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$Ga_{10}[Si(SiMe_3)_3]_6$, $[Ga_{10}(SitBu_3)_6]^-$, and $[Ga_{13}(SitBu_3)_6]^-$—Syntheses and Structural Characterization of Novel Gallium Cluster Compounds[†]

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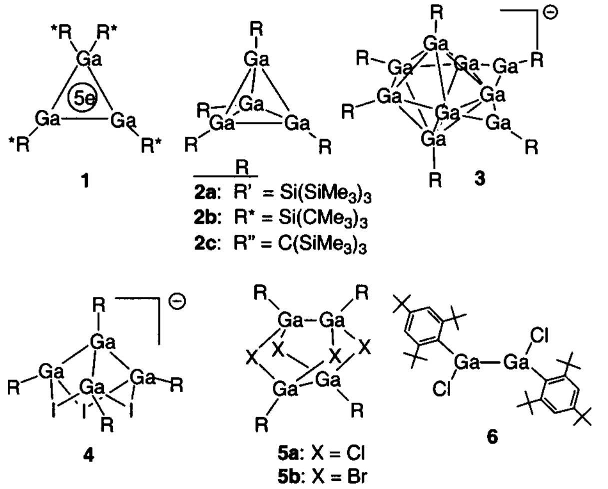
The novel neutral and anionic gallium clusters $Ga_{10}R'_6$ and $[Ga_{10}R^*_6]^-$ as well as $[Ga_{13}R^*_6]^-$ are obtained by reaction of "GaI", prepared sonochemically from gallium and iodine, with $Li(THF)_3R'$ ($R' = Si(SiMe_3)_3$ = hypersilyl) and $Na(THF)_2R^*$ ($R^* = SitBu_3$ = supersilyl), respectively. Both of the Ga_{10} clusters may be considered as *conjuncto* clusters consisting of two edge-sharing octahedrons. In $Ga_{10}R'_6$, these contain a $Ga_4R'_4$ and a $Ga_2R'_2$ unit, and in $[Ga_{10}R^*_6]^-$, they contain two $Ga_3R^*_3$ units. In addition to the syntheses and X-ray structure analyses of these three clusters, some hypersilylgallium halides are described, namely the $[Li(THF)_2]^+$ and $[Li(THF)_3]^+$ salts of $[R'GaI_3]^-$ as well as the $[Li(THF)_2]^+$ salts of $[R'_2Ga_2Br_4]^{2-}$ and $[R'_2Ga_2I_4]^{2-}$.

Introduction

Over the past few years, the chemistry of cluster compounds of the heavier main group III elements has made rapid progress (see refs 1 and 2[1,2] and references cited therein). In particular, gallium clusters Ga_nR_m with fewer, equal, or more gallium atoms than substituents R such as hypersilyl ($Si(SiMe_3)_3 = R'$) and supersilyl ($Si(CMe_3)_3 = R^*$) were investigated. Examples (Chart 1) are $Ga_3R^*_4$ (**1**) with $n < m$,[3] Ga_4R_4 (**2**) with $n = m$,[4−7] and $[Ga_9R'_6]^-$ (**3**) with $n > m$[8] (the first polyhedral gallium compound with more gallium atoms than substituents). Even higher is the n/m ratio in the gallium cluster compounds $Ga_{22}R_8$ ($R = R'$,[9] $Ge(SiMe_3)_3$),[10] $[Ga_{26}R'_8]^{2-}$,[11] and $\{Ga_{19}[C(SiMe_3)_3]_8\}^-$.[12] Furthermore, gallium halide clusters such as the $[Li(THF)_4]^+$ salt of the tetragallanide $[R'_4Ga_4I_3]^-$ (**4**),[8] the dimer of $R'_2Ga_2X_2$ (**5**) with X = Cl, Br,[9,13] or the nonaggregated species $R_2Ga_2Cl_2$ (**6**) with R = supermesityl ($2,4,6$-$tBu_3C_6H_2$)[14] have been prepared.

Chart 1. Gallium and Gallium Halide Cluster Compounds



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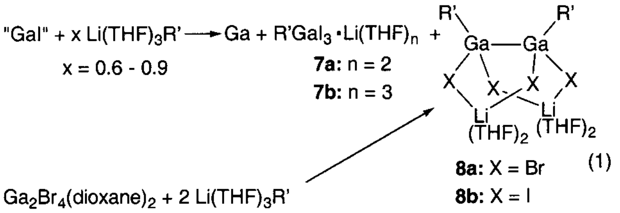
Herein, we report on novel types of gallium cluster compounds which were obtained during our ongoing studies on the use of sonochemically prepared "GaI"[15] as a source of subvalent gallium compounds. In addition, gallium bromides and iodides of types $[\text{Li(THF)}_p][\text{R}'\text{GaI}_3]$ (p = 2, 3) and $[\text{Li(THF)}_2]_2\,[\text{R}'_2\text{Ga}_2\text{X}_4]$ (X = Br, I) are described.

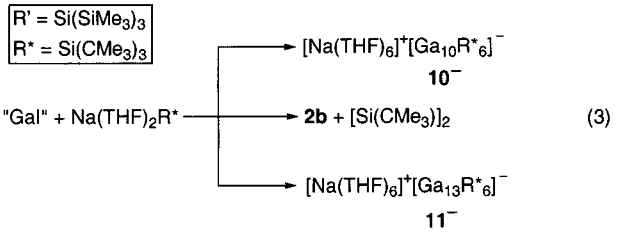
Results and Discussion

Reactions. When gallium is treated with 1 equiv of iodine in toluene in an ultrasonic bath, a greenish product called "GaI" is obtained.[15] According to Raman studies,[16] it is a mixture of gallium subhalides, predominantly consisting of Ga_2I_3 $(=(\text{Ga}^+)_2[\text{Ga}_2\text{I}_6]^{2-})$.[17] If "GaI" is reacted with $\text{LiSi(SiMe}_3)_3{\cdot}3\text{THF}$ (LiR′), a number of reaction products are formed: for example, the $[\text{Li(THF)}_4]^+$ salts of $[\text{Ga}_9\text{R}'_6]^-$ (**3**) [8] and $[\text{R}'_4\text{Ga}_4\text{I}_3]^-$ (**4**).[8] The nature of the products obtained as well as their yields are sensitive to the reaction conditions. If "GaI" is treated in toluene with less than 1 equiv of LiR′, disproportionation of the gallium subhalide is observed (eq 1). **7a** and **8b** are the only hypersilylated compounds which are obtained, if this reaction is performed at 0 °C. The bromine analogue **8a** of the heteroleptic digallane **8b** is easily obtained from $\text{Ga}_2\text{Br}_4{\cdot}2(\text{dioxane})$ (eq 1). Both **8a** and **8b** are formally $\text{Li(THF)}_2\text{X}$ adducts of compounds of type **6**.



