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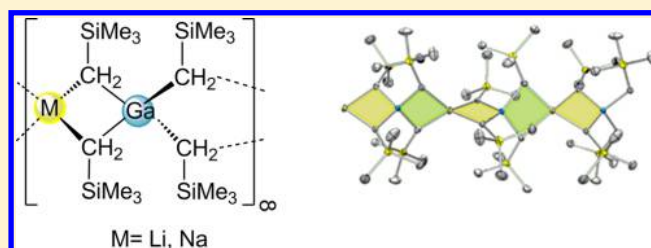
Co-complexation Syntheses, Structural Characterization, and DFT Studies of a Novel Series of Polymeric Alkali-Metal Tetraorganogallates

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S Supporting Information

ABSTRACT: Exploring the co-complexation reactions between the gallium alkyl $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and alkali-metal alkyl $\text{MCH}_2\text{SiMe}_3$ ($\text{M} = \text{Li}, \text{Na}, \text{or K}$) using an arene/hexane solvent mixture has allowed the isolation of solvent-free alkali-metal tetraorganogallates $[\{\text{MGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty]$ ($\text{M} = \text{Li}, \mathbf{1}$; $\text{Na}, \mathbf{2}$) and related benzene adduct $[\{(\text{C}_6\text{H}_6)_2\text{KGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty]$ ($\mathbf{3}$). By combining X-ray crystallography, NMR spectroscopy, and DFT calculations, this study sheds new light on the constitution of these mixed-metal species. X-ray crystallographic studies reveal that all gallates exhibit novel polymeric arrangements, with $\mathbf{1}$ and $\mathbf{2}$ sharing the same linear chain structure, made up exclusively of $\text{M}-\text{C}$ and $\text{Ga}-\text{C}$ bonds, whereas $\mathbf{3}$ displays a significantly more open structural motif, where the K and Ga atoms are connected by a single alkyl bridge and propagation occurs via weaker $\text{K}\cdots\text{Me}$ electrostatic interactions of a methyl from a SiMe_3 group of an alkyl ligand from one monomer to the potassium from a neighboring monomeric unit. Multinuclear NMR spectroscopic studies suggest that in deuterated benzene solutions $\mathbf{1}-\mathbf{3}$ exist as discrete solvent-separated ion-pair species where the alkali-metal is solvated by the arene solvent. DFT calculations show that while the infinite aggregation of these polymeric structures is key for thermodynamically favoring the formation of $\mathbf{1}$ and $\mathbf{2}$, in the case of $\mathbf{3}$ the solvation of unsaturated potassium by two molecules of benzene, via π -electrostatic interactions, appears to be the major contributor to its overall stability.



INTRODUCTION

Pioneered by Dennis in 1932,¹ organogallium compounds have attracted widespread interest from the scientific community over the recent decades due to their diverse applications in areas such as coordination chemistry,² homogeneous catalysis,³ materials science,⁴ and chemotherapeutics.⁵ Combining a moderate Lewis acid character with the presence of relatively low polarity metal–carbon bonds (when compared with other utility homometallic reagents such as organolithium or organomagnesium reagents),⁶ organogallium reagents' use in organic synthesis has increasingly become more prominent,⁷ boasting distinct reactivities from those observed for related group 13 (organoboron and organoaluminum) compounds. Thus, these gallium reagents find widespread application as selective alkylating reagents in transition-metal-catalyzed cross-coupling reactions⁸ and addition reactions to activated olefins,⁹ aldehydes, and ketones,¹⁰ as well as promoting effective carbometallation (carbogallation) reactions of carbon–carbon triple bonds.¹¹

Recent advances in mixed-metal chemistry have shown that by pairing metals with different polarities within the same molecule (as for example Mg , Zn , or Al with an alkali-metal), novel bimetallic ('ate') reagents can be prepared that display unique synergic chemical profiles, including a superior reactivity and functional group tolerance, combined with selectivity patterns distinct from those exhibited by their monometallic

components.¹² Important landmarks in this area include the development of Turbo Grignard reagents "RMgX·LiCl", whose enhanced nucleophilicity allows access to highly functionalized Grignard reagents via Mg –halogen exchange reactions¹³ or the use of heterobimetallic amides in alkali-metal-mediated metalation (AMMM) processes, which facilitate direct zincation, magnesiation, aluminatation, or manganation of a wide range of organic molecules, affording in certain cases synergic regioselectivities, not usually available using single-metal bases.¹⁴ Within the context of mixed-alkali-metal–gallium compounds, *in situ* prepared heteroleptic lithium tetraorganogallates have been employed for the chemoselective transfer of aryl or alkyl groups to acyl chlorides, yielding ketones in excellent yields.¹⁵ These bimetallic combinations can also react effectively with α,β -unsaturated carbonyl compounds to produce the relevant 1,4- and/or 1,2- Michael addition products.¹⁶ Furthermore, Okuda has recently reported the first example of 1,2-insertion reactions of pyridine derivatives mediated by potassium tetraalkyl gallates.¹⁷ In closely related work, Neumüller has shown that the addition of substoichiometric amounts of CsF to trimethyl gallium catalyzes the trimerization of acetonitrile to yield a six-membered-ring metallacycle, where the 'ate' complex $\text{Cs}[\text{GaMe}_3\text{F}]$, postulated

