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Analogies between Group 13 metal clusters in organometallic and intermetallic structures

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This paper is dedicated to Professor Stanisław Pasynkiewicz in recognition of his pioneering contributions to organometallic chemistry, particularly in the area of the chemistry of the Group 13 elements.

Abstract

Analogous metal cluster units are found in organometallic and intermetallic structures containing the Group 13 metals (icosogens) Al, Ga, In, and Tl. The organometallic structures typically contain very sterically hindered alkyl or aryl ligands, whereas the intermetallic structures contain the Group 13 metal and a much more electropositive metal such as an alkali or alkaline earth metal. The Group 13 metal cluster units found in these structures are of the following types: (1) multiply bonded metal dimers such as the organometallics $[RGa{\equiv}GaR]^{2-}$ (R = bulky aryl group) and the anion Ga_2^{5-} in the intermetallic Ca_5Ga_3; (2) metal triangles such as the organometallics $R_3Ga_3^{2-}$ and the anion In_3^{5-} found in the intermetallic $Ca_5In_9Sn_6$, both of which are isoelectronic with the cyclopropenium ions $R_3C_3^+$ and thus may be regarded as metalloaromatic species; (3) metal tetrahedra found in the organometallics R_4M_4 (M = Al, Ga, In, Tl; R = bulky alkyl group), which can be considered to have M–M–M two-electron three-center bonds in each of the four faces of the tetrahedron and which dissociate readily in the solution and gas phases to the monomeric one-coordinate alkyls RM; (4) a metal trigonal bipyramid in $[Li(thf)_4]^+[\{(Me_3Si)_3Si\}_3(Me_3Si)_2Ga_4Si]^-$ with relatively weak $Ga_{eq}{\cdots}Ga_{eq}$ interactions; (5) larger metal deltahedra of which the only structurally characterized organometallic examples are the icosahedral $[Al_{12}i\text{-}Bu_{12}]^{2-}$ obtained as its potassium salt and the pentagonal bipyramidal $[\{(Me_3Si)_3Si\}_4\{(\mu_2\text{-}Me_3Si)_3SiGa\}_2Ga_7]^-$ obtained as its solvated lithium salt. The deltahedra in some of the intermetallic structures exhibit an unusual type of flattening at some of the degree 4 vertices to give polyhedra not yet found in organometallic species. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Group 13; Clusters; Intermetallic; Deltahedra; Multiple bonding

1. Introduction

During the past several years one of us (R.B.K.) has been examining analogies between the chemical bonding in related molecular and solid-state structures. For example, such work has shown how aspects of the structure and bonding in many solid-state ternary transition metal carbides can be understood by analogies to related molecular transition metal organometallic compounds [1,2]. This paper extends this approach to a consideration of analogous organometallic and solid-state structures containing clusters of the Group 13 elements (also known as icosogens [3] or triels [4]) with particular emphasis on gallium in view of recent work from one of our laboratories (G.H.R.) leading to the discovery of the first molecular species containing Ga≡Ga triple bonds [5,6] and Ga_3 metalloaromatic triangles [7–10]. These recent discoveries coupled with the wide variety of unusual polyhedra found in alkali metal/icosogen intermetallics [11–14] suggest that if solid-state/molecular analogies hold for icosogen metal cluster shapes, the field of gallium cluster organometallics will indeed develop into a very fertile area leading to metal clusters of types not found elsewhere in organometallic chemistry.

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2. Background

2.1. Organometallic icosogen clusters

The synthetic approach to organometallic icosogen clusters is conceptually most simple, namely a direct reaction between an organometallic icosogen (Ic) halide and an alkali metal with elimination of the alkali metal halide followed by further reduction with the alkali metal to give an anionic derivative, i.e.:

$$\mathrm{RIcX_2} + 2\mathrm{M^I} \rightarrow 1/n(\mathrm{RIc})_n + 2\mathrm{M^IX} \tag{1a}$$

$$(\mathrm{RIc})_n + z\mathrm{M^I} \rightarrow z\mathrm{M^+} + (\mathrm{RIc})_n^{z-} \tag{1b}$$

The nature of the resulting product depends on the particular icosogen and the organic group R. Bulky R groups, particularly aryl groups with ortho substituents, are most likely to give interesting and characterizable metal cluster structures.

