

Review

Supraicosahedral polyhedra in carboranes and metallacarboranes: The role of local vertex environments in determining polyhedral topology and the anomaly of 13-vertex *closo* polyhedra [☆]

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Abstract

Metal-free carboranes having 13 vertices are anomalous since their *closo* polyhedra having the expected 28 skeletal electrons are not the usual deltahedra with exclusively triangular faces but instead polyhedra with one or two trapezoidal faces obtained by removal of one or more edges from the corresponding 13-vertex deltahedron. Removal of such edges converts degree 6 boron vertices in the 13-vertex deltahedron into more favorable degree 5 boron vertices while lowering the degree of nearby carbon vertices. Thus the anomaly of the 13-vertex carborane *closo* polyhedron can be rationalized by the preference of boron for degree 5 vertices. The 12-vertex tetracarborane carborane (CH₃)₄C₄B₈H₈ with a *nido* electron count of 28 skeletal electrons but with two quadrilateral faces has a solid state structure derived from a 13-vertex “*closo*” polyhedron with one quadrilateral face by removal of a degree 4 vertex to give the second quadrilateral face. However, the corresponding tetraethyl derivative (C₂H₅)₄C₄B₈H₈ has a different solid state structure derived from removal of a degree 6 vertex from an unusual 13-vertex deltahedron with three degree 6 vertices to give an open hexagonal face rather than two quadrilateral faces. In contrast to the 13-vertex *closo* polyhedra, the 14-vertex *closo* polyhedron is a true deltahedron, namely the *D*_{6d} bicapped hexagonal antiprism, which is found in a carborane derivative as well as in several dimetallacarboranes with the metal atoms always at the degree 6 vertices. However, the 15-vertex *closo* polyhedron, so far found only in the metallaborane 1,2-μ-(CH₂)₃C₂B₁₂H₁₂Ru(η⁶-*p*-cymene), is a non-deltahedron with one quadrilateral face.

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[☆] This paper is dedicated to Prof. G. Pályi in recognition of his many important contributions to inorganic and organometallic chemistry.
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1. Introduction

The most stable boron cages, such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$, are based on icosahedral structures [1,2]. In addition, icosahedral cages are found in the stable allotropes of elemental boron and many of the stable metal borides [3,4]. These observations suggest that the favored local vertex environment of a boron atom in a polyhedral cage is a degree 5 vertex, i.e., a vertex where five edges meet similar to all of the vertices of a regular icosahedron [5–8]. Previous papers discuss the role of local vertex environments in determining the most stable and least chemically reactive *closo* [8], *nido* [8], and *arachno* [9] boranes. This method considers boron vertices of degrees differing from the favored degree five to be defective vertices, which must be minimized in number and isolated from each other as much as possible to generate a structure having optimum stability. In addition to accounting for the stability of structures containing boron icosahedra, this approach accounts for the relatively high stability of the neutral binary boranes $B_{10}H_{14}$ and $B_{18}H_{22}$ and the ability of B_6H_{10} to form transition metal complexes [10] such as $(\eta^2-B_6H_{10})Fe(CO)_4$. All of this work has been concerned with icosahedral or subicosahedral borane structures, i.e., structures based on polyhedra with no more than 12 vertices and the 26 skeletal electrons characteristic of stable icosahedral boron cages consistent with the Wade–Mingos rules [11–14].

One of the challenges in borane chemistry has been the synthesis of supraicosahedral boranes, i.e., boranes with structures based on polyhedra having more than the 12 vertices of the regular icosahedron and the 26 skeletal electrons of stable icosahedral boranes. This has not yet been achieved for homoatomic boranes of the type $B_nH_n^{z-}$ ($n > 12$, z typically 2), even though the existence of such boranes has been the subject of a number of theoretical predictions [15–17]. Isoelectronic supraicosahedral carboranes of the type $C_2B_{n-2}H_n$ ($n > 12$) and their substitution products are more tractable synthetic objectives from a practical point of view. However, even here success was achieved only in 2003 with the discovery of the 13-vertex metal-free carborane 1,2- $\mu-C_6H_4(CH_2)_2-3-C_6H_5-1,2-C_2B_{11}H_{10}$ by Welch and co-workers [18]. Structure determination by X-ray diffraction methods indicates that the C_2B_{11} polyhedron of this carborane is not the 13-vertex deltahedron with the required 22 triangular faces (a docosahedron) expected from the Wade–Mingos rules [11–14]. Instead the polyhedron is a 13-vertex hencosahedron with

only 21 faces where 20 of the faces are triangles but the remaining face is a C_2B_2 trapezoid. Subsequent very recent work by Deng et al. [19] resulted in the discovery of another 13-vertex metal-free carborane 1,2- $\mu-(CH_2)_3-3-C_6H_5-1,2-C_2B_{11}H_{10}$, where the 13-vertex polyhedron is neither a docosahedron or a hencosahedron but a ditrapezoidal icosahedron with only 20 faces where two of the faces are trapezoids rather than triangles. More recent work [20] has led to the discovery of the 14-vertex metal-free carborane $(\mu-CH_2)_3C_2B_{12}H_{12}$ in low yield.

This paper surveys the relationships between the polyhedra currently found in supraicosahedral carborane derivatives with the objectives of accounting for the polyhedra already found and suggesting possible structures for larger supraicosahedral carboranes and metallocarboranes.

2. Background

2.1. The three-dimensional aromaticity in polyhedral boranes and carboranes

Consider a borane or carborane polyhedron with n vertices in which all of the vertices are boron or carbon atoms having four-orbital sp^3 valence manifolds. Using one of the four valence orbitals on each vertex atom for external bonding (typically to a hydrogen atom or other monovalent atom or group) leaves three internal valence orbitals per vertex atom for a total of $3n$ internal orbitals for the internal skeletal bonding of the polyhedron. These $3n$ internal orbitals are partitioned into two twin internal or tangential orbitals per boron atom and a single unique internal or radial orbital per boron atom for a total of $2n$ tangential orbitals and n radial orbitals. Pairwise overlap between the $2n$ tangential orbitals is responsible for the surface bonding of the polyhedron and splits these $2n$ orbitals into n bonding and n antibonding orbitals. This bonding is supplemented by an n -center core bond formed by the mutual overlap of the n radial bonding orbitals leading to one additional bonding orbital and $n - 1$ antibonding orbitals. The combination of the surface and core bonding leads to a total of $n + 1$ bonding orbitals. Filling each of these bonding orbitals with an electron pair leads to the $2n + 2$ skeletal electrons required by the Wade–Mingos rules [11–14] for a globally delocalized three-dimensional aromatic system [21,22].