(1)

$$\text{"GaI"} + \text{Li(THF)}_3\text{R}' \longrightarrow 2 + 3 + 4 + 7 + \underset{\mathbf{9}}{\text{Ga}_{10}\text{R}'_6} \qquad (2)$$



(3)

The formation of elemental gallium is almost unobservable in a reaction similar to eq 1a, if a "GaI"/LiR′ ratio of at least 1:1 is applied. In this case, **7b** forms along with gallium cluster compounds **2a**, **3**, and **4** (eq 2). Furthermore, black prisms of the novel cluster $\text{Ga}_{10}\text{R}'_6$ (**9**) crystallize from pentane extracts of the product mixture. If $\text{NaSi(CMe}_3)_3{\cdot}2\text{THF}$ (NaR*) instead of LiR′ is reacted with "GaI" in toluene at −78 °C, the gallatetrahedrane **2b** is isolated in 31% yield from a pentane extract of the product mixture (eq 3). The residue insoluble in pentane is dissolved in a THF/toluene mixture. Tiny, dark red needles of the $[\text{Na(THF)}_6]^+$ salt of the anionic cluster $[\text{Ga}_{10}\text{R}^*_6]^-$ (**10**$^-$) crystallize from the solution. The cluster is accompanied by small black cubes of the $[\text{Na(THF)}_6]^+$ salt of the anionic cluster $[\text{Ga}_{13}\text{R}^*_6]^-$ (**11**$^-$). In addition, superdisilane $t\text{Bu}_3\text{Si}{-}\text{Si}t\text{Bu}_3$,[5] obviously a product of redox processes, is isolated. The spectroscopic characterization of the cluster compounds **9**, **10**$^-$, and **11**$^-$ proved to be difficult. Despite the bulky silyl substituents and the resulting hydrophobic surface, the cluster compounds showed very low solubilities in pentane, toluene, or THF when crystallized. The same was observed for other higher gallium clusters, i.e., $[\text{Ga}_9\text{R}'_6]^-$ [8], $\text{Ga}_{22}\text{R}'_8$,[9] and $[\text{Ga}_{26}\text{R}'_8]^{2-}$,[11] as well as for $\text{R}^*_8\text{In}_{12}$.[25]

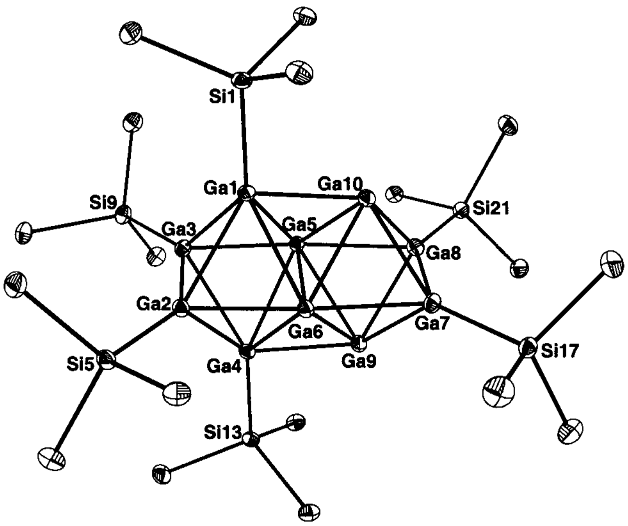


Figure 1. ORTEP view of the cluster **9**, the methyl groups have been omitted for clarity. Selected bond lengths (Å) for **9**: Ga(1)−Si(1) = 2.468(1), Ga(2)−Si(5) = 2.457(1), Ga(3)−Si(9) = 2.443(1), Ga(4)−Si(13) = 2.465(1), Ga(7)−Si(17) = 2.408(1), Ga(8)−Si(21) = 2.401(1), Ga(1)−Ga(10) = 2.5452(8), Ga(1)−Ga(3) = 2.7186(8), Ga(1)−Ga(5) = 2.7402(9), Ga(1)−Ga(6) = 2.7497(9), Ga(1)−Ga(2) = 2.7870(8), Ga(2)−Ga(3) = 2.5758(8), Ga(2)−Ga(6) = 2.5925(8), Ga(2)−Ga(4) = 2.7440(9), Ga(3)−Ga(5) = 2.6017(8), Ga(3)−Ga(4) = 2.753(1), Ga(4)−Ga(9) = 2.5332(8), Ga(4)−Ga(5) = 2.7278(7), Ga(4)−Ga(6) = 2.7754(8), Ga(5)−Ga(9) = 2.6945(9), Ga(5)−Ga(10) = 2.7008(8), Ga(5)−Ga(8) = 2.7149(8), Ga(5)−Ga(6) = 2.9827(8), Ga(6)−Ga(7) = 2.6748(8), Ga(6)−Ga(9) = 2.7117(9), Ga(6)−Ga(10) = 2.7321(8), Ga(7)−Ga(9) = 2.6091(8), Ga(7)−Ga(8) = 2.6095(8), Ga(7)−Ga(10) = 2.6227(9), Ga(8)−Ga(9) = 2.5839(8), Ga(8)−Ga(10) = 2.6047(9).

X-ray Structure Determinations. Gallium Clusters. The gallium atoms of decagallane **9**, which crystallizes in the monoclinic space group $P2_1/n$ together with two molecules of toluene, arrange in two octahedra, sharing an edge (Ga(5), Ga(6)). The distance between these Ga atoms is 2.983 Å (Figure 1), the longest among all neighboring Ga atoms in the cluster. On the other hand, the tops Ga(4)−Ga(9) and Ga(1)−Ga(10) have distances as short as 2.54 Å. The other gallium−gallium bond lengths in **9** range from 2.58 to 2.79 Å. Compared to other metal-rich clusters such as $\text{Ga}_{22}\text{R}'_8$[9,10] and $[\text{Ga}_{26}\text{R}'_8]^{2-}$,[11] these are quite short distances, which are comparable to those in **2** and **3**.

Only six gallium atoms bear hypersilyl groups, namely the four gallium atoms Ga(2), Ga(3), Ga(7), and Ga(8), which, together with the shared edge, make up the base

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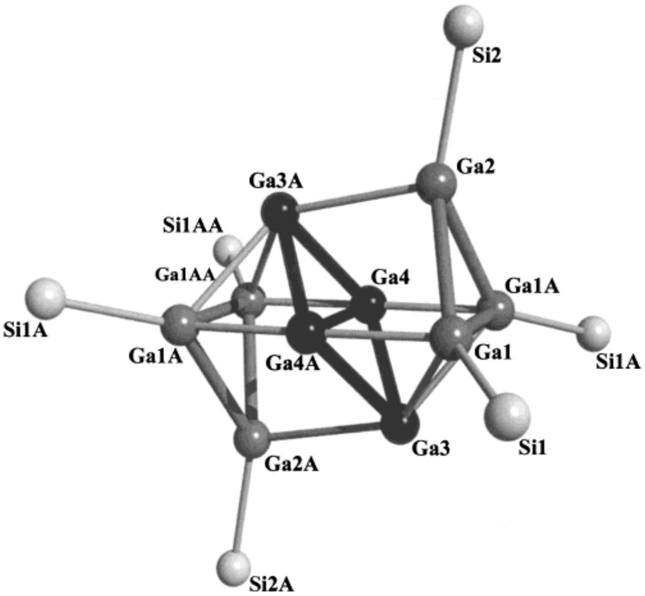

