

## Preparation and Structural Characterization of the First Germylaluminate

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The reaction of  $\text{LiGePh}_3$  with  $\text{Me}_2\text{AlCl}$  in ether yields the trisgermylaluminate  $\text{Li}(\text{OEt}_2)_n[(\text{Ph}_3\text{Ge})_3\text{AlMe}]$ . The Ge–Al

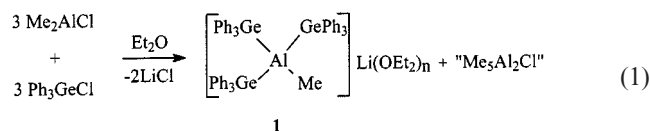
bond length is 2.520 Å and the geometry around the Al center almost tetrahedral.

## Introduction

The chemistry of compounds with direct bonds between boron atoms and group 14 elements has found increased interest in recent years. Silylboranes and stannylboranes have proved to be versatile reagents in organic synthesis<sup>[1]</sup> and they are particularly useful for transition metal-catalyzed addition reactions to unsaturated organic compounds.<sup>[2]</sup> More recently, compounds containing Si–Al<sup>[3]</sup> or Si–Ga<sup>[4]</sup> bonds moved into focus because the  $(\text{Me}_3\text{Si})_3\text{Si}$  or  $(\text{Me}_3\text{C})_3\text{Si}$  groups stabilize polyhedral aluminum, gallium and indium clusters;<sup>[5]</sup> silylalanines and silylaluminates are also known. The molecular structures of the adducts  $(\text{Me}_3\text{Si})_3\text{Al}\cdot\text{L}$ <sup>[6]</sup> [ $\text{L} = \text{THF}$ ,  $\text{NMe}_3$ ,  $\text{P}(\text{SiMe}_3)_3$ ] and  $\text{Ph}_2\text{Al}\text{--}\text{Si}(\text{SiMe}_3)_3\cdot\text{THF}$ <sup>[7]</sup> have been described, as well as those of  $(\text{Me}_3\text{Si})_3\text{Si}\text{--}\text{Al}(\text{tmp})_2$  ( $\text{tmp} = 2,2,6,6\text{-tetramethylpiperidino}$ ),<sup>[8]</sup>  $(t\text{Bu}_3\text{Si})_2\text{Al}\text{--}\text{Al}(\text{Si}t\text{Bu}_3)_2$ ,<sup>[9]</sup>  $\text{Si}(\text{AlCl}_2\cdot\text{OEt}_2)_4$ ,<sup>[10]</sup>  $[\text{Ph}_2\text{PAI}(\text{SiMe}_3)_2]_2$ <sup>[11]</sup> and silylaluminates such as  $\text{Li}(\text{THF})_4[\text{Cl}_3\text{AlSi}(\text{SiMe}_3)_3]$  and  $\text{Na}(\text{THF})_2[\text{Al}(\text{SiMe}_3)_4]$ .<sup>[12]</sup> As far as we are aware no molecular compound containing an Al–Ge bond has been structurally characterized. Dufaut et al.<sup>[13]</sup> reported that the reduction of digermanes with  $\text{LiAlH}_4$  yields various germylaluminates amongst which only  $\text{Li}(\text{Ph}_3\text{GeAlH}_3)\cdot\text{THF}$  was identified by microanalysis; all other compounds were identified from the products of their controlled hydrolysis. Rösch et al.<sup>[14]</sup> succeeded in the preparation of  $\text{Al}(\text{GeMe}_3)_3\cdot\text{THF}$  by reacting  $\text{Hg}(\text{GeMe}_3)_2$  with elemental aluminum. A structural characterization by X-ray methods was, at the time, not standard. Here we report the synthesis and molecular structure of a novel germylaluminate.

Because salt elimination is the most straightforward pathway to synthesize B–Ge bonds<sup>[15]</sup> we also utilized this method for the synthesis of new molecules with Al–Ge bonds. To this end a solution of triphenylgermyllithium<sup>[16]</sup> in  $\text{Et}_2\text{O}$  was allowed to react with an equimolar amount of dimethylaluminum chloride [Equation (1)]. The reaction mixture was monitored by  $^{27}\text{Al}$  NMR spectroscopy. The spectrum showed two signals at  $\delta = 189$  and 62.