For all boranes and carboranes having from six to twelve vertices the globally delocalized borane polyhedron is the most spherical deltahedron (Fig. 1), i.e., a polyhe-

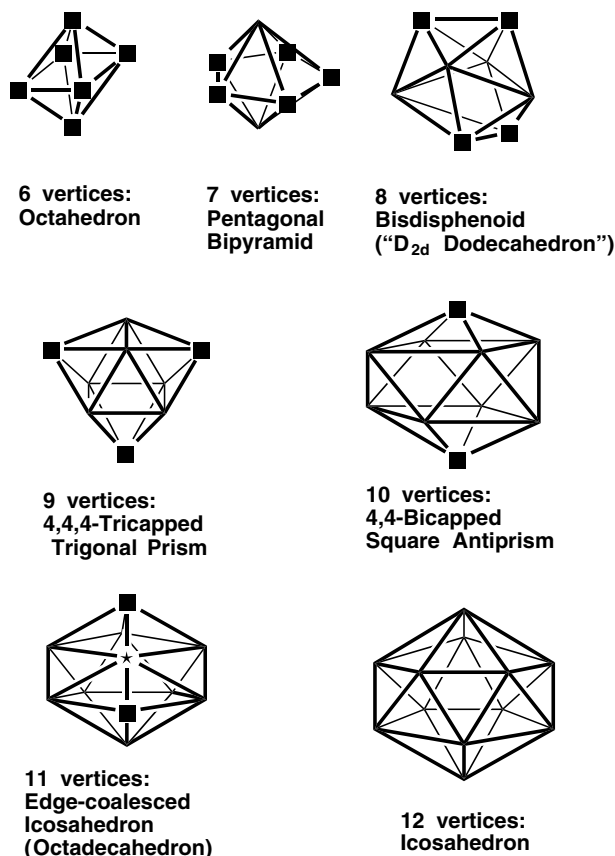


Fig. 1. The most spherical deltahedra (*closo* polyhedron) having from 6 to 12 vertices. In all of the figures the vertices of degrees 3, 4 and 6 are labeled ▲, ■, and ★, respectively, whereas the vertices of degree 5 are unlabeled.

dron with only triangular faces and all vertex degrees as nearly equal as possible. Such deltahedra are often called *closo* deltahedra. However, there is nothing about the model for three-dimensional aromaticity in boranes [21] presented above that requires the underlying polyhedron to be a deltahedron, i.e., to have all faces triangles. In fact, the three-dimensional aromaticity model does not consider any aspects of the detailed topology of the polyhedron, i.e. which pairs of vertices are connected by edges. Instead this model only requires the three-dimensional aromatic polyhedron to be approximated by a sphere. The reasons are presented below why the most spherical electronically *closo* 13-vertex polyhedron need not be a deltahedron but instead can have a single quadrilateral face in addition to the remaining triangular faces.

2.2. Preferred local vertex environments in borane and carborane polyhedra: the Frank–Kasper deltahedra

Degree 5 boron vertices are preferred for borane polyhedra [5–8]. The most spherical subicosahedral deltahedra (Fig. 1) have only degree 4 and degree 5 vertices except for the 11-vertex deltahedron which is required topologically to have a single degree 6 vertex [23]. In polyhedra containing both carbon and boron atoms (i.e., carborane

polyhedra) the lowest energy structures have the carbon atoms at the lowest degree vertices [12,24].

Supraicosahedral boranes and carboranes with deltahedral structures necessarily have one or more vertices of degree 6 or higher. In such structures the degree 6 vertices can be considered to be defective vertices [8] and in the most stable structures the degree 6 vertices should be as far apart as possible. This was already recognized in 1958 by Frank and Kasper in a study of metal alloy structures [25]. They showed that there are only four deltahedra having only degree 5 and 6 vertices with no pair of degree 6 vertices connected by an edge (Fig. 2) including the trivial case of a regular icosahedron having only degree 5 vertices. The non-trivial Frank–Kasper deltahedra include the 14-vertex D_{6d} bicapped hexagonal prism with the two degree 6 vertices in antipodal positions, a 15-vertex D_{3h} deltahedron with the three degree 6 vertices at the vertices of an equilateral macrotriangle, and the 16-vertex T_d tetracapped truncated tetrahedron with the four degree 6 vertices at the vertices of a macrotetrahedron. The Föppl designation 3:[(3):3]₂ for the 15-vertex Frank–Kasper deltahedron refers to the five layers of three vertices. The three vertices in each layer are related by the C_3 axis.

Note that there is no 13-vertex Frank–Kasper deltahedron. The most spherical 13-vertex deltahedron is a dicosahedron with 22 faces as well as two degree 6 vertices, one degree 4 vertex, and 10 degree 5 vertices (Fig. 3). The hexagons surrounding the two degree 6 vertices in this 13-vertex dicosahedron share two edges in contrast to the hexagons surrounding the two degree 6 vertices in the 14-vertex bicapped hexagonal antiprism (Fig. 2), which are completely disjoint with no edges in common.