Figure 2. Schakal plot of one orientation of the cluster ion $\mathbf{10}^-$ (local symmetry C_i). The CMe_3 groups have been omitted for clarity. Selected bond lengths (Å) for $\mathbf{10}^-$: Ga(1)−Si(1)/Ga(1AA)−Si(1AA) = 2.477(5), Ga(1A)−Si(1A)/Ga(1A)−Si(1A) = 2.494(6), Ga(2)−Si(2)/Ga(2A)−Si(2A) = 2.477(5), Ga(1)−Ga(1A)/Ga(1A)−Ga(1AA) = 2.697(3), Ga(1)−Ga(2)/Ga(1AA)−Ga(2A) = 2.709(4), Ga(1A)−Ga(2)/Ga(1A)−Ga(2A) = 2.697(3), Ga(1)−Ga(3)/Ga(1AA)−Ga(3A) = 2.606(7), Ga(1A)−Ga(3)/Ga(1A)−Ga(3A) = 2.629(6), Ga(1)−Ga(4A)/Ga(1AA)−Ga(4) = 2.536(9), Ga(1A)−Ga(4)/Ga(1A)−Ga(4A) = 2.503(9), Ga(3)−Ga(4)/Ga(3A)−Ga(4A) = 2.45(1), Ga(3)−Ga(4A)/Ga(3A)−Ga(4) = 2.536(9), Ga(2)−Ga(3A)/Ga(2°)−Ga(3) = 2.874(6), Ga(4)−Ga(4A) = 2.88(1).

plane, and the apical atoms Ga(1) and Ga(4). Thus, one of the octahedra bears four hypersilyl substituents and the other one only two. This imbalance of crowding in the molecule influences the gallium−silicon bond lengths. The sterically more strained part of the molecule has longer gallium−silicon bonds (2.443(1)−2.468(1) Å) than the other. The average gallium−gallium distances in the $Ga_6R'_4$ part of the molecule are 0.046 Å longer than in the $Ga_6R'_2$ part. Ga(1) and Ga(4) have longer Ga−Ga contacts, than Ga(9) and Ga(10). At first glance, the seemingly unfavorable distribution of the substituents in **9** is surprising.

The salt $[Na(THF)_6]^+\mathbf{10}^-$ crystallizes in the monoclinic space group $C2/m$. The sodium cation is coordinated octahedrally by six THF molecules. The cluster anion $\mathbf{10}^-$ has a more symmetrically distributed substituent sphere than does **9** (Figure 2). Six GaR* fragments form a trigonal antiprism, which is stretched along its C_3 axis. The remaining four gallium atoms form a four-membered ring, which is embedded between the two Ga_3 rings. As a consequence of the C_3/C_4 symmetry mismatch of the cluster building units, the four-membered ring is disordered over three equivalent positions.

All Ga−Ga distances range from 2.453 to 2.880 Å (Figure 2), which is similar to the case for **9**. If Ga−Ga distances up to 3.25 Å are taken into account, the relationship to **9** becomes obvious. While the distance between Ga(4) and Ga(4A), forming the shared edge of the octahedrons, is the longest of all neighboring Ga atoms, it is 0.010 Å shorter than the corresponding bond in $Ga_{10}R'_6$ (Figure 1). The distances of the tops of the octahedrons (2.874 Å) are now nearly the longest in the cluster, whereas the distances Ga(3)−Ga(4A)/Ga(3A)−Ga(4A) and Ga(3)−Ga(4A)/Ga(3A)−Ga(4) are short (2.453 and 2.536 Å, respectively). The gallium−supersilyl bond lengths average 2.483 Å. They are longer than the gallium−hypersilyl distances in **9** but are in the typical range for gallium supersilyl compounds such as **2b** and $Ga_2R^*_3$.[5,18]

The salt $[Na(THF)_6]^+\mathbf{11}^-$ crystallizes in the orthorhombic space group $Pmc2_1$. All crystals of **11** examined were very thin plates and diffracted extremely weakly; thus, every image on the IPDS required 60 min of irradiation time. Consequently, the crystal structure analysis of **11** is preliminary and allows only a tentative discussion of the cluster core. The carbon atoms of the supersilyl groups and the residual electron density between the clusters [$Na(THF)_6{}^+$−counterions, solvent] were not included in the refinement. The unit cell contains two independent cluster molecules, both residing on a crystallographic mirror plane. These molecules differ only in their degree of disorder. Hence, only the less disordered cluster is discussed.

$\mathbf{11}^-$ has a cluster core of 13 gallium atoms (Figure 3). The 7 ligand-free gallium atoms are located at 7 corners of a cube. The missing corner is occupied by a $Ga_3R^*_3$ ring. The remaining three GaR* fragments reside over the three faces of the Ga_7 unit. All Ga−Ga distances range from 2.400 to 2.906 Å, which is similar to the case for **9** and $\mathbf{10}^-$. The gallium−supersilyl bond lengths average 2.453 Å, like those in $\mathbf{10}^-$.

Gallium Halide Clusters. The gallates **7a** and **7b** crystallize in the orthorhombic space group $P2_12_12_1$. **7a** (Figure 4) is the $Li(THF)_2I$ adduct of $R'GaI_2$. The gallium as well as the lithium atom are tetrahedrally coordinated. The lithium atom bonds to two iodine atoms and two THF molecules, and the gallium atom is surrounded by three iodine atoms and a hypersilyl group. **7b** (Figure 5) contains one more THF molecule; thus, the tetrahedrally coordinated lithium atom has only one iodine contact. The Ga−Si distance in **7a** and **7b** is 2.379 Å (Figures 4 and 5). This is in the normal range for hypersilyl gallium halides.[19] The terminal gallium−iodine bonds (2.57−2.59 Å) are shorter than the ones to iodine atoms having lithium contacts (2.64−2.65 Å).

The digallane **8b** crystallizes in the triclinic crystal system, space group $P\bar{1}$. **8a** forms pale yellow rhombs of the monoclinic space group $P2_1/c$. Both molecules are quite similar. They only differ in the Li−X and Ga−X bond lengths (Figure 6). Therefore, only the structure of **8a** (Figure 6) is described in detail. Both gallium atoms are coordinated tetrahedrally by two bromine atoms, a silicon atom, and a gallium atom. Each bromine atom is connected via a lithium atom to a bromine atom of the neighboring gallium atom. Thus, five-membered rings consisting of lithium and two gallium and two bromine centers are formed. The lithium atoms are coordinated tetrahedrally as well. An alternative structure with four-membered $GaBr_2Li$ rings according to the structure of **7a** seems to be less stable.

