STRUCTURAL AND BONDING PATTERNS IN CLUSTER CHEMISTRY

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I. Introduction

This is one of two articles in this volume concerned with the borane–carborane structural pattern. In the other (see Williams, this volume, p. 67) Williams has shown how the pattern reflects the coordination number preferences of the various atoms involved. The purpose of the present article is to note some bonding implications of the pattern, and to show its relevance to a wide range of other compounds, including metal clusters, metal–hydrocarbon π complexes, and various neutral or charged hydrocarbons.

Aspects of this theme have been explored in many recent publications (*12, 31b, 43, 96a, 96b, 105a, 128, 137, 158, 161, 163a, 166a, 172a, 173, 173a, 183, 199–205a*) in which boranes, once regarded as obscure chemical rule-breakers, have featured increasingly as pattern-makers for a surprisingly wide range of substances. Arguments derived from borane or carborane chemistry enable us to forecast the probable structures of new metal carbonyl clusters or carbo cations, to devise new syntheses of cluster compounds, to put their redox and acid–base chemistry on a common systematic footing, to predict the likely sites of nucleophilic or electrophilic attack, and to envisage the specific skeletal rearrangements that may accompany such reactions. They also provide us with a type of approach that can profitably be used in other areas of chemistry, where the borane structural pattern itself does not apply.

Boranes and carboranes may be regarded as cluster compounds in the sense defined by Cotton (*48*); they contain a finite group or skeleton of atoms held together entirely, mainly, or at least to a significant extent by bonding directly between those atoms, even though some other atoms may be associated intimately with the cluster. Examples of their structural pattern, however, can be found far beyond the confines of what is normally regarded as cluster chemistry, so this survey includes many systems not commonly referred to as clusters, e.g., cyclic and even acyclic systems, as well as conventional clusters. Because such a wide area of chemistry is involved, it is not possible to be comprehensive, although the examples chosen are intended to illustrate the arguments in sufficient detail, and for a wide enough range of substances, to allow their application to systems not actually covered here. It is hoped that drawing attention to the relationships between areas that had previously been regarded as quite distinct will allow developments in each area to find more rapid general application.

In the following sections, the ways in which the polyhedral structures of boranes and carboranes reflect the numbers of electrons holding them together are outlined, and similar relationships are noted for some metal–carbonyl clusters. Skeletal electron-counting procedures are then given showing that many mixed clusters, containing both transition metals and main group elements, conform to the same structural and bonding pattern. The π complexes formed extensively by transition metals are next shown to be particularly important examples of such mixed clusters. Later sections deal with the question of the sizes (interatomic distances) of borane-type clusters and with some general reaction types. Some other types of cluster are discussed briefly at the end.

II. The Borane-Carborane Structural Pattern

From the early structural studies carried out on boranes, it appeared that most of these compounds adopted structures based on arrangements of their boron atoms that defined fragments of icosahedra. That other triangular-faced polyhedra were important became apparent during the 1960s (*141*, *145*, *164*, *166*, *212*), as the structures of key materials such as the borane anions $B_nH_n{}^{2-}$ and carboranes $C_2B_{n-2}H_n$ were determined, although it was as recently as 1971 that the full structural pattern was first elaborated in a perceptive article by Williams (*213*), who has

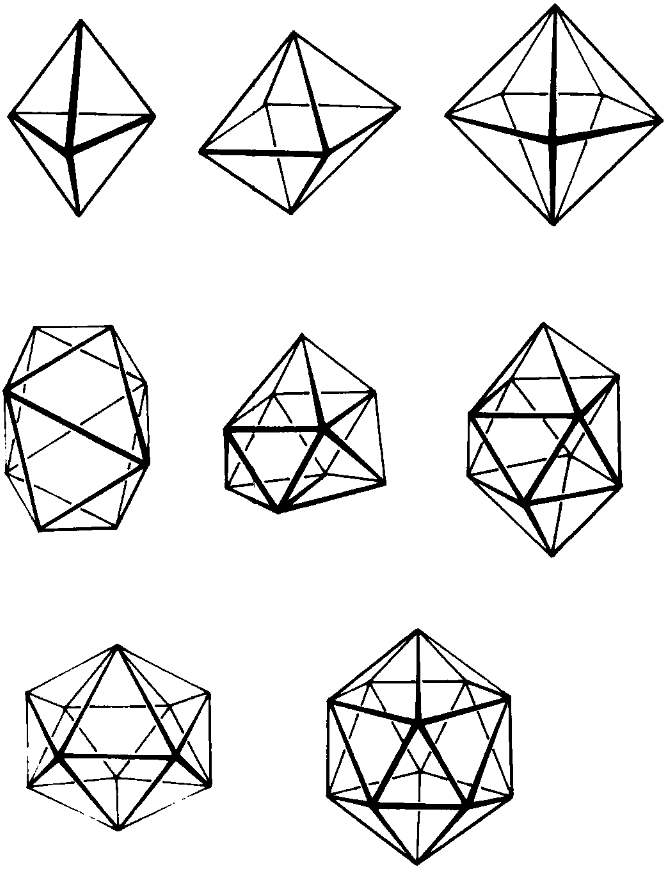


FIG. 1. Polyhedra that form the bases for the structures of *closo*-borane anions $B_nH_n{}^{2-}$ and carboranes $C_2B_{n-2}H_n$.

profusely illustrated the pattern in the following article of this volume. Here we need concern ourselves only with the main features, outlined in the following.

There are three main structural types, closo, nido, and arachno. Closo structures are adopted by borane anions $B_nH_n^{2-}$ ($n = 6 \rightarrow 12$), carboranes $C_2B_{n-2}H_n$ ($n = 5 \rightarrow 12$), and related isoelectronic species. Their n skeletal boron (or carbon) atoms define the vertices of the triangular-faced polyhedra shown in Fig. 1.

The same polyhedra serve as the basis for the structures of nido and arachno compounds, too, although for these boranes and carboranes the polyhedra are incomplete. Nido structures are adopted by neutral boranes B_nH_{n+4}, carboranes $CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$, $C_3B_{n-3}H_{n+1}$ and $C_4B_{n-4}H_n$, and related ionic species, whose n skeletal boron (or carbon) atoms occupy all but one of the vertices of the appropriate ($n + 1$)-vertex polyhedron (see Fig. 2 for examples). Arachno structures are

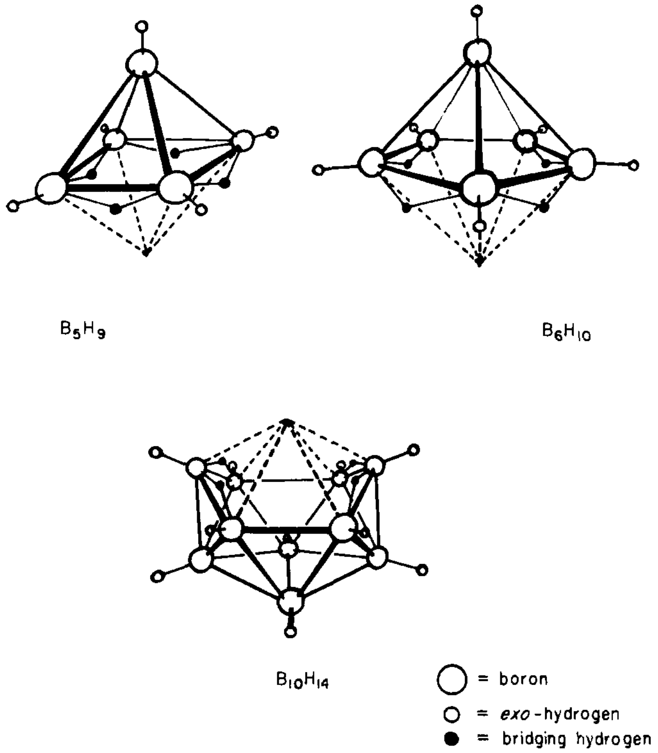


FIG. 2. The *nido*-boranes B_5H_9, B_6H_{10}, and $B_{10}H_{14}$, showing the fundamental polyhedra.

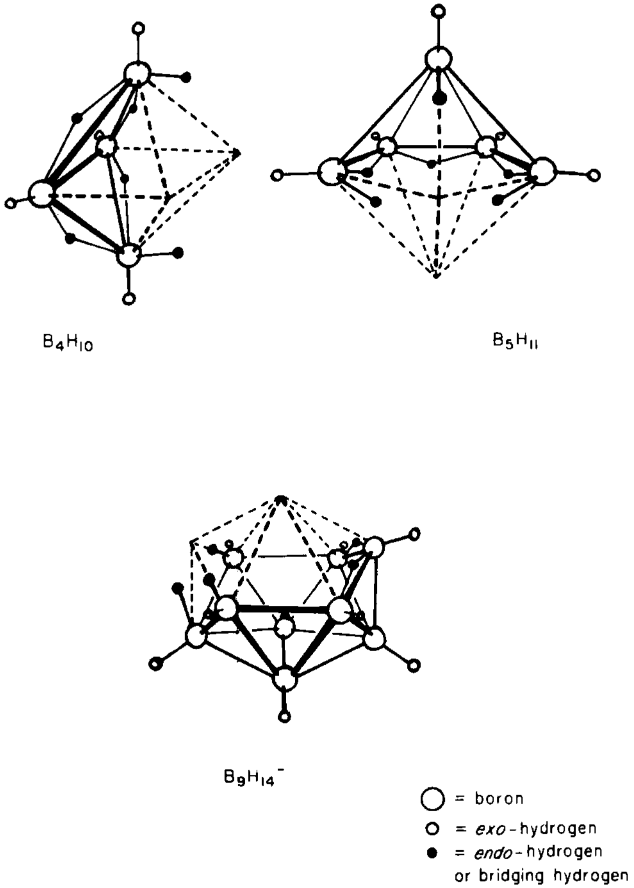


FIG. 3. The *arachno*-boranes B_4H_{10}, B_5H_{11}, and $B_9H_{14}^-$, showing the fundamental polyhedra (Williams, this volume, p. 67).

adopted by boranes B_nH_{n+6} and isoelectronic carboranes $C_2B_{n-2}H_{n+4}$, etc. Their n skeletal atoms define all but 2 of the vertices of the appropriate $(n+2)$-vertex polyhedron (Fig. 3). Table I lists formulas of typical *closo*-, *nido*-, and *arachno*-boranes and -carboranes (*12a, 95, 158a, 166a, 181a, 183, 200,* also Williams, this volume).

The positions of the hydrogen atoms in boranes and carboranes are worth noting. In *closo*-borane anions $B_nH_n^{2-}$, the n BH units are aligned so that the B—H bonds point radially outward away from the centers of the B_n polyhedra and are referred to as *exo*-B—H bonds. The CH units of isoelectronic *closo*-carboranes $CB_{n-1}H_n^-$ or $C_2B_{n-2}H_n$ are similarly orientated. When anions $B_nH_n^{2-}$ or $CB_{n-1}H_n^-$ are protonated to form

TABLE I

TYPICAL *closo-*, *nido-*, AND *arachno*-BORANES AND -CARBORANES[a,b]

No. of skeletal bond pairs	No. of polyhedron vertices	Fundamental polyhedron (symmetry)	*closo* species $B_nH_n^{2-}$	*nido* species $B_nH_n^{4-}$	*arachno* species $B_nH_n^{6-}$
6	5	Trigonal bipyramid (D_{3h})	$C_2B_3H_5$	—	$B_3H_8^-$
7	6	Octahedron (O_h)	$B_6H_6^{2-}$ CB_5H_7 $C_2B_4H_6$	B_5H_9 $C_2B_3H_7$	B_4H_{10} —
8	7	Pentagonal bipyramid (D_{5h})	$B_7H_7^{2-}$ $C_2B_5H_7$	B_6H_{10};$B_6H_{11}^+$ $C_xB_{6-x}H_{10-x}$ ($x = 1 \rightarrow 4$)	B_5H_{11} —
9	8	Dodecahedron (D_{2d})	$B_8H_8^{2-}$ $C_2B_6H_8$ $C_3B_5H_7$	— — —	B_6H_{12}
10	9	Tricapped trigonal prism (D_{3h})	$B_9H_9^{2-}$ $C_2B_7H_9$	B_8H_{12} $C_2B_6H_{10}$	—
11	10	Bicapped Archimedean antiprism (D_{4d})	$B_{10}H_{10}^{2-}$ $CB_9H_{10}^-$ $C_2B_8H_{10}$	$B_9H_{12}^-$ $C_2B_7H_{11}$ —	B_8H_{14} — —
12	11	Octadecahedron (C_{2v})	$B_{11}H_{11}^{2-}$ $CB_{10}H_{11}^-$ $C_2B_9H_{11}$	$B_{10}H_{14}$ CB_9H_{13} $C_2B_8H_{12}$	B_9H_{15} $C_2B_7H_{13}$ —
13	12	Icosahedron (I_h)	$B_{12}H_{12}^{2-}$ $CB_{11}H_{12}^-$ $C_2B_{10}H_{12}$	$CB_{10}H_{13}^-$ $C_2B_9H_{11}^{2-}$ $C_4B_7H_{11}$	$B_{10}H_{15}^-$ $B_{10}H_{14}^{2-}$ —

[a] For the cation $B_6H_{11}^+$, see Ref. (*126*).

[b] The compound $C_4H_4B_6Me_6$ is not a *nido*-carborane, but has an adamantane-type structure (*30a, 170a*).

$B_nH_{n+1}^-$ or $CB_{n-1}H_{n+1}$, the extra hydrogen atom apparently occupies a bridging position either between 2 boron atoms (over an edge of the n-cornered polyhedron) or for 3 atoms (over a polyhedron face). In the (distorted) octahedral carborane CB_5H_7, for example, the extra hydrogen atom is believed, on the basis of a microwave spectroscopic study (*150*), to be in or over one B_3 octahedral face, which is bounded by longer B—B bonds than the others.

nido-Boranes B_nH_{n+4} contain n *exo*-BH units orientated like those of the closo species, pointing away from the centers of the fundamental polyhedra, which for these species have $(n + 1)$ vertices. The extra 4 hydrogen atoms generally occupy BHB bridging positions, "stitching-up" the open face where the polyhedron is incomplete (see, e.g., B_5H_9,

B_6H_{10}, and $B_{10}H_{14}$ in Fig. 2), i.e., these BHB bridging hydrogen atoms are located roughly over the centers of incomplete faces of the fundamental polyhedron.

arachno-Boranes, B_nH_{n+6}, too, have n *exo*-BH units pointing outward away from the centers of $(n + 2)$-vertex fundamental polyhedra (Fig. 3). Their extra 6 hydrogen atoms are found in two types of position: either like their counterparts in *nido*-boranes, occupying BHB bridging positions, or in *endo*-B—H positions, terminally attached to particular boron atoms by B—H bonds orientated *tangentially* with respect to the pseudospherical surface of the fundamental polyhedron, which place these *endo*-hydrogen atoms over incomplete edges or faces of the fundamental polyhedra.