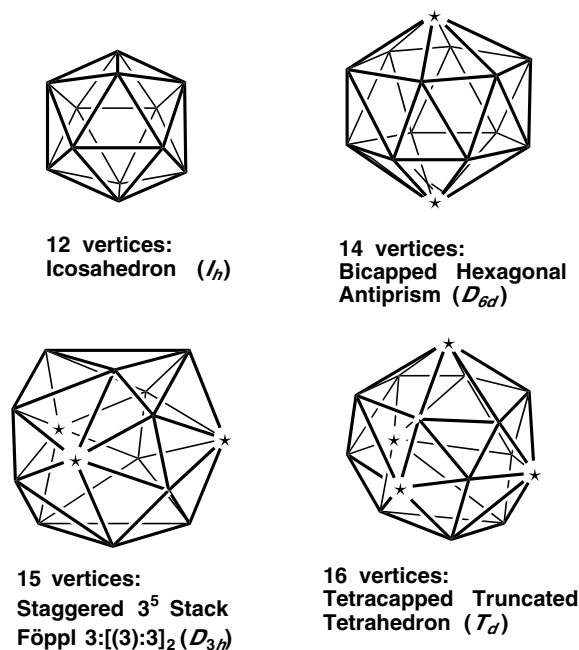


Fig. 2. The four Frank–Kasper deltahedra.

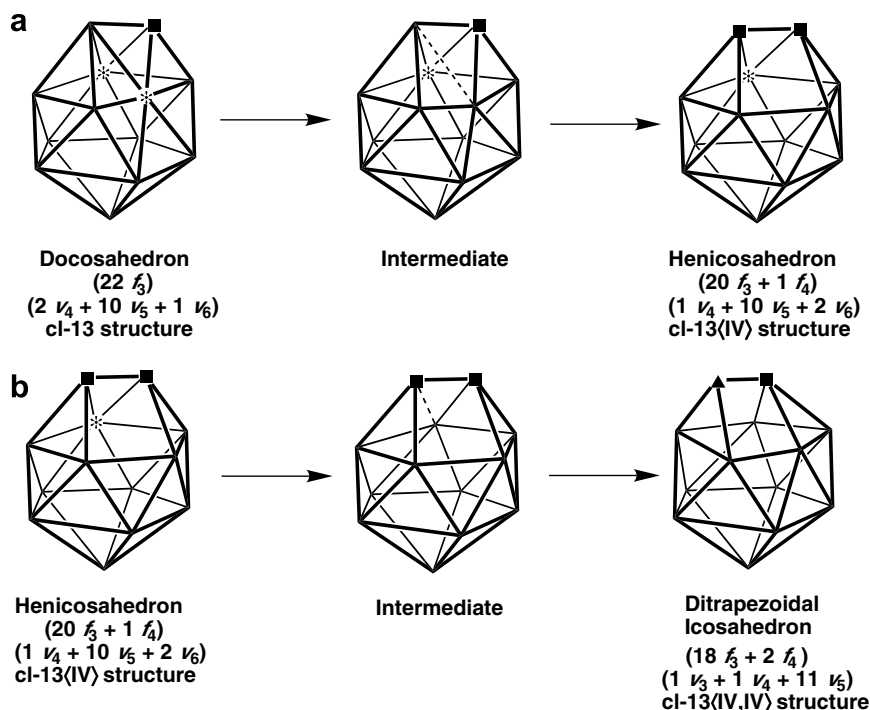


Fig. 3. Relevant 13-vertex polyhedra: (a) Conversion of a docosahedron into a henicosahedron by rupture of an edge connecting a degree 6 vertex with a degree 5 vertex; (b) Conversion of a henicosahedron into a ditrapezoidal icosahedron by rupture of an edge connecting a degree 6 vertex with a degree 4 vertex.

The unfavorability of degree 6 vertices for carbon and boron atoms is undoubtedly a factor in the difficulty of preparing metal-free supraicosahedral boranes and carboranes. However, degree 6 vertices are so favorable for many transition metal vertices that substitution of such vertices for boron or carbon vertices can lead to polyhedra in metallaboranes and metallacarboranes that are topologically different from those found in the corresponding metal-free molecules. For example, the most spherical 10-vertex deltahedron found in metal-free boranes and carboranes (e.g., $B_{10}H_{10}^{2-}$ and $C_2B_8H_{10}$) is the *closo* D_{4d} bicapped square antiprism with two degree 4 vertices and eight degree 5 vertices with the degree 4 vertices in antipodal

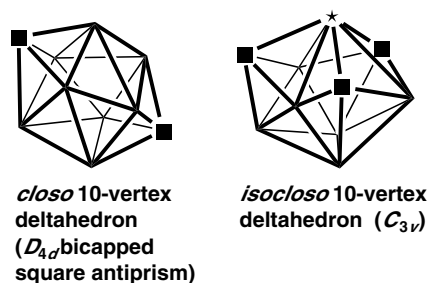


Fig. 4. A comparison of the *closo* 10-vertex deltahedron with two degree 4 vertices and eight degree 5 vertices with the *isocloso* 10-vertex deltahedron with three degree 4 vertices, six degree 5 vertices, and one degree 6 vertex. In 10-vertex *isocloso* metallaboranes, the metal atom occupies the (starred) unique degree 6 vertex.

positions (Fig. 4). However, introduction of a transition metal moiety into the 10-vertex system can lead to rearrangement into a so-called *isocloso* C_{3v} deltahedron having six degree 5 vertices, three degree 4 vertices, and the transition metal located at the unique degree 6 vertex such as in the derivative $(\eta^5-C_5H_5)_2Fe_2C_2B_6H_8$ (Fig. 4) [26]. The preference of transition metal moieties for degree 6 vertices in metallaborane and metallacarborane polyhedra led early in the history of metallacarborane chemistry to the discovery of some supraicosahedral metallacarboranes with the metal atoms located at all of the degree 6 vertices including several 13-vertex $(\eta^5-C_5H_5)CoC_2B_{10}H_{12}$ docosahedral isomers [27] and the 14-vertex $(\eta^5-C_5H_5)_2Co_2C_2B_{10}H_{12}$ bicapped hexagonal antiprismatic isomers [28]. The difficulty in preparing supraicosahedral metal-free carboranes appears to be related to the difficulties of having strong interactions between a degree 6 boron or carbon vertex and all six of its immediate neighbors.

