

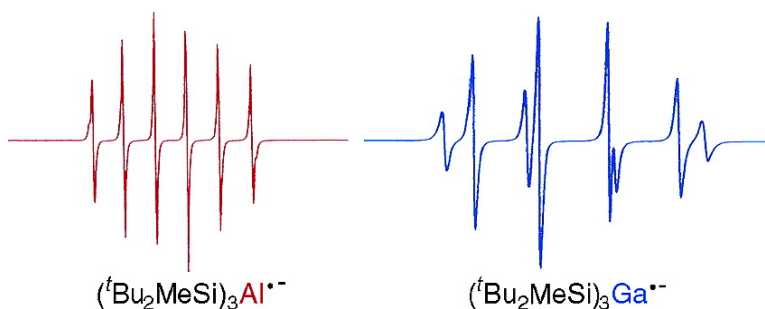
Communication

**Stable Mononuclear Radical Anions of Heavier Group 13
 Elements: [(BuMeSi)E]·[K(2.2.2-Cryptand)] (E = Al, Ga)**

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Stable Mononuclear Radical Anions of Heavier Group 13 Elements: [$(t\text{Bu}_2\text{MeSi})_3\text{E}^{\cdot-}$] $\cdot[\text{K}^+(\text{2.2.2-Cryptand})]$ (E = Al, Ga)

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The chemistry of the radical anions of the group 13 elements has been a topic of discussion for a long time.^{1,2} EPR studies of $\text{H}_3\text{E}^{\cdot-}$ (E = B, Al, Ga) suggest that the borane radical anion is planar,³ like the isoelectronic methyl radical. Indeed, a planar geometry around the B atom in the lithium salt of $[\text{BMe}_3]^{+\cdot-}$ (Mes = 2,4,6-trimethylphenyl) was reported by Power et al.^{2b} In contrast, the alane and gallane radical anions, the heavier congeners of $\text{H}_3\text{B}^{\cdot-}$, are pyramidal,^{4,5} similar to the cases of the isoelectronic silyl and germyl radicals. The large isotope ^{27}Al or ^{69}Ga and ^{71}Ga hyperfine splitting constants of $\text{H}_3\text{Al}^{\cdot-}$ and $\text{H}_3\text{Ga}^{\cdot-}$ correspond to ca. 16% unpaired electron population in the Al 3s and Ga 4s orbitals, respectively. As the stable heavier radical anions of Al, Ga, and In, dimetallanes of the type $[\text{R}_2\text{EER}_2]^{+\cdot-}$, and clusters of the types $[\text{E}_4\text{R}_4]^{+\cdot-}$, $[\text{E}_6\text{R}_6]^{+\cdot-}$, or $[\text{E}_9\text{R}_9]^{+\cdot-}$ have been recently reported.⁶ However, despite a great interest in the heavier congeners of $\text{R}_3\text{B}^{\cdot-}$, the stable $\text{R}_3\text{E}^{\cdot-}$ (E = Al, Ga, In) species are missing due to the synthetic difficulty associated with concomitant formation of metal under the reaction conditions.⁷ Meanwhile, we have reported the effective steric protection by di-*tert*-butylmethylsilyl groups that permits us to isolate stable heavier group 14 element radical species, including tris(di-*tert*-butylmethylsilyl)silyl,⁸ -germyl,⁸ and -stannyl⁹ radicals, which undergo both one-electron reduction and oxidation to produce the corresponding anionic¹⁰ and cationic¹¹ species, respectively. Thus, it is quite interesting to introduce three bulky $t\text{Bu}_2\text{MeSi}$ groups on the heavier group 13 elements to design the precursors of the radical anions. In this communication, we report the synthesis of stable tris(di-*tert*-butylmethylsilyl)aluminum and gallium radical anions, the first stable species in which both unpaired electron and negative charge are situated on the same atom, which has been fully characterized by X-ray crystallography and EPR spectroscopy.

First, we synthesized $(t\text{Bu}_2\text{MeSi})_3\text{Al}$ (**1**) by the reaction of AlCl_3 with 3 equiv of $t\text{Bu}_2\text{MeSiNa}$ in pentane to yield yellow crystals of **1** in 71% yield. In a similar manner, $(t\text{Bu}_2\text{MeSi})_3\text{Ga}$ (**2**) was also prepared in 32% yield. Both compounds were unambiguously identified by NMR and X-ray analysis.¹² The interesting structural features of **1** and **2** are as follows: (1) all methyl substituents at the peripheral Si atoms are arranged in a clockwise manner, thus minimizing the steric repulsion of the bulky *t*Bu groups, (2) the sum of the bond angles around the central aluminum or gallium atom is 360.0° , (3) the average bond lengths of Al–Si in **1** and Ga–Si in **2** are 2.5468(7) Å and 2.5105(11) Å, respectively.

