Gallium Clusters

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Main-Group-Metal Clusters Stabilized by N-Heterocyclic Carbenes

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aromaticity · carbene ligands · cluster compounds · gallium · Wade's rules

The chemistry of boron is characterized by its marked propensity for the formation of cluster compounds in order to compensate the formal electron deficiency of the boron atoms by electron delocalization.[1] The formation of single-shell homo- and heteronuclear clusters is preferred. These may be classified as *closo*, *nido*, or *arachno* species, containing $n+1$, $n+2$, or $n+3$ cluster electron pairs according to Wade's rules (where n corresponds to the number of boron atoms which constitute the cluster).[2] Subhalides B_nX_n and the tetraboron compound $B_4(CMe_3)_4$ display a lower electron count with n electron pairs.[3] Clusters of the heavier Group 13 elements aluminum to thallium have only been described in the last decade, and Wade-like single-shell deltahedral compounds remain particularly scarce.[4] The first species of this type to be reported was $K_2[Al_{12}iBu_{12}]$, which features a *closo* configuration with an icosahedral arrangement of twelve aluminum atoms.[5] Neutral, tetrahedral compounds E_4R_4 (E = Al, Ga, In, Tl) with four skeleton electron pairs have been isolated in greater numbers and contain metal atoms in the formal oxidation state +I.[4,6]

In a series of remarkable publications, Robinson et al. recently reported a new synthetic approach to low-valent p-block-element compounds. Dinuclear compounds containing low-coordinate HB=BH, Si=Si, and P–P units (Scheme 1) were prepared by reduction of suitable element halides with alkali metals in the presence of N-heterocyclic carbenes (NHCs).[7–9] The stability of these very unusual species may be attributed to the steric protection induced by bulky substituents on the carbene. Modification of the NHC ligand may therefore permit access to higher aggregates.[10] The synthesis of a new deltahedral gallium cluster now proved the utility of this approach.[11] Reduction of the Ga^{III} NHC complex $[GaCl_2(Mes)L]$ (Mes = 2,4,6-$Me_3C_6H_2$, L = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with potassium in toluene yielded the neutral hexagallium cluster **1**, which features six gallium atoms in a slightly distorted octahedral arrangement (Ga–Ga 251.1(1) to 259.1(1) pm; Figure 1). Thus, **1** shows the

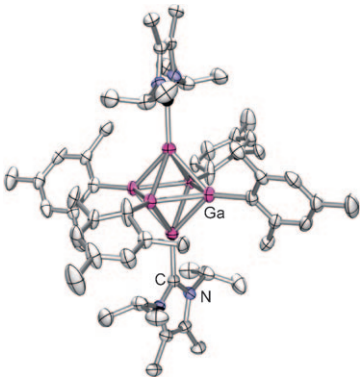
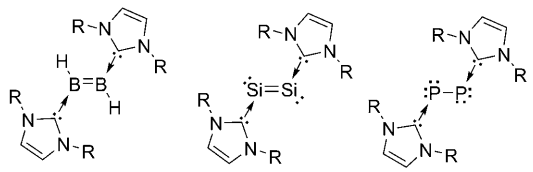


Figure 1. Molecular structure of **1**.

characteristic deltahedral structure of a *closo* cluster analogous to $B_6H_6^{2-}$.[12] One mesityl group is bound to each of the equatorial metal atoms, while the axial gallium atoms are each coordinated by a neutral NHC ligand, which acts as a two-electron donor. The weak tetragonal compression of the octahedron is caused by the different formal oxidation states of the gallium atoms (+I for the equatorial ones and ±0 for the axial ones). Contribution of three electrons from each of the two axial metal atoms and two electrons from each of the four equatorial atoms results in a total of seven skeleton electron pairs, which corresponds to a *closo* configuration.

Compound **1** formally resembles the dianionic cluster **2** (Scheme 2), synthesized by Linti et al. using a different route. Compound **2** displays four silyl substituents and two benzyl groups bound to gallium, the latter of which are in a *cis* arrangement.[13] The same research group also obtained the neutral hexagallium cluster **3**, which possesses only six skeleton electron pairs and hence shows a distorted *precloso*



Scheme 1. Carbene-stabilized diboron, disilicon, and diphosphorus compounds (R = 1,3-$iPr_2C_6H_3$).