Carbon atoms in carborane polyhedra prefer lower coordination numbers than boron atoms and thus generally occupy lower degree vertices than boron atoms [12,24]. This can lead to lengthening or even rupture of C–C and C–B edges in carborane polyhedra. Thus 12-vertex 1,2- $R_2C_2B_{10}H_{10}$ derivatives are known [29] in which the C–C edge of the original icosahedron stretches to the extent that the two triangular faces sharing the C–C edge merge to a quadrilateral face corresponding to the “diamond–square” portion of a diamond–square–diamond rearrangement. The resulting 12-vertex polyhedron is then better

described as an enneadecahedron with 18 triangular faces and one quadrilateral face rather than an icosahedron with 20 triangular faces. A related process is involved in the stretching of C–B edges in the relatively spherical 13-vertex deltahedron (the docosahedron) with 22 triangular faces to give first a hencosahedron with 20 triangular faces and one trapezoidal face and then a ditrapezoidal icosahedron with 18 triangular faces and two trapezoidal faces (Fig. 3). In such cases stretching the C–B edge not only reduces the degree of the carbon vertex from five to a reasonable four but also the degree of the boron vertex from six to a very favorable five.

2.3. Electron-rich *nido* and *arachno* polyhedra

Consider a *nido* borane or carborane polyhedron with n vertices and $2n + 4$ skeletal electrons. Such a polyhedron can be generated in the following two ways [30]:

1. Addition of two electrons to the corresponding *closo* polyhedron having n vertices and $2n + 2$ skeletal electrons to generate a *nido* polyhedron having n vertices and $2n + 4$ skeletal electrons. The *nido* polyhedron has a more open structure than the corresponding *closo* polyhedron with one additional non-triangular face so that this process is conveniently called *polyhedral puncture*.
2. Removal of one vertex from the *closo* polyhedron having $n + 1$ vertices and $2(n + 1) + 2 = 2n + 4$ skeletal electrons to give a *nido* polyhedron having n vertices and likewise $2n + 4$ skeletal electrons [31]. In most, but not all cases the vertex of highest degree is removed from the *closo* polyhedron to generate the corresponding *nido* polyhedron. This process is conveniently called *polyhedral excision*.

In this paper the *nido* polyhedra are generated by polyhedral excision, i.e., by removal of a vertex from a *closo* polyhedron having $n + 1$ vertices. Similarly *arachno* polyhedra are generated by removal of two vertices from a *closo* polyhedron having $n + 2$ vertices. If the two vertices removed from the *closo* polyhedron are adjacent vertices, a new single large hole will be added to form the corresponding *arachno* polyhedron. However, if the two vertices removed from the *closo* polyhedron are non-adjacent vertices, then two new non-triangular faces will be generated in the *arachno* polyhedron. The procedure for generating *nido* and *arachno* polyhedra having n vertices from *closo* polyhedra having $n + 1$ and $n + 2$ vertices, respectively, by vertex removal allows such a *closo* \rightarrow *nido* \rightarrow *arachno* set of polyhedra to be classified by a constant number of skeletal electrons.

The *nido* and *arachno* structures are designated in this paper by a notation introduced by Williams [24] where $ni-n-(R)$ ($R =$ Roman numeral) is used to describe a *nido* structure with n vertices having all triangular faces except for one larger face with R edges. Replacing “ni” in the

above designation by “ar” indicates an *arachno* structure with two open faces or one large open face. This notation can also be adapted to electronically *closo* polyhedra with a non-triangular face. Thus the 13-vertex hencosahedron in $1,2-\mu-C_6H_4(CH_2)_2-3-C_6H_5-1,2-C_2B_{11}H_{10}$ and the ditrapezoidal icosahedron in $1,2-\mu-(CH_2)_3-3-C_6H_5-1,2-C_2B_{11}H_{10}$ can be designated as a $cl-13-(IV)$ and $cl-13-(IV,IV)$, respectively.

3. Structures of supraicosahedral carboranes and metallacarboranes and related compounds

3.1. Polyhedra with 24 skeletal electrons derived from the 11-vertex *closo* carborane $C_2B_9H_{11}$

The 11-vertex system, although a subicosahedral system, is relevant to the discussion in this paper since an 11-vertex deltahedron is the smallest deltahedron required by topology to have a single degree 6 vertex [23], a necessary structural feature for the larger supraicosahedral deltahedra discussed later in this paper. Furthermore, the 11-vertex deltahedral borane anion $B_{11}H_{11}^{2-}$ and the corresponding carboranes $CB_{10}H_{11}^-$ and $C_2B_9H_{11}$ are known experimentally [32] so information is available about the chemical bonding around a degree 6 boron vertex.

The most informative study on the 11-vertex deltahedron is some recent experimental and theoretical work on the vibrational spectrum, structure and electronic density distribution of the $2-CB_{10}H_{11}^-$ anion [33]. The electron density distribution indicated the absence of bond critical points around four of the six edges coming from the unique degree 6 vertex of the 11-vertex deltahedron. Experimentally, four of these edges are unusually long, namely 2.053 Å, 2.043 Å, 2.023 Å, and 2.015 Å in $[Et_4N][2-Ph-closo-2-CB_{10}H_{10}]$ in contrast to all of the other edges of the 11-vertex deltahedron in the range 1.64–1.85 Å [34]. This suggests some relatively weak interactions between the degree 6 vertex in the 11-vertex deltahedron and the adjacent vertices indicating that the corresponding edges are relatively easily broken in accord with the fluxionality of 11-vertex deltahedral structures [34,35]. Thus a degree 6 boron vertex does not appear to have strong direct interactions with all six of its immediate neighbors.

A variety of 24-skeletal electron $ni-10-(VI)$ *nido* species are known with structures obtained by removal of the unique degree 6 vertex from the 11-vertex deltahedron. The best known such species is *nido* decaborane-14, $B_{10}H_{14}$, which is among one of the most stable binary boron hydrides and was one of the original boron hydrides discovered by Stock [36]. Metallaboranes, such as $(\eta^6\text{-arene})RuB_{10}H_{10}$ (Ref. [37]), are also known with the transition metal atom at the degree 6 vertex. However, these metallaboranes are *isocloso* compounds with a different skeletal bonding scheme rather than true *closo* compounds since they have only 22 rather than 24 skeletal electrons [38].

