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A Neutral Ga_6 Octahedron: Synthesis, Structure, and Aromaticity

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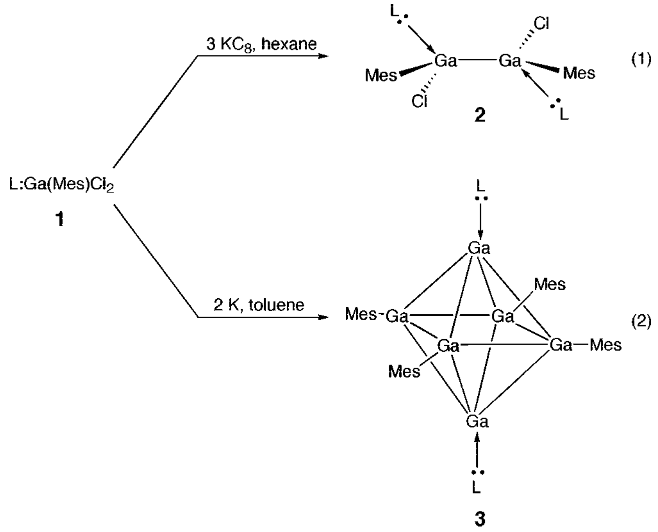
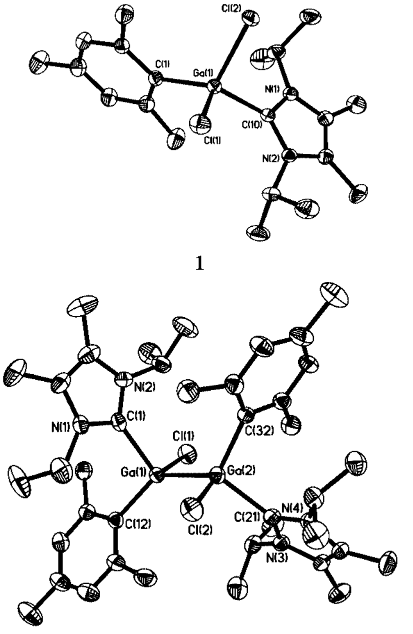
While the chemistry of anionic boron clusters such as *closo*-$B_nH_n^{2-}$ ($6 \le n \le 12$) is well-established, the last two decades have witnessed a rapid development of the corresponding chemistry of the heavier group 13 elements.[1−4] Although the preparation of $K_2[Al_{12}i\text{-}Bu_{12}]$[5] and $[Ga_6\{Si(CMe_3)_3\}_4(CH_2C_6H_5)_2]^{2-}$ [6] are notable advances, the experimental realization of neutral aromatic assemblies of heavier group 13 elements continues to present a challenge.[1] Indeed, the neutral aromatic Ga_6R_4 octahedron has yet to be prepared. However, Ga_6R_4 [R = Si(*t*-Bu$_3$)] is postulated to be a reactive intermediate in the formation of Ga_8R_6.[7] The complexation of gallium halide clusters by Lewis bases, exemplified by triethylphosphine in $Ga_8I_8(PEt_3)_6$,[8] is an interesting approach. Can N-heterocyclic carbenes, serving as Lewis bases, stabilize group 13 metallic clusters? Utilizing this strategy, we recently stabilized a group of highly reactive diatomic molecules, including neutral diborenes [L:(H)B=B(H):L],[9,10] disilicon (L:Si=Si:L),[11] and diphosphorus (L:P−P:L).[12] We now report the syntheses,[13] molecular structures,[13] and computations[14] of three new carbene-stabilized organogallium compounds: L:Ga(Mes)Cl_2 (**1**), L:(Mes)(Cl)Ga−Ga(Cl)(Mes):L (**2**), and L:Ga[Ga_4Mes_4]Ga:L (**3**), where L: = :C{(*i*-Pr)NC(Me)}$_2$ and Mes = 2,4,6-$Me_3C_6H_2$. Notably, compound **3** is the first example of a neutral aromatic Ga_6 octahedron.

