A Simple Synthesis of [(Cp*A1)] and Its Conversion to the Heterocubanes [(Cp*A1)Se] and [(Cp*A1)O] (Cp* = η5-C5H4CH2) **

By Stephan Schulz, Herbert W. Roessky,* Hans Joachim Koch, George M. Shedrick, Dietmar Stalke, and Annya Kuhn

Dedicated to Professor Harry Emeléus 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 I. Only a few contain aluminum in the oxidation state I. One of these is the [(Cp*Al)] tetrahedron (1) synthesized by Schönckel et al. from AlCl3 and [MgCp2] (Cp* = η5-C5H4CH2) in 1991. The synthesis of the starting material AlCl3 from HCl and Al at 1200 K is rather difficult. We report here on a simple alternative synthetic route to 1 as well as the first reactions of this compound.

Freshly prepared [(Cp*Al)] 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%.

Compound 1 is extremely thermally stable and decomposes at 205°C turning to a brown solid. Only one signal with 100% intensity for monomeric Cp*Al (M = 162 g mol⁻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 oxide and/or aluminum hydroxide compounds. This chemical inertness is a result of the steric shielding of the Al₄ tetrahedron by interlocked Cp* rings. Because of the poor solubility of 1 NMR investigations in C₆D₆ were performed in the temperature range 40 to +78°C. In the ¹H NMR spectrum a singlet appears for the methyl protons at δ = 1.89 and two signals occur in the ¹³C NMR spectrum for the methyl-C and for the ring-C atoms at δ = 11.35 and 114.21, respectively. The ²⁷Al NMR spectrum shows, in contrast to the previously published results, only one signal at δ = -78.33 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. In addition to finding a facile access to [(Cp*Al)] 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 AICI3, 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...
formation of the Al-Se and Al-Te heterocubanes, 2 and 3, respectively. Moreover, 3 is the second organometallic

\[
[[\text{Cp}^*\text{AlSe}_{3}]] \quad 2 \\
[[\text{Cp}^*\text{AlTe}_{3}]] \quad 3
\]

Al-Te compound characterized by X-ray crystallography.123 Compounds of the type RAIE (E = Se, Te) are isolobal with those of the type RAIXR (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 RAIE and AIE 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 following the removal of the insoluble material by filtration.

\[
[[\text{Cp}^*\text{Al}_{3}]] + 4 \text{E} \longrightarrow [[\text{Cp}^*\text{AlE}_{4}]] \\
1, \ E = \text{Se} \\
3, \ E = \text{Te}
\]

X-ray structural analysis of 3 can be obtained from toluene by slow evaporation of the solvent over a week. Figure 1 shows the molecular structure of 2. Suitable crystals for a single-crystal

\[\text{Fig. 1. Crystal structure of 2. Selected bond lengths [pm] and angles [°]: Al(1)-Se(1) 249.70(10), Al(1)-Se(1a) 246.16(10), Al(1)-Se(1b) 247.13(10), Al(1)-Se(1)-Al(1a) 85.38(4), Al(1)-Se(1)-Al(1b) 84.62(3), Al(1)-Se(1a)-Al(1a) 85.75(4). Se(1b)-Al(1)-Se(1a) 95.28(4), Se(1a)-Al(1)-Se(1b) 95.28(4), Se(1a)-Al(1)-Se(1) 94.16(4).}\]

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°, 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 \(\eta^1\)-ligand\(^{118}\) (Al-Cp\(^*\)(center) [pm]: 194.9 in 2 and 196.5 in 3; 201.5 in \([[\text{Cp}^*\text{Al}_{3}]]\)).

Noteworthy is the analogous construction of these Al heterocubanes to the [RAINE\(^3\)]\(^{-}\) compounds described by Veith\(^1\) in a review on cage molecules. These compounds exhibit a cubic Al\(_n\)N\(_2\) framework. The facile formation of this organometallic Al-Te compound under very mild reaction conditions in good yield is quite surprising. It illustrates again the strong desire of aluminum in the oxidation state I (as occurs in 1) to attain the more stable oxidation state III. 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**

All reactions were carried out under a nitrogen atmosphere and with dry solvents.