An early example of an organometallic icosogen cluster was the 1991 report [15] on the dark red icosahedral organoaluminum cluster $K_2[i\text{-}Bu_{12}Al_{12}]$, which was isolated in very low yield from the reaction of $i\text{-}Bu_2AlCl$ with potassium metal in n-hexane. This compound represents the first (and still only known example) of a molecular Al_{12} icosahedron analogous to the well-known and very stable icosahedral $B_{12}H_{12}^{2-}$. The compound $K_2[i\text{-}Bu_{12}Al_{12}]$ is much more stable in air than the typically air-sensitive or even pyrophoric aluminum alkyls just as salts of the icosahedral borane anion $B_{12}H_{12}^{2-}$ are unusually stable relative to simple boron hydrides thereby manifesting the special aromaticity of icosahedral icosogen derivatives of the general type $Ic_{12}R_{12}^{2-}$.

The use of aryl groups with bulky ortho substituents has allowed a major expansion of the field of organometallic icosogen clusters synthesized by the above method. Thus, the use of the 2,6-dimesitylphenyl group (mesityl = 2,4,6-trimethylphenyl) has allowed the preparation of Ga_3 triangles of the type $R_3Ga_3^{2-}$ analogous to the cyclopropenium ion [5,6], whereas use of the even larger 2,6-bis(2,4,6-triisopropylphenyl)phenyl group allows the dimers $Ga_2R_2^{2-}$ isoelectronic with the alkynes RC≡CR to be isolated [7–10].

2.2. Intermetallic structures with icosogen clusters

Alkali metals are also the reducing agents of choice for the preparation of solid-state icosogen clusters, but in this case the icosogen substrate is the elemental icosogen and the reactions are conducted at relatively high temperatures [11,12]. The numerous intermetallic compounds of this type are summarized in several review articles [16,17]. Such reactions can yield solid-state structures containing not only novel icosogen clusters but other unusual species, e.g. Ic^{5-} with the electronic configuration of the next rare gas but with the icosogen in the super-reduced − 5 formal oxidation state. Thus, the recently reported [18] intermetallic Ca_8Al_3 has a structure in which none of the aluminum atoms is within bonding distance of any other aluminum atoms so that this compound can be given the classical valence formulation $(Ca^{2+})_8(Al^{5-})_3e^-$.

3. Known analogies between organometallic and solid-state icosogen cluster structures

3.1. Multiply bonded metal dimers: how short is a gallium–gallium multiple bond?

Gallium is the icosogen forming the largest number of dinuclear clusters containing discrete Ga_2 or R_2Ga_2 units. Of interest in the structures of these clusters is the Ga–Ga bond length with the hope of correlating bond