3.2. Polyhedra with 26 skeletal electrons derived from the regular icosahedron or other less symmetrical 12-vertex boron deltahedra

The regular icosahedron is clearly the favored 12-vertex *closo* deltahedron relating to its high symmetry with all vertices having the favored degree 5. It is found in a variety of very stable B_{12} clusters including the $B_{12}H_{12}^{2-}$ anion and the isoelectronic carboranes $CB_{11}H_{12}^-$ and $C_2B_{10}H_{12}$ as well as various boron-rich metal borides and boron carbide, B_4C . However, in a few cases substitution of other atoms for the boron vertices in a 12-vertex cluster can lead to non-icosahedral structures.

Most 12-vertex *closo* metallaboranes and metallacarboranes, e.g., $(\eta^5-C_5H_5)CoC_2B_9H_{11}$, have icosahedral structures with the transition metal at a degree 5 vertex. An interesting exception is the anion $[\{(\eta^3-C_3H_5)(OC)_2Mo\}(PhC)_2B_9H_9]^-$, which is shown by X-ray diffraction to have a non-icosahedral structure with two degree 6 vertices, two degree 4 vertices, and eight degree 5 vertices (Fig. 5) [39]. The two carbon atoms are located at the degree 4 vertices and the molybdenum atom is located at one of the degree 6 vertices in accord with the preference of carbon for lower degree vertices and that of molybdenum for degree 6 vertices. The steric hindrance between the two external phenyl groups on the carbon vertices may play an important role in leading to this non-icosahedral structure since the closely related anion $[\{(\eta^3-C_3H_5)(OC)_2Mo\}(PhC)(CH)B_9H_9]^-$ with only one external phenyl substituent has an icosahedral structure with all degree 5 vertices.

3.3. Polyhedra with 28 skeletal electrons derived from a 13-vertex *closo* polyhedron

Analogy with subicosahedral boron cluster chemistry suggests that the 13-vertex *closo* polyhedron should be a dicosahedron with 22 triangular faces, two degree 6 vertices, and one degree 4 vertex (Fig. 3). This polyhedron is found in numerous 13-vertex metallacarboranes of which $(\eta^5-C_5H_5)CoC_2B_{10}H_{12}$ was the first to be discovered [27]. In complexes of this type the metal atom is located at one of the degree 6 vertices and one of the carbon atoms is located at the degree 4 vertex in accord with their preferred vertex degrees. Similarly the paramagnetic 13-vertex

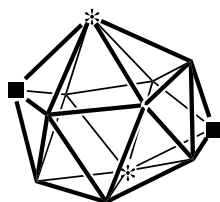


Fig. 5. The MoC_2B_9 12-vertex non-icosahedral deltahedron found in the anion $[\{(\eta^3-C_3H_5)(OC)_2Mo\}(PhC)_2B_9H_9]^-$. The molybdenum atom is located at the “top” degree 6 vertex and the two carbon atoms are located at the two degree 4 vertices.

dimetallatricarborane $(\eta^5-C_5H_5)_2Fe_2C_3B_8H_{11}$ having 27 rather than 28 skeletal electrons has a dicosahedral structure with iron atoms at both degree 6 vertices and one of the carbon atoms at the degree 4 vertex [40].

In 13-vertex deltahedral metallacarboranes based on an MC_2B_{10} dicosahedron with the metal at one of the two degree 6 vertices, the edge connecting the carbon at a degree 5 vertex to the unique boron at the other degree 6 vertex is readily broken to give a cl-13-⟨IV⟩ structure (Fig. 3a). This converts the dicosahedron with 22 triangular faces into a hencicosahedron with 20 triangular faces and one trapezoidal face with both carbon atoms now at favored degree 4 vertices, the metal atom at the remaining degree 6 vertex, and all ten boron vertices having the preferred degree of five. Known examples of such cl-13-⟨IV⟩ hencicosahedral metallaboranes [41] include $\mu-1,2-(CH_2)_3-4-(\eta^5-C_5H_5)Co-1,2-C_2B_{10}H_{10}$ and $\mu-1,2-(CH_2)_3-4-(\eta^6-p-cymene)Ru-1,2-C_2B_{10}H_{10}$.

The same cl-13-⟨IV⟩ hencicosahedral structure is also found in the metal-free 13-vertex *closo* carborane [18] $1,2-\mu-C_6H_4(CH_2)_2-3-C_6H_5-1,2-C_2B_{11}H_{10}$ having the favored 28 skeletal electrons ($=2n+2$ for $n=13$) suggested by the Wade–Mingos rules [11–14]. However, this cl-13-⟨IV⟩ structure still has a boron atom at a degree 6 vertex. Breaking an edge between this boron atom and a carbon atom so that all 11 boron vertices have the favored degree 5 leads to the ditrapezoidal icosahedral cl-13-⟨IV,IV⟩ structure (Fig. 3b), which has been found [19] in $1,2-\mu-(CH_2)_3-3-C_6H_5-1,2-C_2B_{11}H_{10}$. So far metal-free 13-vertex carboranes of the C_2B_{11} variety are only known when the pair of carbon atoms is bridged to form an exopolyhedral ring so that they are forced to remain adjacent. The nature of the bridge (*o*-xylylene versus trimethylene) affects the topology of the underlying C_2B_{11} polyhedron. In any case the “*closo*” 13-vertex metal-free carborane polyhedra are the non-deltahedral hencicosahedron with one trapezoidal face and the ditrapezoidal icosahedron with two trapezoidal faces (Fig. 3).