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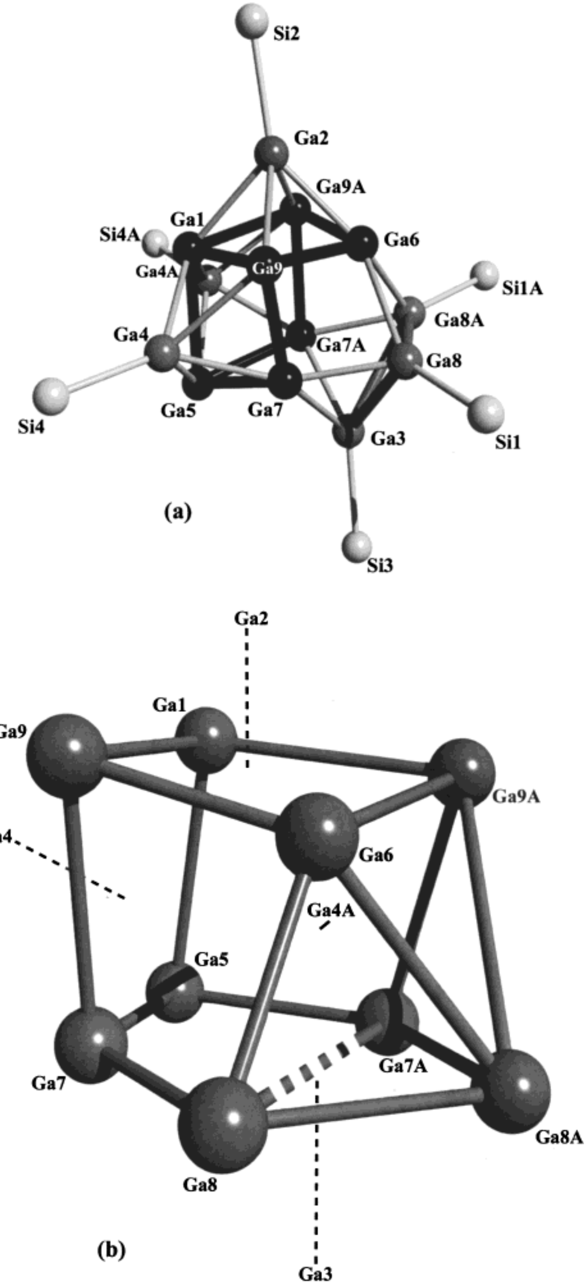

Figure 3. (a, top) Schakal plot of one of the independent cluster ions **11**$^-$. The positions of Ga(6), Si(4), and Si(4A) are doubly split (shown is one split position; local symmetry C_s for the averaged split forms). The CMe$_3$ groups have been omitted for clarity. (b, bottom) Illustration of the *closo*-Ga$_9$ cluster in **11**$^-$ (capped cube), four faces of which are capped by GaR* groups (cf. also Figure 3a).

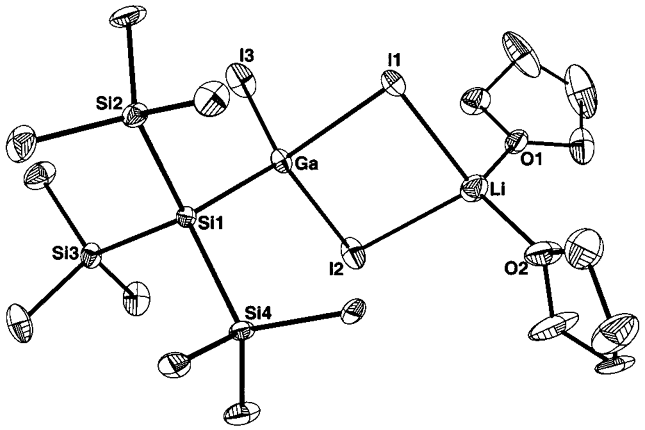

Figure 4. ORTEP view of a molecule of **7a**. The methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **7a**: I(1)−Ga = 2.652(1), I(1)−Li = 2.80(2), I(2)−Ga = 2.635(1), I(2)−Li = 2.79(2), I(3)−Ga = 2.572(2), Ga−Si(1) = 2.375(2), O(1)−Li = 1.91(2), O(2)−Li = 1.86(3); Ga−I(1)−Li = 81.9(4), Ga−I(2)−Li = 82.3(5), Si(1)−Ga−I(3) = 118.29(9), Si(1)−Ga−I(2) = 113.38(9), I(3)−Ga−I(2) = 103.97(5), Si(1)−Ga−I(1) = 113.89(6), I(3)−Ga−I(1) = 103.90(5), I(2)−Ga−I(1) = 101.54(4).

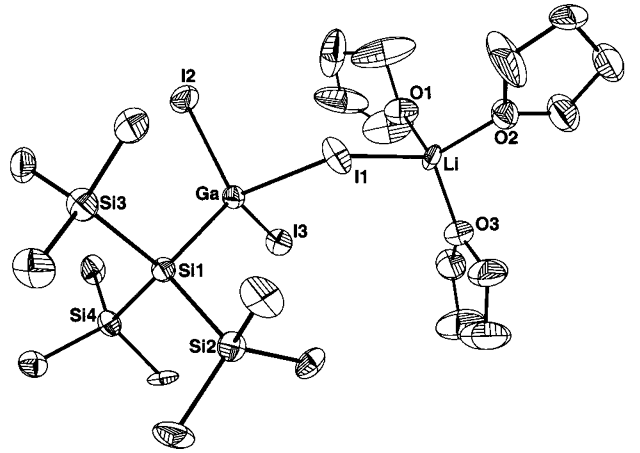

Figure 5. ORTEP view of a molecule of **7b**. The methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **7b**: Ga−I(3) = 2.590(3), Ga−I(2) = 2.595(3), Ga−I(1) = 2.641(3), I(1)−Li = 2.86(5), Ga−Si(1) = 2.377(6), Li−O(3) = 1.84(4), Li−O(2) = 1.88(4), Li−O(1) = 1.91(4); Si(1)−Ga−I(3) = 114.9(2), Si(1)−Ga−I(2) = 116.1(2), I(3)−Ga−I(2) = 105.2(1), Si(1)−Ga−I(1) = 111.1(2), I(3)−Ga−I(1) = 104.64(9), I(2)−Ga−I(1) = 103.8(1), Ga−I(1)−Li = 107.7(7), O(1)−Li−I(1) = 108(2).

The gallium−gallium bond in **8a** is 2.477(1) Å long. This is shorter than in **5a** and **5b**, where the bulky silyl substituents are ecliptic.[9,13]

RI-DFT Calculations on Neutral and Anionic Ga$_{10}$H$_6$ Clusters. To obtain more insight into the different Ga$_{10}$R$_6$ structures present in **9** and **10**$^-$, calculations on the neutral Ga$_{10}$H$_6$ species **9a** and **10a**, as well as on their corresponding reduced, anionic species **9a**$^-$ and **10a**$^-$, were performed on the RI-DFT level (BP86 functional, SV(P)base).[20−24] The calculated structures **9a** and **10a**$^-$ are in good agreement with **9** and **10**$^-$ (Figure 7, Table 1). According to these calculations, isomerization of **9a** into **10a** costs 45 kJ mol^{-1} (Table 2). With regard to the reduced species, **9a**$^-$ is still more stable than **10a**$^-$, but the difference is only 16 kJ mol^{-1}. This means that adding an electron to cluster **10a** gains more energy (246 kJ mol^{-1}) than the reduction of **9a** (218 kJ mol^{-1}).

