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Chemical applications of topology and group theory. Part 36. Deltahedral and fused deltahedral organometallic gallium and indium clusters[☆]

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Abstract

This paper surveys the structures and chemical bonding in several recently discovered organometallic gallium and indium clusters including the tricapped trigonal prism $Ga_9(CMe_3)_9$, the bicapped octahedron $In_8[Si(CMe_3)_3]_6$, fused deltahedra such as $Ga_{10}[Si(SiMe_3)_3]_6$ and $In_{12}[Si(CMe_3)_3]_8$, and the more complicated supraicosahedral structures $[Ga_{19}\{C(SiMe_3)_3\}_8]^{2-}$, $Ga_{22}[Si(SiMe_3)_3]_8$, and $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$. The Wade–Mingos $2n+2$ and Jemmis $2n+2m$ electron-counting rules appear to be applicable to most of these clusters. The deltahedra found in the supraicosahedral Group 13 metal clusters can be derived from the 12-vertex cuboctahedron and related 13-vertex polyhedra by capping all of the non-triangular faces. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Group 13 metals; Organometallic clusters; Topology

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1. Introduction

Boron is well known to form a variety of deltahedral structures including the very stable deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) having external B–H bonds as well as isoelectronic derivatives in which one to three of the boron vertices have been replaced by carbon vertices, e.g. the monoanions $CB_{n-1}H_n^-$ and the neutral carboranes $C_2B_{n-2}H_n$. These deltahedral boranes are considerably more stable than the long-known neutral binary boron hydrides of the types B_nH_{n+4} and B_nH_{n+6}. The heavier congeners of boron, namely the triels or icosogens Ic (Ic = Al, Ga, In, Tl), form much weaker Ic–H bonds and thus the corresponding deltahedral $Ic_nH_n^{2-}$ derivatives remain unknown. However, replacement of the relatively weak Ic–H bonds with stronger Ic–C bonds has recently been shown to give stable deltahedral clusters of the general type $Ic_nR_n^{z-}$ (Ic = Al and Ga; $z = 0$, 1, and 2 in the known examples). The first such compound to be prepared was the icosahedral aluminum cluster $K_2[i\text{-}Bu_{12}Al_{12}]$ (i-Bu = *iso*-butyl), which was found to be considerably more stable in air than the typically air sensitive or even pyrophoric aluminum alkyls [2]. Within the last 2 years the number of such known deltahedral clusters of Al, Ga, and In has escalated including single deltahedra of the general type $Ga_9(CMe_3)_9$ [3]; the bicapped octahedron $In_8[Si(CMe_3)_3]_6$ [4]; fused deltahedra such as $Ga_{10}[Si(SiMe_3)_3]_6$ [5] and $In_{12}[Si(CMe_3)_3]_8$ [6]; and the more complicated supraicosahedral structures of the types $[Ga_{19}\{C(SiMe_3)_3\}_8]^{2-}$ [7], $Ga_{22}[Si(SiMe_3)_3]_8$ [8] and $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$ [9]. The deltahedra found in these organometallic metal clusters are closely related to the deltahedra found in deltahedral boranes in contrast to the flattened hypoelectronic deltahedra found in alkali-metal intermetallics of Ga, In, and Tl related to Zintl ions [10,11]. Linti and Schnöckel [12] have recently reviewed their work on organogallium clusters.

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2. Three-dimensional aromaticity and electron counting in icosogen deltahedra

2.1. Isolated deltahedra

The four valence orbitals, sp^3, on each vertex atom in a delocalized polyhedral icosogen cluster may be conveniently divided into one external orbital, two equivalent twin internal orbitals, and one unique internal orbital [13–16]. The external orbital is used to form a σ bond to an external alkyl or aryl group in the organometallic icosogen clusters analogous to its σ bond to hydrogen in the case of the corresponding boranes $B_nH_n^{2-}$. The unique internal orbitals, also called radial orbitals [17], form a single multicenter core bond in the center of the polyhedron. The twin internal orbitals, also called tangential orbitals [17], overlap pairwise to form two-center bonds in the surface of the polyhedron. In the case of a globally delocalized deltahedron, corresponding to a three-dimensional aromatic system [13,15,16] the core bond is an n-center bond requiring two-skeletal electrons. Furthermore, the surface bonding in a globally delocalized deltahedron having n vertices may be regarded as a resonance hybrid of canonical structures consisting of n pairwise interactions of the tangential orbitals requiring $2n$ skeletal electrons. This leads to the '$2n+2$' skeletal electron rule for globally delocalized (aromatic) deltahedra with n vertices first observed by Williams [18] and studied in further detail by Wade [19] and Mingos [20,21].