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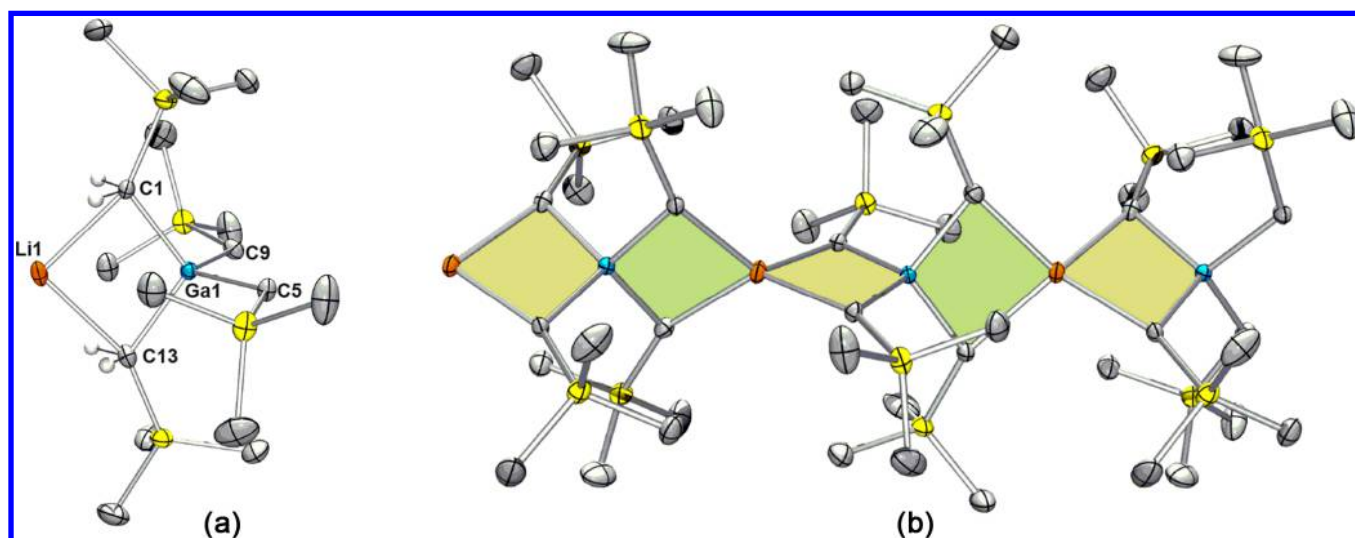
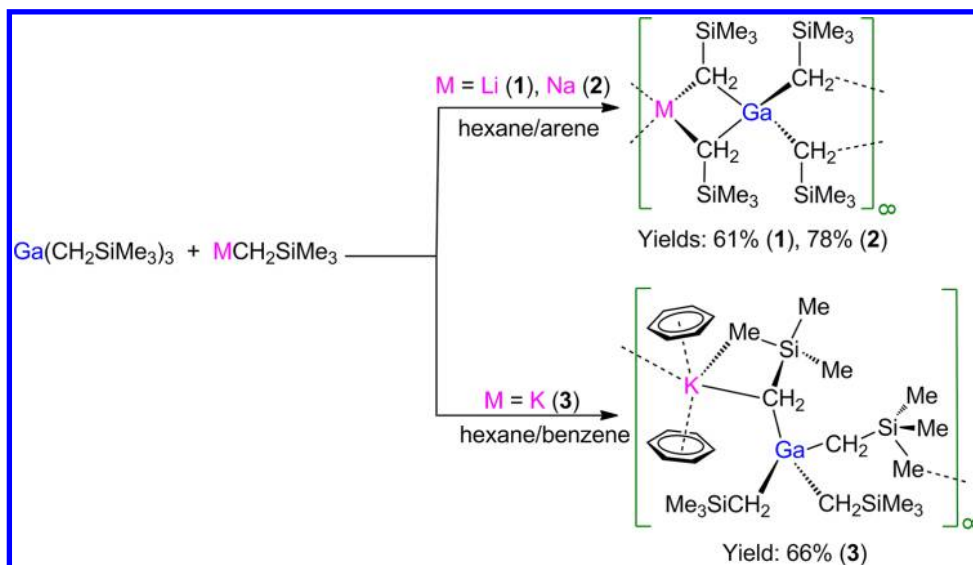
Scheme 1. Co-complexation Reactions of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ with $\text{MCH}_2\text{SiMe}_3$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$)

Figure 1. Solid-state structure of **1** as determined by single-crystal X-ray crystallography with $[\text{LiGaC}]$ rings shaded in yellow and green (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms, except those of CH_2 bridges in Figure 1a, have been omitted for clarity): (a) asymmetric unit; (b) section of the 1D polymeric chain.

to be the active species of the reaction, facilitates the deprotonation of the nitrile, initiating the trimerization process.¹⁸

Surprisingly, despite this growing interest that alkali-metal tetraorganogallates are attracting and their synthetic usefulness, there is an extensive lack of information on the constitution of these bimetallic species, which more often than not are prepared *in situ*.^{15,16} Thus, despite a handful of structural studies on solvated alkali-metal gallium tetraorganogallates,^{17,19} to date the structures of unsolvated compounds have proved elusive with the exception of heteroleptic $[\text{Li}\{\text{tBu}_2\text{Ga}(\text{CH}_2\text{N}^i\text{Pr}_2)_2\}]$ reported by Mitzel, in which the amido N^iPr_2 groups act as internal donors coordinating to Li, giving rise to a monomeric cyclic structure.²⁰

Herein we provide new synthetic and theoretical insights into the formation of homoleptic alkali-metal gallates by systematically studying the co-complexation reactions of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ with a homologous series of alkali-metal alkyl compounds $\text{MCH}_2\text{SiMe}_3$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$). By performing these

reactions in the absence of a Lewis donor, we isolate and present the first structural elucidations of polymeric alkali-metal tetraorganogallates, including solvent-free $[\text{MGa}(\text{CH}_2\text{SiMe}_3)_4]_n$ ($\text{M} = \text{Li}, \text{1}; \text{Na}, \text{2}$) and benzene-solvated $[\{(\text{C}_6\text{H}_6)_2\text{KGa}(\text{CH}_2\text{SiMe}_3)_4\}]_n$ (**3**). The constitutions of these novel bimetallic species are revealed by multinuclear NMR spectroscopy. Furthermore, with the aid of DFT calculations, we establish that aggregation and π -arene coordination play major roles in thermodynamically driving these co-complexation reactions of the homometallic reagents.

RESULTS AND DISCUSSION

Syntheses. Recent studies in alkali-metal chemistry have found that group 1 alkyl complexes containing silyl-substituted methyl groups can display an enhanced stability.²¹ This is primarily due to their lack of β -hydrogens as well as to their considerable steric bulk and electronic stabilization, when compared to carbon-only-based alkyl groups.²² Furthermore, some of our own previous work on the synthesis of alkali-metal