More interesting are the structural changes induced by the reduction of **9a** and **10a** to **9a**$^-$ and **10a**$^-$, respectively. In case of **9a**, the effects of reduction to **9a**$^-$ are relatively small. The major change is an

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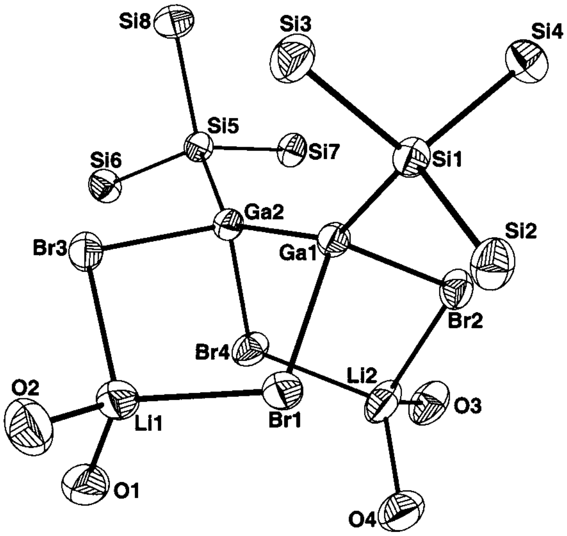


Figure 6. ORTEP view of a molecule of **8a**. The methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ga(1)−Si(1) = 2.410(2), Ga(2)−Si(5) = 2.417(2), Ga(1)−Ga(2) = 2.477(1), Ga(1)−Br(1) = 2.524(1), Ga(1)−Br(2) = 2.490(1), Ga(2)−Br(3) = 2.500(1), Ga(2)−Br(4) = 2.523(1), Br(1)−Li(1) = 2.55(2), Br(2)−Li(2) = 2.49(2), Br(3)−Li(1) = 2.49(1), Br(4)−Li(2) = 2.54(1); Si(1)−Ga(1)−Ga(2) = 142.71(6), Si(1)−Ga(1)−Br(2) = 101.11(6), Ga(2)−Ga(1)−Br(2) = 103.39(4), Si(1)−Ga(1)−Br(1) = 103.79(6), Ga(2)−Ga(1)−Br(1) = 99.55(4), Br(2)−Ga(1)−Br(1) = 99.20(4), Si(5)−Ga(2)−Ga(1) = 141.84(6), Si(5)−Ga(2)−Br(3) = 102.37(6), Ga(1)−Ga(2)−Br(3) = 103.74(4), Si(5)−Ga(2)−Br(4) = 103.41(6), Ga(1)−Ga(2)−Br(4) = 99.05(4), Br(3)−Ga(2)−Br(4) = 99.74(4), Ga(1)−Br(1)−Li1 = 105.4(3), Ga(1)−Br(2)−Li(2) = 96.4(4), Li(1)−Br(3)−Ga(2) = 96.9(4), Ga(2)−Br(4)−Li(2) = 106.1(4), Br(3)−Li(1)−Br(1) = 105.7(5), Br(2)−Li(2)−Br(4) = 104.4(5). Selected bond lengths (Å) and angles (deg) for **8b**: Ga(1)−Si(1) = 2.440(7), Ga(2)−Si(5) = 2.433(7), Ga(1)−Ga(2) = 2.497(4), I(1)−Ga(1) = 2.722(3), I(2)−Ga(1) = 2.720(3), I(3)−Ga(2) = 2.726(3), I(4)−Ga(2) = 2.732(3), I(1)−Li(2) = 2.69(6), I(2)−Li(1) = 2.66(6), I(3)−Li(1) = 2.75(6), I(4)−Li(2) = 2.70(4); Li(2)−I(1)−Ga(1) = 103.9(9), Li(1)−I(2)−Ga(1) = 103(1), Ga(2)−I(3)−Li(1) = 104(1), Li(2)−I(4)−Ga(2) = 99.1(11), Si(1)−Ga(1)−Ga(2) = 138.6(2), Si(1)−Ga(1)−I(2) = 102.4(2), Ga(2)−Ga(1)−I(2) = 104.6(1), Si(1)−Ga(1)−I(1) = 103.3(2), Ga(2)−Ga(1)−I(1) = 103.2(1), I(2)−Ga(1)−I(1) = 98.2(1), Si(5)−Ga(2)−Ga(1) = 140.3(2), Si(5)−Ga(2)−I(3) = 102.5(2), Ga(1)−Ga(2)−I(3) = 102.9(1), Si(5)−Ga(2)−I(4) = 100.9(2), Ga(1)−Ga(2)−I(4) = 104.4(1), I(3)−Ga(2)−I(4) = 99.3(1), I(2)−Li(1)−I(3) = 105(2), I(1)−Li(2)−I(4) = 107(2).

elongation of bonds involving the Ga_2H_2 unit up to 0.015 Å. In contrast, on reduction of **10a** to **10a**$^-$ some very long GaGa contacts shorten drastically. Most striking is the shortening of the central GaGa bond (Ga(5)−Ga(6)) by 0.030 Å.

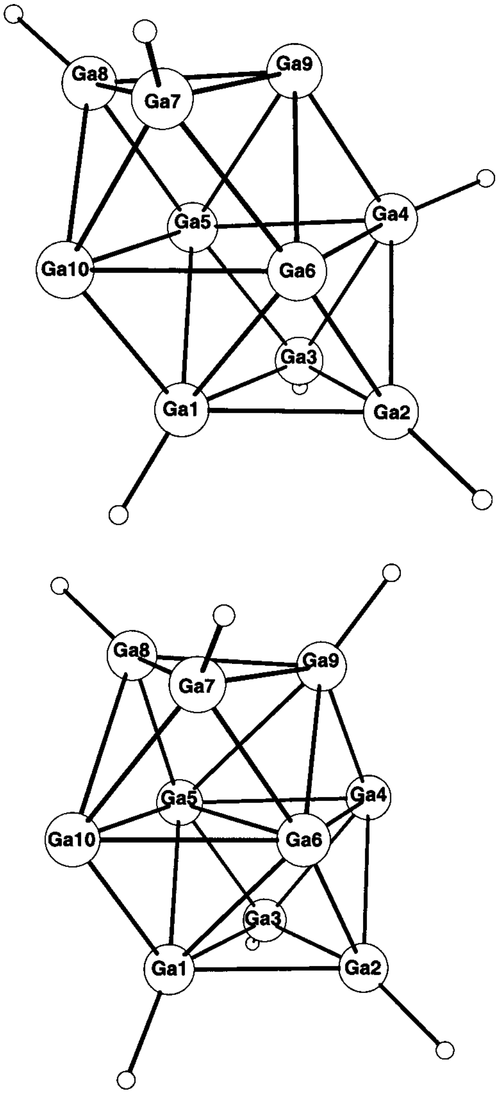


Figure 7. Calculated structures of **9a** (a, top) and **10a**$^-$ (b, bottom).