Table 1
Some Ga–Ga distances in gallium dimers and clusters

Compound	Ga–Ga (Å)	Ga–Ga bond order	Literature
$[\mathrm{ArylGa{\equiv}GaAryl}]^{2-}$ Aryl = 2,4,6-$i\mathrm{Pr_3C_6H_2}$	2.32	3	[5]
$[\mathrm{Trip_2Ga{-}GaTrip_2}]^-$	2.34	1.5	[19]
$[\{\mathrm{(Me_3Si)_2CH}\}_2\mathrm{Ga{-}Ga}\{\mathrm{CH(SiMe_3)_2}\}_2]^-$	2.40	1.5	[20]
Ga=Ga in $Na_{22}Ga_{39}$	2.43	2	[21]
cyclo-$[(\mathrm{Mes_2C_6H_3})_3\mathrm{Ga_3}]^{2-}$	2.44	1.33	[7,8]
$[\{\mathrm{(Me_3Si)_3Si}\}_3\mathrm{(Me_3Si)_2Ga_4Si}]^-$ Ga_{eq}–Ga_{ax}	2.44	1	[45]
Ga_5^{2-} unit in Ca_5Ga_3	2.49	2.5	[22]
$\mathrm{(Me_4C_5H_6N)_2Ga{-}Ga(NC_5H_6Me_4)_2}$	2.52	1	[23]
$\mathrm{[(Me_3Si)_3C]_2Ga{-}Ga[C(SiMe_3)_3]_2}$	2.54	1	[24]
$\mathrm{(^tBu_3Si)_4Ga_4}$	2.57	0.67	[25]
$\mathrm{[(Me_3Si)_3Si]_4Ga_4}$	2.58	0.67	[26]
$\mathrm{[(Me_3Si)_3C]_4Ga_4}$	2.69	0.67	[27]
$\mathrm{[(Me_2EtSi)_3C]_4Ga_4}$	2.71	0.67	[28]
$[\{\mathrm{(Me_3Si)_3Si}\}_3\mathrm{(Me_3Si)_2Ga_4Si}]^-$ Ga_{eq}–Ga_{eq}	2.79	<1	[45]

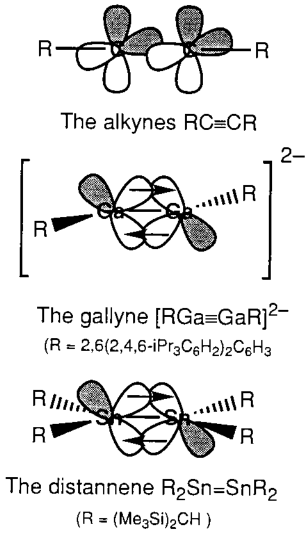


Fig. 1. (Top) The carbon–carbon triple bond in alkynes, RC≡CR, which consists of one σ-bond and two orthogonal π-bonds. (Middle) The gallium–gallium multiple bond in gallynes [RGa≡GaR]$^{2-}$ (R = 2,6(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$), which consists of one σ-bond and two opposing donor–acceptor bonds. (Bottom) The tin–tin multiple bond in distannenes R$_2$Sn=SnR$_2$ (R = (Me$_3$Si)$_2$CH), which likewise consists of one σ-bond and two opposing donor–acceptor bonds.

length with bond order. In this connection the Ga–Ga bond distances in a variety of Ga$_2$ dimers as well as larger gallium clusters are given in Table 1. In Table 1 the Ga–Ga bond order is calculated as the number of bonding electron pairs per Ga–Ga interaction and ranges from 2/3 in the tetrahedral derivatives R$_4$Ga$_4$ where there are four bonding electron pairs for the six Ga–Ga interactions along the edges of the tetrahedron to 3 in the acetylene analogue [ArylGa≡GaAryl]$^{2-}$ where there are six bonding electron pairs for a single Ga–Ga interaction.

The following two Ga$_2$ dimers are of particular interest.

3.1.1. The acetylene analogue

The anion found in Na$_2$[ArylGa≡GaAryl] (Aryl = 2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) [5] is isoelectronic with the alkynes RC≡CR and its Ga≡Ga distance is among the shortest known Ga–Ga distances (Table 1). However, whereas the R–C–C angles in alkynes are linear (180°) in accord with the requirements of the sp hybridization of the alkyne carbons, the corresponding C–Ga–Ga angles occur in the range 129–134°.