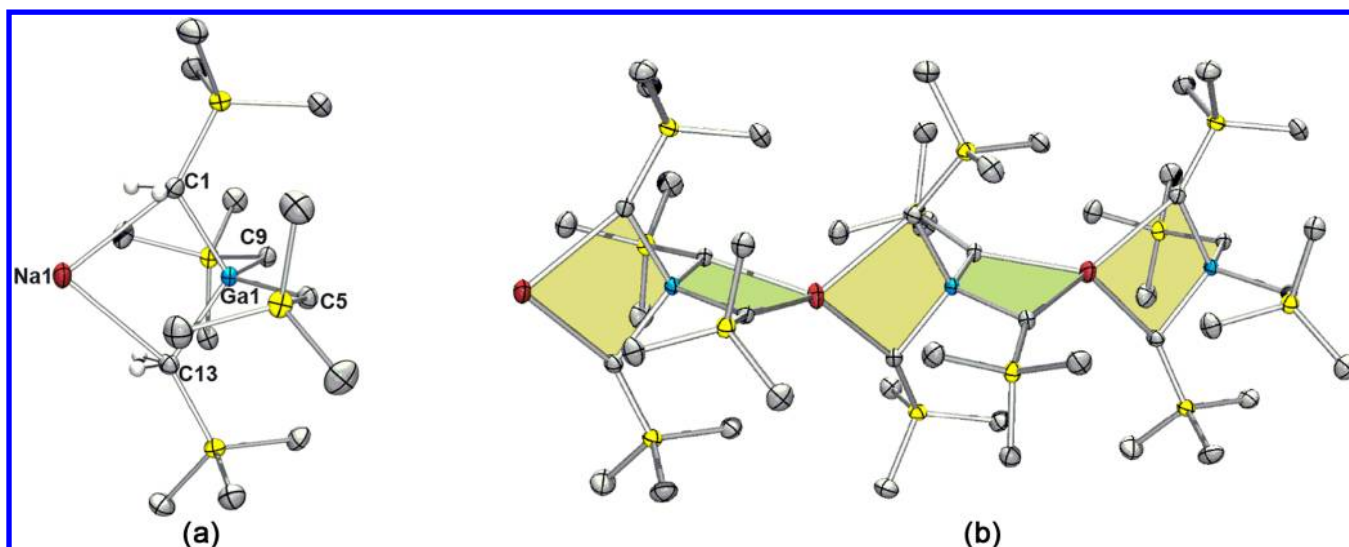


Figure 2. Solid-state structure of **2** as determined by single-crystal X-ray crystallography with [NaCGaC] rings shaded in yellow and green (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms, except those of CH₂ bridges in part a, have been omitted for clarity): (a) asymmetric unit; (b) part of the 1D polymeric chain.

magnesiates has shown that bimetallic compounds containing these alkyl groups exhibit an excellent solubility in nonpolar solvents such as hexane or benzene.²³ Thus, we chose the monosilyl CH₂SiMe₃ group as the anionic ligand for our study. First we studied the co-complexation reactions of equimolar amounts of the monometallic alkyls Ga(CH₂SiMe₃)₃²⁴ and LiCH₂SiMe₃²⁵ using noncoordinating hexane as a solvent, which resulted in the immediate precipitation of a white solid, suggesting the formation of a mixed-metal complex, since on their own both homometallic reagents are highly soluble in hexane. Addition of toluene and gently heating of the resulting suspension afforded a colorless solution, which deposited colorless needle-shaped crystals of the tetraorganogallate [LiGa(CH₂SiMe₃)₄]_∞ (**1**) in 61% isolated yield. Using the same co-complexation approach for the heavier alkali-metal alkyls MCH₂SiMe₃ (M = Na,²⁶ K²⁷), but employing benzene rather than toluene as a cosolvent, led to the isolation of the congeneric sodium [{NaGa(CH₂SiMe₃)₄]_∞ (**2**) and potassium [{(C₆H₆)₂KGa(CH₂SiMe₃)₄]_∞ (**3**) gallates in yields of 78% and 66%, respectively (Scheme 1).

Homoleptic alkali-metal gallates **1–3** were characterized by multinuclear NMR spectroscopy, and their structures were elucidated by X-ray crystallography, which confirmed their bimetallic constitution (see Experimental Section for details).

Solid-State Structures. Unsolvated alkali-metal gallates **1** and **2** share the same structural motif in the solid state (Figure 1 and Figure 2), displaying a polymeric structure comprising {MGa(CH₂SiMe₃)₄} units (M = Li, **1**; Na, **2**) where two of the alkyl groups act as bridges between the alkali-metal and Ga to form a planar four-membered [MCGaC] ring (shaded in yellow in Figures 1b and 2b; sum of the internal angles, 359.9° and 359.5° for **1** and **2** respectively). The remaining two alkyl groups on Ga bond to an alkali-metal of a neighboring unit through their methylene anion, closing a second planar four-membered [GaCMC] ring (shaded in green in Figures 1b and 2b; sum of the internal angles 360.0° and 359.5° for **1** and **2**, respectively), which gives rise to a 1D chain structure made up of an infinite near-linear arrangement [as evidenced by M⋯Ga⋯M, 177.5(13)° and 173.43(3)°; Ga⋯M⋯Ga, 178.95(19)° and 172.13(4)°, for **1** and **2**, respectively] of

[MCGaC] and [GaCMC] rings, fused by their metal vertexes, in a staggered orthogonal disposition. Interestingly, while the angles between these four-membered planes fused by a Ga atom are close to 90° [89.8° and 89.6° for **1** and **2**, respectively], a significant deviation from orthogonality is observed for the angles of these planes which shared a alkali-metal vertex, which is especially significant in the case of **1** [68.0° vs 85.6° for **2**].

A close inspection of the different alkali-metal–carbon distances in **1** and **2** (Table 1) revealed that there is no

Table 1. Selected Bond Distances (Å) for Gallates **1–3**

	M = Li (1)	M = Na(2)	M = K (3)
Ga1–C9	2.050(3)	2.056(3)	2.028(6)
Ga1–C5	2.044(3)	2.047(3)	2.041(6)
Ga1–C1	2.045(3)	2.062(3)	2.072(6)
Ga1–C13	2.041(3)	2.054(3)	2.047(6)
mean Ga–C	2.045	2.054	2.047
M–C1	2.366(6)	2.712(3)	3.155(6)
M–C13	2.333(5)	2.692(3)	
M–C5'	2.380(6)	2.690(3)	
M–C9'	2.351(6)	2.692(3)	
mean M–C	2.357	2.697	
K–C2			3.298(7)
K–C10'			3.401(7)

significant variations that would define a specific molecular unit [i.e., Li–C bond distances in the asymmetric unit of **1** are 2.366(6) and 2.333(5) Å vs 2.380(6) and 2.351(6) Å for the Li–C contacts with the neighboring {LiGaR₄} unit]. Furthermore these distances [average M–C, 2.357 Å for M = Li; 2.697 Å for M = Na] are similar to those found in discrete lithium²⁸ and sodium²⁹ ate compounds and in monometallic alkyl species³⁰ containing bridging monosilyl groups. Similarly, very little difference is observed within the Ga–C bond lengths of **1** and **2** [ranging from 2.050(3) to 2.041(3) Å for **1** and from 2.047(3) to 2.062(3) Å for **2**], which lie in a range similar to those found in other gallate compound containing bridging alkyl groups,^{23b,31} but, as expected, they are considerably

elongated compared to those of monomeric $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ [average Ga–C, 1.959 Å], where the alkyl groups bind terminally to Ga.²⁴ Thus, the extended chain structures displayed by **1** and **2** can be envisaged as the result of a regular arrangement of alkali-metal (M) and Ga cations that are held together by a combination of relatively short (strong) electron-deficient M–C and Ga–C bonds.