1. \(\text{AlCl}_3\) (4.00 g, 30 mmol) was dissolved in hexane (60 mL), treated with \([\text{Cp}^*\text{SeMe}_2]\) (6.25 g, 30 mmol), and heated under reflux for 1 h. Subsequently the solvent and the Me\(_2\)SiCl formed were removed under vacuum. The white solid residue was then dissolved in toluene (60 mL) and treated with K (2.75 g, 77 mmol) and heated for 1.5 h. The insoluble material was then filtered off from the hot solution: the temperature of the solution must not be allowed to drop below 80-90 °C. Compound 2 precipitated from the hot solution on cooling in the form of yellow crystals. Yield: 0.95 g (1.5 mmol) (30%). IR (nujol, CsI): \(\nu_{\text{cm}}^{-1} = 1480, 1370, 1307, 1261, 1169, 1094, 1019, 800, 733, 595, 558, 352\).

2. A mixture of 1 (0.32 g, 0.5 mmol) and Se (0.31 g, 4 mmol) in toluene (60 mL) was stirred for 4 d at room temperature. Subsequently all insoluble material was filtered off and the solvent was slowly removed under vacuum over a period of 2 d to afford 2. Yield: 0.38 g (0.39 mmol) (78%). \(\nu_{\text{H}}\) NMR (400 MHz, \(\text{C}_6\text{D}_6\), 25 °C, TMS): \(\delta = 1.99\); \(\nu_{\text{C}}\) NMR (100 MHz, \(\text{C}_6\text{D}_6\), 25 °C, TMS): \(\delta = 12.07, 115.68\). \(\nu_{\text{Al}}\) NMR (100 MHz, \(\text{C}_6\text{D}_6\), 25 °C, ACI): \(\delta = -36.40\). IR (nujol, CsI): \(\nu_{\text{cm}}^{-1} = 2161, 1095, 1064, 1021, 800, 727, 694, 661, 627, 591, 435, 387\). MS (EI): \(m/\text{z} = 966 (M^+ , 2\%), 831 (M^- - \text{Cp}^*\text{Se}, 8), 162 (\text{AlCp}^*\text{Se}, 100)\). Correct elemental analysis.

3. A mixture of 1 (0.32 g, 0.5 mmol) and Te (0.50 g, 4 mmol) were stirred for 6 d in toluene (60 mL) at room temperature. After removal of the insoluble material by filtration, the solvent was slowly removed under vacuum. Compound 3 precipitated in the form of octahedral crystals. Yield 0.65 g (0.43 mmol) (86%). \(\nu_{\text{H}}\) NMR (400 MHz, \(\text{C}_6\text{D}_6\), 25 °C, TMS): \(\delta = 1.96\); \(\nu_{\text{C}}\) NMR (100 MHz, \(\text{C}_6\text{D}_6\), 25 °C, TMS): \(\delta = 12.91, 116.44\). \(\nu_{\text{Al}}\) NMR (100 MHz, \(\text{C}_6\text{D}_6\), 25 °C, ACI): \(\delta = -112.69\) IR (nujol, CsI): \(\nu_{\text{cm}}^{-1} = 1262, 1168, 1019, 949, 799, 589, 446\).
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 the studies of the heterometal amide [Me₆Si(NSiMe₃)₂]₂INi(1), an example of a class of molecular complexes that has still not been investigated in detail.[3] Compound I can easily be prepared according to Equation (a).

\[ 2\text{Me}_6\text{Si(NSiMe}_3)_2\text{Li}_2 + \text{InCl}_3 \rightarrow 3\text{LiCl} + [\text{Me}_6\text{Si(NSiMe}_3)_2]\text{INi} \]

According to the X-ray crystal structure analysis,[4] (Fig. 1) the trivalent indium and the monovalent lithium atom in I are bound close together in a tricycle of four-membered rings (In...Li = 2.748(9) Å). The \( ^{1}H \), \( ^{13}C \), \( ^{11}B \), and \( ^{29}Si \) NMR spectra of I at room temperature in toluene (see Experimental Procedure) are not consistent with the molecular structure represented in Figure 1. Thus, only one resolved signal is found for both the dimethylsiloylene and trimethylsilyl groups in the \( ^{13}C \) NMR spectrum, whereas a double set of signals would be expected because of the low C₆ symmetry of the molecule (the twofold axis passes through the two metal atoms).

If a toluene solution of I is cooled, \( ^{1}H \), \( ^{13}C \), and \( ^{29}Si \) NMR spectra are obtained at lower temperature (as an example of the spectrum of the compound cooled to 185 K).

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**] Prof. Dr. M. Veith, M. Zimmer, Dr. S. Müller-Becker
Institut für Anorganische Chemie der Universität
Postfach 10 40 51, D-60049 Saarbrücken (FRG)
Telefax: Int. code + (681)920-3995

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