

[2,6-Mes₂C₆H₃]₂Ga⁺Li[Al{OCH(CF₃)₂]₄]₂⁻ (Mes = 2,4,6-Me₃C₆H₂): A Compound Containing a Linear Unsolvated Two-Coordinate Gallium Cation

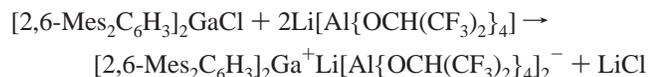
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Cationic organoaluminum compounds have been the target of numerous research groups with the aim of developing highly reactive transition metal free polymerization catalysts.¹⁻⁴ In general, the activity of these compounds increases with decreasing coordination number, and early attempts of isolating the very reactive two-coordinate aluminum ions, R₂Al⁺ (R = alkyl), were unsuccessful due to degradation of the anion B(C₆F₅)₄⁻.⁵ By employing a more robust anion, Reed and co-workers⁶ recently obtained the compounds Et₂Al(CB₁₁H₆X₆) (X = Cl, Br), which contain the aluminum ion-like cation Et₂Al⁺. This cation is stabilized by weak Al···X interactions with the anion, leading to C–Al–C angles of 136.6 or 130.0°. While these angles are wider than expected for tetrahedral or trigonal geometry, they are still considerably smaller than the 180° expected for a “free” two-coordinate aluminum cation. As an alternative approach to generate two-coordinate aluminum cations, we have begun to investigate the use of bulky *m*-terphenyl substituents.^{7,8} It can be seen by simple modeling that two of these large chemically robust bowl-shaped substituents might be able to shield the central cation from interaction with the solvent or the anion. To test this hypothesis, we have prepared the new compound [2,6-Mes₂C₆H₃]₂Ga⁺Li[Al{OCH(CF₃)₂]₄]₂⁻ (**1**) (Mes = 2,4,6-Me₃C₆H₂) as a prototype containing the less Lewis-acidic and therefore less reactive gallium. Here we report the synthesis, characterization, and initial reactivity studies of **1**.

The metathesis reaction of [2,6-Mes₂C₆H₃]₂GaCl⁹ with 2 equiv of Li[Al{OCH(CF₃)₂]₄¹⁰ in chlorobenzene at room temperature afforded the title compound **1** as colorless crystals in moderate yields.¹¹ It has been characterized by ¹H, ¹³C{¹H}, ¹⁹F, and ²⁷Al NMR spectroscopy and X-ray crystallography.¹²



The structure of **1** consists of isolated [2,6-Mes₂C₆H₃]₂Ga⁺ cations (Figure 1) and Li[Al{OCH(CF₃)₂]₄⁻ anions. The gallium center is two-coordinate with an essentially linear C(15)–Ga(1)–C(39) array (175.69(7)°). With values of 1.9130(14) and 1.9145(16) Å, the Ga–C bond is shortened by 2.5–4.5% with respect to the Ga–C bonds in the precursor⁹ and related three-coordinate diaryl-gallium compounds.^{13,14} The bowl-shaped terphenyl substituents are arranged in a staggered conformation that envelopes the gallium cation almost completely (Figure 2). For example, the planes of the central gallium bonded aryl rings are rotated 73.0° with respect to each other, and the flanking mesityl rings are rotated between 68.3 and 86.7° with respect to the central rings. There are no distortions in the substituents which would lead to close Ga···C contacts that could balance the positive charge on the gallium cation with the electron density of the aromatic rings. In fact, the only significant distortion in **1** is probably caused by steric or packing effects. The C(39) terphenyl substituent is slightly bent out of the

