Two-coordinate Group 13 Element (Al, Ga) Centered Cations Formed by Silyl Group Migration: Synthesis and Characterization

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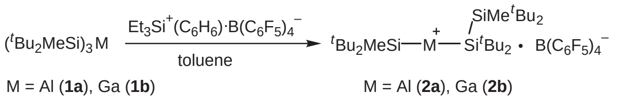
Two-coordinate, sp-hybridized aluminum and gallium cationic species (**2a** and **2b**) were synthesized by the methyl group abstraction from the t-Bu_2MeSi group by Et_3Si^+ followed by 1,2-silyl group migration from group 13 element to the cationic silicon center. X-ray crystal structure analyses confirmed these species to be free cations stabilized by hyperconjugation with a neighboring Si–Si σ bond.

Alkylaluminum compounds, which are among the most fundamental Lewis acids, play an important role in synthetic and polymer chemistry.[1] Low-coordinate cationic organoaluminum complexes have recently received great attention because the cationic dialkylaluminum compounds $[R_2Al^+]$ are of interest as polymerization catalysts.[2] Although Lewis base-stabilized group 13 element cations have been well investigated,[3] the number of examples of two-coordinate aluminum cations reported so far is very limited because of their high reactivity and synthetic difficulties.[4,5] The most general method for the preparation of low-coordinate aluminum cations is halide, hydride, or alkyl abstraction from the corresponding tri-coordinate aluminum compounds by the action of a Lewis acid. Intra- or intermolecular stabilization by the Lewis base is usually necessary to stabilize the newly formed cationic aluminum center. Recent advances in the preparation of bulky ligands for kinetic protection and weakly coordinating anions facilitated the study of these low-coordinate highly reactive cationic species.[6] Recently, Wehmschulte et al. reported aluminum and gallium cations with the two bulky terphenyl ligands,[4] and Reed et al. reported a diethylaluminum cation with a carborane counter anion.[5] Although these compounds are considered as "free" or "free-like" ions in the solid state, the former species are stabilized by intramolecular π-coordination and the latter is stabilized by a weakly coordinating counter anion. Herein, we report a new reaction to synthesize stable two-coordinate aluminum and gallium cationic species, stabilized by σ–π hyperconjugation with a neighboring Si–Si σ bond, which was supported by the solid-state structure analysis and theoretical calculations.

We have shown previously that triethylsilylium tetraarylborates $Et_3Si^+(C_6H_6){\cdot}Ar_4B^-$ are powerful reagents for methyl and halogen abstraction.[7] Indeed, when tris(di-*tert*-butylmethylsilyl)aluminum[8] (200 mg, 0.40 mmol) was treated with $Et_3Si^+(C_6H_6){\cdot}B(C_6F_5)_4^-$ (350 mg, 0.40 mmol) in oxygen-free dry toluene (2 mL) at room temperature, there was an immediate formation of a yellow viscous oil. When the reaction was complete (15 min), the reaction mixture was allowed to separate into two layers: an intense yellow viscous oil as a lower layer and a slightly yellow solution as an upper layer. In the upper layer, triethylmethylsilane (Et_3MeSi) was detected by NMR analysis. The ^1H, ^{13}C, and ^{29}Si NMR spectra of the lower layer confirmed the exclusive formation of $[(t\text{-}Bu_2MeSi)Al^+(Sit\text{-}Bu_2\text{–}SiMet\text{-}Bu_2)][B(C_6F_5)_4^-]$ (**2a**), which was isolated as an air- and moisture-sensitive yellow solid in 78% yield (365 mg) (Scheme 1).[9] Similarly, the reaction of $(t\text{-}Bu_2MeSi)_3Ga$ (**1b**)[8] with $Et_3Si^+(C_6H_6){\cdot}B(C_6F_5)_4^-$ gave the corresponding gallium cationic analog **2b** in 64% yield (Scheme 1).[9]



Scheme 1.

The structures of both **2a** and **2b** were satisfactorily confirmed by NMR spectroscopy, and their molecular structures were determined by X-ray crystallographic analysis.[9,10] Thus, the ^{29}Si NMR chemical shifts of **2a** and **2b** in C_6D_6 displayed three signals (δ 37.0, 18.5, 12.3 for **2a**; 47.8, 33.8, 17.1 for **2b**), of which the low-field signals (δ **2a**: 37.0 and 18.5; **2b**: 47.8 and 33.8) were assigned to the silicon atom attached to the cationic Al and Ga atoms, respectively. These values are considerably shifted to low field compared with the starting **1a** (δ 10.9)[8] and **1b** (δ 20.2)[8] because of the influence of the positive charge.