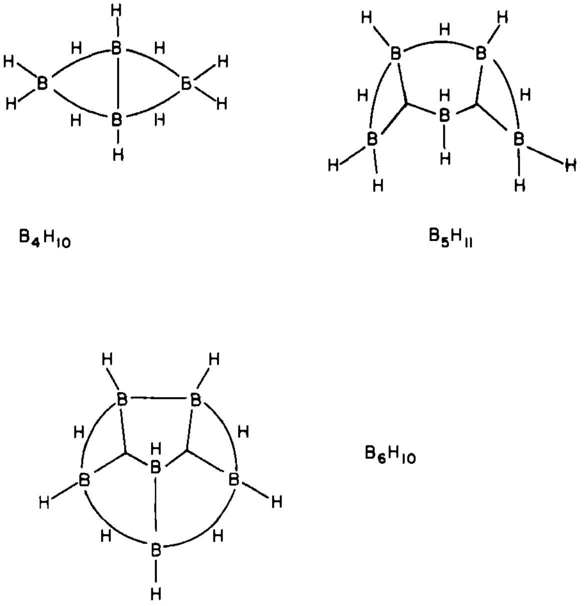
The hydrogen atoms of boranes are, thus, of two distinct structural types, for which distinct bonding descriptions are required. One type of hydrogen atom, the exo type, is located over a polyhedron vertex, bound to the skeletal atom occupying that vertex. The other type of hydrogen atom includes both the BHB bridging and endo-terminal BH hydrogens; these are located nearer to the pseudospherical surface of the fundamental polyhedron and are clearly more intimately associated with the skeletal bonding electrons. Alternative ways of treating their bonding are outlined below.

III. Bonding in Boranes and Carboranes

A. LOCALIZED BOND TREATMENTS

Although the structural pattern outlined in the foregoing can be rationalized at a simple qualitative level by using a molecular orbital approach to the skeletal bonding of boranes and carboranes (see Section III, B) it is useful to consider first what problems are encountered if one attempts to describe the bonding in terms of localized bonds.

Boranes and carboranes are *electron deficient* (*200*) in the sense that they contain more "bonds"—points of contact between adjacent, covalently bound, atoms—than electron pairs. To describe their bonding in terms of localized bonds, it is, therefore, necessary to resort to three-center or other multicenter bonds. Once the aptness of three-center bonds for describing the bonding in simple boranes had been pointed out by Longuet-Higgins (*146*) (see, for example, the bonding schemes for B_4H_{10}, B_5H_{11}, and B_6H_{10} in Fig. 4), it soon became customary to use two- and three-center bonds and occasionally other multicenter bonds for describing the bonding in electron-deficient compounds in general. For boranes in particular, Lipscomb (*145*) developed an ingenious topo-



B_4H_{10}

B_5H_{11}

B_6H_{10}

FIG. 4. Localized two- and three-center bond schemes for the boranes B_4H_{10}, B_5H_{11}, and B_6H_{10}.

logical treatment of localized bonds allowing not only known atom networks to be rationalized but also the existence of other networks to be predicted.

Lipscomb's basic assumptions are that each boron atom in a borane is involved in four bonds, and that these bonds can be two-center BH or BB bonds or three-center BHB or BBB bonds. The total number of electron pairs available, and so the total number of bonds, can be calculated simply from the molecular formula, since each boron atom supplies 3 electrons, and each hydrogen atom supplies 1 electron, for bonding. We have already seen that boranes B_nH_{n+m} consist of n *exo*-BH units and m extra hydrogen atoms. The n BH groups are held together by the $2n$ electrons that they supply for skeletal bonding, together with the m electrons from the extra hydrogens. Thus, there are $(2n + m)$ electrons available for the skeletal bonding that holds the n BH groups together (there are as many skeletal electrons as there are atoms in the molecule), and Lipscomb allocated these in pairs to s three-center BHB bonds, t three-center BBB bonds, y two-center BB bonds, and x two-center BH bonds. The numbers of different types of bond, s, t, y, and x, for a borane B_nH_{n+m} can be shown quite simply to be related by the following equations:

$$x = m - s \qquad t = n - s \qquad 2y = s - x$$

From these equations one can work out what sets of *styx* numbers are possible for known or hypothetical boranes B_nH_{n+m} and so rationalize known atomic networks or predict new ones. For example, the *styx* numbers for the compounds shown in Fig. 4 are B_4H_{10}, 4012; B_5H_{11}, 3203; and B_6H_{10}, 4220.

In the hands of Lipscomb and others (*76, 143, 145a, 153, 189, 190*), such localized bond schemes, particularly when obtained via self-consistent field (SCF) molecular orbital (MO) treatments, have proved particularly valuable for rationalizing the shapes and interatomic distances and estimating the charge distribution in many higher boranes.

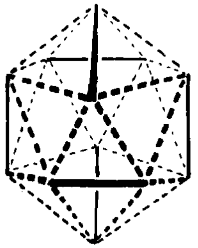


FIG. 5. An apparently satisfactory localized skeletal bond scheme for a hypothetical icosahedral anion $B_{12}H_{12}{}^{4-}$ (two-center B—B bonds are represented by full lines, three center BBB bonds by triangles with exclusively broken-line edges).

However, used qualitatively, localized bond schemes are less satisfactory for rationalizing the shapes of such relatively symmetrical species as the closo anions $B_nH_n{}^{2-}$, for most of which it is not possible to find a single localized bond arrangement that appears appropriate for the symmetry. For example, the equations of balance for the anion $B_6H_6{}^{2-}$ require its 6 BH units to be held together by three two-center BB bonds and four 3-centre BBB bonds, a combination which fits the known octahedral symmetry but poorly. Again, the three two-center BB bonds and ten three-center BBB bonds required for anion $B_{12}H_{12}{}^{2-}$ appear to suit the icosahedral anion far less appropriately than the combination of six two-center BB bonds and eight three-center BBB bonds that could be used for a hypothetical icosahedral anion $B_{12}H_{12}{}^{4-}$ (Fig. 5) (*200*). In short, for the polyhedral *closo*-borane anions and related carboranes, two- and three-center bond schemes are generally unsatisfactory. They give poor fits to the shapes of known species, and, as in the case of the hypothetical anion $B_{12}H_{12}{}^{4-}$, lead one to expect the existence of other species than are actually found, e.g., compounds B_nH_{n+4} with closo structures.

B. SIGNIFICANCE OF THE NUMBERS OF SKELETAL BONDING ELECTRON PAIRS

1. Closo Species

The problems outlined in the previous section can be avoided if, instead of allocating the skeletal bonding electron pairs to localized bonds, one simply compares their number with the number of skeletal bonding MO's (*199*). The closo, nido, and arachno structures of boranes and carboranes can then be seen to reflect the numbers of skeletal bond pairs that are available to hold their skeletal atoms together.

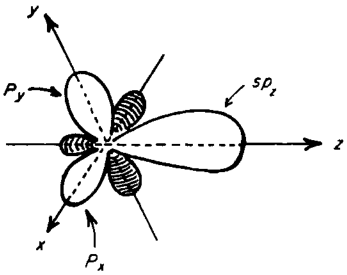
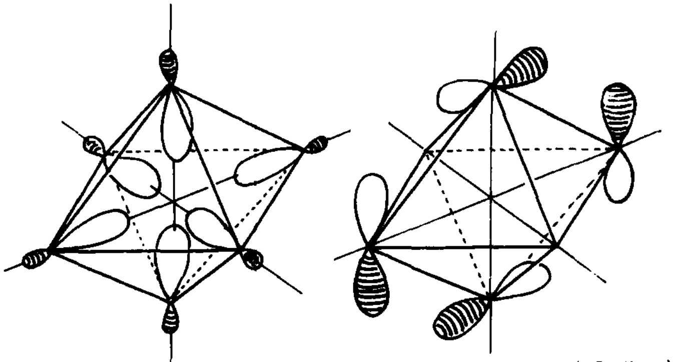


FIG. 6. The radially orientated *sp* hybrid atomic orbital (AO) and tangentially orientated *p* AO's that a BH unit can supply for skeletal bonding.

The number of bonding MO's appropriate for a particular structure is best illustrated by considering first the *closo*-borane anions $B_nH_n^{2-}$. These adopt the polyhedral structures shown in Fig. 1, and each contains n exo-BH units held together by $(n + 1)$ skeletal bond pairs. (Effectively, one skeletal bond pair is supplied by each BH unit; the remaining pair arises from the charge on these closo anions.) If one assigns to the BH bond one *sp* hybrid orbital on each boron atom, pointing radially outward away from the center of the cluster, there remain three atomic orbitals (AO's) on each boron atom available for cluster bonding (see Fig. 6). One of these is an inward-pointing, radially orientated, *sp* hybrid orbital; the other two are *p* orbitals, orientated tangentially with respect to the pseudospherical surface of the cluster. The symmetries of the polyhedra shown in Fig. 1 are such that, in each case, $(n + 1)$ bonding MO's are generated by interactions of the $3n$ AO's available (*113–116*, *139*, *145*, *147*, *148*, *163*, *164*). For example, an octahedral arrangement of six BH groups generates seven bonding MO's (*147*): a unique orbital of a_{1g} symmetry resulting from in-phase interactions of the six radial *sp* AO's (see Fig. 7) and two triply degenerate sets of MO's, of symmetries t_{2g} and t_{1u}, to which the tangentially orientated *p* orbitals make the major contribution.


a_{1g} (radial *sp* hybrid AO's)

t_{2g} (+2 others) (tangential *p* AO's)

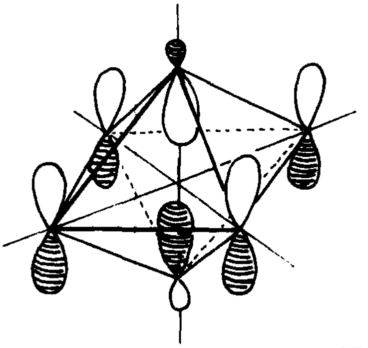

t_{1u} (+2 others)

FIG. 7. The skeletal bonding molecular orbitals of $B_6H_6^{2-}$ (*147*). (AO, atomic orbital.)

For the higher borane anions $B_nH_n^{2-}$, although the sets of bonding MO's become progressively more numerous as n increases (*139*, *145*, *148*, *163*, *164*), features of the $B_6H_6^{2-}$ MO pattern persist. Of the $(n + 1)$ bonding MO's, there is invariably one, of a_1 or a_g symmetry, representing an in-phase combination of the radially orientated *sp* hybrid orbitals, to which the tangentially orientated *p* orbitals make no contribution. The remaining n bonding MO's are primarily polyhedron surface orbitals in that they result from interactions of the $2n$ tangentially orientated p AO's, although some have stabilizing contributions from combinations of radially orientated sp hybrid orbitals, as in the case of the t_{1u} bonding MO's for $B_6H_6^{2-}$. These features can be seen in the MO diagram for the icosahedral *closo*-borane anion $B_{12}H_{12}^{2-}$ (Fig. 8), a species of particular interest as its existence was predicted, on the basis of an LCAO-MO treatment, by Longuet-Higgins and Roberts (*148*) some years before salts of the anion were actually prepared.

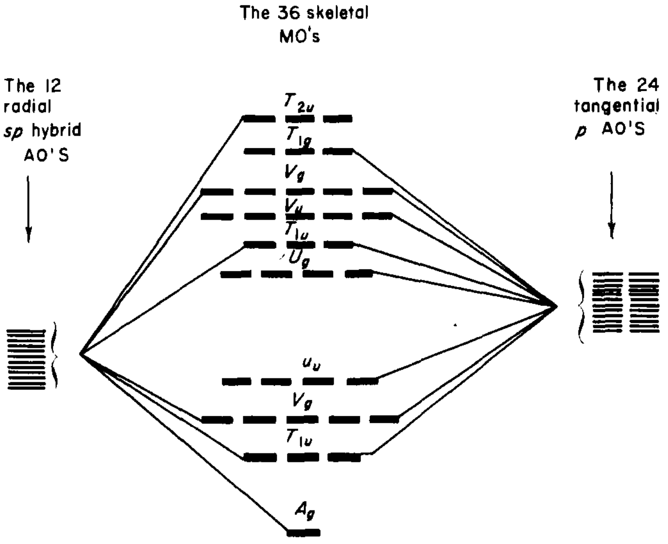


FIG. 8. Relative energy levels and degeneracies of the 13 bonding and 23 antibonding skeletal molecular orbitals (MO's) of the icosahedral anion $B_{12}H_{12}^{2-}$ (*148*). (AO, atomic orbital.)

The division of the $(n + 1)$ bonding AO's into two types, a unique radial orbital and n "surface" orbitals, incidentally is also a feature of a free-electron MO treatment (*198*) which has been applied to borane polyhedra, as distinct from the linear combination of atomic orbitals (LCAO)-MO treatments mentioned above.

The polyhedra in Fig. 1 thus represent suitable shapes for cluster species with n skeletal atoms (each of which can furnish three AO's for use in skeletal bonding) and with $(n + 1)$ skeletal bond pairs. Since it is the cluster symmetry that determines the number of bonding MO's, the same polyhedra can serve as the basis for the structures of a whole range of isoelectronic species, including neutral carboranes of formula $C_2B_{n-2}H_n$, bismuth clusters, such as the trigonal-bipyramidal Bi_5^{3+}, which as Corbett pointed out (*43*) has six skeletal bond pairs to hold its 5 atoms together if one allocates a "lone pair" to each bismuth atom, and many other systems as outlined below.

For a recent photoelectron spectroscopic study of some *closo*-carboranes $C_2B_{n-2}H_n$ ($n = 5$, 6, 7, or 12) which supports this skeletal bonding treatment, see Ref. (*82a*).

2. *Nido and Arachno species*

The structures of *nido*- and *arachno*-boranes and carboranes can be rationalized in a similar manner to those of the closo species if one considers the hypothetical anions, $B_nH_n{}^{4-}$ and $B_nH_n{}^{6-}$, from which they are formally derived. Since each BH unit can contribute 2 electrons for skeletal bonding, these two anions contain $(n + 2)$ and $(n + 3)$ skeletal bond pairs, respectively. Nido species related to the hypothetical anions $B_nH_n{}^{4-}$ thus contain the number of skeletal bond pairs, $(n + 2)$, appropriate for an $(n + 1)$-vertex polyhedral arrangement of their n skeletal atoms, one vertex being left vacant, whereas arachno species formally derived from hypothetical anions $B_nH_n{}^{6-}$ contain the number of skeletal bond pairs, $(n + 3)$, appropriate for a polyhedron with $(n + 2)$ vertices, two of which are left vacant. Even though not all the vertices of the polyhedra are occupied by skeletal atoms, the symmetries of the nido and arachno fragments ensure in each case that the number of skeletal bonding MO's is one more than the number of polyhedron vertices. (This point is illustrated in Fig. 9 for species formally related to $B_6H_6{}^{2-}$.)