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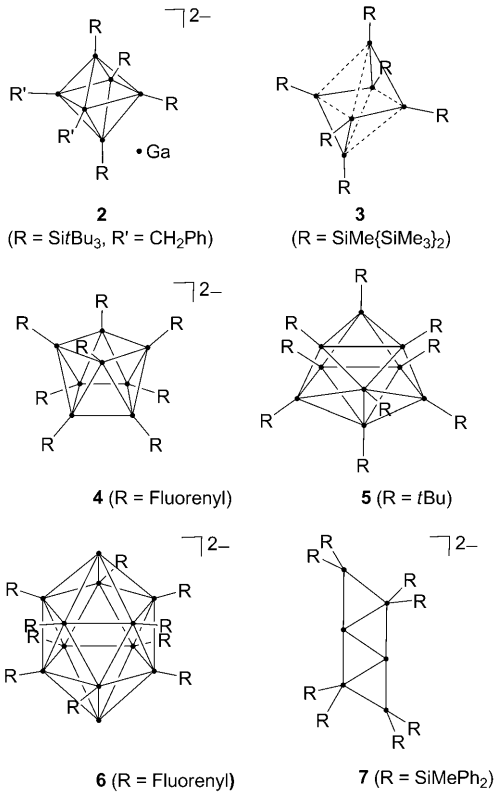

Scheme 2. Selected clusters with six to twelve gallium atoms.

structure. Removing two electrons from the degenerate highest occupied molecular orbitals (HOMOs) of the dianion $[Ga_6R_6]^{2-}$ thus effects a strong distortion of the octahedron in $[Ga_6R_6]$ (Jahn–Teller effect).[13]

Wade's rules can be employed for describing compounds **1–3** but do not accurately predict the structures of other gallium clusters. For example, a triangular dodecahedron may be expected for the *closo* octagallium compound **4** owing to its nine skeleton electron pairs, whereas a square antiprismatic structure is in fact observed (Scheme 2).[14] The Ga_9 cluster **5** has nine electron pairs available for cluster bonding, which is one less than formally required for a *closo* cluster. Nevertheless, it displays a typical closed-shell, deltahedral geometry in the form of a tricapped trigonal prism.[15] Although a *nido* structure would be expected because of its 14 skeleton electron pairs, the $[Ga_{12}R_{10}]^{2-}$ cluster **6** features a Ga_{12} icosahedron.[16] Compound **6** resembles the hexagallium cluster **1** in that it displays two singular, axial gallium atoms which each donate three electrons to the cluster. The rhombic Ga_6 cluster $[Ga_6R_8]^{2-}$ (**7**) further illustrates the limitations of the Wade rules in gallium cluster chemistry.[17] Similar to other clusters containing ligand-free metal atoms, **7** shows a "metalloid" structure related to β-gallium.[18]

Quantum chemical methods can be utilized to understand the bonding situation of such clusters and to unravel systematic relationships.[11,13–20] For example, the stability of the $[Ga_8R_8]^{2-}$ cluster **4** may be inferred from its orbital sequence, which shows the typical pattern for a *closo* cluster analogous to $B_8H_8^{2-}$.[14] However, the electronic structures of gallium clusters often deviate from those of the polyboranes. In these cases, application of the Wade–Mingos concept is doomed to failure, and the intuitive prediction of a certain structural motif can be misleading.[18–20] One important factor stabilizing polyhedral clusters is their spherical aromaticity, which can be quantified by calculating nucleus-independent chemical shifts (NICS).[19,21,22] To date, quantum chemical investigations of the aromatic character of electron-poor Group 13 element clusters appear to be largely limited to polyhedral boranes[21] and ligand-free, planar systems such as Al_4^{2-}.[23] DFT calculations demonstrate the aromatic character of **1** (NICS = −10.2).[11] The dianionic clusters $B_6H_6^{2-}$ (NICS = −27.5) and $Ga_6H_6^{2-}$ (NICS = −27.3) display even more negative values. A systematic analysis of the aromaticity of interrelated clusters might provide a new starting point for explaining experimental observations.[24]

In summary, the neutral, octahedral hexagallium compound **1** was isolated as the first carbene-stabilized *closo* cluster. The synthesis of further interesting gallium clusters and homologous aluminum and indium compounds may be expected in the future. Access to the corresponding boron congeners is equally conceivable and may provide an important addition to this long-established field of chemistry. Considering the ready availability of N-heterocyclic carbenes and their very advantageous steric and electronic properties,[25] a broad range of novel cluster compounds appears to be within reach. Thus, the pioneering work of Robinson et al. doubtlessly has the potential to initiate a further fascinating development of Group 13 element cluster chemistry.

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