These data indicate the formation of methylalanines as well as possibly a pentacoordinated aluminum species.<sup>[17]</sup> On layering a concentrated toluene solution with hexane single



crystals separated which were suitable for an X-ray structure analysis. The crystalline product was unambiguously identified as lithium{methyltris(triphenylgermyl)aluminate} (1). Its elemental analysis indicated that five molecules of ether are coordinated but the crystal structure analysis showed only three ether molecules. Compound 1 is responsible for the high field Al NMR signal and is similar to the  $^{27}\text{Al}$  NMR signal for  $\text{Li}[\text{Al}(\text{SiMe}_3)_4]$ .<sup>[17]</sup> The filtrate contained no other germanium compound, although its  $^{27}\text{Al}$  NMR spectrum showed the presence of an aluminum species with  $\delta^{27}\text{Al} = 189$ . We assigned this broad signal to  $\text{Me}_5\text{Al}_2\text{Cl}$  as we found a  $^{27}\text{Al}$  NMR signal for  $\text{Me}_2\text{AlCl}$  at  $\delta = 165$  in ether solution, and at  $\delta = 179$  in hexane solution. That only a single signal is observed for “ $\text{Me}_5\text{Al}_2\text{Cl}$ ” can be explained by substituent exchange, which is common in the chemistry of aluminum alkyls.<sup>[18]</sup> Compound 1 crystallizes in the space group  $P2_1/c$  with four formula units in the unit cell. The unit cell contains methyltris(triphenylgermyl)aluminate anions and ether-solvated lithium cations. The ether molecules are highly disordered. No accurate coordination geometry was found. Much more interesting is the anionic part of compound 1 (see Figure 1). It shows three Al–Ge bonds of almost equal lengths with an average of 2.520(2) Å. This value is slightly longer than the sum of the covalent radii of these two atoms [ $\text{Al} = 1.25$ ,  $\text{Ge} = 1.22$ ;  $\Sigma = 2.47$  Å].<sup>[10]</sup> This complies with the presence of a tetracoordinated Al center. As far as we are aware this is the first Al–Ge bond length determined in a molecular unit. The Al atom in 1 shows only a minor distortion from a tetrahedral environment. The Ge–Al–Ge angles were determined to be on average 110.2(3)°, whereas the average Ge–Al–C bond angle is 108.6(2)°. This indicates that the methyl group almost demands as much space as a  $\text{Ph}_3\text{Ge}$  group.

The unexpected formation of 1 described in Equation (1) can be explained on the basis that  $\text{Me}_2\text{AlCl}$  was added to  $\text{Ph}_3\text{GeLi}$ . Thus at the beginning of the reaction there is a

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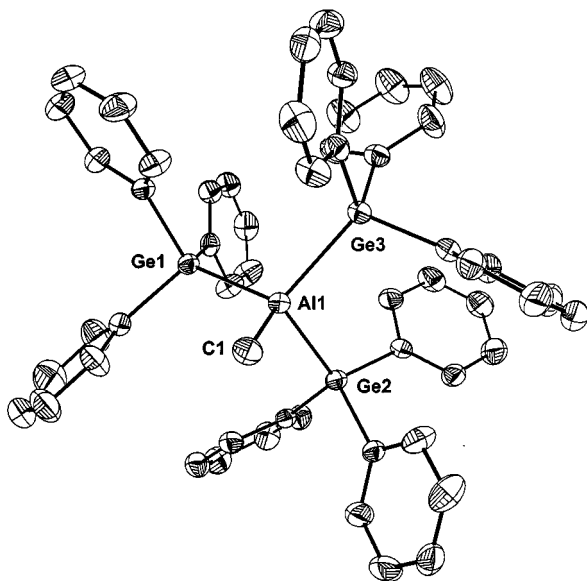


Figure 1. View of the anionic part of the molecular structure of **1**; thermal ellipsoids are shown at a 25% probability level and hydrogen atoms are omitted for clarity; selected interatomic distances [Å] and angles [°]: Ge1–Al1 2.526(2), Ge2–Al1 2.511(2), Ge3–Al1 2.523(2), C1–Al1 1.982(6); C1–Al1–Ge1 110.1(2), C1–Al1–Ge2 107.0(2), C1–Al1–Ge3 108.9(2), Ge1–Al1–Ge2 109.8(1), Ge1–Al1–Ge3 113.3(1), Ge2–Al1–Ge3 107.5(1)

large excess of the germyllithium compound. In the first step an aluminate  $[(\text{Ph}_3\text{Ge})\text{AlMe}_2\text{Cl}]^-$  is expected to be formed. This anion will lose a chloride, with formation of insoluble  $\text{LiCl}$ , producing  $\text{Ph}_3\text{GeAlMe}_2$ . This latter, on reaction with a second equivalent of  $\text{Ph}_3\text{GeLi}$ , will generate  $\text{Li}[(\text{Ph}_3\text{Ge})_2\text{AlMe}_2]$  as an intermediate which may either directly react with  $\text{Me}_2\text{AlCl}$  to form  $(\text{Ph}_3\text{Ge})_2\text{AlMe}$  and  $\text{LiCl}$  or methylate  $\text{Me}_2\text{AlCl}$  with formation of  $\text{AlMe}_3$ . This and  $\text{Me}_2\text{AlCl}$  will produce “ $\text{Me}_5\text{Al}_2\text{Cl}$ ”. Substituent exchange reactions are well-known in alkyl aluminum chemistry.<sup>[18]</sup> Further investigations of the chemistry of Al–Ge compounds are in progress.