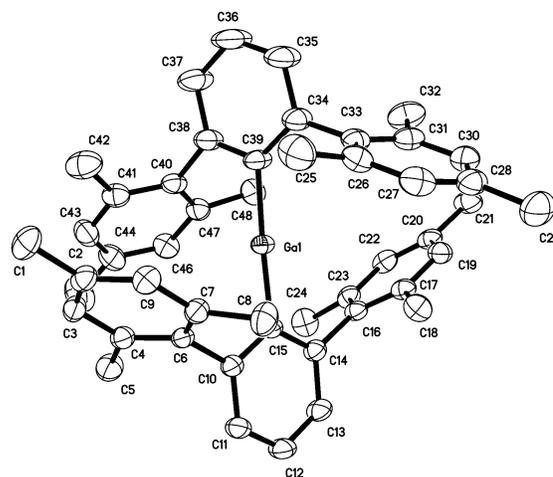


Figure 1. Structure of cation in **1** (thermal ellipsoid plot; H atoms are not shown). Selected bond lengths [Å] and angles [deg]: Ga1–C15 = 1.9130(14), Ga1–C39 = 1.9145(16), C15–Ga1–C39 = 175.69(7), C14–C15–C10 = 121.70(14), C14–C15–Ga1 = 121.23(13), C10–C15–Ga1 = 117.05(11), C38–C39–C34 = 121.60(15), C34–C39–Ga1 = 128.85(13), C38–C39–Ga1 = 109.55(13).

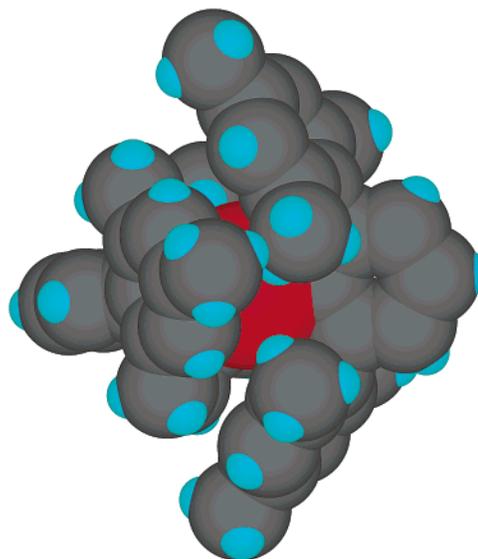


Figure 2. Space filling model of the [2,6-Mes₂C₆H₃]₂Ga⁺ cation in **1**, illustrating the protection of the gallium cation by the terphenyl substituents.

symmetrical alignment as expressed by the 10.2° angle between the Ga(1)–C(39) and C(39)–C(36) vectors or the difference in the Ga–C–C angles with values of 109.55(13) and 128.85(13)°. This leads to the closest nonbonding Ga···C contacts with values of 2.718 Å for Ga(1)···C(38) and 2.773 Å for Ga(1)···C(40), which are only

slightly shorter than the unperturbed corresponding Ga(1)···C(10) and Ga(1)···C(6) distances with values of 2.840 and 3.015 Å, respectively.

The structure of the $\text{Li}[\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4]_2^-$ anion closely resembles the one previously described in the compound [1-Et-3-Me-1,3- $\text{C}_3\text{H}_3\text{N}_2$][$\text{Li}[\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4]_2$].¹⁵ This anion is formed readily when $\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4^-$ is present next to $\text{Li}[\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4]$. For example, the reaction of [2,6-Mes₂C₆H₃]₂GaCl with 1 equiv of $\text{Li}[\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4]$ in chlorobenzene also afforded **1**, but unreacted [2,6-Mes₂C₆H₃]₂GaCl could be recovered from the reaction mixture. While there are several examples of cationic diorganogallium compounds, these species are at least three-coordinate via complex formation with a Lewis base.^{16,17} Compound **1** is so far the only two-coordinate cationic diorganogallium species in the condensed phase.

Under anhydrous and anaerobic conditions, crystalline **1** is stable for months, and C₆D₅Cl solutions of **1** remain unchanged for days at room temperature and are also not affected by brief (30 min) heating to ca. 70 °C. Compound **1** is soluble in chlorobenzene, but only slightly soluble in benzene or toluene. In these solvents, dense liquid phases (liquid clathrates)¹⁸ are obtained, which seems to be typical for ionic organometallic compounds consisting of large cations and anions.