2.2. Fused deltahedra

Balakrishnarajan and Jemmis [22,23] have recently extended the electron counting rules from isolated borane deltahedra to fused borane deltahedra, which are the three-dimensional analogues of polycyclic aromatic hydrocarbons such as naphthalene. They arrive at the requirement of $n+m$ skeletal electron pairs corresponding to $2n+2m$ skeletal electrons for such fused deltahedra having n total vertices and m individual deltahedra. This electron count corresponds to pairwise surface bonding in these fused deltahedral structures ($2n$) supplemented by a multicenter core bond in the center of each individual deltahedron ($2m$). Note that for a single deltahedron (i.e. $m=1$) the Jemmis $2n+2m$ rule reduces to the Wade–Mingos $2n+2$ rule.

The vertices in fused deltahedral boranes shared by two or more deltahedra have no external groups. Therefore, all four orbitals of the boron sp^3 manifold become internal orbitals and all of the boron valence electrons become skeletal electrons. Thus a boron vertex without an external group shared between two deltahedra is a donor of three-skeletal electrons in contrast to a B–H group belonging to a single deltahedron which is a donor of only two-skeletal electrons. Similar electron counting rules naturally apply to the related clusters of the heavier icosogens discussed in this paper.

Table 1
The dimensions of some tricapped trigonal prismatic clusters

Cluster	v/h ratio	Literature reference
18-skeletal electron clusters		
B_9Cl_9	1.14	[24]
B_9Br_9	1.14	[24]
$Ga_9(CMe_3)_9$	1.12	[3]
19-skeletal electron cluster		
$B_9Br_9^-$	0.91	[24]
20-skeletal electron clusters		
$B_9Br_9^{2-}$	0.89	[24]
$B_9H_9^{2-}$	0.97	[26]
$B_7H_7C_2Me_2$	0.90	[26]
Ge_9^{2-}	1.03	[27]
22-skeletal electron cluster		
Bi_9^{5+}	1.15	[28]

3. Simple deltahedral structures

The first deltahedral cluster of a heavier Group 13 element to be prepared was the icosahedral aluminum cluster $K_2[i\text{-}Bu_{12}Al_{12}]$ [2], which is isoelectronic and isostructural with the icosahedral borane anion $B_{12}H_{12}^{2-}$ with 26 skeletal electrons corresponding to the $2n+2$ for the icosahedron. No further simple deltahedral clusters of the heavier Group 13 metals were known until the very recent discovery [3] of the nine-vertex gallium cluster $Ga_9(CMe_3)_9$ from the reaction of $GaCl_3$ with $LiCMe_3$. This tricapped trigonal prismatic deltahedral cluster is an 18-skeletal electron cluster corresponding to $2n$ rather than $2n+2$ skeletal electrons for $n=9$. This anomalous electron count is analogous to that found in the stable neutral boron halides B_9X_9 (X = Cl, Br, I). In fact deltahedral (tricapped trigonal prismatic) nine-vertex clusters are known with 18, 19, 20, and 22 skeletal electrons (Table 1).

Approximately 20 years ago [25] I noted the relationship of the skeletal electron count of a tricapped trigonal prism to its geometry as measured by the ratio of the length of the prism 'height' (i.e. vertical distance, v) to the basal edge length (i.e. horizontal distance, h) depicted in Fig. 1a. Thus the v/h ratio (Table 1) was found to be in the range 0.9–1.0 for 20-skeletal electron clusters such as $B_9H_9^{2-}$ [26], $B_7H_7C_2Me_2$ [26], and Ge_9^{2-} [27] but 1.15 for the 22-skeletal electron cluster Bi_9^{5+} [28]. The large amount of additional structural data that have become available during the last 20 years continue to support the observation that tricapped trigonal prismatic clusters