The structure of **2a** revealed that one of the silicon atoms (Si1), attached to the aluminum atom, was disordered and the major fraction with an occupancy factor of 0.90 is shown in Figure 1.[10] The closest distance between the aluminum and fluorine atoms of $B(C_6F_5)_4^-$ is 6.68 Å, which is much greater than the sum of the van der Waals radii (3.43 Å) of Al and F.[11] Thus, the aluminum species **2a** is a free cation in the solid state. The Si1–Al1–Si2 bond angle is 170.32(4)°, which is nearly linear, indicating that compound **2a** has sp-hybridization of the

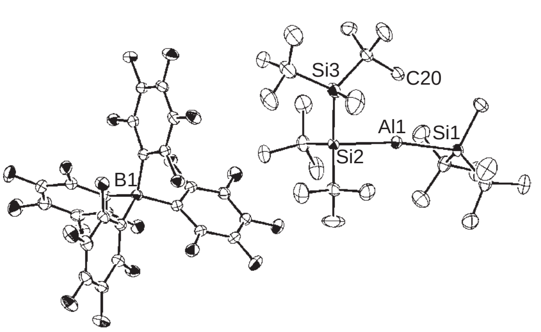
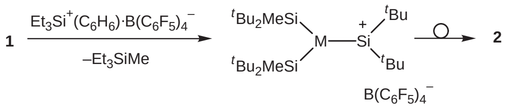


Figure 1. ORTEP drawing of **2a** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. One of the silicon atoms (Si1) was disordered and the major fraction with an occupancy factor of 0.90 is shown. Selected bond lengths (Å) and angles (deg): Al1–Si1 = 2.4969(9), Al1–Si2 = 2.4581(9), Si2–Si3 = 2.4165(9), Si1–Al1–Si2 = 170.32(4), Al1–Si2–Si3 = 97.79(3).



M = Al (**3a**), Ga (**3b**)

Scheme 2.

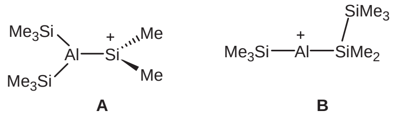
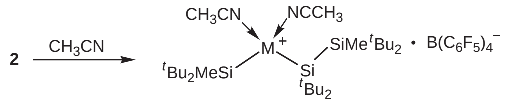


Chart 1.



M = Al (**4a**), Ga (**4b**)

Scheme 3.

aluminum center. The Al–Si bond lengths are 2.4969(9) Å for Si1–Al1 and 2.4581(9) Å for Si2–Al1. Both Al–Si bond lengths are shortened by ca. 2.7% compared with those of the neutral precursor **1a** (av. 2.5468(7) Å).[8] This is apparently due to the increased s-character of aluminum in **2a**: from sp^2-hybridization in **1a** to sp-hybridization in **2a**. It should be noted that the two Al–Si bond lengths are different; the Si2–Al1 bond length is 1.6% shorter than that of Si1–Al1, despite the bulky t-Bu$_2$MeSi group bonded to the Si2 atom. This is due to the hyperconjugative interaction of the Si2–Si3 σ bond with the cationic aluminum center, resulting in the shortening of the Si2–Al bond. To promote such effective hyperconjugation, the bond angle Al1–Si2–Si3 is appreciably reduced to 97.79(3)°. The decrease in the bond angle is also possibly caused by the interaction of a C–H bond of one of the methyls on a terminal *tert*-butyl group (C20) with the cationic aluminum center. Indeed, the Al1–C20 interatomic distance of 2.60 Å is much shorter than the sum of the van der Waals radii (3.90 Å) of C and Al.[11] However, we do not have any spectroscopic evidence for CH–Al$^+$ interaction in solution, even at low temperature.

What is the mechanism to form **2** by the reaction of **1** with Et$_3$Si$^+$? Firstly, demethylation of **1** by Et$_3$Si$^+$ occurred to produce the transient silyl cation **3** and triethylmethylsilane, as shown in Scheme 2. The subsequent migration of the t-Bu$_2$MeSi group to the cationic silicon center resulted in the formation of **2**, facilitated by the hyperconjugative stabilization of the cationic group 13 element center. This is also supported by DFT calculations at the B3LYP/6-31G* level on the relative stability of the model cations **A** and **B** (Chart 1). The two-coordinate aluminum cation **B** is more stable than the three-coordinate silyl cation **A** by 56.4 kJ/mol.

Both cations **2a** and **2b** readily react with acetonitrile to give the acetonitrile adducts, the four-coordinate cation $[(t\text{-Bu}_2\text{MeSi})\text{Al}^+(\text{MeCN})_2(\text{Si}t\text{-Bu}_2\text{–SiMe}t\text{-Bu}_2)][\text{B}(\text{C}_6\text{F}_5)_4{}^-]$ (**4a**) and $[(t\text{-Bu}_2\text{MeSi})\text{Ga}^+(\text{MeCN})_2(\text{Si}t\text{-Bu}_2\text{–SiMe}t\text{-Bu}_2)][\text{B}(\text{C}_6\text{F}_5)_4{}^-]$ (**4b**), respectively, which were quantitatively obtained by the addition of an excess amount of acetonitrile to the two-coordinate cations (Scheme 3).[12] However, in the case of other nucleophiles, such as LiAlH$_4$, MeLi, and Bu$_4$NBr, the reactions were very messy, resulting in unidentified products, probably due to the breaking of the Al–Si bond.