Table 1. Calculated Ga−Ga Distances (Å) for 9a, 9a$^-$, 10a, and 10a$^-$

	9a	9a$^-$	10a	10a$^-$
Ga(1)−Ga(2)	2.684	2.638	2.879	2.784
Ga(1)−Ga(3)	2.673	2.632	2.887	2.783
Ga(1)−Ga(5)	2.754	2.743	2.704	2.646
Ga(2)−Ga(3)	2.503	2.549	2.546	2.479
Ga(2)−Ga(4)	2.685	2.634	3.117	2.840
Ga(3)−Ga(5)	2.590	2.546	2.643	2.558
Ga(4)−Ga(5)	2.757	2.747	2.944	2.932
Ga(4)−Ga(6)	2.754	2.746	3.521	3.032
Ga(5)−Ga(6)	3.191	3.169	3.378	3.074
Ga(5)−Ga(8)	2.621	2.582	2.456	2.507
Ga(5)−Ga(10)	2.866	2.870	3.529	3.022
Ga(6)−Ga(7)	2.644	2.585	2.639	2.634
Ga(6)−Ga(10)	2.841	2.854	2.951	3.009
Ga(7)−Ga(8)	2.539	2.638	2.535	2.471
Ga(7)−Ga(9)	2.634	2.593	2.882	2.861
Ga(7)−Ga(10)	2.635	2.605	2.505	2.590
Ga(8)−Ga(9)	2.648	2.765	2.855	2.624
Ga(8)−Ga(10)	2.642	2.788	3.166	3.206

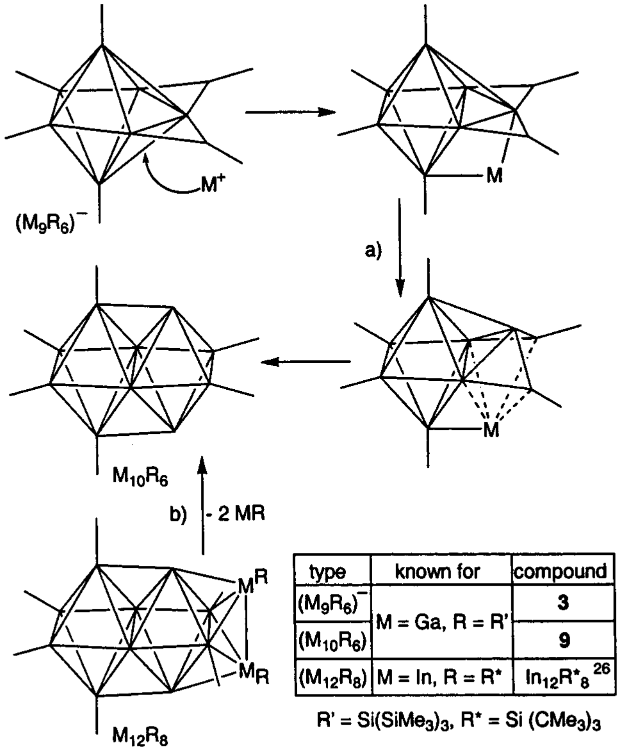
This can be explained by inspecting the frontier orbitals of compounds **9a** and **10a**. For **9a** the HOMO is located predominantly where the lone pairs of the “naked” gallium atoms are expected. In addition, it is bonding for the Ga(5)−Ga(6) interaction. Occupation of the LUMO of **9a** with electrons would mainly affect peripheral cluster bonds involving the Ga_2H_2 and the Ga_4H_4 unit of the cluster, thus explaining the calculated structural differences. In contrast, the HOMO of **10a**$^-$ (the same is valid for the LUMO of **10a**) is bonding with respect to the Ga(5)−Ga(6) contact. Consequently, occupation of the LUMO of **10a** with an electron affords a shortening of the Ga(5)−Ga(6) distance.

In this context, it may be worth commenting on the relevance of discussing Ga−Ga interactions up to 3 Å. In electron-precise oligogallanes, Ga−Ga single bonds are between 2.35 and 2.58 Å.[2] In gallatetrahedrane Ga−

Table 2. Calculated Total Energies (hartrees) for Species 9a, 9a$^-$, 10a, and 10a$^-$ as well as Energy Differences (kJ mol^{-1}) between the Species

9a	−19 252.682 432 56	**9a** → **10a**	45
9a$^-$	−19 252.765 586 45	**9a**$^-$ → **10a**$^-$	16
10a	−19 252.665 315 02	**10a** → **10a**$^-$	246
10a$^-$	−19 252.759 352 13	**9a** → **9a**$^-$	216

Scheme 1. Topological Relation between 3 and 9 (a) as well as 3 and $In_{12}R^*_8$ ($R^* = SitBu_3$) and 9 (b)



type	known for	compound
$(M_9R_6)^-$	M = Ga, R = R′	3
$(M_{10}R_6)$		9
$(M_{12}R_8)$	M = In, R = R*	$In_{12}R^*_8$ 26

R′ = Si(SiMe$_3$)$_3$, R* = Si (CMe$_3$)$_3$

Ga distances of up to 2.70 Å are observed.[1] On the other hand, in elemental gallium distances between neighboring gallium atoms of 2.47−2.80 Å are typical. If we rely on population analyses (in this case Ahlrichs−Heinzmann population analyses),[25] we find significant shared electron density between the gallium atoms forming the connecting edge.

Discussion

Recently, the metal-rich clusters $In_{12}R^*_8$ with $R^* = SitBu_3$[26] and $[Al_{12}\{N(SiMe_3)_2\}_8]^-$[27] have been reported. They can be described as $M_{10}R_6$ clusters with a structure similar to **9**, to which two MR units are added. This relationship—in an inverse manner—is depicted in Scheme 1b. Thus, the gallium core of **9** might be described as a small sector of a close packing, which is observed in the structure of elemental Al and In and is also approached in one of the modifications of gallium (gallium(III)).[28] The $Ga_9R'_6$ cluster anion **3**, which we have described earlier,[8] is in close relation to **9** as well. As is summarized in Scheme 1a, formal reaction of **3** with a Ga cation and a consequent slight topological rearrangement leads directly to **9**. Thus, the surprising distribution of Si(SiMe$_3$)$_3$ groups in **9** would be a result of the relationship between **3** as well as $In_{12}R^*_8$ and **9**. For the bulkier Si(CMe$_3$)$_3$ groups a cumulation of four neighboring ligands in $[Ga_{10}R^*_6]^-$—as is found in $In_{12}R^*_8$ with the larger indium cluster—is obviously less stable for steric reasons.