Nido structures with 12 vertices and 28 skeletal electrons can be derived from various “*closo*” 13-vertex structures by removal of one of the vertices. Thus two different 12-vertex polyhedra (Fig. 6) for tetracarboranes of the general formula $R_4C_4B_8H_8$ are found to be in equilibrium in

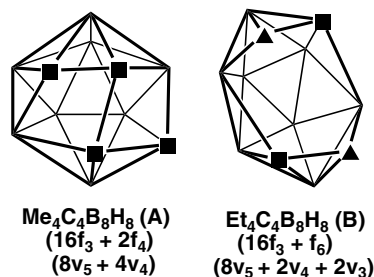


Fig. 6. The two polyhedra found in $R_4C_4B_8H_8$ derivatives. The carbon atoms are located at the degree 3 and degree 4 vertices designated as ▲ and ■, respectively.

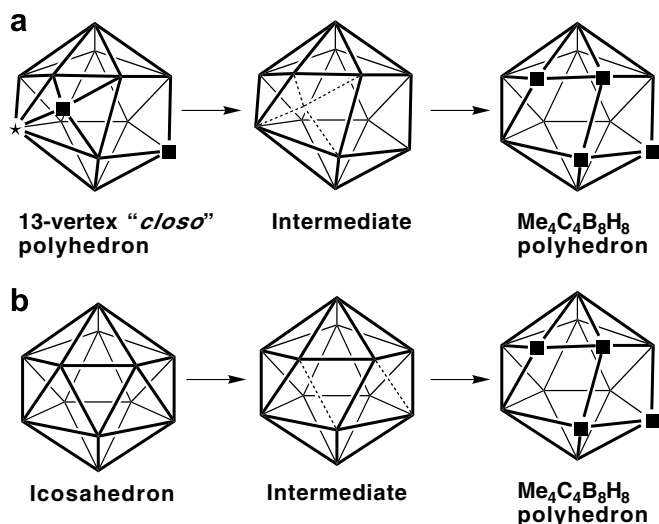


Fig. 7. (a) Generation of the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron by removal of a degree 4 vertex from a 13-vertex "closo" polyhedron (actually a hencosahedron with one quadrilateral face). (b) Generation of the $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron by removal of two edges from an icosahedron. The carbon atoms in the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron are located at the degree 4 vertices designated as ■.

solution based on NMR studies [42]. The favored structure in the solid state depends upon the alkyl substituents R. Thus the tetramethyl derivative $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ was found by X-ray diffraction [43] to have a solid state structure with two quadrilateral faces, 16 triangular faces, and 28 skeletal electrons (Fig. 7a), which can be derived from a *closo*-13-⟨IV⟩ hencosahedron with one quadrilateral face by removal of a degree 4 vertex to generate a second quadrilateral face. Thus the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron can be described as a ni-12-⟨IV,IV⟩ structure and the presence of two quadrilateral faces in a structure with a *nido* skeletal electron count can be rationalized. Note, however, that the hencosahedron used to generate the $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron has only one degree 4 vertex adjacent to the unique degree 6 vertex whereas the hencosahedron found in $1,2\text{-}\mu\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-}3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{11}\text{H}_{10}$ has both degree 4 vertices adjacent to the unique degree 6 vertex. This structural difference undoubtedly is a consequence of the forced adjacency of the two carbon vertices in $1,2\text{-}\mu\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-}3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{11}\text{H}_{10}$ combined with the preference of carbon over boron for the degree 4 vertices.

This *nido*-12-⟨IV,IV⟩ $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron can also be derived from a C_4B_8 icosahedron by placing the carbon atoms in a zigzag manner on four adjacent vertices of the icosahedron and then breaking the two C–C edges (Fig. 7b). However, this does not rationalize the *nido* skeletal electron count of 28 rather than the *closo* skeletal electron count of 26 for $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$.

A more open *nido*-⟨VI⟩ structure with one hexagonal face rather than two quadrilateral faces is found for the corresponding tetraethyl derivative $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ in the solid state (Fig. 6) [42]. This structure can be derived from a rather unusual 13-vertex deltahedron with three degree 6

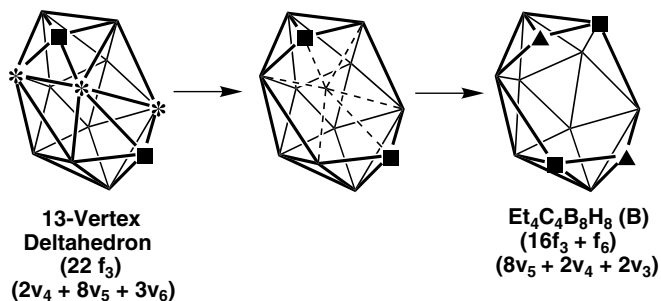


Fig. 8. Conversion of a deltahedron with three adjacent degree 6 vertices to the 12-vertex polyhedron found in $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ by removal of the central degree 6 vertex.

vertices in a line partially compensated by two degree 4 vertices (Fig. 8). The *nido*-⟨VI⟩ $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ polyhedron is derived from this deltahedron by removal of the central degree 6 vertex in the lineup of three degree 6 vertices. This avoids adjacent degree 6 vertices. The four carbon atoms are located at the degree 3 and 4 vertices in the open face.

3.4. Polyhedra with 30 skeletal electrons derived from a 14-vertex *closo* polyhedron

The obvious 14-vertex *closo* deltahedron is the D_{6h} bicapped hexagonal antiprism, which is one of the Frank–Kasper polyhedra (Fig. 2) and in which the two degree 6 vertices are isolated as much as possible from each other in antipodal positions on the C_6 polyhedral axis. Dimetallacarboranes having this structure and with the