Both Ga and M centers exhibit distorted tetrahedral environments (Table 2). Reflecting the more covalent character

Table 2. Selected Bond Angles (°) for Compounds **1**–**3**

	M = Li (1)	M = Na (2)	M = K (3)
C13–Ga1–C5	108.97(13)	107.12(11)	111.7(3)
C13–Ga1–C1	107.62(12)	113.97(11)	109.4(3)
C5–Ga1–C1	109.54(13)	107.36(11)	105.8(2)
C13–Ga1–C9	110.44(13)	107.51(11)	108.3(3)
C5–Ga1–C9	108.77(12)	113.16(11)	110.6(2)
C1–Ga1–C9	110.59(13)	107.86(12)	111.1(3)
mean C–Ga–C	109.32	109.49	109.48
C13–M1–C9'	133.2(3)	139.04(9)	
C13–M1–C1	89.13(19)	79.39(10)	
C9'–M1–C1	108.4(2)	122.13(9)	
C13–M1–C5'	109.1(2)	123.78(9)	
C9'–M1–C5'	89.40(19)	79.02(10)	
C1–M1–C5'	134.3(2)	118.69(9)	
mean C–M–C	110.58	110.34	
C1–K1–C10'			136.87(19)
C2–K1–C10'			78.98(17)
Ct1–K1–Ct2			167.94

of the Ga–C vs the M–C bonds, this distortion is considerably more severe for the geometry around M (τ_4 parameters³² 0.66 and 0.69 for **1** and **2**, respectively) than for that of Ga (τ_4 parameters 0.94 and 0.99 for **1** and **2**, respectively). Furthermore, both **1** and **2** display almost identical Ga–C distances (mean distance of 2.045 Å in **1** and 2.054 Å in **2**) to those described for the solvent-separated yttrium gallate [$\{\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_4\}^+\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_4\}^-$] (mean distance, 2.041 Å), where the four monosilyl groups bind terminally to Ga.³³ This can be rationalized in terms of the concept of anchoring and ancillary bonding in mixed-metal compounds introduced by Mulvey.³⁴ Thus, the foundation of the structure is provided by anchoring σ -based Ga–C bonds, as they comprise the stronger, more covalent interactions, whereas

the alkali metal ions affix to this framework via ancillary bonds to give contacted ion pairs.³⁵

As far as we can ascertain, **1** and **2** represent the first examples of unsolvated alkali-metal tetraorganogallates to be structurally defined with the exception of heteroleptic [$\text{Li}\{\text{Bu}_2\text{Ga}(\text{CH}_2\text{N}^i\text{Pr}_2)_2\}$] reported by Mitzel,²⁰ which contrastingly with **1** and **2** exhibits a monomeric arrangement where the bis(amino)methylgallate anion coordinates to Li as a bidentate anion through its N-donor appendages, forming a six-membered [LiNCGaCN] ring. Furthermore, highlighting the scarcity of structural studies on mixed alkali-metal gallium chemistry and the general novelty of **1** and **2**, a search of the CSD³⁶ revealed no hits for either solvated or unsolvated sodium tetraorganogallates. The closest precedent to **2** is the trimethylhypersilanidogallate [$\{(\text{toluene})\text{Na}(\mu\text{-Me})_2\text{Ga}(\text{Hsi-Me})_\infty\}$] (Hsi = $\text{Si}(\text{SiMe}_3)_3$), in which the terminal methyl attached to Ga interacts with the Na center of a neighboring unit, giving rise to a polymeric chain.^{37,38} The polymeric ring-fused chain assembly of **1** and **2** has no precedents in mixed-metal chemistry; however it is somewhat reminiscent of the recently reported structures for the carbene complex $^t\text{Bu}_8\text{Mg}_4\cdot 2\text{IPr}$ (resulting from the trapping of a tetranuclear fragment of presumably polymeric $^t\text{Bu}_2\text{Mg}$)³⁹ and lithium magnesiate [$\{(\text{dioxane})\text{Li}_2\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_6\}_\infty$], whose core contains a [MgCMgC] planar four-membered ring that is orthogonal to two adjacent [LiCMgC] rings, although in this case the lithium atoms are also solvated by dioxane, which act as linkers between the $\{\text{Li}_2\text{Mg}_2(\text{CH}_2\text{SiMe}_3)_6\}$ units.^{23b}

The infinitely aggregated structures of **1** and **2** contrast with previous solvated structures of alkali-metal tetraorganogallates, which depending on the hapticity and donor ability of the Lewis base employed can exhibit a contacted ion-pair structure like that described for dimeric [$\{(1,4\text{-dioxane})_3(\text{LiGa}(\text{CH}_2\text{SiMe}_3)_4)_2\}$]^{19c} or a solvent-separated ion-pair structure (like for example that reported for [$\{\text{Li}(\text{THF})_4\}^+\{\text{Ga}(\text{fluorenyl})_4\}^-$]),^{19a} which precludes any possible type of metal–metal communication between the alkali-metal and gallium.^{12b}

Switching to the heavier alkali-metal potassium led to the isolation of benzene-solvated potassium gallate **3** (Figure 3). Displaying also a polymeric arrangement, the basic repeat unit in **3** features a significantly more open structural motif (Figure 3a), where both metals are connected by a single alkyl group, which coordinates to potassium in an unusual ambidentate fashion through its methylene unit [K1–C1, 3.155(6) Å] and one methyl of the SiMe_3 group [K1–C2, 3.298(7) Å], closing a

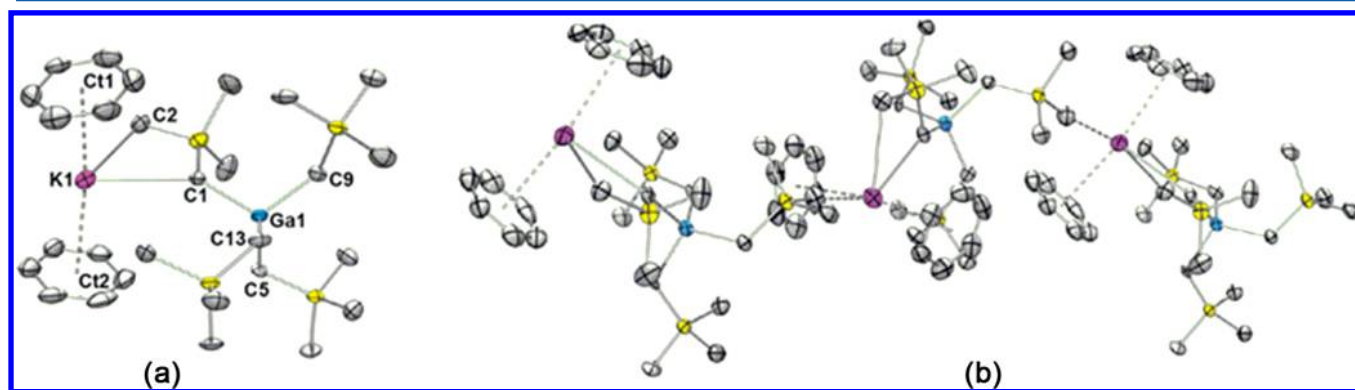


Figure 3. Solid-state structure of **3** as determined by single-crystal X-ray crystallography (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms have been omitted for clarity): (a) asymmetric unit; (b) part of the 1D polymeric chain.