Given that compound **1** was developed as a less reactive model for the potentially industrially important aluminum cations, we have begun to investigate its reactivity. Here, it is of interest how far the steric bulk of the substituents interferes with the reactivity of the cationic center. On the other hand, the existence of [2,6-Mes₂C₆H₃]₂GaX (X = Cl,⁹ Br¹⁹) and [2,6-Mes₂C₆H₃]₂GaR (R = Me, *t*-Bu)²⁰ and the range of the C–Ga–C angles in these compounds with values of 153.5(2)°, 153.5(2)°, 135.1(7)°, and 113.2(1)°, respectively, indicates that the [2,6-Mes₂C₆H₃]₂Ga⁺ system is flexible enough to accommodate a third ligand and thus display some catalytic activity. The relative Lewis acidity of **1** was probed by addition of the Lewis bases THF, pyridine, and 4-(dimethylamino)pyridine (DMAP) to solutions of **1** in C₆D₅Cl, C₆D₅Cl/C₆D₆ mixtures, or C₇D₈, and the adduct formation was monitored by ¹H NMR spectroscopy. The addition of THF did not cause any changes in the NMR spectrum, but the addition of both pyridine and DMAP resulted in line broadening and splitting of the *o*-Me signals of the substituent, indicating adduct formation. Two broadened singlets have also been observed for the *o*-Me signals in [2,6-Mes₂C₆H₃]₂Ga(*t*-Bu),²⁰ whereas in the halide and methyl derivatives, only one set of signals was observed for the eight *o*-Me groups. As addition of excess pyridine or DMAP did not affect the appearance of the terphenyl signals, it may be concluded that the observed dynamic process is caused by hindered rotation of the aryl groups and not Lewis base exchange. No reaction was observed when 1-octene was added to a solution of **1** in C₆D₅-Cl, not even after heating at 70 °C for 30 min. On the other hand, cyclohexene oxide is consumed immediately after addition, and broad signals appear in the cyclohexyl oxide region of the spectrum. Repeating this reaction on a preparative scale (0.6 mL of cyclohexene oxide added to a solution of **1** (25 mg) in C₆H₅Cl (5 mL))

resulted in an immediate exothermic reaction. After workup, a colorless solid was obtained, which was identified as polycyclohexeneoxide by ¹H NMR spectroscopy.²¹

In summary, application of bulky *m*-terphenyl substituents allows the isolation of a compound featuring a linear two-coordinate gallium cation. Investigations of the properties of this compound and the extension toward the more reactive aluminum analogues are under way.

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Supporting Information Available: X-ray data (PDF and CIF) for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Chlorobenzene (10 mL) was added to a mixture of [2,6-Mes₂C₆H₃]₂GaCl (0.35 g, 0.48 mmol) and $\text{Li}[\text{Al}\{\text{OCH}(\text{CF}_3)_2\}_4]$ (0.67 g, 0.96 mmol), and the resulting cloudy solution was stirred for 2 days at room temperature. Filtration followed by concentration to ca. 3 mL and cooling to –40 °C afforded colorless crystals of **1**. Yield: 33%. Mp 130–135 °C. ¹H NMR (300 MHz, C₆D₅Cl): 7.27 (t, *J* = 7.8 Hz, *p*-H, 2H), 6.81 (s, *m*-H(Mes), 8H), 6.74 (d, *J* = 7.8 Hz, *m*-H, 4H), 4.80 (sept, *J*_{H–F} = 5.6 Hz, OCH, 8H), 2.16 (s, *p*-Me, 12H), 1.53 (s, *o*-Me, 24H). ¹³C{¹H} NMR (75.45 MHz, C₆D₅Cl): 147.87, 144.28, 140.89, 137.18, 136.79, 134.53, 130.58, 128.67, 122.90 (q, *J*_{C–F} = 284 Hz, CF₃), 71.50 (sept., *J*_{C–F} = 33 Hz, OCH), 21.68 (*o*-Me), 21.21 (*p*-Me). ¹⁹F NMR (282.35 MHz, C₆D₅Cl): –77.41 (d, *J*_{H–F} = 5.6 Hz). ²⁷Al{¹H} NMR (78.19 MHz, C₆D₅Cl): 55.5 (s, broad, *w*_{1/2} = 700 Hz).
- Crystal data for **1**·0.25C₆H₅Cl at 153 K with Mo Kα (λ = 0.71073 Å) radiation: *a* = 16.4399(8) Å, *b* = 18.2990(9) Å, *c* = 18.6637(9) Å, α = 61.1830(10)°, β = 64.6210(10)°, γ = 75.4100(10)°, triclinic, space group *P*-1, *Z* = 2, *R*1 = 0.0470 for 15 215 (*I* > 2σ(*I*)) data, *wR*2 = 0.1518 for all (18 247) data.
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