### Synthesis and Characterization of Gallium(III) and Germanium(II) Chlorides Bearing the C<sub>6</sub>F<sub>5</sub>-Substituted $\beta$ -Diketiminate HC[(CMe)(NC<sub>6</sub>F<sub>5</sub>)]<sub>2</sub> Ligand

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Dedicated to Professor Achim Müller on the Occasion of his 70<sup>th</sup> Birthday

**Abstract.** The germanium(II) and gallium(III) organochlorides containing the C<sub>6</sub>F<sub>5</sub>-substituted  $\beta$ -diketiminate ligand LGeCl (2) and LGaCl<sub>2</sub> (3) (L = HC[(CMe)(NC<sub>6</sub>F<sub>5</sub>)]<sub>2</sub>) were synthesized. Salt elimination reactions of the C<sub>6</sub>F<sub>5</sub>-substituted  $\beta$ -diketiminato lithium salt with the corresponding germanium(II) and gallium(III) chlorides led to the organochlorides respectively. Compounds 2

# and 3 were characterized by spectroscopic and elemental analyses, and 2 was further investigated by single crystal X-ray structural analysis.

Keywords: Gallium; Germanium;  $C_6F_5$ -substituted;  $\beta$ -Diketiminate ligand

### Introduction

Germanium and gallium halides are involved in most of the germanium and gallium containing reactions. They are important for germanium and gallium chemistry [1, 2]. Reduction of gallium halides can result in Ga<sup>I</sup> or Ga-Ga bond containing compounds [3]. Hydrolysis of germanium and gallium halides lead to gallium and germanium terminal hydroxide compounds [4, 5]. Recent research in our group showed that organic germanium chloride reacts with H<sub>3</sub>Al·NMe<sub>3</sub> to result in an unusual monomeric germanium(II) compound with terminal hydride [6]. Bulky encumbered  $\beta$ -diketiminate ligands are usually used to stabilize the metal center due to their electronic and/or steric properties. The bulky ligands can avoid the condensation of molecules to form oligomeric compounds. A noticeable point is the ability of these ligands to stabilize low coordination numbers at the metal atoms, rare coordination geometries, or low oxidation states owing to their ability to tune properly between the steric and electronic factors. Using this kind of ligands, we can selectively change the functionalities on the metal center, design and control the reaction process. In 2002, Power et al. reported on a new  $C_6F_5$  substituted  $\beta$ -diketiminate ligand  $HC[(CMe)(NC_6F_5)]_2$  (L) [7]. Moreover *Cowley* et al. prepared a Lewis acid stabilized compound with a

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boron-oxygen double bond using this ligand [8], and they also reported on the single crystal X-ray structure of the ligand (LH) and on LLi · (OEt<sub>2</sub>), LAlMe<sub>2</sub>, and LGaMe<sub>2</sub> respectively [9]. Recently LAlBr<sub>2</sub>, LAl(Me)Cl, LAl(Me)I, and (LAlMe)<sub>2</sub>( $\mu$ -O) were reported from our group [10]. In these papers, it was demonstrated that this ligand exhibits very interesting reaction properties. Until now there are still no germanium and gallium halides reported with this ligand. Herein, we describe the synthesis and characterization of germanium and gallium chlorides supported by the HC[(CMe)(NC<sub>6</sub>F<sub>5</sub>)]<sub>2</sub> ligand.

### **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. LH [7] was prepared as described in the literature. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on Bruker AM 300 and 500 spectrometers and IR spectra on a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and were not corrected.