Table 3. Chemical Shifts (ppm) in the ^1H and ^{13}C NMR Spectra of the Standards $\text{Li}(\text{CH}_2\text{SiMe}_3)$, $\text{Na}(\text{CH}_2\text{SiMe}_3)$, $\text{K}(\text{CH}_2\text{SiMe}_3)$, and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and the New Gallates 1–3 in Deuterated Benzene Solution

compound	$\delta^1\text{H}(\text{CH}_2)$	$\delta^1\text{H}(\text{CH}_3)$	$\delta^{13}\text{C}(\text{CH}_2)$	$\delta^{13}\text{C}(\text{CH}_3)$
$\text{Li}(\text{CH}_2\text{SiMe}_3)$	−2.03	0.16	−4.45	3.36
$\text{Na}(\text{CH}_2\text{SiMe}_3)^a$	−2.44	0.15		
$\text{K}(\text{CH}_2\text{SiMe}_3)^a$	−2.60	0.18		
$\text{Ga}(\text{CH}_2\text{SiMe}_3)$	0.13	0.13	12.69	2.49
$[\{\text{LiGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty] (1)^b$	−1.13	0.24	1.73	3.48
$[\{\text{NaGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty] (2)$	−1.06	0.25	3.00	3.58
$[\{\text{C}_6\text{H}_6\}_2\text{KGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty] (3)$	−1.01	0.31	4.33	3.91

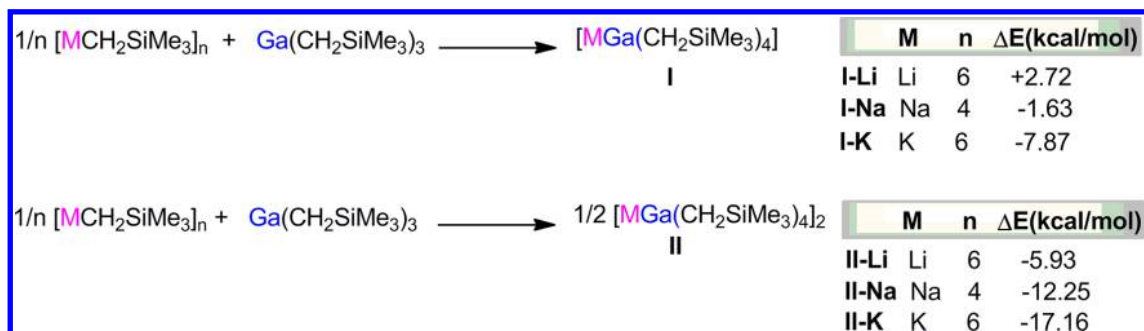
^aLow solubility and poor stability of $\text{M}(\text{CH}_2\text{SiMe}_3)$ ($\text{M} = \text{Na}, \text{K}$) precluded the acquisition of meaningful ^{13}C NMR spectra. ^bNMR spectra of 1 showed the presence of small amounts of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and tetramethylsilane.

four-membered $\{\text{KCSiC}\}$ ring. Potassium completes its coordination by engaging with the $\text{C}=\text{C}$ π -bonds of two molecules of benzene, which lie approximately *trans* to each other [$\text{Ct1}-\text{K}-\text{Ct2}$, 167.9° , where Ct represents the centroid of the benzene ring].⁴⁰ Analysis of the $\text{K}-\text{C}_{\text{benzene}}$ distances shows that while one of the benzene molecules is essentially η^6 -coordinated by the K atom [$\text{K}-\text{C}$ distances lie in the narrow range 3.360–3.507 Å; $\text{K}-\text{Ct1}$, 3.134 Å], the remaining molecule binds in an η^3 -fashion [with the shorter $\text{K}-\text{C}$ distances in the range 3.220–3.384 Å and longer distances between 3.554 and 3.690 Å; $\text{K}-\text{Ct2}$, 3.183 Å]. Noticeably, the $\text{K}-\text{C}(\text{methylene})$ distance in 3 is considerably elongated compared to those reported for homometallic $[\{\text{PMDETA}-\text{K}(\text{CH}_2\text{SiMe}_3)\}_\infty]$ (PMDETA = N,N,N',N'',N''' -pentamethyldiethylenetriamine),²¹ which also exhibits a chain structure where the potassium atoms are connected by bridging alkyl groups [average $\text{K}-\text{C}$, 2.975 Å]. These facts coupled with the remarkably long intermetallic distance $\text{K}\cdots\text{Ga}$ [4.971(2) Å] and much wider $\text{K}-\text{C1}-\text{Ga}$ bond angle [$143.1(3)^\circ$] when compared to those found in 1 and 2 [2.855(5) and 3.193(2) Å, and $81.09(16)^\circ$ and $82.77(9)^\circ$, respectively] suggest that 3 can be envisaged as an intermediate between solvent-separated ion pair $[\{\text{K}(\text{benzene})_2\}^+\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_4\}^-]$ and a closed four-membered $\{\text{MCGaC}\}$ ring structure similar to those found in contacted ion-pair gallates 1 and 2. Supporting this interpretation, a comparison of the $\text{Ga}-\text{C}$ distances in 3 (Table 1) showed very little variation between that of the bridging alkyl group and those found for the terminal ligands. Furthermore, highlighting the covalent/anchoring character³⁴ of the $\text{Ga}-\text{C}$ bonds present in 3, these distances are also very close to those witnessed in 1 and 2 (Table 1). As mentioned above, 3 displays a polymeric arrangement, where potassium attains a higher coordination number by forming a long-distance electrostatic interaction with one Me of a SiMe_3 group of a terminal alkyl group bonded to Ga from a neighboring $\{(\text{benzene})_2\text{KGa}(\text{CH}_2\text{SiMe}_3)_4\}$ unit [Figure 3b, $\text{K}-\text{C10}'$, 3.401(7) Å], giving rise to a zigzag chain structure, where the monomeric units assemble in a staggered disposition [$\text{K1}\cdots\text{Ga1}\cdots\text{K1}'$, $136.75(2)^\circ$; $\text{Ga1}-\text{K1}'-\text{Ga1}'$, $149.64(3)^\circ$].⁴¹ This propagation mode is in sharp contrast with that observed for unsolvated gallates 1 and 2, where the polymeric chain is constructed by the formation of short (strong) intermolecular bonds of the alkali-metals with the anionic methylene groups of the two terminal alkyl ligands attached to Ga. Within the context of mixed potassium–gallium chemistry, the closest structural precedent to 3 is the unsolvated mixed alkyl-hydride gallate $[\{\text{KGa}(\text{CH}_2\text{SiMe}_3)_3\text{H}\}]$. Although the authors initially describe this compound as a discrete arrangement of separated K^+ and $\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_3\text{H}\}^-$ ions,⁴² a close inspection of the