According to the Wade−Mingos rules,[29] **3** can be regarded as a pentagonal-bipyramidal *closo*-Ga_7 cluster with four hypersilyl groups and two edge-bridging GaR′ ligands. The “naked” Ga atoms and the GaR′ groups are each considered to provide one electron and two electrons, respectively. Thus, $Ga_9R'_6{}^-$ has 16 cluster bonding electrons—that means $2n - 2$ electrons with n = number of framework atoms—which should lead to the formation of a bicapped *closo*-Ga_7 cluster. When these electron bookkeeping rules are applied, **9**, like **3**, would have 16 cluster electrons. These formally lead to a tricapped *closo*-Ga_8 cluster. Indeed, the structure of **9** (as well as of **10**$^-$) is reminiscent of a *conjuncto* polyhedron. On the other hand, **9** and **10**$^-$ fit Cotton’s definition[30] of a metal atom cluster. In fact, the arrangement of the gallium atoms in **9** and **10**$^-$ represents a small section of a close-packing structure of atoms.

Finally, with regard to electron bookkeeping rules (see above), **11**$^-$ has 20 cluster electrons, which formally leads to a 4-fold capped *closo*-Ga_9 cluster. Ga(1), Ga(9), Ga(6), Ga(9A), Ga(5), Ga(7), Ga(8), and Ga(7A) form a distorted cube, capped by Ga(8A), as is shown in Figure 3b. Three Ga_4 faces and a Ga_5 face of this Ga_9 cluster subunit are each capped by a GaR* group (cf. Figure 3; Ga(5) of the Ga_5 face of the cluster obviously does not bind to GaR*).

The chemistry of gallium cluster compounds has developed fruitfully over the last few years. Worthy of note is that the use of “GaI” and the bulky silyl ligands Si(SiMe$_3$)$_3$ and Si(CMe$_3$)$_3$ has allowed the isolation of a number of novel cluster types, unprecedented even in the cluster chemistry of other elements. Therefore, our efforts are directed to a variation of the substituents in order to obtain other novel gallium clusters, possibly even larger ones, and to get insight into the formation mechanisms of such compounds.

Experimental Section

All experiments were performed under purified nitrogen or in vacuo with Schlenk techniques. All yields are referenced to gallium. Elemental analyses were carried out at the microanalytic laboratory of the University of Karlsruhe. NMR: Bruker ACP200 and 250. Mass spectra: Varian MAT711. X-ray crystallography: suitable crystals were mounted with a perfluorated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head.

Data collections were performed with Mo Kα radiation (graphite monochromator) on a STOE STADI4 (**7a**, **7b**, **8a**, **8b**) in a ω-scan mode or on a STOE IPDS (**9**, **10**$^-$, **11**$^-$) diffractometer. Structures were solved and refined with the Bruker AXS Shelxtl 5.1 program package. Refinement was in full matrix against F^2. All non-hydrogen atoms were included as riding models with fixed isotropic U values in the final refinement. For further data, cf. Table 3. Crystallographic data (excluding structure factors and the data for **11**$^-$, which are

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Table 3. Data for the X-ray Structure Determinations

	7a	**7b**	**8a**	**8b**	**9**	**10$^-$**	**11$^-$**
emp form	$C_{17}H_{43}GaI_3$-LiO_2Si_4	$C_{21}H_{51}GaI_3$-LiO_3Si_4	$C_{34}H_{86}Ga_2Br_4$-$Li_2O_4Si_8$	$C_{34}H_{86}Ga_2I_4$-$Li_2O_4Si_8$	$C_{68}H_{162}Ga_{10}Si_{24}$	$C_{102}H_{216}Ga_{10}$-NaO_6Si_6	$C_{72}H_{162}Ga_{13}Si_6$
cryst size, mm	0.8 × 0.6 × 0.5	1.1 × 0.87 × 0.60	1.0 × 0.8 × 0.8	0.35 × 0.2 × 0.12	0.9 × 0.75 × 0.3	0.7 × 0.5 × 0.2	0.05 × 0.05 × 0.05
cryst syst	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$C2/m$	$Pmc2_1$
fw	849.2	921.4	1256.7	1444.7	2351.3	2427.5	2558.5
a, Å	9.615(2)	11.529(2)	14.174(2)	13.560(3)	17.547(4)	24.727(5)	19.902(4)
b, Å	11.106(2)	18.053(3)	24.297(5)	13.662(3)	22.278(5)	19.934(4)	18.392(4)
c, Å	31.197(6)	18.337(3)	18.498(4)	19.198(4)	32.075(6)	13.587(3)	33.068(7)
α, deg	90	90	90	87.38(3)	90	90	90
β, deg	90	90	104.82(2)	89.46(3)	101.30(3)	105.71(3)	90
γ, deg	90	90	90	62.98(3)	90	90	90
V, nm^3	3.3313(11)	3.8165(11)	6.1585(20)	3.1648(11)	12.30(1)	6.45(1)	12.10(1)
Z	4	4	4	2	4	2	4
D(calcd), g cm^{-3}	1.693	1.603	1.355	1.516	1.270	1.293	1.404
F(000)	1640	1800	2568	1428	4864	2640	5328
μ, mm^{-1}	3.761	3.291	3.654	2.982	2.418	2.171	2.948
2θ range, deg	1.95−30.03	1.58−24.95	1.71−25.00	1.67−24.00	1.94−25.95	1.71−23.90	1.63−22.37
no. of collcd rflns	3552	4652	11 879	9916	81 620	20 152	37 986
no. of unique rflns	3552	4190	10 655	9916	23 872	5098	15 711
no. of obsd rflns	3053	2887	7216	6108	13270	3239	10 449
GOF	1.153	1.168	1.162	1.164	0.845	1.139	1.448
wR2 (all data)	0.1053	0.1823	0.1614	0.3389	0.0946	0.3822	0.4030
R1	0.0390	0.0620	0.0519	0.0952	0.0396	0.1405	0.1382
largest diff peak, e Å^{-3}	1.101	1.709	0.479	1.660	0.668	0.774	2.333
deepest diff peak, e Å^{-3}	−0.713	−1.178	−0.378	−1.380	−0.612	−1.120	−2.844

only preliminary) for the structures reported in this paper are available as Supporting Information.

Gallium halides were prepared from the elements;[15,31] the compounds $LiSi(SiMe_3)_3 \cdot 3THF$ (≡LiR′)[32] and $NaSitBu_3 \cdot 2THF$ (≡LiR*)[5] were prepared as described in the literature.

Synthesis of $C_{17}H_{43}GaI_3LiO_2Si_4$ (7a) and $C_{34}H_{86}Ga_2I_4Li_2O_4Si_8$ (8b). Into a vigorously stirred suspension of freshly prepared "GaI"[15] (0.87 g, 4.43 mmol) in 20 mL of toluene was added a solution of $Li(THF)_3Si(SiMe_3)_3$ (1.00 g, 2.20 mol) in THF dropwise at 0 °C. After slow warming to ambient temperature a gallium mirror formed. All volatiles were removed in vacuo, and the residue was extracted with 30 mL of pentane. From the pentane solution **8b** crystallized (1.91 g, 60%) at 0 °C. After concentration of the mother liquor **7a** (0.48 g, 13%) could be isolated by crystallization at −20 °C. The NMR spectra of **7a** and **8b** showed impurities (approximately 5% by integration) of **8b** and **7a**, respectively.