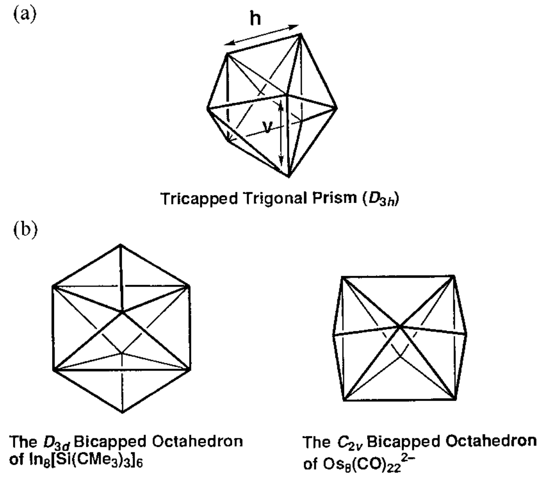

Fig. 1. (a) The tricapped trigonal prism showing the horizontal (*h*) and vertical (*v*) distances. (b) A comparison of the bicapped octahedra found in $In_9[Si(CMe_3)_3]_6$ and $Os_8(CO)_{22}^{2-}$.

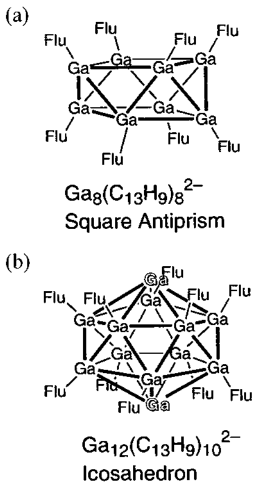

Fig. 2. (a) Square antiprismatic $Ga_8(C_{13}H_9)_8^{2-}$. (b) Icosahedral $Ga_{12}(C_{13}H_9)_{10}^{2-}$. For clarity in these structures the fluorenyl group ($C_{13}H_9$) is abbreviated as Flu.

with the 20 skeletal electrons required by the $2n+2$ rule are more compressed (i.e. have a lower v/h ratio) than those with either more (22 skeletal electrons) or less (18-skeletal electrons). The 19 skeletal electron radical anion $B_9Br_9^-$ also has a small v/h ratio of 0.91 similar to the 20-skeletal electron dianion $B_9Br_9^{2-}$.

An unusual type of deltahedral cluster found in organoindium chemistry but not in deltahedral boron chemistry is the eight-vertex cluster $In_8[Si(CMe_3)_3]_6$ [4] with a structure based on a bicapped octahedron with idealized D_{3d} symmetry of the underlying polyhedron (Fig. 1b). The D_{3d} bicapped octahedron has six degree five vertices and two degree three vertices. In $In_8[Si(CMe_3)_3]_6$ the two In vertices lacking the $Si(CMe_3)_3$ groups are degree five vertices. If the six $(Me_3C)_3SiIn$ vertices are donors of two skeletal electrons and the two 'bare' In vertices have an external lone pair so that they are donors of a single skeletal electron, then $In_8[Si(CMe_3)_3]_6$ is a $(6\times 2)+(2\times 1)=$ 14-skeletal electron structure in accord with its central In_6 octahedron. Thus $In_8[Si(CMe_3)_3]_6$ may be regarded as an 'electron-poor' or hypoelectronic cluster [29] analogous to a variety of osmium carbonyls [30]. Interestingly enough, the structure of $In_8[Si(CMe_3)_3]_6$ is derived from a symmetrical D_{3d} bicapped octahedron whereas the eight-vertex isoelectronic osmium carbonyl anion $Os_8(CO)_{22}^{2-}$ [31] is derived from a less symmetrical C_{2v} bicapped octahedron (Fig. 1b).