This discrepancy in the corresponding angles in acetylene and [ArylGa≡GaAryl]$^{2-}$ can be rationalized by differences in the nature of the triple bond between pairs of carbon atoms and between pairs of gallium atoms [6,29]. In the case of acetylene, the triple bond consists of one σ-bond and two orthogonal π bonds so that the carbon is sp-hybridized with an ideal bond angle of 180° (Fig. 1(top)). However, in the case of [ArylGa≡GaAryl]$^{2-}$ each Ga atom is sp^2-hybridized with ideal bond angles of 120° close to the 129–134° bond angles observed experimentally. One of the sp^2 hybrids forms a two-electron two-center σ-bond with a carbon atom of the Aryl group, a second sp^2 hybrid forms a similar two-electron two-center bond with the other Ga atom, and the third sp^2 hybrid contains a lone pair which can form a donor–acceptor bond with the empty p orbital of the other Ga atom (Fig. 1(middle)). Thus the Ga≡Ga triple bond consists of one σ bond and two donor–acceptor bonds. A similar bonding scheme was proposed by Lappert and co-workers more than 20 years ago [30] for the tin–tin multiple bond in the distannene [(Me$_3$Si)$_2$CH]$_2$Sn=Sn[CH(SiMe$_3$)$_2$]$_2$ (Fig. 1(bottom)). Computational studies [29] suggest that a similar bonding model is favored for the Ga≡Ga triple bond in the hypothetical ‘gallyne’ [Ga$_2$H$_2$]$^{2-}$. In addition Bytheway and Lin [31] have attributed the non-linearity of the [ArylGa≡GaAryl]$^{2-}$ unit to a second-order Jahn–Teller effect arising from a reversal of the energy sequence of the σ* and π* molecular orbitals that leads to a mixing of the in-plane π-HOMO and the σ*-LUMO, which results in decreased π-orbital overlap but overall stabilization of the molecule. In these ways the reluctance of heavy main group elements to form strong π bonds leads to these alternative bonding pictures for gallium–gallium multiple bonds as well as tin–tin multiple bonds.

3.1.2. The NO analogue Ga_2^{5-} in Ca_5Ga_3

At the present time there appears to be no known solid-state analogue to the aryl derivative [ArylGa≡GaAryl]$^{2-}$ discussed above, i.e. solid-state materials containing discrete binuclear Ga$_2^{4-}$ ions analogous to the acetylide ion C$_2^{2-}$ are unknown. The closest analogue is the Ga$_2^{5-}$ ion found in the solid-state material Ca$_5$Ga$_3$ [= (Ca^{2+})$_5$(Ga^{5-})(Ga$_2^{5-}$)]. Analogy of Ga$_2^{5-}$ with the isoelectronic NO suggests a bond order of 5/2. However, the Ga–Ga bond distance in the Ga$_2^{5-}$ anion (2.49 Å) is comparable to the bond distances in neutral Ga–Ga singly bonded compounds such as [(Me$_3$Si)$_3$C]$_2$Ga–Ga[C(SiMe$_3$)$_3$]$_2$ (2.54 Å), suggesting that the high negative charge on Ga$_2^{5-}$ leads to longer bond lengths for a given bond order, possibly due to Coulombic repulsion.

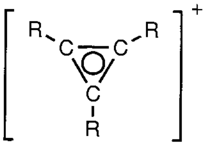
3.2. Triangular clusters: the gateway to metalloaromaticity in cyclopropenium analogues

The first unusual organogallium cluster to be discovered was the cyclotrigallane dianion *cyclo*-[(Mes$_2$C$_6$H$_3$)$_3$Ga$_3$]$^{2-}$ isolated as air-sensitive Na$^+$ and K$^+$ salts and structurally characterized by standard X-ray diffraction methods [7–10]. A solid-state analogue is the anion In$_3^{5-}$ found in the solid-state material Ca$_5$In$_9$Sn$_6$ [= (Ca^{2+})$_5$(In$_3^{5-}$) (In$_6$Sn$_6^{5-}$)] [32]. Both of these anions are isoelectronic and isostructural with the cyclopropenium cations $R_3C_3^+$ with all of these species being two π-electron aromatic systems (Fig. 2) [33].