### $HC[(CMe)(NC_6F_5)]_2GeCl (2)$

To a toluene solution (20 mL) of LH (0.43 g, 1 mmol) at 0 °C was added drop by drop *n*-BuLi (2.5 M, 0.4 mL, 1 mmol). The mixture was stirred and allowed to warm to room temperature. After ad-



ditional stirring for 12 h, the solution was cooled to 0 °C and GeCl<sub>2</sub> · dioxane (0.23 g, 1 mmol) in toluene (10 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuum and washed with cold *n*-hexane twice to yield solid **2**. Yield: (0.45 g, 84 %). Mp 183 °C. Anal. Calcd for  $C_{17}H_7ClF_{10}GeN_2$  (*M*r = 537.29): C, 38.00; H, 1.31; N, 5.21. Found C, 39.05; H, 1.67; N, 4.97 %.

<sup>1</sup>**H** NMR (300.13 MHz, CDCl<sub>3</sub>, 298 K, ppm): δ 2.08 (s, 6 H, β-Me), 5.67 (s, 1 H, γ-CH). <sup>13</sup>C NMR (75.48 MHz, CDCl<sub>3</sub>, 298 K, ppm): δ 23.43 (β-Me), 103.22 (γ-C), 119.22, 137.54, 138.55, 139.15, 139.88, 142.19 (C<sub>6</sub>F<sub>5</sub>), 167.27 (CN). <sup>19</sup>F NMR (188.28 MHz, CDCl<sub>3</sub>, 298 K, ppm): -144.83 (m, 2 F, o-F), -146.63 (m, 2 F, o-F), -154.23 (t, 2 F, p-F), -159.94 (m, 2 F, m-F), CM-MS (%) 538 (59, [M<sup>+</sup>]), 503 (100, [M<sup>+</sup>-C]).

### $HC[(CMe)(NC_6F_5)]_2GaCl_2(3)$

To a toluene solution (40 mL) of LH (4.31 g, 10 mmol) at 0 °C was added drop by drop *n*-BuLi (2.5 M, 4 mL, 10 mmol). The mixture was stirred and allowed to warm to room temperature. After additional stirring for 12 h, the solution was cooled to 0 °C and GaCl<sub>3</sub> (1.73 g, 10 mmol) in toluene (20 mL) was added. The resulting solution was allowed to warm to room temperature and stirred for 12 h. After workup, the insoluble LiCl was removed by filtration and the filtrate was dried in vacuum and washed with *n*hexane twice to yield solid **3**. Yield: (4.67 g, 82 %). Mp 242 °C. Anal. Calcd for  $C_{17}H_7Cl_2F_{10}GaN_2$  (*M*r = 569.87): C, 35.83; H, 1.24; N, 4.92. Found C, 35.60; H, 1.74; N, 4.61 %.

<sup>1</sup>**H NMR** (300.13 MHz, CDCl<sub>3</sub>, 298 K, ppm): δ 2.05 (s, 6 H, β-Me), 5.47 (s, 1 H, γ-CH). <sup>13</sup>C **NMR** (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 23.82 (β-Me), 100.14 (γ-C), 117.06, 137.08, 139.13, 139.91, 141.78, 143.75 (C<sub>6</sub>F<sub>5</sub>), 173.93 (CN). <sup>19</sup>**F NMR** (188.28 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ – 144.24 (m, 4 F, o-F), -153.35 (t, 2 F, p-F), -160.02 (m, 4 F, m-F). **EI-MS**: m/z (%) 570 (100,  $[M^+]$ ).

## Single Crystal X-ray Structure Determination and Refinement

The crystallographic data for compound **2** was collected on a Stoe IPDS II-array detector system with graphite-monochromated  $Mo_{Ka}$  radiation ( $\lambda = 0.71073$  Å). This structure was solved by direct methods (SHELXS-96) [11] and refined against  $F^2$  using SHELXL-97 [12]. All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with  $U_{iso}$  related to the  $U_{iso}$  of the parent atoms.