References and Notes

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9 Spectral data for **2a**: yellow crystals, mp 84–86 °C (dec), ^{1}H NMR (C$_6$D$_6$) $\delta - 0.04$ (s, 6H), 0.80 (s, 18H), 0.98 (s, 18H), 1.03 (s, 18H); ^{13}C NMR (C$_6$D$_6$) $\delta - 7.61$, −2.89, 22.1, 22.3, 25.1, 29.4 (2C), 34.0, 123.8–126.0 (m), 136.7 (d, $^1J_{13\text{C}-19\text{F}} = 248$ Hz), 138.5 (d, $^1J_{13\text{C}-19\text{F}} = 248$ Hz), 148.8 (d, $^1J_{13\text{C}-19\text{F}} = 250$ Hz); ^{29}Si NMR (C$_6$D$_6$) δ 12.3, 18.5, 37.0. Spectral data for **2b**: yellow crystals, mp 90–93 °C (dec), ^{1}H NMR (C$_6$D$_6$) $\delta - 0.01$ (s, 6H), 0.79 (s, 18H), 0.90 (s, 18H), 1.02 (s, 18H); ^{13}C NMR (C$_6$D$_6$) $\delta - 7.48$, −2.80, 21.7, 23.0, 26.6, 29.1 (2C), 33.9, 123.2–126.4 (m), 137.3 (d, $^1J_{13\text{C}-19\text{F}} = 245$ Hz), 138.5 (d, $^1J_{13\text{C}-19\text{F}} = 251$ Hz), 149.4 (d, $^1J_{13\text{C}-19\text{F}} = 249$ Hz); ^{29}Si NMR (C$_6$D$_6$) δ 17.1, 33.8, 47.8. The structure of **2b** was unambiguously determined by X-ray crystallography; however, we do not discuss its structural features here because the refinement is not sufficiently good at this moment.

10 Crystal data for **1a** at 120 K: C$_{50}$H$_{60}$AlBF$_{20}$Si$_3$, M_r 1163.04, monoclinic, space group $P2_1/c$, $a = 18.3910(5)$, $b = 16.8790(3)$, $c = 21.2570(5)$ Å, $\beta = 123.088(2)°$, $V = 5528.5(2)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.397$ g cm^{-3}. The final R factor was 0.0575 ($R_w = 0.1824$ for all data) for 9761 reflections with $I > 2\sigma(I)$. GOF = 1.056.

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12 Spectral data for **4a**: colorless crystals, mp 103–106 °C, ^{1}H NMR (C$_6$D$_6$) δ 0.10 (s, 3H), 0.18 (s, 3H), 0.98 (s, 18H), 1.09 (s, 18H), 1.21 (s, 18H), 1.32 (s, 6H, CH$_3$CN); ^{13}C NMR (C$_6$D$_6$) $\delta - 5.60$, −1.54, 0.10 (*C*H$_3$CN), 21.7, 22.3, 24.1, 29.9, 31.5, 34.1, 123.4–125.6 (m), 136.7 (d, $^1J_{13\text{C}-19\text{F}} = 245$ Hz), 137.6 (CH$_3$*C*N), 138.6 (d, $^1J_{13\text{C}-19\text{F}} = 245$ Hz), 148.7 (d, $^1J_{13\text{C}-19\text{F}} = 242$ Hz); ^{29}Si NMR (C$_6$D$_6$) δ 5.87, 6.24, 11.6. Spectral data for **4b**: colorless crystals, mp 109–111 °C, ^{1}H NMR (C$_6$D$_6$) δ 0.12 (s, 3H), 0.16 (s, 3H), 0.93 (s, 18H), 1.00 (s, 18H), 1.16 (s, 18H), 1.21 (s, 6H, CH$_3$CN); ^{13}C NMR (C$_6$D$_6$) $\delta - 5.94$, −1.96, −0.07 (*C*H$_3$CN), 22.1, 22.3, 25.0, 29.3, 31.1, 33.5, 123.5–125.6 (m), 136.6 (d, $^1J_{13\text{C}-19\text{F}} =$ 249 Hz), 137.6 (CH$_3$*C*N), 138.5 (d, $^1J_{13\text{C}-19\text{F}} = 247$ Hz), 148.8 (d, $^1J_{13\text{C}-19\text{F}} = 249$ Hz); ^{29}Si NMR (C$_6$D$_6$) δ 14.3, 19.4, 24.5.