Most of the deltahedral clusters of the heavier icosogens have bulky spherical external groups such as *tert*-butyl and the bulky silyl groups $-Si(CMe_3)_3$ and $-Si(SiMe_3)_3$. When the flat but still bulky fluorenyl groups are used rather than these bulky spherical groups, then the packing of the external groups rather than the electronic configuration appears to determine the nature of the polyhedral clusters. Thus the two structurally characterized fluorenylgallium clusters are the eight-vertex $Ga_8(C_{13}H_9)_8^{2-}$ [32] and the 12-vertex $Ga_{12}(C_{13}H_9)_{10}^{2-}$ [33] (Fig. 2). Both of these compounds have the fluorenyl groups in antiprismatic configurations in order to provide propeller-like packing of this large flat group. Thus the eight fluorenyl groups in $Ga_8(C_{13}H_9)_8^{2-}$ form a square antiprism whereas the ten fluorenyl groups in $Ga_{12}(C_{13}H_9)_{10}^{2-}$ form a pentagonal antiprism. As a result of this antiprismatic configuration of the external fluorenyl groups, the eight-vertex cluster $Ga_8(C_{13}H_9)_8^{2-}$ has a square antiprismatic structure rather than the *closo*-bisdisphenoidal structure expected for such a $2n+2$ skeletal electron system. An earlier example of a square antiprismatic metal cluster with $18=2n+2$ skeletal electrons for $n=8$ is the cobalt carbonyl carbide anion $Co_8C(CO)_{18}^{2-}$ [34]. The similarity in the energy of the bisdisphenoid and the square antiprism is indicated by the fluxionality of $B_8H_8^{2-}$ [35].

The 12-vertex $Ga_{12}(C_{13}H_9)_{10}^{2-}$ is more unusual since the Ga_{12} unit in this cluster forms a nearly regular icosahedron with only 24 ($=2n$ for $n=12$) rather than the expected 26 ($=2n+2$) skeletal electrons. Such electron counting assumes that the two 'bare' gallium vertices have an external lone pair and thus donate a single skeletal electron. However, density functional calculations [33] lead to the formulation of $Ga_{12}(C_{13}H_9)_{10}^{2-}$ as a 28- rather than a 24-skeletal electron system suggesting that the two 'bare' gallium atoms are three-skeletal electron donors by using all of their valence electrons. These two 'bare' gallium atoms in $Ga_{12}(C_{13}H_9)_{10}^{2-}$ may be similar to the flattened icosogen vertices in the deltahedra found in alkali-metal intermetallics of Ga, In, and Tl [10,11].

4. Fused deltahedral (*conjuncto*) structures

The two reported examples of heavier icosogen clusters consisting of two fused deltahedra are $Ga_{10}[Si(SiMe_3)_3]_6$ [5] and $In_{12}[Si(CMe_3)_3]_8$ [6]. These two clusters have closely related structures (Fig. 3) with edge-sharing pairs of deltahedra, which are octahedra in the case of $Ga_{10}[Si(SiMe_3)_3]_6$ and bisdisphenoids in the case of $In_{12}[Si(CMe_3)_3]_8$. An aluminum cluster radical anion $Al_{12}[N(SiMe_3)_2]_8^-$ is known [36] with a structure closely related to that of $In_{12}[Si(CMe_3)_3]_8$. In both cases the two vertices of the shared edge and two other vertices are bare vertices free of terminal groups. For electron-counting purposes the bare icosogen vertices can be assumed to use all the four orbitals of their sp^3 manifolds and thus all of their valence electrons so that each such vertex is a donor of three-skeletal electrons. With this in mind both of these cluster types can be seen to follow the Jemmis electron counting rules for fused polyhedral clusters [22,23]. Thus $Ga_{10}[Si(SiMe_3)_3]_6$ receives $6 \times 2 = 12$ skeletal electrons from the six RGa groups and $4 \times 3 = 12$ skeletal electrons from the four 'bare' Ga atoms with four internal orbitals. The resulting 24-skeletal electrons correspond to the $2n + 2m$ skeletal electrons required by the ten gallium atoms ($n = 10$) and the two polyhedra ($m = 2$). Similarly $In_{12}[Si(CMe_3)_3]_8$ receives $8 \times 2 = 16$ skeletal electrons from the eight RIn groups and $4 \times 3 = 12$ skeletal electrons from the four 'bare' In atoms. The resulting 28 skeletal electrons again follow the Jemmis rules by corresponding to $2n + 2m$ for $n = 12$ and $m = 2$.