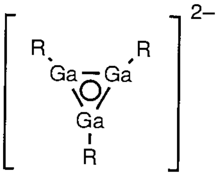
3.3. Tetrahedral clusters: the stabilization of one-coordinate metal alkyls

Gallium(I) and indium(I) form alkyls with bulky alkyl groups which associate into the tetramers, R_4Ic_4, having tetrahedral structures [34,35]. In such tetrahedra each RIc vertex donates two skeletal electrons so that there are eight skeletal electrons available for each Ic_4 tetrahedron. This is less than the 12 skeletal electrons required for two-center two-electron bonds along each of the six edges of the tetrahedron. However, the eight skeletal electrons in the R_4Ic_4 tetramers are exactly the number required for three-center two-electron bonds in each of the four faces of each Ic_4 tetrahedron. This corresponds to an average Ic–Ic bond order of $(8)/(6)(2) = 2/3$ and a relatively weak Ic–Ic bond, which relates to the following observations:

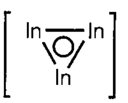
1. The long Ga–Ga bond distances (~ 2.6 Å and even longer) found in R_4Ga_4 derivatives (Table 1).
2. The tendency for tetrahedral Ga(I), In(I), and Tl(I) alkyls of the type $[(R_3Si)_3C]_4Ic_4$ to dissociate into monomers in solution [27,28,36,37] or in the gas phase [27,38] in which the icosogen has a coordination number of only one [34,35].
3. The use of $[(Me_3Si)_3C]_4In_4$ as a source of monomeric $(Me_3Si)_3CIn$ ligands in reactions with metal carbonyls under mild conditions to form the complexes $[\mu\text{-}(Me_3Si)_3CIn]_2\text{–}Mn_2(CO)_8$ [39], $[\mu\text{-}(Me_3Si)_3CIn]_3\text{-}Fe_2(CO)_6$ [40], $[\mu\text{-}(Me_3Si)_3CIn]_2(\mu\text{-}CO)Fe_2(CO)_6$ [41], $[\mu\text{-}(Me_3Si)_3CIn]Fe_2(CO)_8$ [41], $[\mu\text{-}(Me_3Si)_3CIn]_2Fe_3\text{-}(CO)_{10}$ [41], $[\mu\text{-}(Me_3Si)_3CIn](\mu\text{-}CO)Co_2(CO)_6$ [42], $[\mu\text{-}(Me_3Si)_3CIn]_2Co_2(CO)_6$ [42], and $[(Me_3Si)_3CIn]_4\text{-}Ni$ [43].



The cyclopropenium cation $R_3C_3^+$



The cyclogallene anion $R_3Ga_3^{2-}$



The anion In_3^{5-} in $Ca_5In_9Sn_6$

Fig. 2. (Top) The cyclopropenium ions, $R_3C_3^+$. (Middle) The cyclogallene $R_3Ga_3^{2-}$ ($R = 2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$. (Bottom) The ion In_3^{5-} in $Ca_5In_9Sn_6$.

The chemical bonding in the tetrahedral alkyls $[(R_3Si)_3C]_4Ic_4$ appears to be similar to that in the isoelectronic tetrahedral boron halides B_4X_4, which also have the correct skeletal electron count for four three-center two-electron bonds in the B_4 tetrahedra.

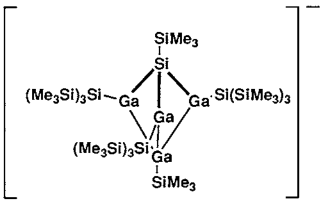
Solid-state analogues of the R_4Ic_4 tetramers would contain Ic_4^{4-} anions in their structures and are apparently unknown. However, the tetrahedral anion Tl_4^{8-} is found in the intermetallic Na_2Tl [44]. This tetrahedral anion has 12 skeletal electrons consistent with edge-localized two-center bonding along each of the six edges of a Tl_4^{8-} tetrahedron rather than the face-localized three-center bonding in each of the four faces found in the R_4Ic_4 tetramers discussed above. Thus, the Tl_4^{8-} anion in Na_2Tl is an isoelectronic as well as an isostructural analogue of white phosphorus, P_4 rather than an analogue of R_4Ic_4 or B_4Cl_4.