### **Results and Discussion**

According to the outline given in Scheme 1, compounds LGeCl (2) and LGaCl<sub>2</sub> (3) were prepared by lithium salt elimination with the corresponding germanium and gallium chloride. The toluene solution of LLi prepared from LH and n-BuLi was used in situ for the reaction with GeCl<sub>2</sub> · dixone and GaCl<sub>3</sub> respectively (The structure of  $LLi \cdot OEt_2$  in ether has been reported by *Cowlev* et al. [9a].). Both compounds were characterized by EI-MS, <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR measurements as well as by elemental analysis. In the <sup>1</sup>H NMR spectrum compounds 2 and 3 exhibit each one resonance for the  $\gamma$ -C-H proton around 5.5 ppm, and one signal for Me protons around 2.0 ppm with the intensity of 1:6, showing the characteristic  $\beta$ -diketiminate resonances. The <sup>19</sup>F NMR spectrum of compound 2 shows five resonances in the ratio of 1:1:1:1:1, while 3 exhibits three resonances in the ration of 2:1:2. These differences can be attributed to the symmetric arrangement of 3 and the asymmetric structure of 2 due to the non-coordinate lone-pair of the germanium atom. In the EI-MS spectra, the most intense peak of compounds 2 and 3 is attributed to



#### Scheme 1



Figure 1 Molecular structure of 2. Thermal ellipsoids are drawn at 50 % level, and the hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances/Å and angles/° for compound 2

the molecular ion  $[M^+]$  (m/z 538, 570) with correct isotopic pattern. In **2**, the ion at m/z = 503 was assigned to  $[M-Cl]^+$ .

Pale vellow single crystals of compound 2 were obtained from saturated toluene solution at -28 °C, and were submitted to X-ray diffraction studies to determine the molecular structure. The structure of 2 shows mononuclear arrangement with germanium at the center that coordinates to the chelating  $\beta$ -diketiminate ligand with the C<sub>6</sub>F<sub>5</sub> groups attached to the ring. Compound 2 crystallizes in the triclinic space group  $P\overline{1}$  with one molecule in the asymmetric unit [13]. The molecular structure of 2 is shown in Figure 1. In 2, the germanium atom is coordinate to two nitrogen atoms of the monoanionic ligand and a terminal chloride atom, resulting in a pyramidal coordination sphere. The Ge-N bond length (av. 1.999 Å) is similar to that (av. 1.993 Å) in compound L'GeCl (L' =  $HC[(CMe)(NAr)]_2$ ,  $Ar = 2,6-iPr_2C_6H_3$  [14]. The Ge-Cl bond length (2.299 Å) is comparable to that of L'GeCl (2.295 Å).

### Conclusion

In summary we report on the synthesis of a germanium and a gallium chloride containing the  $C_6F_5$  substituted  $\beta$ -diketiminate ligand HC[(CMe)(NC<sub>6</sub>F<sub>5</sub>)]<sub>2</sub>GeCl (2) and HC[(CMe)(NC<sub>6</sub>F<sub>5</sub>)]<sub>2</sub>GaCl<sub>2</sub> (3). To our knowledge compound 2 is the first germanium compound supported by this ligand. The germanium(II) compound (2) has carbene-like properties and is therefore a promising candidate for the preparation of other germanium derivatives either by electron donor-acceptor reactions or by chloride metathesis reactions.

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- [13] Crystal data for 2:  $C_{17}H_7ClF_{10}GeN_2$ , Mr = 537.29, triclinic, space group  $P\bar{1}$ , a = 11.0621(6) Å, b = 12.0853(7) Å, c = 15.4740(8) Å,  $\alpha = 112.788(4)^\circ$ ,  $\beta = 93.632(4)^\circ$ ,  $\gamma = 96.160(5)^\circ$ , V = 1883.90(18) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.894$  gcm<sup>-3</sup>, F(000) = 1048,  $1.84 \le \theta \ge 24.77$ , of 28409 reflections collected, 6048 were independent, R(int) = 0.0479,  $R_1 = 0.0260$ ,  $wR_2 = 0.0627$  ( $I > 2\sigma(I)$ ); The residual electron density: 0.893/ -0.906 e Å<sup>-3</sup>. The CCDC reference number 670516. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2IEZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.
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