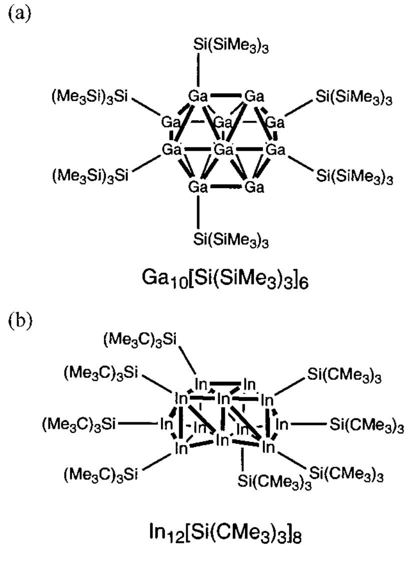

Fig. 3. (a) The fused pair of octahedra in $Ga_{10}[Si(SiMe_3)_3]_6$. (b) The fused pair of bisdisphenoids in $In_{12}[Si(CMe_3)_3]_8$.

5. Supraicosahedral structures

Some larger gallium clusters have been recently prepared which may be interpreted as containing gallium supraicosahedra with a single gallium atom in the center analogous to the centered $Tl@Tl_{12}$ icosahedron found in the intermetallic $Na_3K_8Tl_{13}$ [37]. In all cases the structures of such clusters can be derived by the following procedure:

1. Start with a 12- or 13-vertex gallium polyhedron containing some quadrilateral and/or pentagonal faces. This polyhedron is conveniently called the *core polyhedron*.
2. Cap each of the non-triangular faces of the core polyhedron with one or more additional gallium atoms. This leads to a supraicosahedral deltahedron since the capping process removes all of the non-triangular faces.
3. Place an additional gallium atom in the center of the core polyhedron.
4. Place bulky organic substituents (typically $-C(SiMe_3)_3$ or $-Si(SiMe_3)_3$) on the outermost gallium atoms.

Electron counting in these supraicosahedral gallium clusters has some ambiguities since it is not clear which of the bare vertex atoms of the core polyhedra provide the usual three internal orbitals and which vertex atoms provide four internal orbitals. Typically, it is seen that the Wade–Mingos [17–20] or Jemmis and coworkers [22,23] skeletal electron rule is obeyed if about half of the bare vertex gallium atoms use all four orbitals of their sp^3 manifolds as internal orbitals and thus are donors of three skeletal electrons and the other half of the bare vertex gallium atoms use only three orbitals of their sp^3 manifolds and thus are donors of only a single skeletal electron.

The simplest such supraicosahedral organogallium cluster is that of the anion $[Ga_{19}\{C(SiMe_3)_3\}_6]^-$ which has a structure based on a centered $Ga@Ga_{18}$ deltahedron (Fig. 4) [7]. The structure of this 18-vertex deltahedron can be derived from a cuboctahedron by capping its six square faces with $(Me_3Si)_3CGa$ vertices. A similar hexacapped cuboctahedron is found in the polyoxovanadate $V_{18}O_{42}^{12-}$ when it encapsulates tetrahedral anions such as SO_4^{3-} and VO_4^{3-} [38]. If the 12 vertices of the underlying Ga_{12} cuboctahedron are partitioned in accord with the symmetry so that six use four internal orbitals and six use only three internal orbitals, the electron counting for $[Ga_{19}\{C(SiMe_3)_3\}_6]^-$ can proceed as follows:

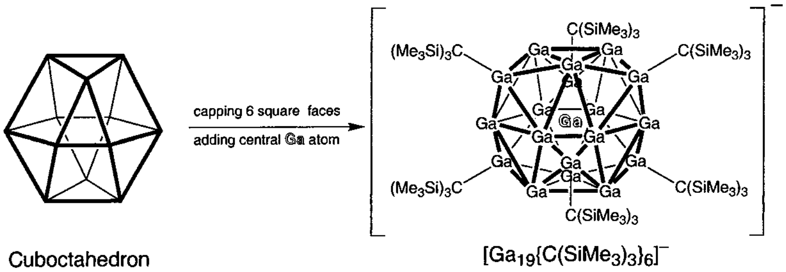

Fig. 4. Generation of the $[Ga_{19}\{C(SiMe_3)_3\}_6]^-$ structure from the cuboctahedron by capping the six square faces and adding a central gallium atom.