3.4. A trigonal bipyramidal cluster with weak equatorial–equatorial bonding

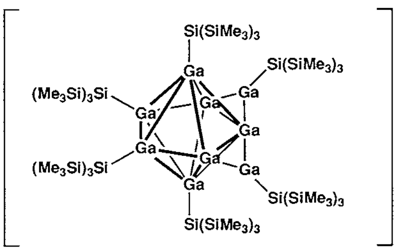
Recent work indicates that one of the triangular faces of a R_4Ic_4 tetramer can be capped to form a five-vertex trigonal bipyramidal cluster. Thus, a black–violet crystalline product of stoichiometry $[Li(thf)_4]^+[\{(Me_3Si)_3Si\}_3(Me_3Si)_2Ga_4Si]^-$ can be isolated from the reaction of Ga_2I_3 with $LiSi(SiMe_3)_3$ [45]. The X-ray structure of this product indicates the presence of a Ga_4Si trigonal bipyramid (Fig. 3(top)) with $Ga_{eq}\text{–}Ga_{ax}$ bond distances of 2.44 Å and much longer $Ga_{eq}\text{–}Ga_{eq}$ bond distances of 2.79 Å. The $Ga_{eq}\text{–}Ga_{ax}$ bond distances of 2.44 Å are close to those expected for Ga–Ga single bonds, whereas the $Ga_{eq}\text{–}Ga_{eq}$ bond distances of 2.79 Å are the longest bonding Ga–Ga distances found in clusters suggesting a fractional $Ga_{eq}\text{–}Ga_{eq}$ bond order (Table 1).

The Ga–Ga bond distances in the Ga_4Si trigonal bipyramid in $[Li(thf)_4]^+\text{–}[\{(Me_3Si)_3Si\}_3(Me_3Si)_2Ga_4Si]^-$ can be rationalized by an edge-localized bonding model with six $Ga_{eq}\text{–}Ga_{ax}$ single bonds and no $Ga_{eq}\cdots Ga_{eq}$ bonding in accord with the following electron-counting scheme:

Three equatorial trigonal $(Me_3Si)_3SiGa$ vertices: $3 \times 2 =$	6 electrons
One axial Me_3SiGa vertex of degree 3: $1 \times 2 =$	2 electrons
One axial Me_3SiSi vertex of degree 3: $1 \times 3 =$	3 electrons
-1 charge on anion	1 electron
Total skeletal electrons	12 electrons



The trigonal bipyramidal cluster $[\{(Me_3Si)_3Si\}_3(Me_3Si)_2Ga_4Si]^-$



The pentagonal bipyramidal cluster $[\{(Me_3Si)_3Si\}_4\{(\mu\text{-}Me_3Si)_3SiGa\}_2Ga_7]^-$

Fig. 3. (Top) The Ga_4Si trigonal bipyramid found in $[\{(Me_3Si)_3Si\}_3(Me_3Si)_2Ga_4Si]^-$; (Bottom) The Ga_7 pentagonal bipyramid found in $[\{(Me_3Si)_3Si\}_4\{(\mu_2\text{-}Me_3Si)_3SiGa\}_2Ga_7]^-$.