Significantly, in the neutral *nido*-boranes B_nH_{n+4} (Fig. 2), treated as anions $B_nH_n{}^{4-}$ to which four H^+ ions have been added, the extra 4 hydrogen atoms occupy BHB bridging positions that preserve so far as possible the symmetry of the system, thus also preserving the number of bonding MO's. Similarly, the extra 6 hydrogen atoms of *arachno*-boranes B_nH_{n+6} (Fig. 3) occupy endo-terminal BH or bridging BHB positions that preserve the symmetry of the system. In B_4H_{10}, for example, the extra 6 hydrogen atoms occupy four BHB bridging sites and two endo-terminal BH sites. Similarly, in B_5H_{11} (Fig. 3), the 6 extra hydrogen atoms occupy three BHB bridging and three endo-terminal BH sites. It should be stressed that the electron pairs that, in a localized bond treatment, would be allocated to *endo*-BH or bridging BHB bonds are here included in the *skeletal* electron count.

That the number of skeletal bonding MO's associated with a particular polyhedral arrangement of BH units need not change if 1 or 2 BH units are removed from the closo species is illustrated in Fig. 9 for species based on an octahedron, namely, the closo anion $B_6H_6{}^{2-}$ and the hypo-

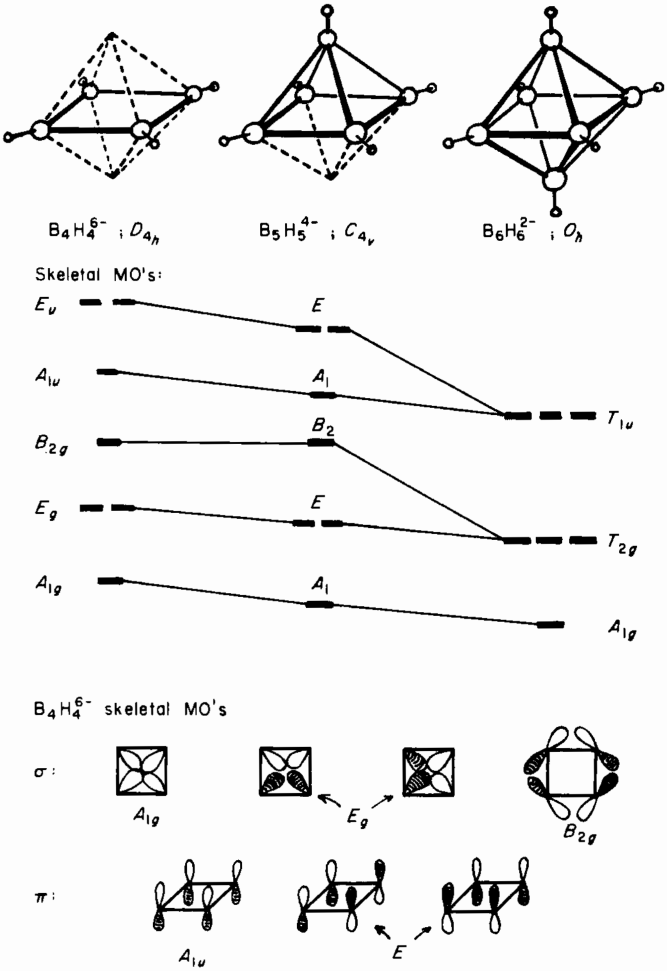


Fig. 9. Orbital correlation diagram for D_{4h} $B_4H_4^{6-}$, C_{4v} $B_5H_5^{4-}$, and O_h $B_6H_6^{2-}$. (MO, molecular orbitals.)

thetical nido and arachno anions $B_5H_5^{4-}$ (C_{4v} symmetry) and $B_4H_4^{6-}$ (D_{4h}). A hypothetical square-planar anion $B_4H_4^{6-}$ (cf the isoelectronic cyclobutadiene dianion $C_4H_4^{2-}$) would have four σ-bonding MO's (of symmetries A_{1g}, B_{1g}, and E_g) and three π-bonding MO's (of symmetries A_{1u} and E_u), which would be stabilized and modified in symmetry, but not added to, if 2 BH^{2+} units were brought up the fourfold axis to complete the octahedron of $B_6H_6^{2-}$. Significantly, the neutral *arachno*-borane B_4H_{10} actually has a C_{2v} arrangement of its 4 skeletal boron atoms (Fig. 3) (formally derived from the octahedral $B_6H_6{}^{2-}$ by removing 2 *cis*- rather than *trans* boron atoms) rather than a D_{4h} square-planar arrangement, probably because the C_{2v} symmetry, but not the D_{4h}, can be preserved for the molecule B_4H_{10}. A square-planar structure, however, appears possible for an anion $B_4H_8{}^{2-}$ which is already known in the form of the coordination complex $B_4H_8Fe(CO)_3$ (*94*) (Fig. 10).

The progressive opening of the molecular skeleton that accompanies formal addition of electron pairs to a *closo*-borane anion $B_nH_n{}^{2-}$ is intelligible in that a pair of electrons is the contribution made to skeletal bonding by a neutral BH unit. Formally adding BH to $B_nH_n{}^{2-}$ to convert it into $B_{n+1}H_{n+1}^{2-}$ has the same effect on the positions of the original n boron atoms as has the addition of a pair of electrons to $B_nH_n{}^{2-}$ to convert it into $B_nH_n{}^{4-}$. In each case, the original n boron atoms move to n of the $(n + 1)$ vertices of the next higher triangular-faced polyhedron (*199*).

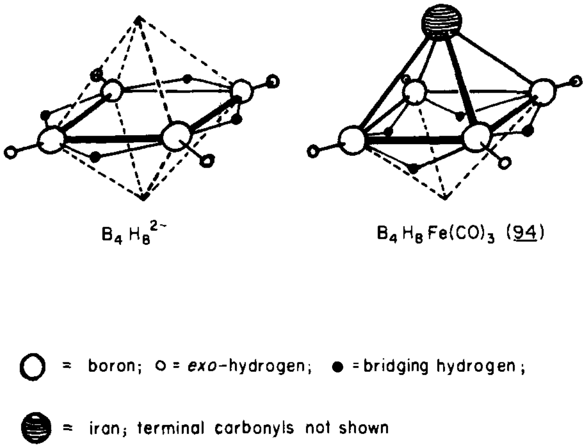


FIG. 10. Possible structures for the arachno anion $B_4H_8{}^{2-}$ and its iron complex $B_4H_8Fe(CO)_3$.

C. SUMMARY OF STRUCTURAL AND BONDING PATTERN

Before exploring other areas to which the borane–carborane structural and bonding pattern is relevant, it is useful to summarize the main features, as follows.

1. The triangular-faced polyhedra shown in Fig. 1 form the bases for the structures of boranes and carboranes.
2. The skeletal boron or carbon atoms occupy all, all but one, or all

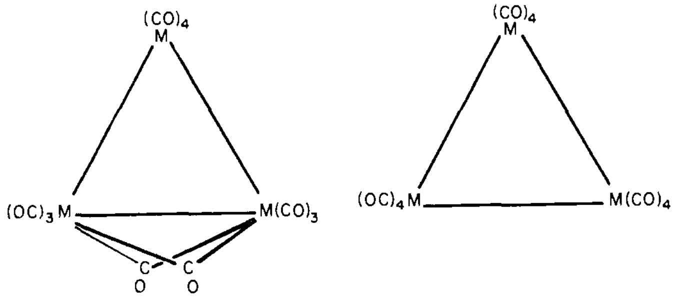
but two of the vertices of the appropriate polyhedron in closo, nido, or arachno compounds, respectively.

3. Each skeletal boron or carbon atom has a hydrogen atom (or some other singly bonded ligand) terminally attached to it, by a bond radiating outward (*exo*) away from the center of the polyhedron, to which a pair of electrons is allocated.
4. The remaining valence shell electrons (b pairs) are regarded as skeletal bonding electrons.
5. Each skeletal boron or carbon is considered to provide three AO's for skeletal bonding.
6. The symmetries of the polyhedra are such as to generate $(n + 1)$ skeletal bonding MO's from these AO's, where $n =$ the number of polyhedron vertices $[n = (b - 1)]$.
7. Compounds with a skeletal atoms and b skeletal bond pairs adopt closo structures if $b = (a + 1)$, nido structures if $b = (a + 2)$, and arachno structures if $b = (a + 3)$.

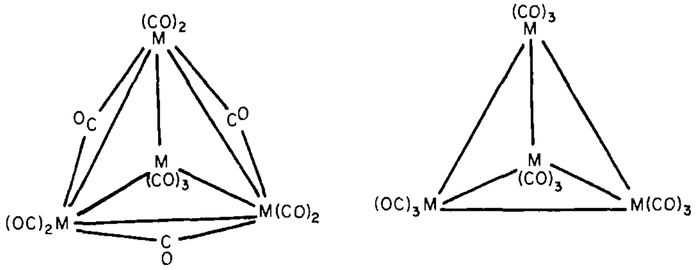
IV. Some Metal–Carbonyl Clusters

That transition metal–carbonyl clusters, which contain an apparent abundance of electrons, might have much in common with boranes and carboranes, notorious for their deficiency of electrons, appears at first sight improbable. However, the structural and bonding relationship between them becomes apparent if one considers certain metal–carbonyl clusters for which localized bond treatments are unsatisfactory.

Among the large numbers of metal–carbonyl clusters now known (*1*, *33*, *127*, *138*, *170*), species based on triangular, tetrahedral, or octahedral arrays of metal atoms are common. For the first two types, exemplified by the iron-group triangular clusters $M_3(CO)_{12}$ [M = Fe (*208*, *210*), Ru (*156*), or Os (*45*)] and the cobalt-group tetrahedral clusters $M_4(CO)_{12}$ [M = Co (*47*, *210*), Rh (*211*), or Ir (*211*)] (Fig. 11), the skeletal bonding can be described in terms of localized two-center metal–metal bonds, it being assumed that each metal atom attains an inert gas configuration (*134*). However, many octahedral clusters that contain the wrong number of electrons for similar localized bond descriptions are now known. For example, the octahedral complex $Rh_6(CO)_{16}$ (Fig. 12) contains a pair of electrons too many to allow its skeletal bonding to be described in terms of twelve two-center rhodium–rhodium bonds along the octahedron edges (*46*), although an equivalent orbital approach suggested it had 2 electrons too few (*135*). The same valence problem is posed by other octahedral clusters such as the



$Fe_3(CO)_{12}$ (208, 211) $Ru_3(CO)_{12}$ (156) $Os_3(CO)_{12}$ (45)



$Co_4(CO)_{12}$ (47, 210), $Rh_4(CO)_{12}$ (211) $Ir_4(CO)_{12}$ (211)

FIG. 11. Triangular and tetrahedral metal clusters.

carbonyl hydride $H_2Ru_6(CO)_{18}$ (*39*) and the carbonyl carbides $Ru_6(CO)_{17}C$ (*125*, *182*) and $Ru_6(CO)_{14}C$(arene) (*125*, *157*) (see Fig. 12).

All these molecules contain 86 electrons associated with the valence shells of the 6 metal atoms (the core carbon atoms of the carbides are considered to contribute all their valence shell electrons to these clusters). In the hydride $H_2Ru_6(CO)_{18}$, for example, the metal atoms supply 48 electrons, the carbonyl ligands 36, and the hydrogen atoms 2. Formally, this hydride may be regarded as derived from the anion $[Ru(CO)_3]_6^{2-}$, which, in turn, can be shown to be formally related to the *closo*-borane anion $B_6H_6^{2-}$ as follows (*199*, *200*).

If 18 electron pairs are assigned to the eighteen metal–carbon bonds (3 on each metal), there remain six AO's on each metal atom, and 25 electron pairs, for use in metal–metal bonding. Since well over half the

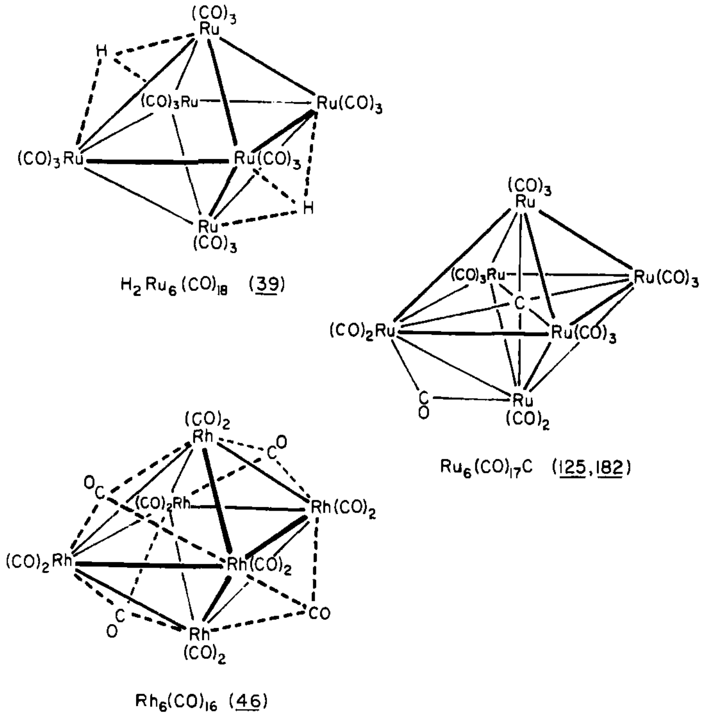


FIG. 12. Some octahedral metal–carbonyl clusters.

available MO's (25 of the 36) will be filled, clearly not all of the electron pairs in them can perform a metal–metal bonding role. Either some must occupy orbitals that are essentially nonbonding, or else the metal–metal antibonding effect of some must nullify the metal–metal bonding effect of others.

For simplicity, one can allocate 3 electron pairs to "nonbonding" orbitals on each metal atom, which leaves three AO's on each metal atom for cluster skeletal bonding, and 7 electron pairs to be accommodated in the bonding MO's these AO's generate. This description is reminiscent of that outlined above (Fig. 7) for $B_6H_6^{2-}$. Each $Ru(CO)_3$ unit of $H_2Ru_6(CO)_{18}$, like each BH unit of $B_6H_6^{2-}$, can contribute three AO's, and 2 electrons, for skeletal bonding (*199, 200*).