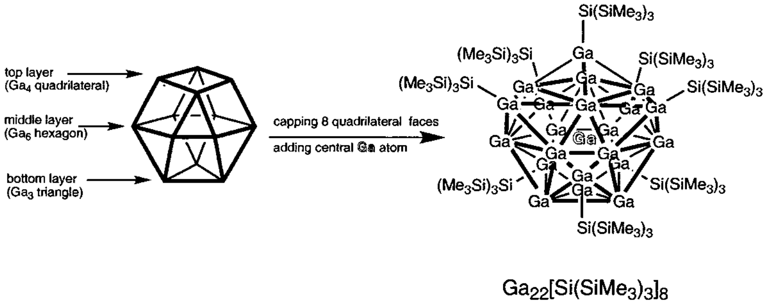

Fig. 5. Generation of the $Ga_{22}[Si(SiMe_3)_3]_8$ structure from a 13-vertex polyhedron with eight quadrilateral faces.

Six outer $(Me_3Si)_3CGa$ vertices: $6\times 2=$	12 electrons
Six Ga atoms in the Ga_{12} cuboctahedron using four internal orbitals: $6\times 3=$	18 electrons
Six Ga atoms in the Ga_{12} cuboctahedron using four internal orbitals: $6\times 1=$	6 electrons
One center Ga atom:	3 electrons
−1 charge	1 electron
Total skeletal electrons	40 electrons

In terms of the Jemmis $2n+2m$ rule [22,23] the 40-skeletal electron count by the above scheme corresponds to $m=2$ for an 18-vertex system ($n=18$) suggesting that the centered 18-vertex deltahedron is partitioned into two polyhedral cavities, each containing a multicenter core bond.

The next most complicated supraicosahedral gallium structure is that of $Ga_{22}[Si(SiMe_3)_3]_8$ in which the gallium atoms form a centered $Ga@Ga_{21}$ 21-vertex deltahedron [8]. The relatively low symmetry 21-vertex deltahedron in $Ga_{22}[Si(SiMe_3)_3]_8$ can be derived from a 13-vertex Ga_{13} polyhedron with eight quadrilateral faces and six triangular faces by capping all the eight of the quadrilateral faces with $(Me_3Si)_3SiGa$ vertices. The underlying 13-vertex polyhedron in $Ga_{22}[Si(SiMe_3)_3]_8$ may be regarded as a three-layer structure with a Ga_4 quadrilateral in the top layer, a Ga_6 hexagon in the middle layer, and a Ga_3 triangle in the bottom layer (Fig. 5). Within the underlying Ga_{13} polyhedron, the six gallium atoms common to three quadrilateral faces and thus bonded directly to four of the $(Me_3Si)_3SiGa$ caps may be regarded as using all four orbitals of their sp^3 valence orbital manifold for skeletal bonding. Each of these six gallium atoms thus is a donor of three skeletal electrons. The other seven gallium atoms of the underlying Ga_{13} polyhedron, which are common to only two quadrilateral faces, may be regarded as using only three orbitals for skeletal bonding and thus each is a donor of only one skeletal electron. The center gallium atom in the $Ga@Ga_{21}$ deltahedron donates all the three of its valence electrons to the skeletal bonding whereas the outer $(Me_3Si)_3SiGa$ vertices are donors of two skeletal electrons. This leads to the following electron counting scheme for $Ga_{22}[Si(SiMe_3)_3]_8$:

Eight outer $(Me_3Si)_3SiGa$ vertices: $8\times 2=$	16 electrons
Six Ga atoms in the Ga_{13} polyhedron common to three square faces: $6\times 3=$	18 electrons
Seven Ga atoms in the Ga_{13} polyhedron common to two square faces: $7\times 1=$	7 electrons
One center Ga atom:	3 electrons
Total skeletal electrons	44 electrons

Note that the 44-skeletal electrons for $Ga_{22}[Si(SiMe_3)_3]_8$ obtained by this electron counting scheme corresponds to $2n+2$ where $n=21$ corresponding to the Ga-centered Ga@Ga_{21} deltahedron. This 21-vertex deltahedron is apparently the largest known deltahedron to follow the $2n+2$ Wade–Mingos skeletal electron counting rules [19–21].