crystallographic data shows that it forms a complicated 3D network made up of intermolecular $\text{K}\cdots\text{alkyl}$ interactions. These polymeric arrangements contrast with the discrete dimeric structure recently reported for the potassium tetra(allyl)gallate $[\{\text{K}(\text{dibenzo-18-c-6})^+\{\text{Ga}(\eta^1\text{-C}_3\text{H}_5)_4\}^-\}]$, where each potassium attains a hexagonal bipyramidal geometry by binding to the oxygen atoms of the crown ether and π -engaging with the $\text{C}=\text{C}$ double bonds of one allyl ligand and the aromatic carbons of a crown ether from another monomeric unit.¹⁷

Solution NMR Spectroscopic Studies. Complementing their solid-state characterization, new alkali-metal gallates 1–3 have also been investigated by multinuclear NMR spectroscopy in deuterated benzene C_6D_6 and deuterated tetrahydrofuran $[\text{D}_8]\text{THF}$ solutions (see Experimental Section and Supporting Information for details). While compounds 2 and 3 showed a good solubility in deuterated benzene at room temperature, the solubility of 1 under these conditions was more limited. However all compounds readily dissolved when the donor solvent deuterated THF was employed. This contrasts with the complete lack of solubility of 1–3 in nonpolar solvents such as hexane or cyclohexane, suggesting that their polymeric lattices observed in the solid state are not retained in solution. Furthermore, the NMR spectra of 1–3 in both deuterated solvents displayed a single set of resonances for the alkyl groups CH_2SiMe_3 , showing that on the NMR time scale all the CH_2 hydrogens and SiMe_3 hydrogens are equivalent. Taking into account the structures found for the asymmetric units of 1–3, where chemically distinct alkyl groups are present, this indicates that either rapid interconversion of the alkyl positions or the formation of solvent-separated species is taking place in solution. Thus, variable-temperature ^1H NMR experiments were undertaken for potassium gallate 3⁴³ using deuterated toluene as a solvent, finding that even at temperatures as low as 213 K a single set of resonances is observed for the alkyl groups. A comparison of the chemical shifts observed for the monosilyl groups in the ^1H and ^{13}C NMR spectra of 1–3 shows very little variation across the three different gallates (Table 3), which coupled with the variable-temperature NMR studies points toward the formation of solvent-separated ion-pair $[\{\text{M}(\text{arene})_x\}^+\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_4\}^-]$ species as the most plausible solution scenario for these mixed-metal species.⁴⁴ This solution constitution appears also to be present when stronger coordinating d_8 -THF solvent was employed, as evidenced by the almost identical chemical shifts observed for the alkyl groups in the three gallates in both ^1H and ^{13}C NMR spectra (Table S1, Supporting Information). Reflecting the bimetallic constitution of 1–3, the resonances observed for the $\text{M}-\text{CH}_2$ group in the ^1H NMR spectrum in d_6 -benzene solutions lie considerably downfield (at −1.13, −1.06, and −1.01 ppm for 1,

Scheme 2. Relative Energies of Modeled DFT Reactions to Yield Metal Gallates I-M and II-M (M = Li, Na, K)

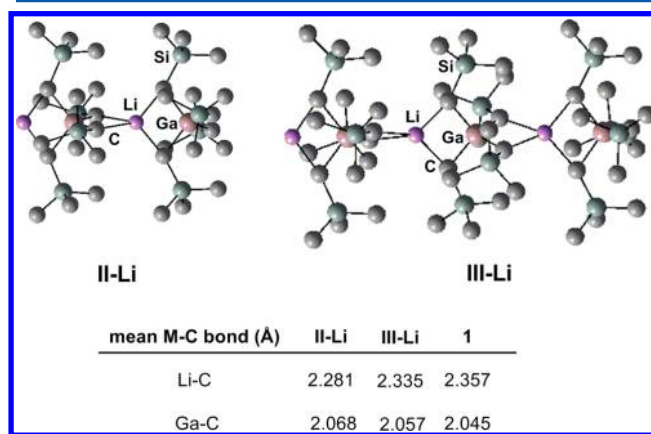


2, and 3, respectively) from those observed for the alkali-metal alkyl precursors $\text{M}(\text{CH}_2\text{SiMe}_3)$ (at -2.03 , -2.44 , and -2.60 ppm for $\text{M} = \text{Li}$, Na , and K , respectively) and much closer to that found for the neutral Ga alkyl species (at 0.13 ppm), indicating that the monosilyl groups, although part of a mixed-metal species, retain much of their “gallium-bonded character”. The trend observed for variation of these chemical shifts has been previously found in mixed-metal chemistry for related alkali-metal magnesiates, zincates, and magnesium–zinc hybrid species.^{23,45}

Regarding the solution stability of **1–3**, it should be mentioned that ^1H NMR analysis of isolated crystalline samples of **1** in deuterated benzene solution showed the presence of small amounts of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ along with tetramethylsilane. Remarkably when deuterated THF was employed, only the resonances attributed to **1** were observed in the ^1H NMR spectrum. This implies that in nonpolar benzene, **1** may be in dynamic equilibrium with its two homometallic components, with the equilibrium lying mainly toward the mixed-metal species. In this regard, although $\text{LiCH}_2\text{SiMe}_3$ could not be detected spectroscopically, the presence of tetramethylsilane in these solutions may be due to partial solvolysis of this lithium alkyl in deuterated benzene.⁴⁶ This partial disproportionation of **1** into its monometallic components may be a consequence of the lower tendency of Li to form π -interactions with arenes when compared to its heavier congeners Na and K,^{47,48} which must greatly contribute to the overall stabilization of the alkali-metal gallate in solution. Further support toward this possible equilibrium was found from theoretical studies (*vide infra*).