Similar bonding descriptions are possible for the other octahedral metal carbonyl clusters. In $Rh_6(CO)_{16}$, for example, 4 electron pairs can be allocated to the four metal–carbon bonds each metal atom is involved in (each metal has two terminal and two triply bridging carbonyl groups attached); 2 more pairs can be allocated to nonbonding orbitals on each metal atom; and 7 electron pairs remain for skeletal bonding.

The relationship between boranes and metal–carbonyl clusters can be extended by considering the compound $Fe_5(CO)_{15}C$, which has the square-based pyramidal structure shown in Fig. 13, with the carbide carbon atom just below the center of the Fe_4 square, clearly contributing all its valence shell electrons to the cluster (*24*). The metal–carbonyl residue $Fe_5(CO)_{14}^{4-}$ formally left by removal of this carbon as C^{4+} has the nido structure appropriate for a cluster with 5 skeletal atoms and seven skeletal bond pairs.

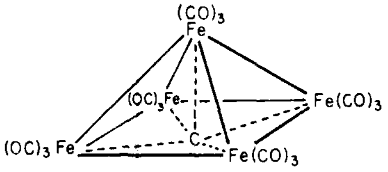


FIG. 13. The *nido*-iron–carbonyl carbide cluster $Fe_5(CO)_{15}C$ (*24*).

It should be stressed that, in this treatment of metal–carbonyl clusters, the number of nonbonding electron pairs allocated to each metal atom [3 pairs for each ruthenium atom of $H_2Ru_6(CO)_{18}$; 2 pairs for each rhodium atom of $Rh_6(CO)_{16}$] is not arbitrary but is chosen with two objectives in mind: (*a*) to reduce the number of electrons formally remaining for skeletal bonding to fewer than the number of orbitals remaining, because only then is it realistic to assume that all these electrons can be accommodated in bonding MO's; and (*b*) to provide a suitable number of electron pairs on each metal atom for metal → carbon dative π bonding to the carbonyl ligands. The so-called nonbonding electrons thus contribute to metal–ligand bonding and, indeed, must also be expected to make a small net metal–metal bonding contribution to the skeletal bonding, as indicated by a recent MO treatment (*162*) of the carbonyl anion (*3*) $Co_6(CO)_{14}^{4-}$.

In addition to the closo- and nido-metal–carbonyl clusters already mentioned, with structures based on the octahedron, another interesting category of structure that is found among metal–carbonyl clusters is one in which n skeletal atoms are held together formally by n skeletal bond pairs. These adopt structures based on polyhedra with $(n - 1)$ vertices, as might be expected. The extra metal atom caps one of the triangular faces of the closo residue, where the three vacant orbitals that it can formally furnish for cluster bonding enable it to bond to the 3 metal atoms defining the face without modifying the number of bonding MO's for the rest of the cluster. Examples include the anion $[Rh_7(CO)_{16}]^{3-}$ (*4*), which has the capped octahedral geometry (Fig. 14) appropriate for its 7 skeletal atoms and seven skeletal bond pairs, and the neutral osmium complex $Os_6(CO)_{18}$ (*73*, *158*), which has a capped trigonal-bipyramidal (or bicapped tetrahedral) structure (Fig. 14) instead of the regular octahedral shape that seemed likely, on a localized bond approach, for an arrangement of six $Os(CO)_3$ units, each capable of forming four two-center bonds.

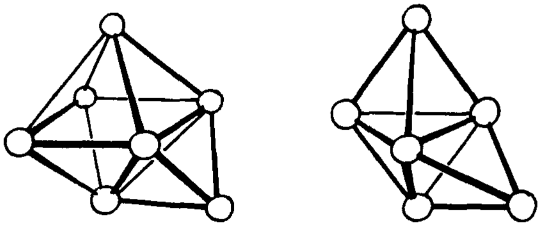


FIG. 14. The capped octahedral skeleton of the anion $[Rh_7(CO)_{16}]^{3-}$ (*4*) and capped trigonal bipyramidal (bicapped tetrahedral) skeleton of $Os_6(CO)_{18}$ (*73*, *158*).

Many further examples could be added to those already cited to support the close relationship between carbonyl clusters and borane clusters, particularly for species based on an octahedron. These other *closo* octahedral clusters include anions such as $Co_6(CO)_{15}{}^{2-}$ (*34*), $[Fe_6(CO)_{16}C]^{2-}$ (*38*, *40*), $[Rh_6(CO)_{15}I]^-$ (*6*), $[Ni_6(CO)_{12}]^{2-}$ (*31*), $[Co_4Ni_2(CO)_{14}]^{2-}$ (*8*), and $[Rh_{12}(CO)_{30}]^{2-}$, in which two Rh_6 octahedra are linked by a metal–metal bond and two bridging carbonyl groups (2).

V. Some Mixed Clusters

A. SKELETAL ELECTRON-COUNTING PROCEDURES

The foregoing examples show the relevance to metal–carbonyl cluster chemistry of the borane–carborane structural and bonding pattern. Its relevance to other areas of chemistry may be explored readily using a systematic skeletal electron-counting procedure (*161*, *201*).

Tables II and III list the numbers of electrons provided by various potential cluster units, assuming that the skeletal atoms make available three AO's apiece for skeletal bonding, and use their remaining valence shell orbital(s) to bond ligands to the cluster. For example, a main group element E (Table II) such as boron can make three AO's available for cluster bonding if it uses its one remaining valence shell AO (an inert

TABLE II

THE NUMBER OF SKELETAL BONDING ELECTRONS ($v + x - 2$) THAT MAIN GROUP CLUSTER UNITS CAN CONTRIBUTE

		Typical cluster unit[b]		
v[a]	Main group element E	E ($x = 0$)	EH, EX ($x = 1$)	EH_2, EL ($x = 2$)
1	Li, Na	[−1]	0	1
2	Be, Mg, Zn, Cd, Hg	0	1	2
3	B, Al, Ga, In, Tl	1	2	3
4	C, Si, Ge, Sn, Pb	2	3	4
5	N, P, As, Sb, Bi	3	4	5
6	O, S, Se, Te	4	5	[6]
7	F, Cl, Br, I	5	[6]	[7]

[a] v = No. of valence shell electrons (periodic group number) of main group element.

[b] x = No. of electrons from ligand(s); X = a 1-electron ligand; L = a 2-electron ligand.

TABLE III

THE NUMBER OF SKELETAL BONDING ELECTRONS ($v + x - 12$) THAT TRANSITION METAL CLUSTER UNITS CAN CONTRIBUTE[a]

		Typical cluster unit			
v	Transition metal M	$M(CO)_2$ ($x = 4$)	$M(\pi\text{-}C_5H_5)$ ($x = 5$)	$M(CO)_3$ ($x = 6$)	$M(CO)_4$ ($x = 8$)
6	Cr, Mo, W	[−2]	−1	0	2
7	Mn, Tc, Re	−1	0	1	3
8	Fe, Ru, Os	0	1	2	4
9	Co, Rh, Ir	1	2	3	5
10	Ni, Pd, Pt	2	3	4	6

[a] v = No. of valence shell electrons on M; x = No. of electrons from ligands.

gas configuration is assumed) either to accommodate a lone pair or to bond a suitable ligand (as in a group EL). The number of electrons that atom E or group EL supplies for cluster bonding is then $v + x - 2$, where v = the number of electrons in the valence shell of the cluster atom E (its periodic group number) and x = the number of electrons supplied by the ligand L. A transition metal atom M, with five more orbitals in its valence shell, can accommodate more ligands and will furnish $(v + x - 12)$ electrons for skeletal bonding (where x represents the total number of electrons supplied by the ligands on M). For mixed clusters containing both transition metal and main group skeletal atoms, the skeletal electron count may be carried out by summing the valence shell and ligand electrons, and subtracting 2 for each main group atom and 12 for each transition metal atom in the cluster (*201*). For example, the skeletal electron count for a simple borane B_nH_{n+m} would be $2n + m$, obtained either by adding the contribution from n BH units (2 electrons from each; see Table II) to the contribution from the m extra hydrogen atoms, or

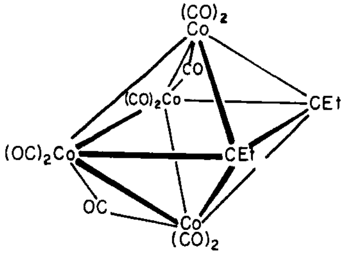


FIG. 15. The closo distorted octahedral structure of the cobalt–carbonyl acetylene complex $Co_4(CO)_{10}C_2Et_2$ (*50*).

by summing the valence shell $(3n)$ and ligand $(n + m)$ electrons and subtracting 2 for each boron atom $(2n)$.

The application of the method to a cluster containing cobalt and carbon skeletal atoms is illustrated by the cobalt–carbonyl acetylene complex $Co_4(CO)_{10}C_2Et_2$ (*50*), which can be prepared from the tetrahedral cobalt carbonyl cluster $Co_4(CO)_{12}$ and diethylacetylene (*142*). Summing the valence shell electrons (4 × 9 from Co_4; 2 × 4 from C_2) and ligand electrons (10 × 2 from the ten carbonyl groups plus 2 × 1 from the two ethyl groups) and subtracting 12 for each cobalt atom and 2 for each carbon atom, leaves 14 electrons, i.e., 7 pairs, appropriate for a *closo*-octahedral arrangement of its 6 (Co_2C_2) skeletal atoms. [The same number of skeletal electrons is arrived at by treating the cluster as containing 4 $Co(CO)_2$ units, 2 EtC units, and 2 extra carbonyl ligands.] In the actual structure (Fig. 15) the octahedral skeleton is distorted because of the differing sizes of the cobalt and carbon atoms.

For mixed main group–transition element clusters containing but one transition element, modifying the above electron-counting procedure to include the 6 nonbonding electron pairs on the transition metal has been advocated (*128*) as a way of bringing the electron count into line with the familiar "18-electron rule" for transition metal complexes. This produces a "$2n + 14$ electron rule" for closo clusters with n skeletal atoms, one a transition metal, and a "$2n + 16$ electron rule" for related nido clusters.

B. METALLO-BORANES AND -CARBORANES

Large numbers of metallo-boranes and -carboranes (*31b*, *68a*, *94a*, *95*, *96a*, *96b*, *172a*, *183*, *195*, *205b*, also Williams, this volume) are now

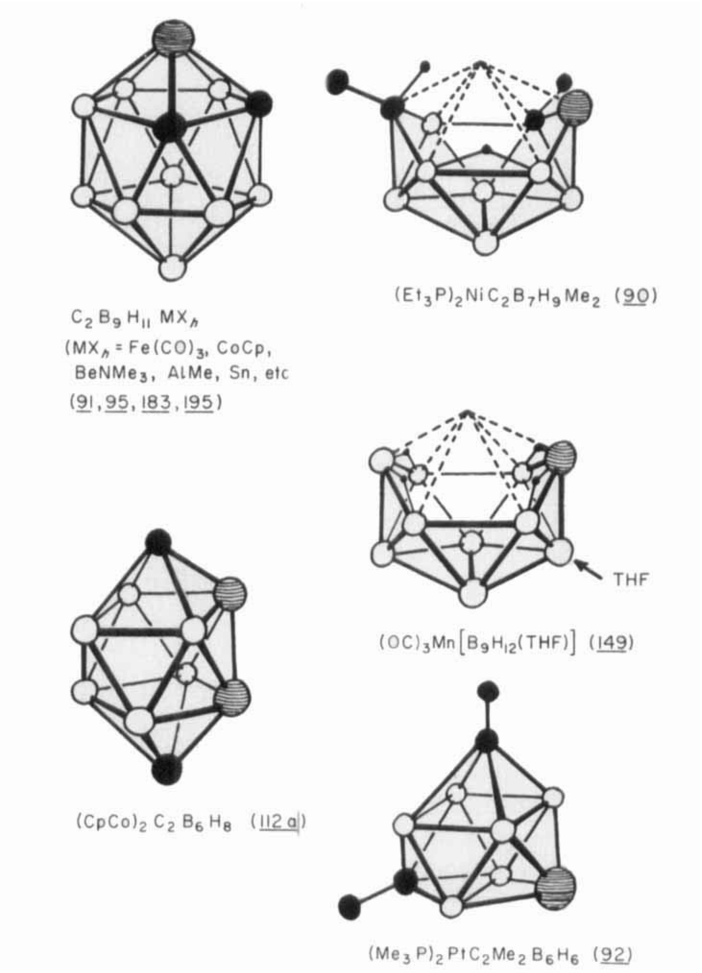


FIG. 16. Some metallocarboranes and a metalloborane (metal ligands and exo-hydrogen atoms omitted). (THF, tetrahydrofuran.)

known in which metal atoms occupy vertices of the fundamental polyhedra. Some typical structures are illustrated in Fig. 16, and formulas of some metallo-boranes and -carboranes are listed in Tables IV and V. Reference to Tables II and III shows that such groups as $M(CO)_3$ ($M = Fe$, Ru, or Os), $M'(h^5\text{-}C_5H_5)$ ($M' = Co$, Rh, or Ir) and $M''(CO)_2$ ($M'' = Ni$, Pd, or Pt), like a BH group, can in principle supply three AO's and 2 electrons for cluster bonding, so it is not surprising to find such units in *closo*-metallo-boranes and -carboranes.