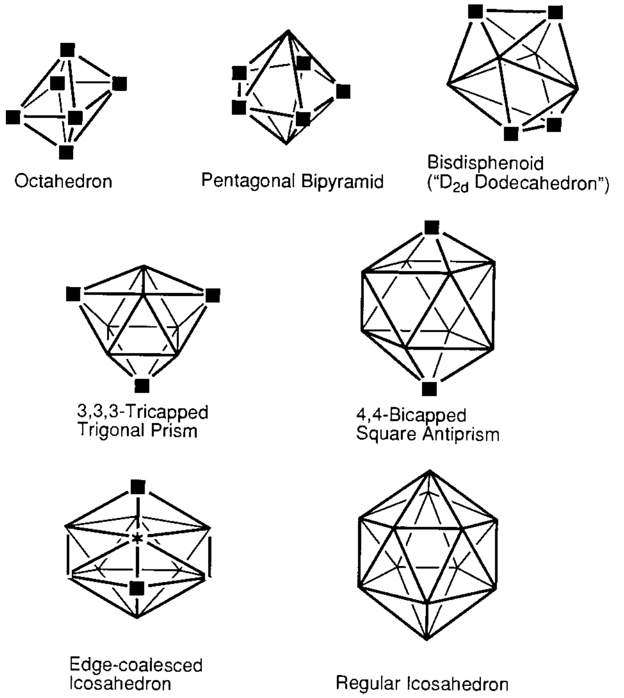

Octahedron
Pentagonal Bipyramid
Bisdisphenoid ("D_{2d} Dodecahedron")
3,3,3-Tricapped Trigonal Prism
4,4-Bicapped Square Antiprism
Edge-coalesced Icosahedron
Regular Icosahedron

Fig. 4. The deltahedra found in the borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$). The degree 4 vertices are indicated by solid squares (■) whereas the single degree 6 vertex of the edge-coalesced icosahedron is indicated by a six-pointed star.

The resulting 12 skeletal electrons are exactly the number required for two-center two-electron bonds along each of the six axial-equatorial edges of the trigonal bipyramid, but no bond along the three equatorial edges. The equatorial RGa vertices in this structure may be considered to be tricoordinate gallium similar to the gallium atom in Me_3Ga since they are each bonded only to the two axial gallium atoms.

3.5. Larger deltahedral clusters: flattened deltahedra

These are two examples of organometallic icosogen clusters based on deltahedra similar to those found in the borane anions. The first example of such a cluster is the organoaluminum icosahedron $K_2[i\text{-}Bu_{12}Al_{12}]$ discussed above (Section 2.1). Very recently a pentagonal bipyramidal Ga_7 cluster has been found in $[Li(thf)_4][\{(Me_3Si)_3Si\}_4\{(\mu_2\text{-}Me_3Si)_3SiGa\}_2Ga_7]$ (Fig. 3(bottom)) isolated from the reaction of 'GaI' with $LiSi(SiMe_3)_3$ [46]. Well-established bonding principles for deltahedral boranes [47–52] are applicable for such deltahedral clusters recognizing the obvious isolobality [53,54] between BH and RIc vertices.

The skeletal electron counting in $\{(Me_3Si)_3Si\}_4\{(\mu_2\text{-}Me_3Si)_3SiGa\}_2Ga_7^-$ (Fig. 3(bottom)) suggests a globally delocalized pentagonal bipyramid similar to that in $B_7H_7^{2-}$ according to the following scheme assuming that each gallium vertex of the pentagonal bipyramid contributes three skeletal orbitals in the normal manner [55]:

Four $(Me_3Si)_3SiGa$ vertices: $4 \times 2 =$	8 electrons
Three bare Ga vertices: $3 \times 1 =$	3 electrons
Two external trigonal μ_2-$(Me_3Si)_3SiGa$ bridges: $2 \times 2 =$	4 electrons
-1 charge on anion:	1 electron
Total skeletal electrons	16 electrons

The 16 skeletal electrons obeys the $2n + 2$ skeletal electron rule ($n = 7$) for a globally delocalized pentagonal bipyramid [55].

There are numerous examples of other icosogen deltahedra in solid-state intermetallic structures which do not yet have any organometallic analogues. Most interestingly, some of the deltahedra found in these intermetallic structures are distinctly different from the more familiar deltahedra found in the borane anions of the type $B_nH_n^{2-}$ ($6 \leq n \leq 12$) [13,14]. Thus the deltahedra found in the $B_nH_n^{2-}$ ($6 \leq n \leq 12$) boranes (Fig. 4) are characterized by a maximum number of degree 4 and 5 vertices where the degree of a vertex corresponds to the number of edges meeting at that vertex. In the deltahedra formed by the heavier icosogens, particularly indium and thallium, so-called flattened structures are found [13,14] in which one or more of the tetragonal pyramidal cavities formed by the degree 4 vertices are flattened (Fig. 5). Examples of such flattened structures are depicted in Fig. 6. The degree 4 vertices of the octahedron, tricapped trigonal prism, and bicapped

