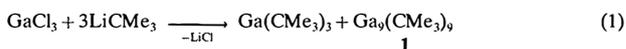


Ga₉(CMe₃)₉, an Important New Building Block in the Structural Chemistry of the Alkylelement(I) Compounds E_nR_n (E = B – In)**

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Numerous organoelement cluster compounds of the elements boron, aluminum, gallium, and indium have been published in recent literature. Most of them are difficult to prepare and were isolated in only very poor yield. They often contain cluster anions such as [Al₇₇{N(SiMe₃)₂]₂₀]²⁻ or [Ga₉{Si(SiMe₃)₃]₆]⁻.^[1] Beside these ionic derivatives a few neutral cluster compounds such as In₈Ar₄ (Ar = 2,6-dimesitylphenyl) or In₁₂{Si(CMe₃)₃]₈^[2] were synthesized in which the number of the cluster atoms exceeds the number of the substituents. To the best of our knowledge there is no systematic approach to the description of their formation and of their fascinating structural chemistry. Element(I) compounds E_nR_n were isolated and structurally characterized before only as monomers ER or as tetrahedral clusters of the type E₄R₄,^[3] in which R denotes very bulky substituents. A neopentylgallium(I) compound was reported in literature,^[4] however, it was not isolated in a pure form. For many years we have tried to control the size of E^I clusters by the systematic variation of the steric demand of their substituents. Smaller groups should lead to the formation of larger clusters, which are of particular interest owing to their bonding and broad preparative application in secondary reactions. However, the tendency to disproportionate as a consequence of insufficient steric shielding prevented the isolation of such derivatives.

The reaction of *tert*-butyllithium with gallium trihalides affords tri(*tert*-butyl)gallium^[5] in a good yield as well as a small quantity of elemental gallium by a redox reaction. By systematically changing the reaction conditions we attempted to stop the partial reduction of trivalent gallium at an intermediate oxidation state. Finally, we obtained a green solution from which black-green crystals of **1** were isolated in 4% yield after separation of the alkylgallium(III) compound [Eq. (1)]. Owing to the easy availability of compound **1** a complete characterization was possible despite its low yield. The crystal structure determination^[6] revealed a tricapped



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