The reaction of **1** and **2** with alkali metals (Li, Na, K) in THF immediately took place, accompanied with a color change from yellow to dark red. After the removal of THF and insoluble materials, the residue was crystallized from hexane to give the corresponding radical anions $[(t\text{Bu}_2\text{MeSi})_3\text{Al}]^{+\cdot-}$ (**3**) and $[(t\text{Bu}_2\text{MeSi})_3\text{Ga}]^{+\cdot-}$ (**4**), which were isolated in the form of the potassium salt as extremely air- and moisture-sensitive, deep red crystals (Scheme 1).¹³

A deep red single crystal of **3** as the solvent-separated ion pair salt was obtained by recrystallization from benzene–THF in the

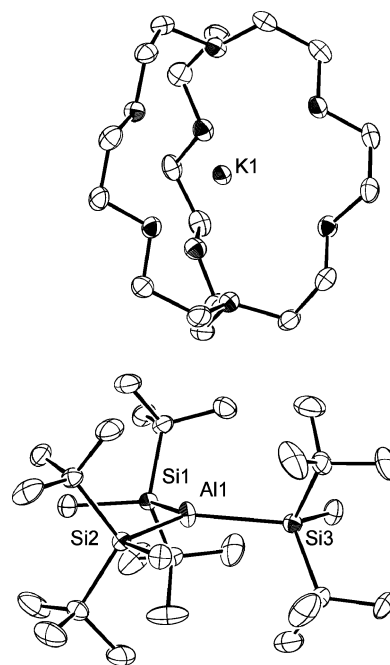
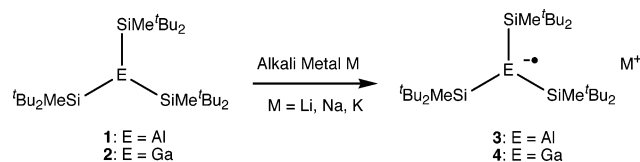


Figure 1. ORTEP drawing of **3**· $[\text{K}^+(\text{2.2.2-cryptand})]$ ·benzene. Hydrogen atoms and benzene molecule are omitted for clarity. Selected bond lengths (Å): Si1–Al1 = 2.5031(10), Si2–Al1 = 2.4997(10), Si3–Al1 = 2.5087(10). Selected bond angles (deg): Si2–Al1–Si1 = 119.55(4), Si2–Al1–Si3 = 118.70(4), Si1–Al1–Si3 = 120.15(4).

Scheme 1



presence of 2.2.2-cryptand (Figure 1).¹⁴ Similar to the precursor **1**, the methyl substituents on the Si atoms all lie in the Al(1)–Si(1)–Si(2)–Si(3) mean plane, apparently to minimize the steric hindrance. The geometry around Al in **3**· $[\text{K}^+(\text{2.2.2-cryptand})]$ is nearly planar (sum of the bond angles = 358.4°), due to both the steric and electronic influences of the bulky electropositive $t\text{Bu}_2\text{MeSi}$ substituents. The average Al–Si bond length in **3** is 2.5038(10) Å, which is slightly shorter than that of the neutral precursor **1** by 0.04 Å. This characteristic bond shortening by one-electron reduction can be rationalized in terms of the hyperconjugative attractive interaction between the SOMO (3pz) and neighboring Si–C(*t*Bu) σ^* orbitals. The existence of the monomeric structure of **3** is ascribed to severe steric repulsion by the three bulky $t\text{Bu}_2\text{MeSi}$ groups, which can force the molecule into a monomeric and nearly planar structure. Consequently, the unpaired electron