The carbene-complexed mesitylgallium dichloride **1** was quantitatively prepared by the reaction of $MesGaCl_2$ with L:.[13] Remarkably, potassium graphite reduction of **1** in hexane (**1**/KC_8 = 1:3) formed air- and moisture-sensitive pale-yellow crystals of **2** (eq 1), while potassium reduction of **1** in toluene (**1**/K = 1:2) resulted in ruby-red crystals of **3** (eq 2):



The four-coordinate gallium atoms in **2** reside in distorted tetrahedral geometries (Figure 1). The formal gallium oxidation numbers in compounds **1** and **2** are +3 and +2, respectively. The Ga−Ga bond length in **2**, 2.447 Å, is comparable to those in gallium(II) iodide amine and phosphane complexes (2.425−2.459 Å).[15] The Ga−$C_{L:}$ distance in **2** (2.101 Å) approaches the Ga−C_{Mes} bond distance (2.028 Å). The Ga−Cl and Ga−C bonds in **2** are only marginally longer than those in **1**.



1

2

Figure 1. Molecular structures of **1** and **2**, with thermal ellipsoids shown at the 30% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å): For **1**: Ga(1)−C(1), 1.978(2); Ga(1)−C(10), 2.048(2); Ga(1)−Cl(1), 2.2468(6); Ga(1)−Cl(2), 2.2444(6). For **2**: Ga(1)−Ga(2), 2.4474(11); Ga(1)−C(1), 2.101(7); Ga(1)−C(12), 2.028(7); Ga(1)−Cl(1), 2.300(2).

The octahedral Ga_6 core is the most striking structural feature of **3**, a carbene-stabilized neutral gallium octahedron (Figure 2). Each gallium atom in **3** is five-coordinate; four Mes−Ga groups occupy the equatorial sites, while two L:Ga moieties populate the axial positions. Thus, one can consider the formal oxidation states of the gallium atoms in the Mes−Ga and L:Ga units to be +1 and zero, respectively. Indeed, **3** resembles the isoelectronic $[Ga_6\{Si(CMe_3)_3\}_4(CH_2C_6H_5)_2]^{2-}$ dianion:[6] both have 14 skeletal electrons, consistent with the Wade−Mingos rules.[1] Although $Ga_6Cp^*_6$ (Cp* = Me_5C_5)[16] is also a neutral Ga_6 octahedron, it has extremely long Ga−Ga distances (> 4.0 Å). Neutral Ga_6R_6 [R = SiMe(SiMe$_3$)$_2$],[6] has only 12 skeletal electrons and a Jahn−Teller-distorted *precloso*-octahedral Ga_6 core. Dianionic $Ga_6R_8^{2-}$ [R = Si(C_6H_5)$_2$Me][17] exhibits a planar Ga_6 frame that is also present in *β*-Ga.

10.1021/ja809945v CCC: $40.75

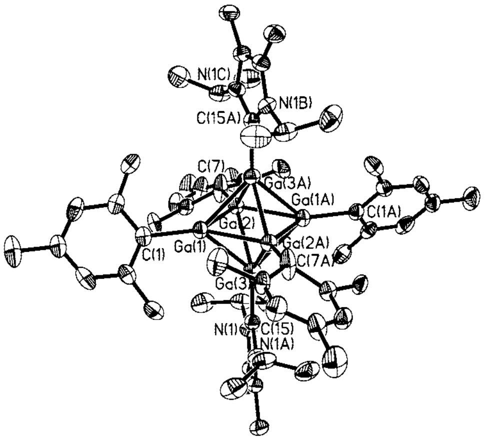


Figure 2. Molecular structure of **3**, with thermal ellipsoids shown at the 30% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ga(1)−Ga(2), 2.5905(11); Ga(1)−Ga(3), 2.5109(12); Ga(2)−Ga(3), 2.5165(12); Ga(2)−Ga(3)−Ga(2A), 93.68(5); Ga(1A)−Ga(3)−Ga(1), 93.44(5); Ga(1A)−Ga(2)−Ga(1), 89.76(5); Ga(3)−Ga(2)−Ga(3A), 86.32(5); Ga(2A)−Ga(1)−Ga(2), 90.24(5); Ga(3)−Ga(1)−Ga(3A), 86.56(5).