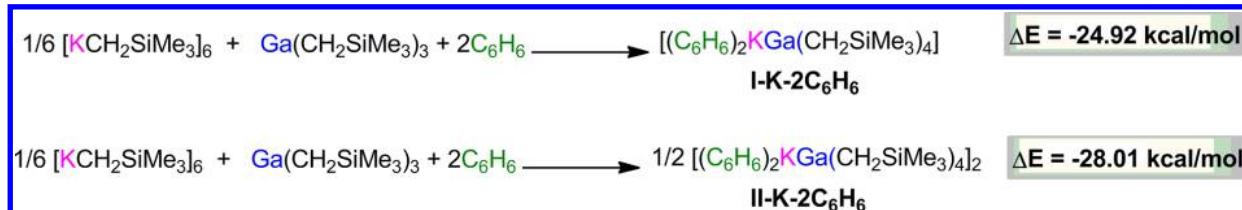
DFT Studies. To gain further understanding of the energetics involved in the formation of these alkali-metal tetraorganogallates, a theoretical study on the co-complexation reactions between $\text{M}(\text{CH}_2\text{SiMe}_3)$ and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ was also carried out. We first performed DFT calculations utilizing the B3LYP functionals⁴⁹ and the 6-311G** basis set (for full details see Supporting Information) for the formation of **1–3**. The resultant optimized geometries were subjected to a frequency analysis. The total energy taken from the DFT calculation was adjusted by inclusion of the zero-point energy contribution. We modeled the reactants $\text{LiCH}_2\text{SiMe}_3$ and $\text{NaCH}_2\text{SiMe}_3$ as a hexamer and tetramer, respectively, since these are the arrangements exhibited by the alkali-metal alkyls in the solid state in the absence of any donor, while $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ was modeled as a simple monomer. Although the structure of unsolvated $\text{KCH}_2\text{SiMe}_3$ has not yet been forthcoming, here it was modeled as a hexamer, since this aggregation state is common in potassium chemistry.⁵⁰ When the alkali-metal gallates were modeled as dinuclear monomers **I–M** ($\text{M} = \text{Li}$, Na , K), the co-complexation reactions were

calculated to be exothermic for **II–Na** and **II–K** by -1.63 and -7.87 kcal/mol, respectively, whereas for **I–Li** the reaction was found to be endothermic by $+2.72$ kcal/mol (Scheme 2 and Supporting Information). However, the thermodynamics of these reactions were greatly affected by changing the aggregation of the resulting mixed-metal species. Thus on modeling tetraorganogallates **1–3** as dimers **II–M** ($\text{M} = \text{Li}$, Na , K), their formation became much more energetically favored (by 10.62 and 9.29 kcal/mol for **II–Na** and **II–K**, respectively, Scheme 2). This is particularly remarkable in the case of **II–Li**, whose formation becomes exothermic by an energy gain of -5.93 kcal/mol, which increased to -11.09 kcal/mol for the corresponding trimer **III–Li**. Matching the polymeric structure described for **1**, the geometrical optimizations of **II–Li** and **III–Li** showed linear arrangements where the metals are connected by two alkyl bridges (Figure 4). A comparison of the calculated

Figure 4. Modeled structures of lithium gallates **II–Li** and **III–Li**.

geometrical parameters for models **II–Li** and **III–Li** shows in general a good agreement with those found experimentally from the X-ray determination of **1**, especially in the case of **III–Li**, the trimeric structure of which is closer to that of **1** (see Figure 4 and Supporting Information for details).⁵¹

These theoretical studies suggest that the success of co-complexation reactions of these homometallic alkyl precursors in forming unsolvated tetraorganogallate species is strongly dependent on the ability of the resulting mixed-metal product to aggregate. Furthermore, a comparison of the calculated energies of **I–M** and **II–M** shows a marked effect of the alkali-metal in the formation of these mixed-metal species, being more favored for K followed by Na, and with the size pattern extending to lithium gallates, as they are the least energetically preferred. Since compounds **1** and **2** exhibit polymeric

Scheme 3. Relative Energies of Modeled DFT Reactions to Yield Potassium Gallates I-K-2C₆H₆ and II-K-2C₆H₆

structures in the solid state of an infinite aggregation, taking into account these theoretical studies, their formation should be extremely thermodynamically favored. As mentioned above, in deuterated benzene solutions, NMR studies suggest that these compounds exist as monomeric solvent-separated ion-pair $[\{\text{M}(\text{benzene})_x\}]^+[\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_4\}]^-$ species. Although π -stabilization of softer alkali-metal Na or K by coordination to neutral arenes is well-documented,⁴⁰ it is much rarer for the smallest alkali-metal, lithium.^{47,48} This fact, coupled with the calculated energy value for monomeric I-Li, which enters endothermic territory (Scheme 2), would offer further support for the partial disproportionation of **1** into its homometallic components, as postulated above on the basis of NMR data.

Since in potassium gallate **3** each potassium atom is solvated by two molecules of benzene, the co-complexation reaction of the homometallic reactants was investigated in the presence of two equivalents of this arene. This showed that the formation of monomeric I-K-2C₆H₆ is substantially more exothermic (−24.92 kcal/mol) than solvent-free I-K (−7.87 kcal/mol) (Scheme 3). On modeling the resulting potassium gallate as dimeric II-K-2C₆H₆, the reaction became only slightly more energetically favored by a modest increase of 3.09 kcal/mol, contrasting with the theoretical studies for unsolvated I-M and II-M, where the higher aggregation of the mixed-metal species seems to be key to thermodynamically drive the co-complexation of the homometallic reactants. Thus, these results suggest that in **3** the major stabilization of coordinated unsaturated potassium comes from its solvation by two molecules of benzene via π -electrostatic interactions rather than by the formation of a polymeric structure. In addition it should be mentioned that comparison of the calculated bond lengths and bond angles in the minimum energy theoretical structure of II-K-2C₆H₆ with the relevant experimental values taken from the X-ray crystallographic study of **3** shows an excellent agreement (Figure S1 and Table S3 in the Supporting Information).

CONCLUSIONS

Using a straightforward co-complexation approach novel unsolvated alkali-metal tetraorgano-gallate species **1** and **2** have been prepared by reaction of equimolar amounts of the homometallic alkyls MCH₂SiMe₃ and Ga(CH₂SiMe₃)₃ using nonpolar hexane/arene solvent mixtures. Reflecting the softer character of potassium, when its alkyl KCH₂SiMe₃ was employed, benzene-solvated gallate **3** was isolated, where potassium coordinates to the π -face of two molecules of benzene. X-ray crystallographic studies of **1–3** revealed unprecedented polymeric arrangements for these mixed-metal species in the solid state. Solvent-free gallates **1** and **2** shared the same structural motif, where the “terminal” alkyl groups bonded to Ga in the monomeric unit $\{\text{M}(\mu\text{-CH}_2\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\}$ interact through their methylene group with the Li atom of a neighboring unit, producing a novel linear chain arrangement made up exclusively of M–C and Ga–C bonds

accommodated in planar four-membered {MCGaC} rings linked in an orthogonal manner. Contrastingly **3** exhibits a much more open structural motif, with K and Ga connected by a single alkyl group in the monomeric unit, with the propagation of the polymer taking place via weaker Me \cdots K electrostatic interactions between a methyl of a SiMe₃ group from a terminal alkyl ligand of one monomer and the neighboring potassium center of another. Significantly, despite the structural differences between **1**, **2**, and **3**, the Ga–C bond distances are almost identical for these three compounds, which highlights the anchoring nature of these strong covalent bonds, which provide the foundation of the structure, whereas the more polar alkali-metals affix to this framework via ancillary M–C bonds.