TABLE IV

SOME *closo*-METALLO-BORANES AND -CARBORANES CONTAINING AT LEAST 1 METAL ATOM IN THE *n*-VERTEX POLYHEDRAL CLUSTER

n	Examples (*95*, *183*, *195*)
6	$(CpCo)_2B_4H_6$ (*159*); $CpCoC_2B_3H_5$ (*159a*); $(OC)_3FeC_2B_3H_5$ (*159a*)
7	$(OC)_3FeC_2B_4H_6$ (*96*); $MeMC_2B_4H_6$ (M = Ga, In) (*98*); $(Ph_3P)_2NiC_2B_4H_6$ (*159a*); $(OC)_3MnC_3B_3H_5Me$; $(CpCo)_2C_2B_3H_5$ (*14*, *159a*); $[(OC)_3Fe]_2C_2B_3H_5$ (*159a*)
9	$(R_3P)_2PtC_2B_6H_6R_2'$ (*92*); $CpCoC_2B_6H_8$ (*72*, *77*); $[(OC)_3MnC_2B_6H_8]^-$; $[CpCoCB_7H_8]^-$; $(CpCo)_2C_2B_5H_7$ (*82*, *159a*); $CpFeC_2B_6H_8$ (*77*); $[Co(C_2B_6H_8)_2]^-$ (*77*)
10	$CpCoC_2B_7H_9$ (*72*, *77*); $[Co(C_2B_7H_9)_2]^-$; $(CpCo)_2C_2B_6H_8$ (*77*, *112a*); $CpNi(CpCo)CB_7H_8$ (*175*); $(CpCo)_3C_2B_5H_7$ (*159a*)
11	$CpCoC_2B_8H_{10}$ (*72*, *77*); $CpFeC_2B_8H_{10}$ (*77*); $(C_2B_9H_{11})CoC_2B_8H_{10}$; $(CpCo)_2C_2B_7H_9$ (*80*, *82*); $[Co(C_2B_8H_{10})_2]^-$ (*77*)
12	$XC_2B_9H_{11}$ [X = CpCo, $(R_3P)_2Pt$ (*91*); L_2Ni, Ge, Sn, Pb, Tl^-, EtAl, [LBe]; $M(C_2B_9H_{11})_2^{x-}$ ($M = Fe, x = 2; M = Co, x = 1; M = Ni, x = 0$); $M(CB_{10}H_{11})_2^{x-}$ ($M = Co, x = 3; M = Ni, x = 2$); $AsCB_{10}H_{11}$; $M(B_{10}H_{10}S)_2^{x-}$ ($M = Fe, x = 2; M = Co, x = 1$) (*195a*); $XB_{10}H_{10}S$ (X = CpCo, L_2Pt) (*195a*); $(CpCo)_2C_2B_8H_{10}$ (*77*, *81*, *82*); $(CpCo)_3C_2B_7H_9$ (*80*, *82*); $CpCoCB_9H_{10}X$ (X = P, As)
13	$CpCoC_2B_{10}H_{12}$ (*35*, *70*, *72*); $(CpCo)(CpFe)C_2B_9H_{11}$ (*71*); $(CpCo)_2C_2B_9H_{11}$ (*82*)
14	$(CpCo)_2C_2B_{10}H_{12}$

Although most known metallocarboranes have only 1 metal atom per polyhedron, the existence of an increasing number of metallocarboranes with 2 or more metal atoms per cluster emphasizes the close relationship between metal clusters and borane clusters. Since they can be synthesized from *closo*-carboranes by replacing BH units by metal–carbonyl or metal–cyclopentadienyl residues, carborane clusters can effectively be used as disposable templates on which to fabricate particular metal clusters (*106*), although alternative, more direct routes to a range of new metal clusters are rapidly being developed.

One particularly interesting category of metallocarborane is that in which a single metal atom is shared between two polyhedra that have a vertex in common. In effect, the metal is sandwiched between two *nido*-carborane residues. Examples are shown in Fig. 17. For such "commo" compounds, the metal can be assumed to contribute three AO's to the skeletal bonding of each polyhedron, when the "$(n + 1)$ rule" for closo clusters is found to be obeyed. For example, the isoelectronic complexes $[Fe(C_2B_9H_{11})_2]^{2-}$, $[Co(C_2B_9H_{11})_2]^-$, and $Ni(C_2B_9H_{11})_2$ may be regarded as complexes in which two *nido*-$C_2B_9H_{11}{}^{2-}$ anions sandwich the isoelectronic d^6 metal ions Fe^{2+}, Co^{3+}, and Ni^{4+}, respectively (*214*), and these adopt symmetrical structures (Fig. 17) (*36, 37, 53, 174, 220*). Significantly, related complexes with 2 or more extra electrons, such as $[Ni(C_2B_9H_{11})_2]^{2-}$, $[Cu(C_2B_9H_{11})]^-$, and $[Cu(C_2B_9H_{11})_2]^{2-}$ (*215, 216*) have "slipped" structures (Fig. 17) in which the metal is displaced from the fivefold axis of the $C_2B_9H_{11}$ residue toward the 3 boron atoms of the pentagonal face, as if based on a polyhedron with 13 vertices.

TABLE V

SOME *nido*-METALLO-BORANES AND -CARBORANES

n^a	Examples
6	$(OC)_3FeB_4H_8$ (*94*); $CpCoB_4H_8$ (*159*)
7	$(OC)_3FeC_2B_3H_7$ (*26, 84, 96*); $(OC)_4FeB_6H_{10}$ (*52*)^b; $R_3MC_2B_4H_7$ (M = Si, Ge)^b; $[(OC)_4Fe(H_3B)B_6H_9]^-$ (*118*)^b
10	$(R_3P)_2PtC_2B_6H_6R_2'$ (*92*); $(OC)_3MnB_9H_{12}OC_4H_8$ (*149*)
11	$(Et_3P)_2MC_2B_7H_9Me_2$ [M = Ni (*90*), Pt (*91*)]; $(Et_3P)_2PtB_9H_{11}PEt_3$ (*195a*); $CpCoC_2B_7H_{11}$ (*31c*)
12	$(Et_3P)_2PtHB_9H_{10}S$ (*195a*); $[Zn(B_{10}H_{12})_2]^{2-}$ (*195a*)

[a] n = No. of vertices on fundamental polyhedron, one of which is left vacant.

[b] In these compounds the metal atoms occupy edge-bridging positions (not polyhedron vertices).

The skeletal changes that accompany changes in skeletal electron numbers are reflected in one of the most widely used routes to metallocarboranes, the so-called polyhedral expansion reaction. This reaction, which has been used to considerable effect by Hawthorne and his coworkers (*68–71, 77–79, 82*), involves conversion of a neutral *closo*-

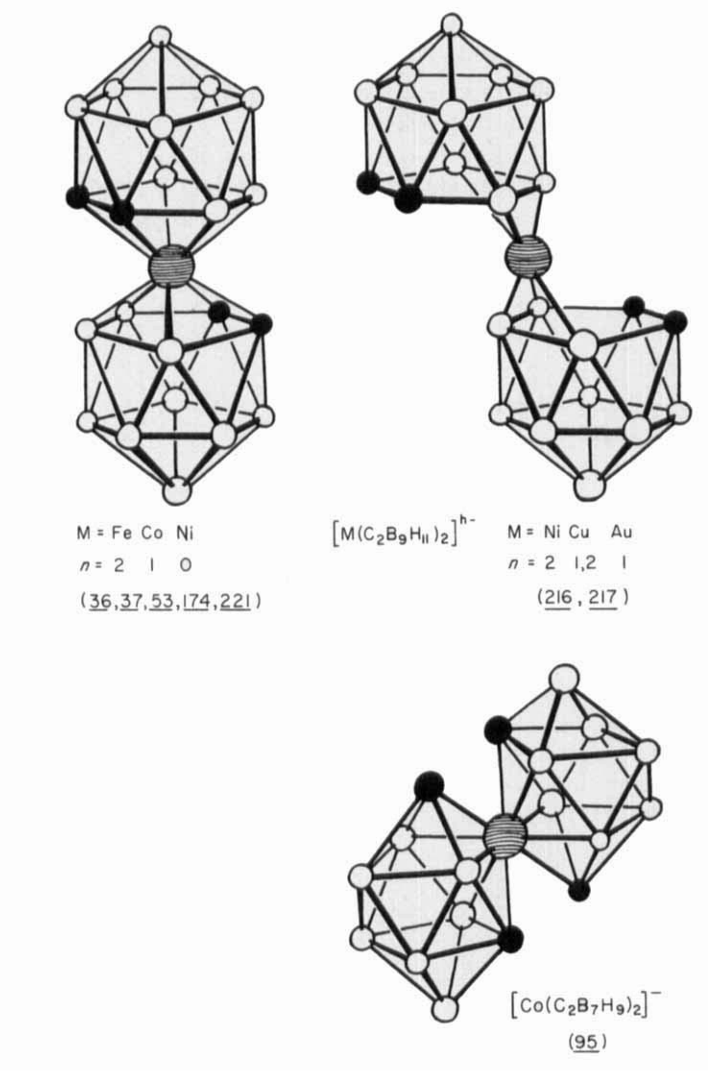


FIG. 17. Metallocarboranes in which the metal is shared between two polyhedra.

carborane into a nido anionic species by adding a pair of electrons to it and then treating it with a suitable metal cation*:

$$\underset{(closo\text{-})}{C_2B_{n-2}H_n} \xrightarrow[\text{THF}]{\text{Na/naphthalene}} \underset{(nido\text{-})}{C_2B_{n-2}H_n^{2-}} \xrightarrow{L_xM^{x+}} \underset{(closo\text{-})}{L_xMC_2B_{n-2}H_n}$$

---

* THF, tetrahydrofuran.

Applied to icosahedral carboranes as the starting materials, it leads to metallocarborane based on 13- or 14-vertex polyhedra, e.g. (*35*, *70*),

$$\begin{tikzcd}
\begin{gathered}C_2B_{10}H_{12}\\(\textit{closo-})\end{gathered} \arrow[r, "Na/C_{10}H_8", "THF"'] & \begin{gathered}C_2B_{10}H_{12}{}^{2-}\\(\textit{nido-})\end{gathered} \arrow[r, "NaC_5H_5", "CoCl_2"'] & \begin{gathered}(C_5H_5)CoC_2B_{10}H_{12}\\(\textit{closo-};\ 13\ \text{vertices})\end{gathered} \arrow[d, "Na/C_{10}H_8"] \\
& \begin{gathered}(C_5H_5)_2Co_2C_2B_{10}H_{12}\\(\textit{closo-};\ 14\ \text{vertices})\end{gathered} & \begin{gathered}[(C_5H_5)CoC_2B_{10}H_{12}]^{2-}\\(\textit{nido-})\end{gathered} \arrow[l, "NaC_5H_5"', "CoCl_2"]
\end{tikzcd}$$

The products have structures (*35*) related to the icosahedron but with 6 atoms instead of 5 in the "tropical" (ortho or meta) rings of atoms (Fig. 18).

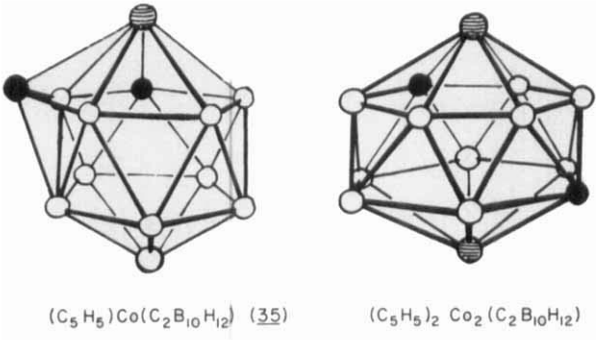


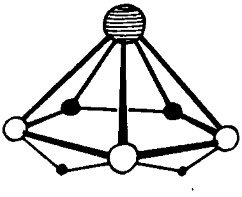
FIG. 18. Skeletons of metallocarboranes with 13 and 14 skeletal atoms.

Similar polyhedral expansion reactions have been used to synthesize metallocarboranes containing 3 metal atoms, e.g., the icosahedral $(C_5H_5Co)_3C_2B_7H_9$ (*80*), or containing two different metals (*71*, *175*), e.g., the bicapped square-antiprismatic $C_5H_5CoCB_7H_8NiC_5H_5$ (*175*).

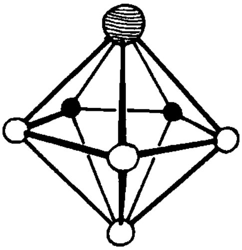
Polyhedral expansion is achieved without the need for a preliminary reduction stage in other syntheses of metallocarboranes, e.g., in the preparation of the closo icosahedral platinum compound $(Me_2PhP)_2$-$PtC_2Me_2B_9H_9$ (*91*) from the *closo*-carborane $C_2Me_2B_9H_9$ and $(Me_2PhP)_3Pt$ (*184*), or in the preparation of mono and dimetallocarboranes from the *closo*-trigonal-bipyramidal $C_2B_3H_5$:

$$\begin{tikzcd}
& C_2B_3H_5Fe(CO)_3 \arrow[r, "Fe(CO)_5"] & C_2B_3H_5[Fe(CO)_3]_2 \\
C_2B_3H_5 \arrow[ur, "Fe(CO)_5"] \arrow[dr, "C_5H_5Co(CO)_2"'] & & \\
& C_2B_3H_5CoC_5H_5 \arrow[r, "C_5H_5Co(CO)_2"] & C_2B_3H_5[CoC_5H_5]_2 \\
\begin{gathered}\textit{closo-}\\(\text{trigonal}\\\text{bipyramid})\end{gathered} & \begin{gathered}\textit{closo-}\\(\text{octahedra})\end{gathered} & \begin{gathered}\textit{closo-}\\(\text{pentagonal bipyramids})\end{gathered}
\end{tikzcd}$$

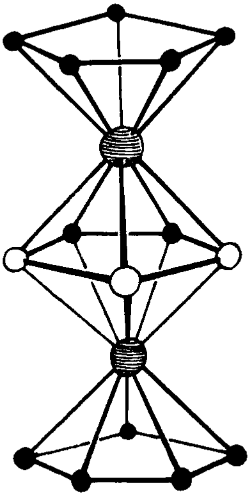
The recent work of Grimes and his co-workers (*14*, *26*, *84*, *96–96b*, *98*, *119*, *191*, *192*) has shown the smaller carboranes to be particularly fertile sources of metal–boron–carbon clusters, of which a few further examples are shown in Fig. 19.



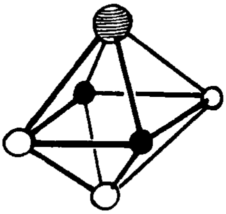
$C_2B_3H_7Fe(CO)_3$ (26)



$C_2B_4H_6GaMe$ (98)



$C_2B_3H_5Co_2(C_5H_5)_2$ (14)



$C_2B_3H_5Fe(CO)_3$

FIG. 19. Metallocarboranes derived from the smaller carboranes. (Terminal hydrogen atoms and carbonyl groups not shown.)