The other supraicosahedral gallium cluster is the dianion $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$ [9]. The underlying polyhedral structure may be regarded as a fusion of a central Ga-centered Ga@Ga_{17} polyhedron with two side bicapped trigonal prisms. The core polyhedron of the $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$ structure is a 13-vertex polyhedron with eight triangular faces, six quadrilateral faces, and two pentagonal faces (Fig. 6). Capping the two pentagonal faces and two of the quadrilateral faces of the core polyhedron leads to a 17-vertex polyhedron, which still has two quadrilateral faces. These two remaining quadrilateral faces are then each capped with Ga_4 units to form with the central Ga atom a nine-vertex tricapped trigonal prismatic cavity on each side. The four gallium atoms corresponding to outer caps in each of these trigonal prismatic cavities bear external $Si(SiMe_3)_3$ groups to provide the remaining two $(Me_3Si)_3SiGa$ vertices.

The problem with counting electrons in $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$ is knowing which bare gallium atoms in this complicated structure use all four orbitals of their sp^3 valence orbitals for internal skeletal bonding and which bare gallium atoms use only three such orbitals for internal skeletal bonding. The former gallium atoms are donors of three skeletal electrons whereas the latter gallium atoms are donors of only a single skeletal electron. If $Ga_{26}[Si(SiMe_3)_3]_8^{2-}$ is considered to be a cluster containing three polyhedra (i.e. $m=3$) and 25 gallium atoms (i.e. $n=25$) then the Jemmis $2n+2m$ rule requires 28 skeletal electrons. This can be obtained as follows:

Eight outer $(Me_3Si)_3SiGa$ vertices: $8\times2=$	16 electrons
Four Ga atoms in the two outer capped trigonal prisms: $4\times1=$	4 electrons
Four 'outer' bare Ga vertices of the central underlying 13-vertex polyhedron using three internal orbitals: $4\times1=$	4 electrons
Nine bare Ga vertices of the central underlying 13-vertex polyhedron using four internal orbitals: $9\times3=$	27 electrons
One central Ga atom: $1\times3=$	3 electrons
−2 charge on ion	2 electrons
Total skeletal electrons	56 electrons

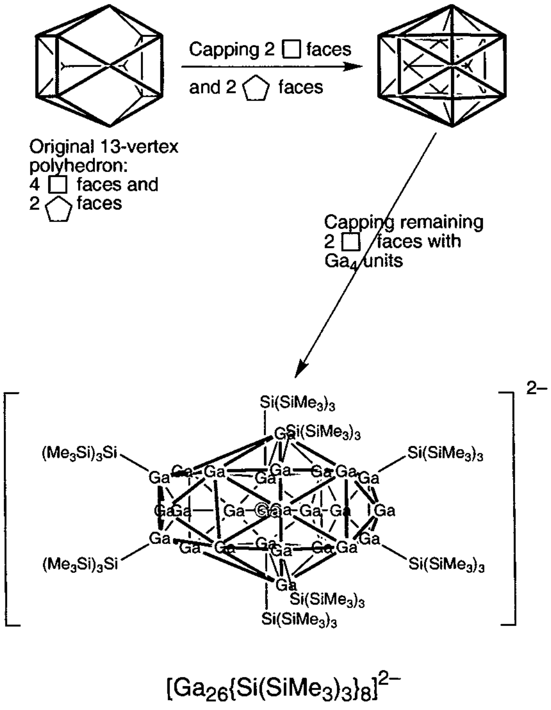

Fig. 6. Generation of the $[Ga_{26}\{Si(SiMe_3)_3\}_8]^{2-}$ structure from a 13-vertex polyhedron with four quadrilateral faces and two pentagonal faces.

6. Summary

The heavier Group 13 metals gallium and indium have recently been shown to form a variety of organometallic clusters having structures consisting of simple and fused deltahedra. Some of these clusters exhibit structures and bonding resembling boron analogues whereas others have structures based on fused deltahedra or supraicosahedral deltahedra not yet found in boron chemistry. The Wade–Mingos $2n+2$ and Jemmis $2n+2m$ electron-counting rules appear to be applicable to most of these clusters. The deltahedra that are found in the supraicosahedral Group 13 metal clusters can be derived from the cuboctahedron and related 13-vertex polyhedra by capping all of the non-triangular faces.

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