## Experimental Section

The experiments were performed under anhydrous conditions under an argon atmosphere using Schlenk techniques.  $\text{LiGePh}_3$  was prepared according to a literature procedure.<sup>[16]</sup> NMR spectra were recorded with a JEOL 400 instrument. For X-ray work a Siemens P4 diffractometer (graphite monochromator,  $\text{Mo-K}_\alpha$  radiation) equipped with an area detector and a low temperature device LT2 was employed. Data collection was performed with the program SMART,<sup>[20]</sup> data reduction with the program SAINT,<sup>[20]</sup> and absorption correction with the program SADABS.<sup>[21]</sup> For all other calculations the program package SHELXTL was used.<sup>[22]</sup> The Li atom and the non-hydrogen atoms of the anion were refined anisotropically. The hydrogen atoms of the Ph and Me groups were placed in calculated positions and included in the final refinement isotropically. The O and C atoms of the ether molecules were included isotropically with free SOR values.

**Lithium{methyltris(triphenylgermyl)aluminate}· $(\text{Et}_2\text{O})_5$  (**1**):** A solution of  $\text{Ph}_3\text{GeLi}$  (1.5 mmol) in approximately 40 mL of  $\text{Et}_2\text{O}$  was cooled to  $-78^\circ\text{C}$  and slowly treated with a hexane solution con-

taining of  $\text{Me}_2\text{AlCl}$  (1.45 mmol). After stirring for 1 h at ambient temperature all volatile components were removed in vacuo. The solid residue was dissolved in 50 mL of toluene, the solution filtered and layered with 20 mL of hexane. This afforded 0.60 g of **1** (yield 90% based on  $\text{Ph}_3\text{GeLi}$ ), as colorless prisms; m.p.  $152^\circ\text{C}$ . –  $^1\text{H}$  NMR (270 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  = 0.49 (s, 3 H  $\text{AlCH}_3$ ), 1.30 (t,  $^3J_{\text{HH}}$  = 8.2 Hz, 16 H,  $\text{OCH}_2\text{CH}_2$ ), 1.65 (br. s, 14 H,  $\text{OCH}_2\text{CH}_2$ ), 3.46 (q,  $^3J_{\text{HH}}$  = 8.2 Hz, 11 H,  $\text{OCH}_2$ ), 3.77 (br. m, 9 H,  $\text{OCH}_2$ ), 7.35 (m, 27 H, *p*-Ph-*H* and *m*-Ph-*H*), 7.76 (m, 18 H, *o*-Ph-*H*). –  $^{27}\text{Al}$  NMR (104 MHz,  $\text{C}_7\text{D}_8$ ):  $\delta$  = 62 ( $h_{1/2}$  = 5850 Hz).

**X-ray Structure Determination:**  $\text{C}_{67}\text{H}_{48}\text{Ge}_3\text{LiO}_3$ , mol. wt. 1152.74, colorless prism, cryst. size:  $0.10 \times 0.20 \times 0.20$  mm,  $a$  = 14.2369(8),  $b$  = 19.5112(1),  $c$  = 22.766(2) Å,  $\beta$  =  $92.523(1)^\circ$ ,  $V$  = 6317.9(7) Å<sup>3</sup>, monoclinic, space group  $P2_1/c$ ,  $Z$  = 4,  $d_{\text{calcd.}}$  = 1.212 Mg/m<sup>3</sup>,  $F(000)$  = 2344, index ranges:  $-15 < h < 12$ ,  $-21 < k < 21$ ,  $-25 < l < 24$ ; 2 $\theta$  range 2–46.52°,  $T$  =  $-80^\circ\text{C}$ ; refl. collected: 27052; refl. unique: 5808;  $R_{\text{int}}$  = 0.0754, no. variables: 607, GOOF 1.1015,  $R_1(4\sigma)$  = 0.628,  $wR_2$  = 0.1605, larg. res. peak: 1.62 e/Å<sup>3</sup>. Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152468. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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