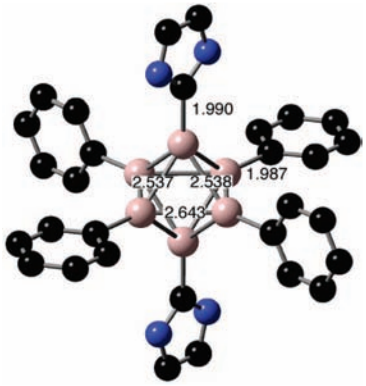


Figure 3. Structure of the **3a** model optimized at the B3LYP/6-311+G** level.

The fact that the diagonal Ga(3)···Ga(3a) distance (3.443 Å) is noticeably shorter than the Ga(1)···Ga(1a) (3.656 Å) and Ga(2)···Ga(2a) (3.671 Å) separations in **3** suggests a tetragonal compression of the Ga_6 octahedron. A more pronounced tetragonal compression was observed in the Tl_6^{6-} octahedral polyanion in CsTl.[18] The distortion of the Ga_6 octahedron in **3** is also illustrated by the longer Ga(1)−Ga(2) bond distance of 2.590 Å in the $(MesGa)_4$ square plane compared with the Ga(1)−Ga(3) and Ga(2)−Ga(3) bond lengths (2.511 and 2.516 Å, respectively). Three twofold axes, through the Ga(1)···Ga(1A), Ga(2)···Ga(2A), and Ga(3)···Ga(3A) diagonals, constitute the D_2 symmetry of **3**.

Density functional theory (DFT) computations on a simplified model of **3**, L′:Ga[Ga_4Ph_4]Ga:L′ [L′: = :C{N(H)C(H)}$_2$] (**3a**) (Figure 3) at the B3LYP/6-311+G** level are in reasonable agreement with the experimental values.[14] Natural bond orbital (NBO)[19] analysis of **3a** shows that the natural atomic orbital indices (NAO) and Wiberg bond indices (WBI) of the $Ga_{L'}-Ga_{Ph}$ bonds (NAO = 0.729, 0.747; WBI = 0.606, 0.647) are larger than those of the $Ga_{Ph}-Ga_{Ph}$ bonds (NAO = 0.679; WBI = 0.548). The skeletal bond orders in **3a**, however, are similar to those for the $B_6H_6^{2-}$ (NAO = 0.766, WBI = 0.683) and $Ga_6H_6^{2-}$ (NAO = 0.683, WBI = 0.646) dianions.

The nucleus-independent chemical shift (NICS)[20] values computed at the cluster centers at the PW91PW91/6-311+G** level indicated that **3a** (NICS = −10.2), although aromatic, was less so than its parent octahedral dianion congeners $[Ga_6H_6]^{2-}$ (NICS = −27.3), $[Al_6H_6]^{2-}$ (NICS = −25.1), and $[B_6H_6]^{2-}$ (NICS = −27.5[21]).

The strong complexing capabilities[22] and "superbasicity"[23] description of N-heterocyclic carbenes are quantified by our B3LYP/6-311+G**+ZPE-computed binding energies for the reactions of the model parent imidazole-based L′: with $GaCl_3$ to give L′:$GaCl_3$ (47.0 kcal/mol), with $C_6H_5GaCl_2$ to give L′:$GaC_6H_5Cl_2$ (**1a**) (37.9 kcal/mol), and with $(C_6H_5)(Cl)Ga-Ga(Cl)(C_6H_5)$ to give L′:$(C_6H_5)(Cl)Ga-Ga(Cl)(C_6H_5)$:L′ (**2a**) (67.2 kcal/mol). The utilization of carbenes in the stabilization of a neutral aromatic Ga_6 octahedron further illustrates the fascinating versatility of these ligands.

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Supporting Information Available: Full details concerning the syntheses, computations, and X-ray crystal determinations as well as CIF files for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) See the Supporting Information for synthetic and crystallographic details.
(14) Computations: All of the structures were optimized at the B3LYP/6-311+G** DFT level, and NICS values were computed at the PW91PW91 DFT level with the 6-311+G** basis set. The Gaussian 03 program was used in all cases. See the Supporting Information.
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