7a. NMR (C_6D_6): $\delta(^1H)$ 3.54 (m, 16H, OCH_2), 1.35 (m, 16H, CH_2), 0.62 (s, 27H, $SiMe_3$); $\delta(^{13}C)$ 69.4 (OCH_2), 26.1 (CH_2), 3.7 ($SiMe_3$). MS (EI): *m*/*z* (%) 570 (0.02, $[R'GaI_2]^{\bullet+}$), 555 (0.04, $R'GaI_2 - CH_3]^+$), 443 (2, $[RGaI]^+$), 374 (100, $[R'I]^{\bullet+}$), 359 (21, $[R'I - CH_3]^+$), 286 (2, $[R'I - SiMe_3]^+$), 174 (57, $[(Me_3Si)_2Si]^+$).

8b. NMR (C_6D_6): $\delta(^1H)$ 3.54 (m, 16H, OCH_2), 1.35 (m, 16H, CH_2), 0.69 (s, 27H, $SiMe_3$). MS (EI): *m*/*z* 691 (7, $[R'_2GaI]^{\bullet+}$), 676 (20, $[R'_2GaI - CH_3]^+$), 564 (9, $[R'_2Ga]^+$), 443 (12, $[R'GaI]^+$), 374 (97, $[R'I]^{\bullet+}$), 359 (85, $[R'I - CN_3]^+$), 316 (100, $[R'Ga]^{\bullet+}$), 301 (54, $[R'Ga - CH_3]^+$).

Synthesis of $C_{21}H_{51}GaI_3LiO_3Si_4$ (7b) and $C_{68}H_{162}Ga_{10}Si_{24}$ (9). The reaction was performed using the procedure above at −78 °C instead of 0 °C using $Li(THF)_3Si(SiMe_3)_3$ (1.4 g, 3.0 mmol) in THF and "GaI" (0.59 g, 3.0 mmol) in toluene. All volatiles were removed in vacuo, and the residue was extracted with pentane. By fractional crystallization at first **7b** (0.21 g, 8%) and then **9** (0.09 g, 13%) were isolated. All volatiles were removed from the mother liquor. The remaining violet-red oily residue (0.3 g) mainly consisted of **2** (identified by ^1H and ^{13}C NMR and MS).[4] On standing at ambient temperature, dark violet crystal plates of **2** grew.

7b. NMR (C_6D_6): $\delta(^1H)$ 3.54 (m, 24H, OCH_2), 1.35 (24H, CH_2), 0.60 (s, 27H, $SiMe_3$); $\delta(^{13}C)$ 69.4 (OCH_2), 26.1 (CH_2), 5.2 ($SiMe_3$). MS (EI): see **7a**. Anal. Calcd for $C_{21}H_{51}GaI_3LiO_3Si_4$: C, 27.38; H, 5.58. Found: C, 27.03; H, 5.22.

9. Due to the high inlet temperature, **9** decomposed and only a few characteristic peaks for **9** could be observed. MS (70 eV, EI, 240 °C inlet temperature): *m*/*z* (%) 1431 (4, $[Ga_{10}R'_3]^+$, 563 (3, $[GaR'_2]^+$), 389 (30, $[R'GaSiMe_3]^+$), 316 (5, $[R'Ga]^{\bullet+}$), 73 (100, $[SiMe_3]^+$). IR (KBr): no bands in the region typical for ν_{GaH} (1850−1950 cm^{-1}).

Synthesis of $C_{34}H_{86}Ga_2Br_4Li_2O_4Si_8$ (8a). $Ga_2Br_4 \cdot 2$(dioxane) (1.90 g, 2.99 mmol) and $Li(THF)_3Si(SiMe_3)_3$ (2.81 g, 5.79 mmol) were each dissolved in 30 mL of THF. The solutions were added simultaneously into 20 mL of THF at −78 °C with vigorous stirring. After slow warming to room temperature and stirring for 24 h, all volatiles were removed in vacuo. The residue was extracted with pentane. From the concentrated pentane solution pale yellow crystals of **8a** (3.43 g, 91%) were recovered in several portions.

8a. NMR (C_6D_6): $\delta(^1H)$ 3.58 (m, 16H, OCH_2), 1.35 (m, 16H, CH_2), 0.66 (s, 27H, $SiMe_3$); $\delta(^{13}C)$ 69.2 (OCH_2), 26.2 (CH_2), 4.7 ($SiMe_3$); $\delta(^{29}Si)$ −7.5 ($SiMe_3$), −115.1 (Si). MS (70 eV, EI): *m*/*z* (%) 875 (12, $\{Ga_2Br_3[Si(SiMe_3)_3]_2\}^+$), 644 (8, $\{GaBr[Si(SiMe_3)_3]_2\}^{\bullet+}$); 629 (30) $\{GaBr[Si(SiMe_3)_3]_2 - CH_3\}^+$), 316 (100, $[GaSi(SiMe_3)_3]^{\bullet+}$). Anal. Calcd for $C_{34}H_{86}Ga_2Br_4Li_2O_4Si_8$: C, 32.50; H, 6.90. Found: C, 31.04; H, 6.15.

Synthesis of $C_{102}H_{216}Ga_{10}NaO_6Si_6$ ($[Na(THF)_6]^+10^-$) and $C_{72}H_{162}Ga_{13}Si_6$ ($[Na(THF)_6]^+11^-$). To a suspension of "GaI" (0.60 g, 3.0 mmol) in 25 mL of toluene was added a solution of $Na(THF)_2Si(CMe_3)_3$ (1.6 g, 4.3 mmol) in 25 mL of pentane dropwise at −78 °C. After it was slowly warmed to ambient temperature, the mixture was stirred for 12 h. Subsequently all volatiles were evaporated in vacuo and the residue was extracted with 50 mL of pentane. The remaining solid was dissolved in 30 mL of a 1:1 toluene/THF mixture. From the pentane solution violet crystals of **2b** (0.36 g, 45%) precipitated at −30 °C (NMR and mass spectra are in agreement with those reported in the literature).[6] From the toluene/THF extract (reduced to half its volume) red plates of $[Na(THF)_6]^+$**10**$^-$ (0.05 g, 8%) accompanied by a few tiny black cubes of $[Na(THF)_6]^+$**11**$^-$ crystallized at 0 °C. Further crystals of $[Na(THF)_6]^+$**10**$^-$ (**11**$^-$) embedded in a matrix of colorless crystals (0.38 g) of LiI·THF (identified by X-ray crystallography) and $tBu_3Si-SitBu_3$ (iden-

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tified by comparison with an authentic sample[5]) were recovered from the concentrated mother liquor at 0 °C. Once crystallized, the $[Na(THF)_6]^+$ salts of **10**$^-$ and **11**$^-$ were insoluble in common NMR solvents; consequently, solution spectra (ESR, NMR) of the products could not be obtained.

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Supporting Information Available: Tables giving crystal data and details of the structure solution and refinement, positional and thermal parameters, and all bond distances and angles for **7a**, **7b**, **8a**, **8b**, **9**, and **10**$^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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