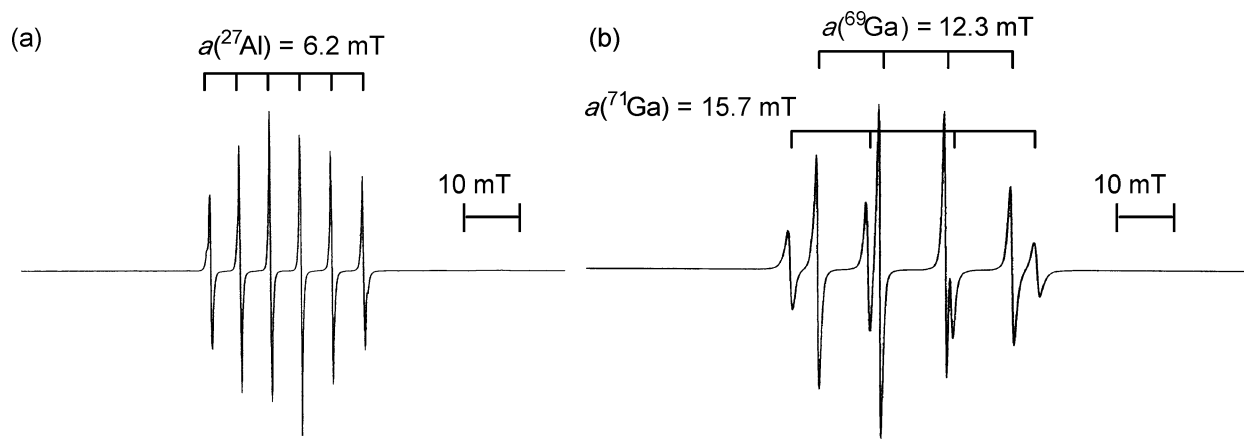


Figure 2. ESR spectra of **3** (a) and **4** (b) in THF solution at 298 K.

predominantly occupies the 3pz orbital of the Al atom. The structural features of **4**·[K⁺(2.2.2-cryptand)] are also similar to those of **3**·[K⁺(2.2.2-cryptand)].¹⁵

The planarity of both **3** and **4** in solution was also evidenced by the EPR study. The EPR spectrum of **3** in THF solution shows a well-resolved sextet (²⁷Al; *I* = 5/2, 100%) at *g* = 2.005 (Figure 2a) with the hyperfine coupling constants of *a*(²⁷Al) = 6.2 mT. In the case of **4**, the EPR spectrum shown in Figure 2b appears as two sets of quartets (⁶⁹Ga; *I* = 3/2, 60.1%; ⁷¹Ga; *I* = 3/2, 39.9%) at *g* = 2.015 with *a*(⁶⁹Ga) = 12.3 mT and *a*(⁷¹Ga) = 15.7 mT. The rather small hyperfine coupling constants for both radical anions relative to H₃Al^{•−} (15.4 mT)⁴ and H₃Ga^{•−} (42.0 mT for ⁶⁹Ga, 53.4 mT for ⁷¹Ga)⁵ clearly indicate that these species are planar π -radicals, as found in the crystal structures. Because the splitting pattern of the central part was independent of the counteranions, these radical anions exist as a solvent-separated ion pair in THF.

The X-ray data and EPR studies of **3** and **4** imply that the addition of one electron to **1** or **2** has a small effect on its structure. Apart from the slight shortening of the Si–E bonds in **3** and **4**, the remaining structural parameters are virtually identical, indicating that the extra electron is mainly localized in the pz orbitals of the heavier group 13 elements, in contrast to H₃Al^{•−} and H₃Ga^{•−}. Both radical anions **3** and **4** readily undergo one-electron oxidation with [Ph₃C⁺][B[−](C₆F₅)₄], giving **1** and **2**.

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Supporting Information Available: Experimental procedures and spectral data for **1**, **2**, **3**, and **4** and tables of crystallographic data including atomic positional and thermal parameters for **1**, **2**, and **3**·[K⁺(2.2.2-cryptand)]·benzene (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) For the experimental procedures, spectral data, and X-ray data of **1** and **2**, see Supporting Information.
- (13) For the experimental procedures of **3** and **4**, see Supporting Information.
- (14) Crystal data for **3**·[K⁺(2.2.2-cryptand)]·benzene at 120 K: MF = C₄₈H₁₀₂-AlKN₂O₆Si₃, MW = 953.67, Triclinic, *P*1, *a* = 12.2120(5), *b* = 14.9660(7), *c* = 16.5990(9) Å, α = 85.441(3), β = 84.227(3), γ = 83.410(3)°, *V* = 2991.3(2) Å³, *Z* = 2, *D*_{calcd} = 1.059 g·cm^{−3}. The final *R* factor was 0.0623 for 8734 reflections (*I*_o > 2σ(*I*_o)) (*R*_w = 0.1915 for all data), GOF = 1.088.
- (15) The structure of **4**·[K⁺(2.2.2-cryptand)]·benzene was determined by X-ray crystallography; however, the refinement was insufficient to discuss the structure in detail.

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