Contrasting with these supramolecular structures in the solid state, NMR spectroscopic studies suggest that in deuterated benzene and deuterated tetrahydrofuran solutions, gallates **1–3** exist as solvent-separated ion-pair $[\{\text{M}(\text{solvent})_x\}]^+[\{\text{Ga}(\text{CH}_2\text{SiMe}_3)_4\}]^-$ species. DFT computational studies on the formation of these mixed-metal species revealed that in the cases of solvent-free gallates **1** and **2** the formation of a polymeric arrangement is the driving force for the success of the co-complexation, whereas for **3** the presence of π -interactions between benzene and potassium seems to play a much more important stabilizing role than the ability of the mixed-metal species to increase its aggregation.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. Ga(CH₂SiMe₃)₃,²⁴ NaCH₂SiMe₃,²⁶ and KCH₂SiMe₃²⁷ were synthesized as described in the literature. LiCH₂SiMe₃ was purchased from Sigma Aldrich Chemicals and used as received. All NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H, 155.50 MHz for ⁷Li, and 100.62 MHz for ¹³C. Elemental analyses were obtained using a Perkin-Elmer 2400 elemental analyzer. Crystallographic data was collected at 123(2) K on an Oxford Diffraction diffractometer with Mo K α (λ = 0.71073 Å) radiation.⁵² Structures were solved using SHELXS-97 and refined to convergence on F^2 against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program.⁵³ Structure **2** was refined as a racemic twin and gave a Flack parameter of 0.489(9). Selected crystallographic and refinement details are given in Table S2 (see the Supporting Information for details).

Synthesis of $[\{\text{LiGa}(\text{CH}_2\text{SiMe}_3)_4\}_\infty]$ (1**).** To a solution of Ga(CH₂SiMe₃)₃ (0.50 g, 1.50 mmol) in hexane (17 mL) was added LiCH₂SiMe₃ (1 M in pentane, 1.50 mL, 1.50 mmol), and the resulting white suspension was stirred at room temperature for 1 h. A crop of colorless, needle-shaped crystals was isolated by filtration, washed with a small amount of *n*-hexane, and dried *in vacuo*. Crystalline solid: yield 0.39 g, 61%. ¹H NMR (400.03 MHz, 298 K, C₆D₆): δ (ppm) −1.13 (8H, s, SiCH₂), 0.24 (36H, s, Si(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, 298 K, C₆D₆): δ (ppm) 1.73 (SiCH₂), 3.48 (Si(CH₃)₃). ⁷Li NMR (155.47 MHz, 298 K, C₆D₆): δ (ppm) −2.38 (LiCH₂). ¹H

NMR (400.03 MHz, 298 K, $[D_8]THF$): δ (ppm) -1.03 (8H, s, $SiCH_2$), -0.11 (36H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, $[D_8]THF$): δ (ppm) 3.45 ($SiCH_2$), 4.19 ($Si(CH_3)_3$). 7Li NMR (155.47 MHz, 298 K, $[D_8]THF$): δ (ppm) -0.46 ($LiCH_2$). Anal. Calcd for $C_{16}H_{44}GaLiSi_4$: C, 45.16; H, 10.43. Found: C, 45.27; H, 11.15.

Synthesis of $[NaGa(CH_2SiMe_3)_4]_{\infty}$ (2). To a suspension of $NaCH_2SiMe_3$ (0.30 g, 2.72 mmol) in hexane (10 mL) were added $Ga(CH_2SiMe_3)_3$ (0.90 g, 2.72 mmol) and benzene (7 mL), and the resulting solution was stirred at room temperature for 12 h, upon which a white suspension formed. A crop of colorless, needle-shaped crystals was isolated by filtration, washed with a small amount of *n*-hexane, and dried *in vacuo*. Crystalline solid: yield 0.94 g, 78%. 1H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) -1.06 (8H, s, $SiCH_2$), 0.25 (36H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 3.00 ($SiCH_2$), 3.58 ($Si(CH_3)_3$). 1H NMR (400.03 MHz, 298 K, $[D_8]THF$): δ (ppm) -1.03 (8H, s, $SiCH_2$), -0.10 (36H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, $[D_8]THF$): δ (ppm) 3.38 ($SiCH_2$), 4.10 ($Si(CH_3)_3$). Anal. Calcd for $C_{16}H_{44}GaNaSi_4$: C, 43.52; H, 10.04. Found: C, 42.91; H, 10.14.

Synthesis of $[[(C_6H_6)_2KGa(CH_2SiMe_3)_4]_{\infty}]$ (3). Following the same procedure mentioned above for the synthesis of **2**, to a suspension of KCH_2SiMe_3 (0.38 g, 3.00 mmol) in hexane (10 mL) were added $Ga(CH_2SiMe_3)_3$ (0.99 g, 3.00 mmol) and benzene (3 mL), and the resulting colorless solution was stirred at room temperature for 1 h. The solution was cooled at -30 °C for 12 h. Colorless, needle-shaped crystals were isolated by filtration, washed with a small amount of hexane, and dried *in vacuo*. It should be noted that the two coordinated benzene molecules observed in the solid-state structure are lost upon drying *in vacuo*. Crystalline solid: yield 0.91 g, 66%. 1H NMR (400.03 MHz, 298 K, C_6D_6): δ (ppm) -1.01 (8H, s, $SiCH_2$), 0.31 (36H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, C_6D_6): δ (ppm) 3.91 ($Si(CH_3)_3$), 4.33 ($SiCH_2$). 1H NMR (400.03 MHz, 298 K, $[D_8]THF$): δ (ppm) -1.04 (8H, s, $SiCH_2$), -0.11 (36H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, $[D_8]THF$): δ (ppm) 3.42 ($SiCH_2$), 4.09 ($Si(CH_3)_3$). Anal. Calcd for $C_{16}H_{44}GaKSi_4$: C, 41.99; H, 9.69. Found: C 42.38; H, 9.23.

■ ASSOCIATED CONTENT

■ Supporting Information

CIF files giving crystallographic results, computational details, and copies of the NMR spectra are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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