By no means do all metallocarboranes have the metal atoms occupying vertices of the basic polyhedra. Apart from many derivatives in which σ-bonded metal residues occupy exo sites attached to particular skeletal atoms, several metalloboranes and -carboranes are known in which the metal occupies an edge-bridging site, effectively replacing a bridging hydrogen atom of the parent borane. Many are nido species related to B_6H_{10}, for example, the μ-silyl and μ-germyl carboranes,

μ-$R_3MC_2B_4H_7$ (R = H, Me; M = Si, Ge) (*192*) (Fig. 20) and the anion $[\mu\text{-}Fe(CO)_4B_7H_{12}]^-$, which is formally derived from B_6H_{10} by replacing 2 bridging hydrogen atoms by BH_3 and $Fe(CO)_4$ units (Fig. 20) (*118*). From its formula, this last anion appears capable of being treated as an 8-atom cluster (FeB_7) with 12 electron pairs available to hold the cluster together, i.e., in Williams's terminology (see following article, this volume) this might be a rare example of a hypho species based on the 11-vertex polyhedron but with 3 vertices unoccupied by skeletal atoms. It seems significant that instead it adopts a structure based on a pentagonal bipyramid with but 1 vertex unoccupied, using its "surplus"

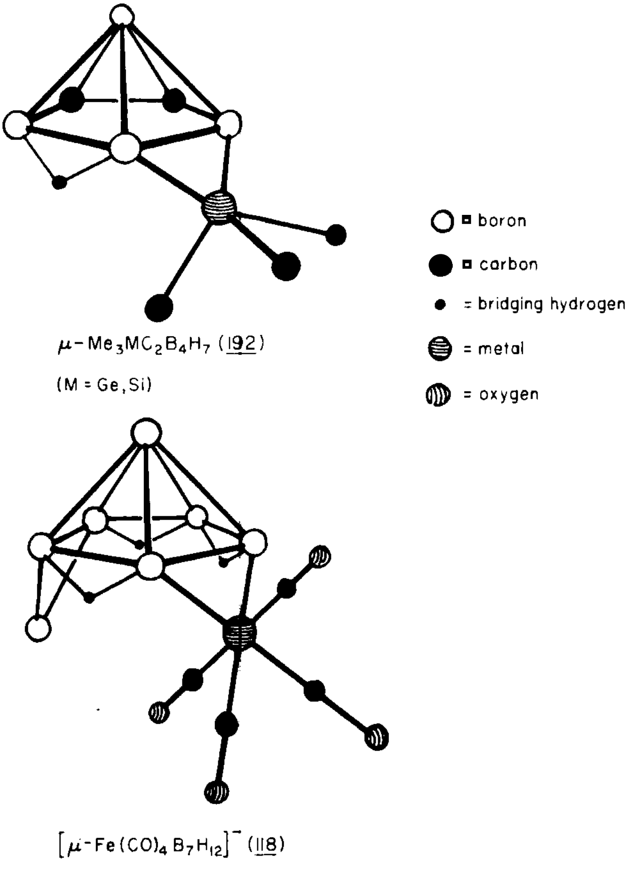


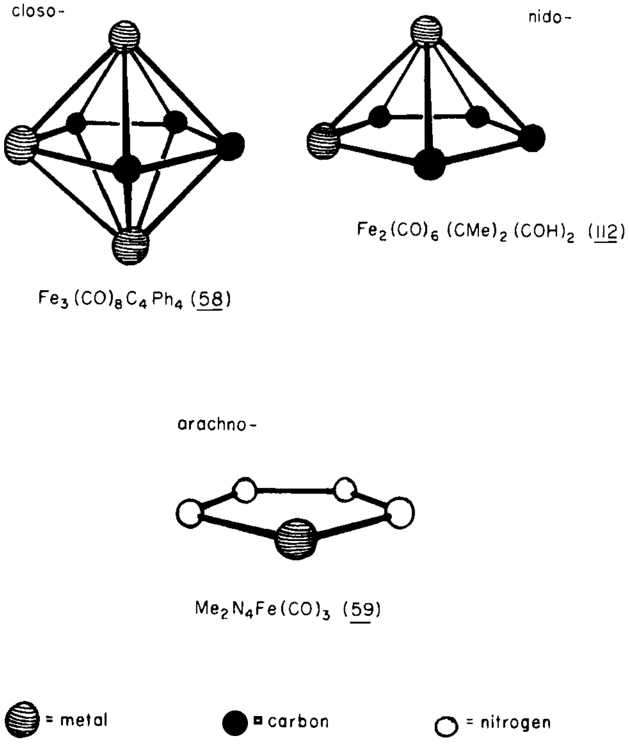
FIG. 20. Metalloboranes with metal atoms in bridging positions. (Terminal hydrogen atoms not shown.)

electron pairs to bond carbonyl groups or hydrogen atoms to the bridging iron and boron atoms, thereby coordinatively saturating them.

More surprising departures from the normal borane–carborane polyhedral pattern have been found among some metallocarboranes containing platinum (*91*, *92*) which adopt nido rather than the expected closo structures. These are the compounds $(Et_3P)_2PtC_2B_7H_7Me_2$ (*91*) and $(R_3P)_2PtC_2B_6H_6R_2'$ (*92*), which have structures based on a very distorted bicapped square antiprism and very distorted tricapped trigonal prism, respectively; the distortions are ones that might have been expected had these compounds contained an extra pair of hydrogen atoms apiece. A closo isomer of the latter compound is known (*92*).

C. Other Mixed Clusters

The metal–carbonyl clusters and metalloboranes and -carboranes already mentioned illustrate the range of substances that conform to the



$Fe_3(CO)_8C_4Ph_4$ (58)

$Fe_2(CO)_6(CMe)_2(COH)_2$ (112)

$Me_2N_4Fe(CO)_3$ (59)

FIG. 21. Skeletons of some mixed clusters with 8 skeletal bond pairs.

borane structural pattern. Some further examples not containing boron but, nevertheless, incorporating both metal and nonmetal skeletal atoms are shown in Figs. 21–23 and listed in Table VI.

Examples with a skeletal electron count of 8 pairs, and with structures formally based on a pentagonal bipyramid, include the *closo*-ferracyclopentadiene complex $Fe_3(CO)_8C_4Ph_4$ (*58*) and the related nido pentagonal-pyramidal complex $[Fe(CO)_3]_2(CMe)_2(COH)_2$ (*112*). Different types of arachno structure based on the same polyhedron are exemplified by complexes $Fe(CO)_3N_4Me_2$ (*55*, *59*) and $Ir(CO)(PPh_3)_2N_4(C_6H_4F)_2$ (*74*) (Fig. 21).

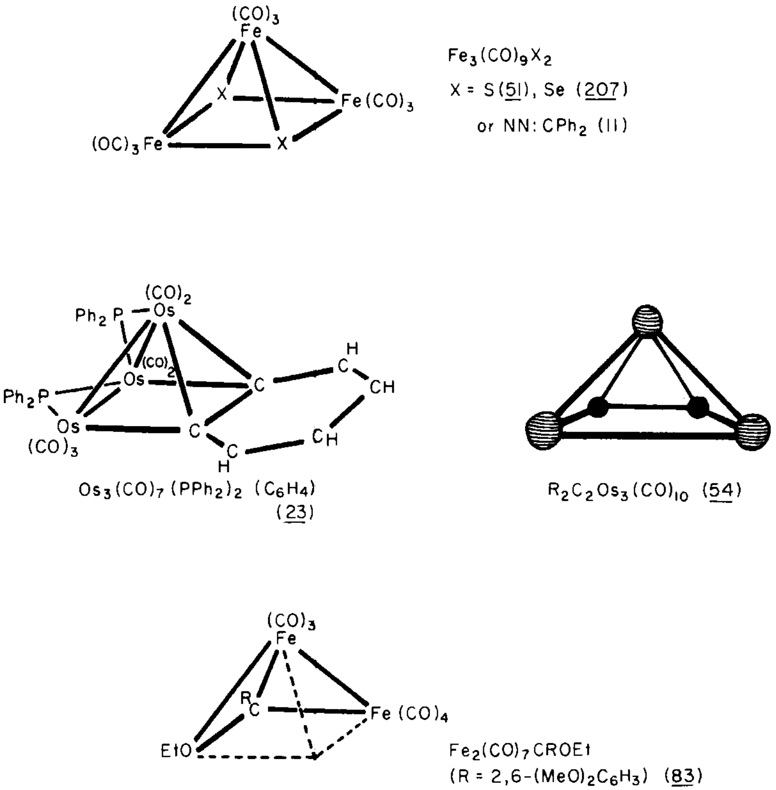
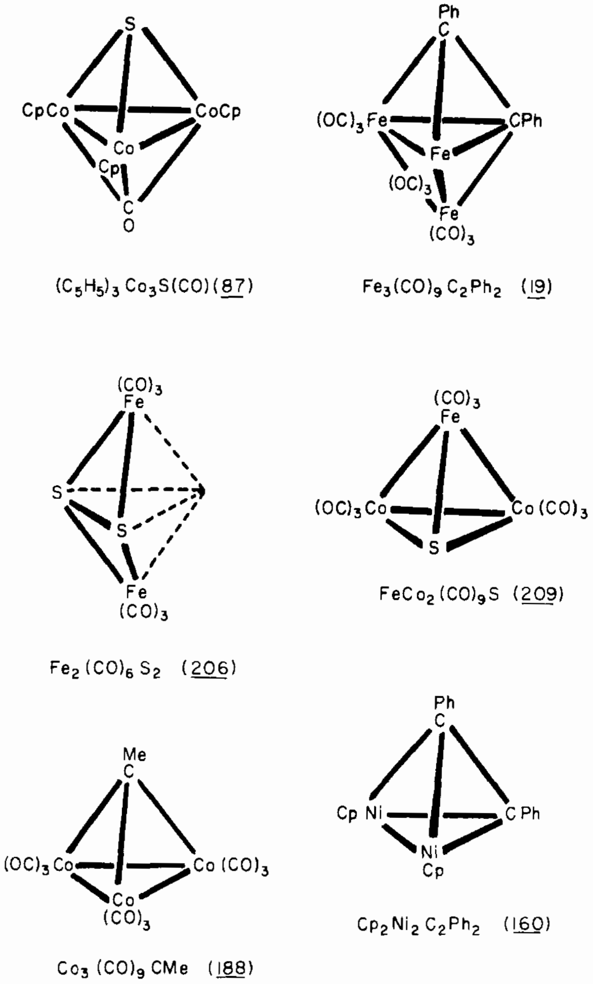


FIG. 22. Some mixed clusters with 7 skeletal bond pairs.

The mixed cluster $Co_4(CO)_{10}(C_2Et_2)$ (*50*) has already been quoted (Fig. 15) as an example of a closo cluster with 6 skeletal atoms and 7 skeletal bond pairs. Nido clusters also formally based on an octahed-



$(C_5H_5)_3Co_3S(CO)$ (87) $Fe_3(CO)_9C_2Ph_2$ (19)

$Fe_2(CO)_6S_2$ (206) $FeCo_2(CO)_9S$ (209)

$Co_3(CO)_9CMe$ (188) $Cp_2Ni_2C_2Ph_2$ (160)

FIG. 23. Some mixed clusters with 6 skeletal bond pairs.

ron include the series of compounds $Fe_3(CO)_9X_2$ [where $X = S$ (*51*), Se (*207*), or NN:CPh_2 (*11*)] all of which have distorted square-pyramidal structures (Fig. 22). Another 5 skeletal atom–7 skeletal bond pair mixed cluster, although less readily recognized as such, is the benzyne complex $Os_3(CO)_7(PPh_2)_2(C_6H_4)$ (*23*) which has a distorted square-pyramidal arrangement of its Os_3C_2 skeleton (Fig. 22). The electron count for this cluster includes 2 electrons from the $Os_3(CO)_7$ residue, 6 electrons (3

TABLE VI

MIXED CLUSTERS WITH CLOSO, NIDO, OR ARACHNO STRUCTURES[a]

Fundamental polyhedron	b	Closo species ($a = b - 1$)	Nido species ($a = b - 2$)	Arachno species ($a = b - 3$)
Trigonal bipyramid	6	$C_2Ph_2Fe_3(CO)_9$ (*19*) $Co_3(C_5H_5)_3(CO)S$ (*87*)	$SFeCo_2(CO)_9$ (*209*) $MeCCo_3(CO)_9$ (*188*) $Fe_2(CO)_6S_2$ (*206*)	$O(CH_2)_2$ $RN(CH_2)_2$ $M(I)M_2(II)\ (CO)_{12}$[b]
Octahedron	7	$[Co_4Ni_2(CO)_{14}]^{2-}$ (*8*)	$Fe(_3CO)_9X_2$[c] $Os_3(CO)_7(PPh_2)_2C_6H_4$ (*23*) $C_2R_2Os_3(CO)_{10}$ (*54*)	$Fe_2(CO)_7C(OEt)C_6H_3(OMe)_2$ (*83*)
Pentagonal bipyramid	8	$C_4Ph_4Fe_3(CO)_8$ (*58*)	$C_4Me_2(OH)_2Fe_2(CO)_6$ (*112*)	$N_4Me_2Fe(CO)_3$ (*55, 59*)

[a] a = No. of skeletal atoms; b = No. of skeletal bond pairs.

[b] M(I), M(II) = Fe, Ru, Os. For illustrative structures, see Figs. 15, 21, 22, and 23.

[c] X = S (*51*), Se (*207*), or NN:CPh_2 (*11*).

apiece) from the bridging diphenylphosphino ligands, and 6 electrons from the benzyne residue (cf an acetylene C_2R_2). Figure 22 also shows an example of an arachno species formally based on an octahedral fragment, namely, the carbene complex $Fe_2(CO)_7C(OEt)C_6H_3(OMe)_2$ (*83*).

Mixed clusters formally containing 6 skeletal bond pairs are also common. The acetylene complex $Fe_3(CO)_9C_2Ph_2$ has a distorted trigonal-bipyramidal (closo) arrangement of its Fe_3C_2 skeleton, with apical carbon and iron atoms (Fig. 23) (*19*). Most clusters with 6 skeletal bond pairs are, however, systems with 4 skeletal atoms arranged at the corners of a tetrahedron. As such, they appear to be n-vertex closo species that contravene the $(n + 1)$ bond pair rule. However, the tetrahedron differs from the triangular-faced polyhedra in Fig. 1 in that its symmetry is such as to generate $(n + 2)$ rather than $(n + 1)$, bonding MO's from the three AO's contributed by each skeletal atom at its corners. Formally, the tetrahedron may be regarded as derivable from the trigonal bipyramid by removal of one apex, so tetrahedral clusters are effectively 4-atom, 6 bond pair nido systems.

The tetrahedron is unique in another respect, in that each vertex is directly linked to only 3 others, so that the three AO's contributed by each skeletal atom can be employed in forming six two-center bonds along the six tetrahedron edges, as illustrated by the mixed clusters $FeCo_2(CO)_9S$ (*209*), $MeCCo_3(CO)_9$ (*188*), and $Co_3(C_5H_5)_3(CO)S$ (*87*). This last compound has the carbonyl group triply bridging the metal atoms, effectively completing the trigonal bipyramid (Fig. 23).