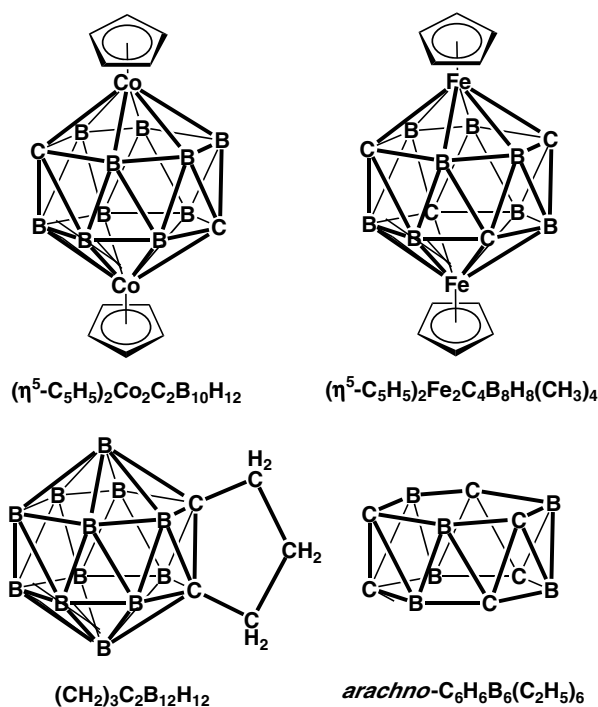


Fig. 9. Examples of polyhedral borane structures derived from the D_{6d} bicapped hexagonal antiprism. External hydrogens and alkyl groups are omitted for clarity.

metal atoms at the two degree 6 vertices (Fig. 9) have been known since the discovery of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_{10}\text{H}_{12}$ in 1974 [28]. Much more recently Welch and co-workers [44] have synthesized a variety of other 14-vertex dimetallacarboranes including $(\eta^6\text{-}p\text{-cymene})_2\text{Ru}_2\text{C}_2\text{B}_{10}\text{H}_{12}$ as well as the heterobimetallic derivatives of the types $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^6\text{-}p\text{-cymene})\text{RuC}_2\text{B}_{10}\text{H}_{12}$ and (diphos)- $\text{Ni}(\eta^6\text{-}p\text{-cymene})\text{RuC}_2\text{B}_{10}\text{H}_{12}$. All of these compounds have bicapped hexagonal antiprismatic structures with the two transition metal atoms at the two degree 6 vertices consistent with the preference of transition metals for degree 6 vertices.

Fourteen-vertex dimetallacarboranes with $\text{M}_2\text{C}_4\text{B}_8$ cages containing four carbon vertices can be prepared by the dimetallation of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$. Thus four isomers of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_4\text{B}_8\text{H}_8(\text{CH}_3)_4$ have been structurally characterized [45]. The two initially produced isomers do not have 14-vertex deltahedral structures but instead structures with either a quadrilateral or pentagonal open face. However, pyrolysis of these isomers leads to two isomers with the expected bicapped hexagonal antiprismatic structures with the two metal atoms at the degree 6 vertices (Fig. 9) so that these bicapped hexagonal appear to be the most thermodynamically stable structures for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{C}_4\text{B}_8\text{H}_8(\text{CH}_3)_4$.

The preparation of a metal-free 14-vertex *closo* carborane is considerably more difficult and was achieved only in 2005 [20] with the synthesis of $(\mu\text{-CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}$ in low yield. The expected bicapped hexagonal prismatic structure with boron atoms at the degree 6 vertices (Fig. 9) was confirmed by X-ray diffraction.

Removal of one or both of the degree 6 vertices from the D_{6d} bicapped hexagonal antiprism is expected to lead to *nido* or *arachno* structures with one or two hexagonal faces with retention of the 30 skeletal electrons of the original bicapped hexagonal antiprism. The *arachno* ar-14-(VI,VI) hexagonal antiprismatic hexacarborane $\text{C}_6\text{H}_6\text{B}_6(\text{CH}_3)_6$ (Fig. 9) has been synthesized and structurally characterized [46].

3.5. A 15-vertex metallocarborane with 32 skeletal electrons

No 15-vertex metal-free carboranes are known. However, a 15-vertex metallocarborane of the type $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}\text{Ru}(\eta^6\text{-arene})$ (arene = *p*-cymene) was recently reported by Welch and collaborators [47] as an unexpected pyrolysis product of the corresponding 14-vertex $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{11}\text{H}_{11}\text{Ru}(\eta^6\text{-arene})$ derivative. The $\text{RuC}_2\text{B}_{12}$ polyhedron in $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}\text{Ru}(\eta^6\text{-arene})$ is a cl-15-(IV) pentacosahedron derived from the 15-vertex Frank–Kasper deltahedron (Fig. 2) by rupture of one of the edges connecting a degree 6 boron vertex to a degree 5 carbon vertex (Fig. 10). This process is completely analogous to the conversion of the most spherical 13-vertex deltahedron (the dicosahedron in Fig. 3) into the hencosahedron. In both cases the degree of one of the boron vertices decreases from six to a more favorable five and the degree of a carbon vertex decreases from five to a more favorable four.

3.6. Prospects for synthesizing larger supraicosahedral carboranes and metallocarboranes

The 14-vertex structures with 30 skeletal electrons (e.g., Fig. 9) are the largest known polyhedral carboranes having structures constructed from a single polyhedron rather than fused subicosahedral polyhedra (e.g., $\text{B}_{18}\text{H}_{22}$) [48,49]. A key question in the area of supraicosahedral borane chemistry is whether boranes and carboranes based on a single polyhedron with 15 or more vertices and with 32 or more skeletal electrons can be synthesized.

The syntheses of the known supraicosahedral carboranes and metallocarboranes are based on the following two-step polyhedral expansion procedure:

1. A *closo* deltahedral carborane or metallocarborane is reduced to the corresponding *nido* dianion with an open face (generally a hexagonal face) using an alkali metal in a suitable inert solvent.

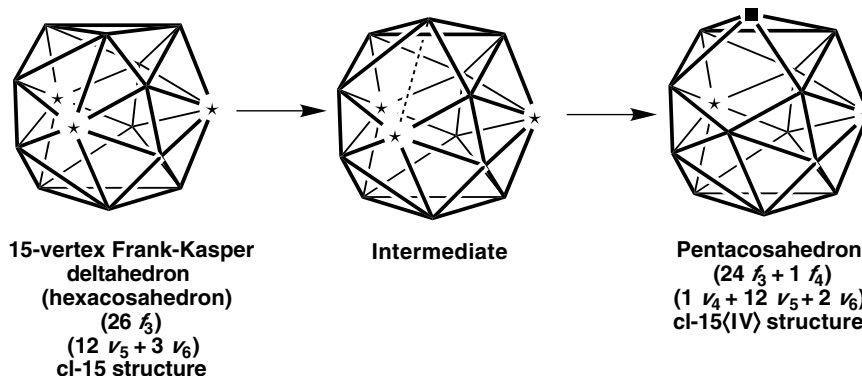


Fig. 10. Conversion of the 15-vertex Frank–Kasper deltahedron (the hexacosahedron) into the pentacosahedron found in the $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}\text{Ru}(\eta^6\text{-arene})$ metallocarborane. In this metallocarborane the ruthenium atom is located at one of the degree 6 vertices (starred in the figure) and a boron atom at the other degree 6 vertex. A carbon atom is located at the single degree 4 vertex.