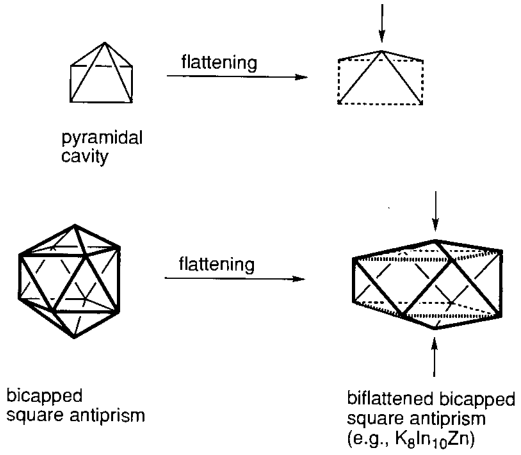


Fig. 5. (Top) Flattening a pyramidal cavity of a larger deltahedron. (Bottom) An example of a flattening process converting a bicapped square antiprism similar to that found in $B_{10}H_{10}^{2-}$ to the biflattened bicapped square antiprism found in the intermetallic $K_8In_{10}Zn$.

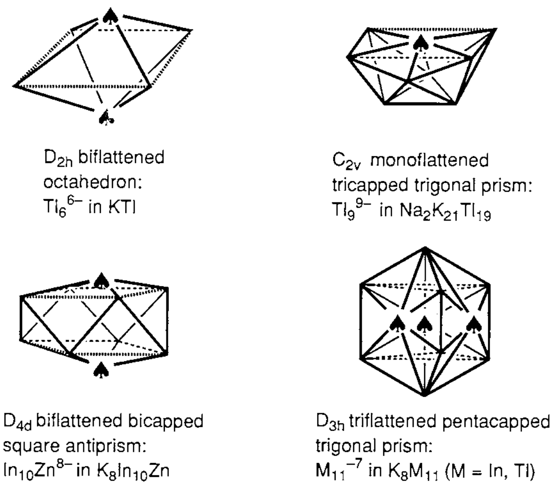
square antiprism are particularly susceptible to such flattening processes.

Flattening has the following effects:

square antiprism are particularly susceptible to such flattening processes.

1. Flattening opens at least some of the edges connecting the basal vertices of the original pyramidal cavity.
2. Flattening pushes the relevant degree 4 vertex closer to the center of the polyhedron.
3. Flattening of a pyramidal cavity reduces the local curvature of the polyhedral surface at the apex but increases the local curvature at the basal vertices of the original pyramidal cavity.

The flattened polyhedra have lower apparent skeletal electron counts in stable anions than the deltahedra from which they are derived. However, skeletal electron counts corresponding to those in the original deltahedra can be obtained if each of the vertices participating in the flattening process contribute an extra electron pair corresponding to the participation of one of their d orbitals as well as the usual four orbitals of their sp^3 manifolds [13,14]. Through such a process an otherwise non-bonding pair in a vertex atom d orbital can become available for skeletal bonding.


D_{2h} biflattened octahedron: Tl_6^{6-} in KTl

C_{2v} monoflattened tricapped trigonal prism: Tl_9^{9-} in $Na_2K_{21}Tl_{19}$

D_{4d} biflattened bicapped square antiprism: $In_{10}Zn^{8-}$ in $K_8In_{10}Zn$

D_{3h} triflattened pentacapped trigonal prism: M_{11}^{-7} in K_8M_{11} (M = In, Tl)

Fig. 6. Some examples of flattened deltahedra found in intermetallics containing indium and thallium. The vertices involved in the flattening process are indicated by spades (♠).

No examples of flattened deltahedra similar to those depicted in Fig. 6 have been found thus far in any organometallic compounds including icosogen derivatives isoelectronic with the anions found in the intermetallic structures. However, the analogies between organometallic and intermetallic icosogen clusters demonstrated in other structures suggests the synthesis and characterization of organometallic icosogen flattened deltahedral clusters as an interesting future research objective.

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