4(1), N1-In-N2 76.2(1), N1-In-N2′ 127.3(1), N1-Li-N1′ 105.4(3).

nance signal is found for both the dimethylsilylene and trimethylsilyl groups in the ¹³C NMR spectrum, whereas a double set of signals would be expected because of the low C_2 symmetry of the molecule (the twofold axis passes through the two metal atoms).

If a toluene solution of 1 is cooled, ¹H, ¹³C, and ²⁹Si NMR spectra are obtained at lower temperature (as an ex-

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