- The new open face of the *nido* dianion is then capped by reaction with a suitable RBX_2 reagent to introduce a new boron vertex or a suitable transition metal reagent to introduce a transition metal vertex.

This synthetic procedure has the following limitations:

- It does not appear to be adaptable to the *closo* deltahedral borane dianions $\text{B}_n\text{H}_n^{2-}$ since the high negative charge inhibits the reduction of $\text{B}_n\text{H}_n^{2-}$ to $\text{B}_n\text{H}_n^{4-}$. Thus this chemistry might well be limited to the neutral *closo* carboranes $\text{C}_2\text{B}_{n-2}\text{H}_n$ and related neutral metallacarboranes.
- In order to go beyond the icosahedron using polyhedral expansion it appears necessary to start with a *closo* carborane with adjacent carbon atoms and tie them together with a bridge such as a phenylene or trimethylene bridge before the two-electron reduction to the *nido* dianion. So far attempts to carry out this cage expansion chemistry on carborane derivatives without the adjacent carbon atoms tied together have led to separation of the carbon atoms in the cage followed by boron extrusion so that a supraicosahedral carborane is not obtained [18].

A 15-vertex trimetallacarborane based on the 15-vertex Frank–Kasper polyhedron (Fig. 2) with transition metals at the three degree 6 vertices is an interesting synthetic objective since both the metal and boron vertices have the favored degrees. However, the synthesis of such a trimetallacarborane may present another more serious fundamental difficulty. In a possible 14-vertex dimetallacarborane starting material for polyhedral expansion, namely $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_{10}\text{H}_{12}$, the degree 6 vertices are located in antipodal positions on the C_6 axis of the underlying bicapped hexagonal antiprism. However, in the possible trimetallacarborane product $(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}_3\text{C}_2\text{B}_{10}\text{H}_{12}$, the three degree 6 vertices are located at the vertices of a large equilateral triangle consistent with the D_{3h} symmetry of the underlying 15-vertex Frank–Kasper deltahedron (Fig. 2). Thus a polyhedral rearrangement moving the degree 6 vertices already present in the 14-vertex Frank–Kasper deltahedron is necessary for the expansion of the 14-vertex Frank–Kasper polyhedron to the 15-vertex Frank–Kasper deltahedron (Fig. 2). This may present an obstacle for the polyhedral expansion of a 14-vertex metallacarborane to a 15-vertex metallacarborane. However, the recent synthesis [47] of the 15-vertex metallacarborane $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}\text{Ru}(\eta^6\text{-arene})$ in fairly good yield (67% in an apparently clean reaction) by pyrolysis of a corresponding 14-vertex metallacarborane suggests that the necessary structural rearrangements might be rather facile so that it would be reasonable to explore such syntheses.

4. Summary

The 13-vertex $\text{cl-13-}\langle\text{IV}\rangle$ and $\text{cl-13-}\langle\text{IV,IV}\rangle$ metal-free carboranes are anomalous since the *closo* polyhedra having

the expected $28 (= 2n + 2 \text{ for } n = 13)$ skeletal electrons are not deltahedra with exclusively triangular faces but instead are polyhedra having one or two trapezoidal faces obtained by removal of one or two edges from the corresponding 13-vertex deltahedron. Such edge removal converts degree 6 boron vertices in the 13-vertex deltahedron into more favorable degree 5 boron vertices while simultaneously reducing the degree of carbon vertices. Thus the anomaly of the 13-vertex carborane *closo* polyhedron can be rationalized by the preference of boron for degree 5 rather than degree 6 vertices. The 12-vertex tetracarbon carborane $\text{ni-12-}\langle\text{IV,IV}\rangle (\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ with a *nido* electron count of 28 skeletal electrons has a solid state structure with two quadrilateral faces derived from a 13-vertex “*closo*” polyhedron with one quadrilateral face by removal of a degree 4 vertex to give the second quadrilateral face. However, the corresponding tetraethyl derivative $(\text{C}_2\text{H}_5)_4\text{C}_4\text{B}_8\text{H}_8$ has a different $\text{ni-12-}\langle\text{VI}\rangle$ solid state structure derived from removal of a degree 6 vertex from an unusual 13-vertex deltahedron with three degree 6 vertices to give an open hexagonal face. In contrast to the 13-vertex *closo* polyhedron the 14-vertex *closo* polyhedron is a true deltahedron, namely the D_{6d} bicapped hexagonal antiprism which has the two degree 6 vertices as isolated as possible, i.e., in antipodal positions. This 14-vertex deltahedron is found in a carborane derivative as well as a number of dimetallacarboranes. Furthermore, removal of the two antipodal degree 6 vertices from this 14-vertex deltahedron gives the hexagonal antiprism found in the known *arachno* $\text{ar-12-}\langle\text{VI,VI}\rangle$ hexagonal antiprismatic hexacarborane $\text{C}_6\text{H}_6\text{B}_6(\text{CH}_3)_6$. The 15-vertex *closo* polyhedron, so far found only in the metallaborane $1,2\text{-}\mu\text{-}(\text{CH}_2)_3\text{C}_2\text{B}_{12}\text{H}_{12}\text{Ru}(\eta^6\text{-}p\text{-cymene})$, is a $\text{cl-15-}\langle\text{IV}\rangle$ non-deltahedron with one quadrilateral face like the 13-vertex *closo* polyhedron.

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