Not all such species conform to the electron count expected for tetrahedral or trigonal-bipyramidal species. For example, the tetrahedral clusters $SCo_3(CO)_9$ (*209*) and $BuNNi_3(C_5H_5)_3$ (*131*) formally have 1 electron too many, and the trigonal bipyramidal clusters $S_2Co_3(C_5H_5)_3$ (*87*) and $S_2Ni_3(C_5H_5)_3$ (*87*) have 2 and 5 electrons, respectively, in excess of the number appropriate for 5-atom closo species. Such trigonal-bipyramidal clusters have been the subject of a careful study by Dahl and his co-workers, who have shown, by studying the metal–metal distances, that the extra electrons are accommodated in metal–metal *antibonding* MO's (*87*). These and other examples show that adding extra electrons to a closo cluster, at least one containing metal atoms, may simply increase the *size* of the cluster rather than change its shape to one based on a higher polyhedron.

The remaining structure illustrated in Fig. 23 is that of the 4-atom nido cluster $Fe_2(CO)_6S_2$, with 2 apical iron atoms and 2 equatorial sulfur atoms arranged about an incomplete trigonal bipyramid (*206*). Similar structures are adopted by various diaza complexes of general formula $Fe_2(CO)_6(RNNR)$ (*109*).

VI. Hydrocarbon Systems Conforming to the Borane Pattern

Although boranes and hydrocarbons are more notable for their differences than for any similarities, there are several important hydrocarbon systems that adopt structures that conform to the borane pattern (*202*). They include metal–hydrocarbon π complexes, various aromatic systems, and certain other neutral or charged hydrocarbons. Representative examples are listed in Table VII.

The relationship between borane clusters and metal–hydrocarbon π complexes is illustrated by metal cluster –acetylene complexes such as those already cited, namely, $Co_4(CO)_{10}C_2Et_2$ (*50*) (Fig. 15) and $Fe_3(CO)_9$-C_2Ph_2 (*19*) (Fig. 23), whose octahedral and trigonal-bipyramidal skeletons, respectively, are directly analogous to those of the *closo*-carboranes $B_4H_4C_2H_2$ and $B_3H_3C_2H_2$ (*151*). Both types of cluster can be prepared by reactions between acetylenes and appropriate homonuclear clusters (metal–carbonyl clusters or boranes). Both types of cluster, when heated, can rearrange to separate the carbon atoms originally triply bonded to each other (*18*, *95*). The dimerization of acetylenes that can take place at metal centers, as in the formation of the ferracyclopentadienyl compound $Fe_3(CO)_8C_4Ph_4$ (*58*) (Fig. 21), can also take place at borane centers, as in the formation of C-methylated tricarba-*nido*-hexaboranes $C_3H_2MeB_3H_4$ from B_4H_{10} and HC:CH (*97*). However, the close bonding relationship between metal cluster–acetylene complexes and carboranes is obscured by the different ways in which their bonding is normally treated. Whereas the bonding in carboranes is not usually discussed in terms of localized two-center bonds, this approach is used for bonding in the carbon skeleton or metal–acetylene complexes (indeed of metal–hydrocarbon π complexes in general) (*41*); attention is normally focused on the interactions between metal orbitals and hydrocarbon bonding or antibonding π orbitals, the electrons in the C—C σ bonds being ignored. If the C—C σ-bonding electrons are included in the skeletal electron count, then the parallel between boranes and metal–hydrocarbon π complexes becomes apparent.

For example, the pentagonal-pyramidal shape of the C_5M skeleton of pentahaptocyclopentadienyl–metal complexes, as exemplified by $(C_5H_5)Mn(CO)_3$ (Fig. 24), is the nido structure appropriate for a set of 6 atoms held together by eight skeletal bond pairs [3 electrons from each CH unit; 1 electron from the $Mn(CO)_3$ residue]. Two such pentagonal pyramids sharing a common apex are present in ferrocene, $(C_5H_5)_2Fe$ (*22*) (Fig. 24). Similarly, cyclobutadiene complexes (*197*) such as $C_4H_4Fe(CO)_3$ (Fig. 24) have the square-pyramidal geometry appropriate for clusters with 5 skeletal atoms and 7 skeletal bond pairs, whereas

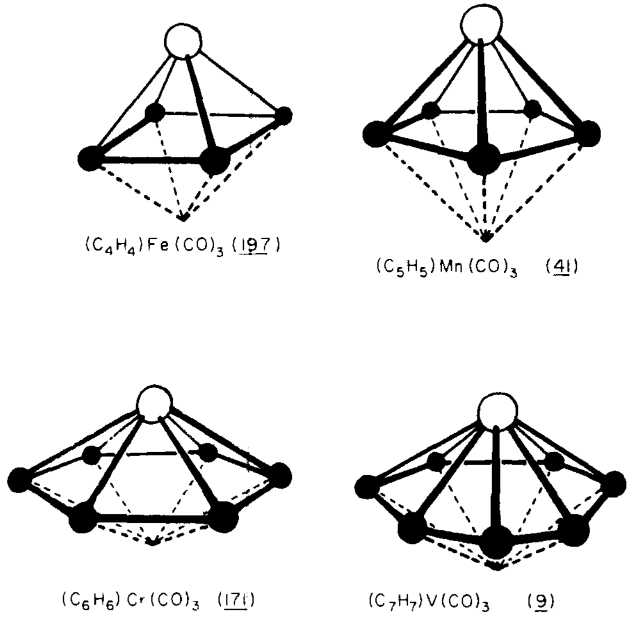
TABLE VII

EXAMPLES OF CLOSO, NIDO, AND ARACHNO RELATIONSHIPS AMONG HYDROCARBONS AND THEIR METAL COMPLEXES[a]

Fundamental polyhedron	b	Closo species ($a = b - 1$)	Nido species ($a = b - 2$)	Arachno species ($a = b - 3$)
Trigonal bipyramid	6	$C_2Ph_2Fe_3(CO)_9$ (*19*)	$C_2Ph_2Co_2(CO)_6$ $C_2Ph_2Ni_2(C_5H_5)_2$ (*160*)	$C_2H_4Pt(PPh_3)_3$ $(CH_2)_3$
Octahedron	7	$C_2Et_2Co_4(CO)_{10}$ (*50*)	C_4Ph_4CoCp (*197*) $C_5H_5{}^{+b}$	$(\pi\text{-allyl})Co(CO)_3$ $C_4H_4{}^{2-}$
Pentagonal bipyramid	8	$C_4Ph_4Fe_3(CO)_8$ (*58*)	$(C_5H_5)Mn(CO)_3$ $C_6Me_6{}^{2+}$ (*117*)	(butadiene)$Fe(CO)_3$ (*93*) $C_5H_5{}^-$
Hexagonal bipyramid	9	—	$(C_6H_6)_2Cr$	benzene
Dodecahedron	9	—	—	benzvalene, $Me_2AlC_5H_5$ (*61*)
Heptagonal bipyramid	10	—	$C_7H_7V(CO)_3$ (*9*)	$C_7H_7{}^+$

[a] a = No. of skeletal atoms; b = No. of skeletal bond pairs.

[b] References *56*, *108*, *140*, *154*, *155*, *187*, *213*.



$(C_4H_4)Fe(CO)_3$ (197)

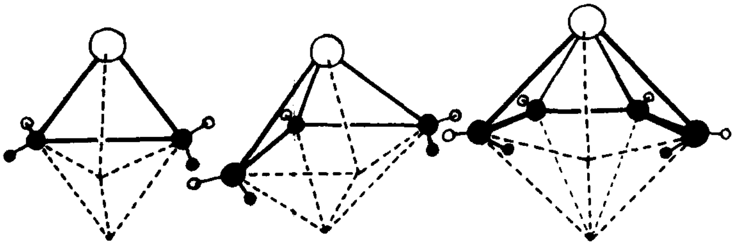
$(C_5H_5)Mn(CO)_3$ (41)

$(C_6H_6)Cr(CO)_3$ (171)

$(C_7H_7)V(CO)_3$ (9)

FIG. 24. The nido structures of some metal–hydrocarbon π complexes containing C_nH_n ring systems.

related butadiene complexes such as $(CH_2{:}CHCH{:}CH_2)Fe(CO)_3$ (Fig. 25), with 2 more skeletal electrons but the same number of skeletal atoms, adopt arachno structures based on pentagonal bipyramids. That the metal atom of a butadiene complex occupies an axial, not an equatorial, vertex of the pentagonal bipyramid is apparently in order to allow the 2 extra hydrogen atoms (those bound by skeletal electrons), 1 on



$(CH_2{:}CH_2)Fe(CO)_4$ $(CH_2CHCH_2)Co(CO)_3$ $(CH_2{:}CHCH{:}CH_2)Fe(CO)_3$

FIG. 25. The arachno structures of some metal–hydrocarbon π complexes. (Carbonyl ligands not shown.)

each methylene group of the butadiene, to be accommodated in endo positions without displacing the remaining methylene hydrogen atoms from their preferred exo positions, directed radially away from the center of the cluster. Significantly, the ^1H NMR chemical shift of the endo-hydrogen atoms (9.78τ) (*93*) reveals the influence of their proximity to the metal. A planar C_4Fe skeleton for a complex $(CH_2{:}CHCH{:}CH_2)$-$Fe(CO)_3$ which also in principle appears possible for an arachno 8-electron pair system, would only allow an exo orientation of four CH groups if the remaining 2 hydrogens were in C···H···C or C···H···Fe bridging positions. Isoelectronic species without these 2 extra hydrogen atoms, e.g. complexes of chelating ligands such as RN:C(R′)C(R′):NR or RCOCOR, can and do form planar five-membered C_2N_2M or, C_2O_2M rings in their metal complexes. Similar arguments may be applied to rationalize the nonplanar C_3M skeletons or π-allyl complexes, which, as arachno species based on an octahedron (Fig. 25), might also in principle be planar.

Further examples of organometallic compounds with hydrocarbon residues ranging in complexity from monoolefins or -acetylenes to the cycloheptatrienyl ring are listed in Table VII. Species with 6, 7, or 8 skeletal bonding electron pairs have skeletal structures that can be related to the same fundamental polyhedra (trigonal bipyramid, octahedron, or pentagonal bipyramid, respectively) as can cage boranes or transition metal carbonyl clusters. However, species with 9 or 10 skeletal bond pairs, such as $(C_6H_6)Cr(CO)_3$ (*171*) or π-$C_7H_7V(CO)_3$ (*9*) adopt structures clearly related to the hexagonal or heptagonal bipyramid (Fig. 24) rather than to the D_{2d} dodecahedron or D_{3h} tricapped trigonal prism of $B_8H_8^{2-}$ and $B_9H_9^{2-}$, respectively (*99*, *100*) (Fig. 1). Although this shows there is not one unique fundamental polyhedron for each of the 9- and 10-electron pair cases from which skeletal structures are formally derived, it is, nevertheless, apparent that both $(C_6H_6)Cr(CO)_3$ and $(C_7H_7)V(CO)_3$ are *nido* species, i.e., in which the number of skeletal bond pairs exceeds the number of skeletal atoms by 2 and the skeletal structure is clearly recognizable as based on a triangular-faced polyhedron, 1 vertex of which is left vacant. Expressed another way, the carbocyclic systems $C_4H_4^{2-}$, $C_5H_5^-$, C_6H_6, $C_7H_7^+$ (and $C_8H_8^{2+}$) and aromatic ring systems isoelectronic with these form a set of arachno species capable of conversion into *nido* derivatives by coordination to a metal–carbonyl fragment that provides three AO's, but no electrons, for cluster bonding (*202*).

A corollary of this treatment is that *closo* species appear capable of preparation from these arachno-ring systems by coordination to *two* metal–carbonyl residues in apical positions, on each side of the C_nH_n

ring. Thus, it might be possible to prepare species such as $(CO)_3Mn(C_4H_4)Mn(CO)_3$, $(CO)_3M(C_5H_5)Mn(CO)_3$ (M = Cr, Mo, or W), or $(CO)_3M(C_5H_5)Fe(C_5H_5)M(CO)_3$ as well as coordination polymers such as $[(C_4H_4)M]_n$ (M = Fe, Ru, or Os) or $[(C_5H_5)M]_n$ (M = Mn, Tc, or Re) consisting of octahedra or pentagonal bipyramids, respectively, linked by shared apical metal atoms. The ferracyclopentadienide $Fe_3(CO)_8C_4Ph_4$ (Fig. 21) (*58*) has a metal–carbonyl residue on each side of an FeC_4 ring and so is of the structural type envisaged, as is the metallocarborane $(C_5H_5)_2Co_2C_2B_3H_5$ (*14*) (Fig. 19).

The only complex containing a *complete* cyclopentadienyl ring sandwiched between 2 metal atoms that has been the subject of an X-ray crystallographic study is the triple-decker sandwich compound $[(C_5H_5)Ni(C_5H_5)Ni(C_5H_5)]^+BF_4^-$ (Fig. 26) (*66*, *176*) which can be prepared from nickelocene:

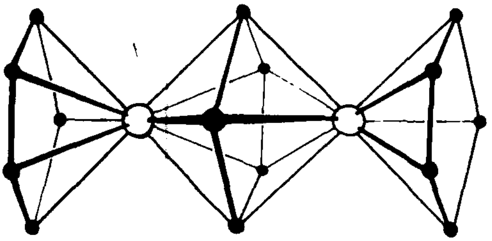
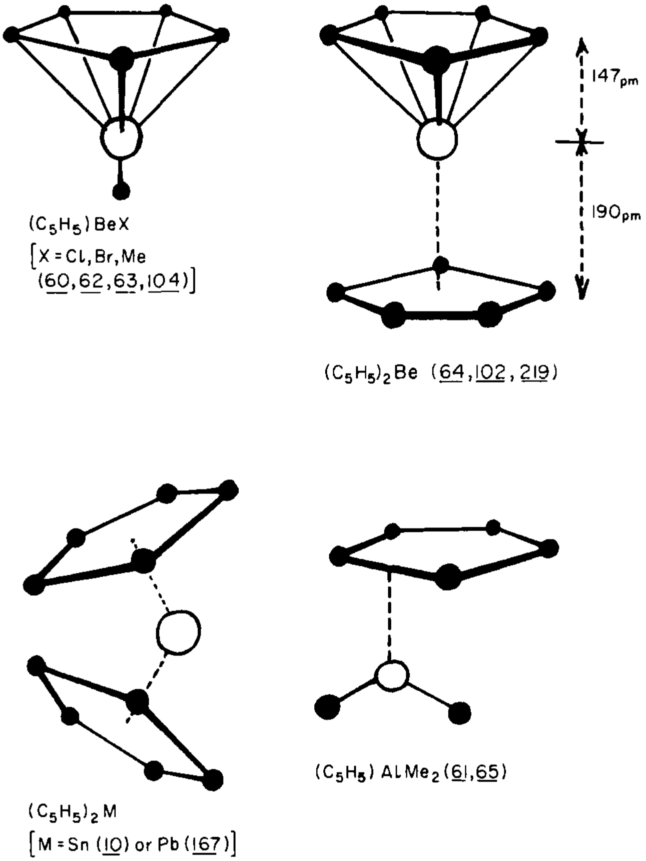


FIG. 26. The triple-decker sandwich structure of cation $[(C_5H_5)Ni(C_5H_5)Ni(C_5H_5)]^+$ (*66*, *176*).

$$2(C_5H_5)_2Ni + R^+X^- \rightarrow [(C_5H_5)Ni(C_5H_5)Ni(C_5H_5)]^+X^- + C_5H_5R$$
$$(R = Ph_3C, C_7H_7; \quad X = BF_4, PF_6)$$

Like nickelocene itself, this complex has 2 electrons more than the number expected using the electron-counting approach outlined in this article. Interestingly, the iron analog $[(C_5H_5)_3Fe_2]^+$, for which such a triple-decker structure appears appropriate on an electron count, has been detected in mass-spectroscopic studies on ferrocene (*179*) and on the cyclopentadienyl iron carbonyl tetramer $[C_5H_5FeCO]_4$ (*136*).

Many main group metal derivatives of unsaturated hydrocarbons adopt structures recognizably nido or arachno in type. Nido structures are, for example, adopted by a range of pentahaptocyclopentadienyl derivatives including $MeBe(C_5H_5)$ (*60*, *62*), $ClBe(C_5H_5)$ (*60*, *63*), $BrBe(C_5H_5)$ (*104*), $HC{:}CBe(C_5H_5)$ (*104*), $(C_5H_5)_2Be$ (*64*, *102*, *218*), $(C_5H_5)_2Mg$ (*103*), $(C_5H_5)In$ (*85*, *181*), $(C_5H_5)Tl$ (*196*), $(C_5H_5)_2Sn$ (*10*), and $(C_5H_5)_2Pb$ (*167*) (Fig. 27). The pentahapto geometry of the bis(cyclopentadienyls) $(C_5H_5)_2M$ (M = Mg, Sn, or Pb) can formally be reconciled with the borane pattern only if these metals use more than four valence shell orbitals. Bis(cyclopentadienyl)beryllium $(C_5H_5)_2Be$ in the crystal (*218*) significantly has one pentahapto- and one monohapto-cyclopentadienyl group, as appropriate for the four AO's available in the beryllium valence shell. The unsymmetrical sandwich structure (Fig. 27) of this compound in the vapor phase may be interpreted similarly, although it has been pointed out (*64*, *102*) that repulsions between the ring π electrons may not allow a symmetrical ferrocene-type structure to be adopted.



$(C_5H_5)BeX$ [X = Cl, Br, Me (60, 62, 63, 104)]

$(C_5H_5)_2Be$ (64, 102, 219)

$(C_5H_5)_2M$ [M = Sn (10) or Pb (167)]

$(C_5H_5)AlMe_2$ (61, 65)

FIG. 27. Cyclopentadienyl derivatives of some main group metals.

Arachno structures among main group metal–hydrocarbon complexes are represented by the di- or trihaptocyclopentadienylaluminum compound $(C_5H_5)AlMe_2$ (*61*, *65*) (Fig. 27) and possibly also by certain lithium derivatives of aromatic hydrocarbons. Compounds such as $Ph_3CLi(Me_2NC_2H_4NMe_2)$ (*29*), the bis(quinuclidine) adduct of fluorenyllithium (*27*) and the tetramethylethylenediamine adduct of naphthalene dilithium (*28*) have structures in which the lithium atoms are evidently bonded directly to 3 or 4 carbon atoms of the hydrocarbons, although

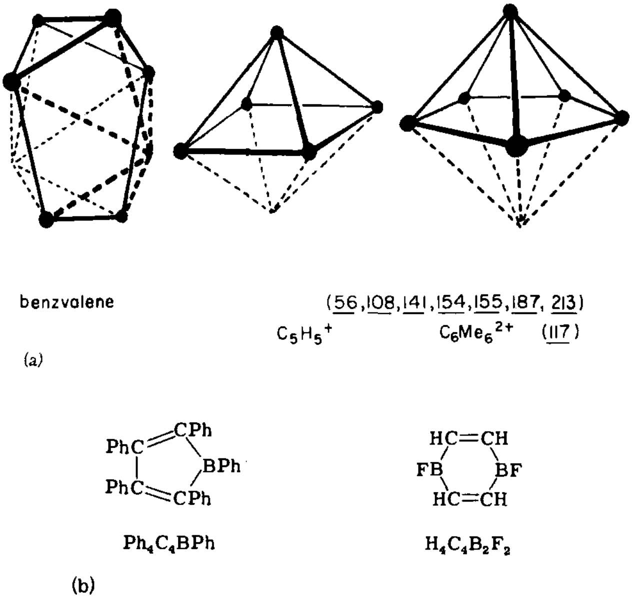


FIG. 28. (a) The arachno structure of benzvalene and nido structures of $C_5H_5^+$ and $C_6Me_6^{2+}$. (b) The boron heterocycles Ph_4C_4BPh and $H_4C_4B_2F_2$.

analysis of these complex structures in terms of fragments of 6- or 7-cornered polyhedra is necessarily somewhat arbitrary.

Other hydrocarbon systems that clearly conform to the borane structural pattern include the benzene isomer benzvalene, C_6H_6 (Fig. 28), which has an arachno structure based on a D_{2d} dodecahedron (*cf.* $B_8H_8^{2-}$ in Fig. 1), and the *nido*-carbo cations $C_5H_5^+$ (*56*, *108*, *140*, *154*, *155*, *187*, *213*) and $C_6Me_6^{2+}$ (*117*), which are believed to adopt the nido-pyramidal structures shown in Fig. 28 instead of planar cyclic structures like the parent *arachno*-aromatic systems, $C_5H_5^-$ and C_6Me_6. Interestingly, the related organoborane, Ph_4C_4BPh, apparently adopts a five-membered borole ring structure (Fig. 28) (*25*, *75*) in which form it is, not surprisingly, highly reactive. It should be possible to prepare a square-pyramidal isomer of this compound.

Another boron heterocycle with a formula apparently appropriate for a nido-pyramidal structure is the compound $H_4C_4B_2F_2$ (*193*) (Fig. 28). The fluorine substituents in this molecule, however, can π-bond to the boron atoms, thereby generating a quinonoid electronic structure. Elsewhere in boron cluster chemistry, the presence of halogen substituents appears to modify the skeletal electron requirements of the cluster.

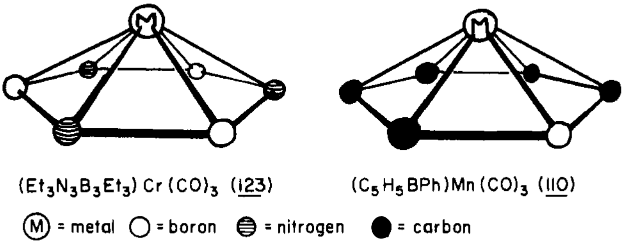


FIG. 29. The nido skeletons of the hexaethylborazine complex $(Et_3N_3B_3Et_3)$-$Cr(CO)_3$ and borabenzene complex $(C_5H_5BPh)Mn(CO)_3$.

For example, the neutral chloride B_8Cl_8 (*169*) and hydride anion $B_8H_8{}^{2-}$ (*100*) both adopt D_{2d} dodecahedral structures (Fig. 1) despite their differing numbers of skeletal bond pairs, but, significantly, the interatomic distances in the former are longer. Again, both B_9Cl_9 (*122*) and $B_9H_9{}^{2-}$ (*99*) have tricapped trigonal-prismatic structures, although with different interatomic distances.

Other unsaturated boron heterocycles, such as borazines and borabenzenes, form transition metal complexes with the expected nido geometry, as exemplified by compounds $(Et_3N_3B_3Et_3)Cr(CO)_3$ (*123*) and $(C_5H_5BPh)Mn(CO)_3$ (*110*) (Fig. 29).

VII. Interatomic Distances in Clusters

Whereas the main object of this survey is to explore how the *shapes* of various substances reflect the number of electron pairs holding them together, it is worth considering also how their *sizes* can be rationalized using the electron-counting approach already outlined (*203*).

In a closo-cluster species such as a borane anion $B_nH_n{}^{2-}$, in which the n skeletal atoms are held together by $(n + 1)$ bond pairs, the interatomic distances—the edge lengths of the B_n polyhedron—can be rationalized if one regards the skeletal atoms as held together by a network of fractional order two-center bonds along the polyhedron edges. The number of electron pairs associated with each edge will be the effective bond order of the two-center link represented by that edge.

The average edge bond order for a particular closo species can be calculated by dividing the total number of skeletal bond pairs $(n + 1)$ by the number of edges, which, for exclusively triangular-faced polyhedra with n vertices, is $(3n - 6)$. This leads directly to the formal boron–boron bond order for those borane anions [$B_6H_6^{2-}$ (*177*) and $B_{12}H_{12}^{2-}$ (*219*)] in which all the polyhedron edges are the same length. The octahedral anion $B_6H_6^{2-}$ has a formal boron–boron bond order of 0.58 and a B—B distance of 169 pm, whereas the icosahedral anion $B_{12}H_{12}^{2-}$ has a formal bond order of 0.43 and a B—B distance of 177 pm.

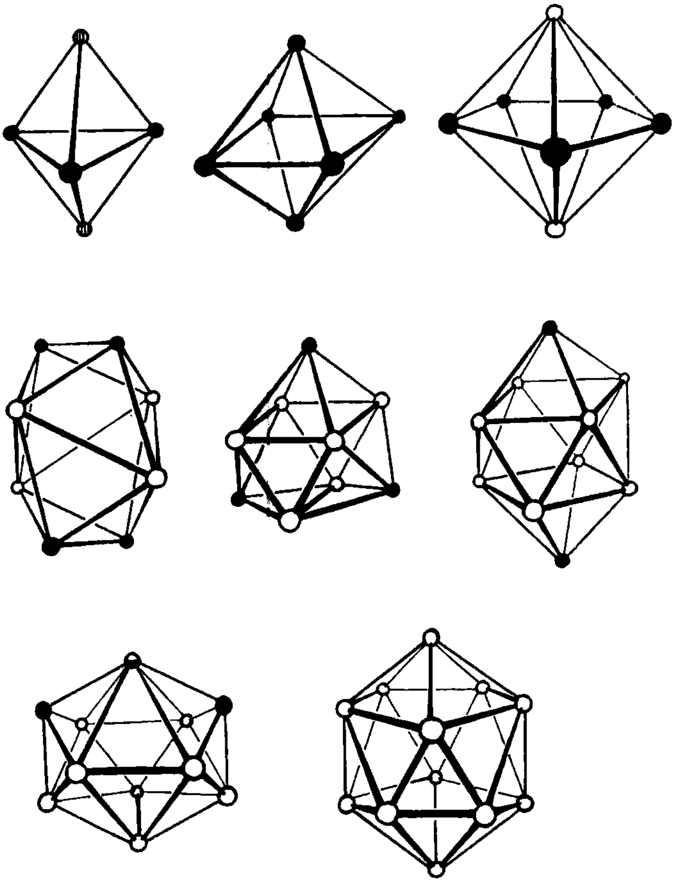


FIG. 30. Skeletal coordination numbers: ◍ = 3; ● = 4; ○ = 5; ◒ = 6.

The less symmetrical polyhedra contain two or more distinct types of edge, linking vertices of similar or different coordination numbers (Fig. 30), and understandably differing in length (see Table VIII) (*57, 99, 100*). Some insight into these lengths can be obtained by assuming that, for the homonuclear closo clusters $B_8H_8^{2-}$ (*100*), $B_9H_9^{2-}$ (*99*), and $B_{10}H_{10}^{2-}$ (*57*) the $(n + 1)$ skeletal electron pairs are distributed evenly among the n skeletal atoms. This gives each skeletal atom $(n + 1)/n$ electron pairs with which to form bonds to its x skeletal neighbors, where x is the "skeletal coordination number" or order of that vertex (Fig. 30). A skeletal atom with x skeletal neighbors can supply $(n + 1)/nx$ electron pairs to each of the two-center links it forms. The two-center link between 2 skeletal atoms of coordination numbers x_1 and x_2, respectively, will thus contain a total of $[(n + 1)/nx_1 + (n + 1)/nx_2]$ electron pairs, i.e., $(n + 1)\ (x_1 + x_2)/nx_1x_2$, which is the bond order expected using this approach.

TABLE VIII

SKELETAL (POLYHEDRON-EDGE) BOND ORDERS FOR ANIONS $B_nH_n^{2-}$

Anion $B_nH_n^{2-}$	Skeletal coordination numbers of linked atoms x_1	x_2	Edge bond order[a] $(n + 1)\ (x_1 + x_2)/nx_1x_2$	Interatomic distance (pm)
$B_6H_6^{2-}$	4	4	0.58	169 (*177*)
$B_7H_7^{2-}$	4	4	0.57	167[b]
	4	5	0.51	175[b]
$B_8H_8^{2-}$	4	4	0.56	156 (*100*)
	4	5	0.51	174
	5	5	0.45	193
$B_9H_9^{2-}$	4	5	0.50	171 (*99*)
	5	5	0.44	189
$B_{10}H_{10}^{2-}$	4	5	0.50	173 (*57*)
	5	5	0.44	183
$B_{11}H_{11}^{2-}$	4	5	0.49	170[b]
	4	6	0.45	178[b]
	5	5	0.44	179[b]
	5	6	0.40	195[b]
$B_{12}H_{12}^{2-}$	5	5	0.43	177 (*219*)

[a] Estimated, assuming that the skeletal bonding electrons are distributed equally among the skeletal atoms.

[b] Predicted (see text).

Bond orders calculated on this basis for the various types of two-center link in anions $B_8H_8^{2-}$ (*100*), $B_9H_9^{2-}$ (*99*), and $B_{10}H_{10}^{2-}$ (*57*) are given in Table VIII, together with the interatomic distances. The approach leads consistently to the correct qualitative sequence of bond orders for each of these anions—the strongest bonds, and therefore shortest edges, in a particular polyhedron link the atoms of lowest coordination number. However, it underestimates the *extent* to which the various types of bond differ. Judged by their lengths alone, the shortest and longest bonds in $B_8H_8^{2-}$ appear to have orders of about 1.0 and 0.3, respectively. The differences in length are in part, although not entirely, due to the familiar dependence of bond length on coordination number. That the bonds linking atoms of low coordination number are significantly shorter than would be expected on the basis of equal sharing of the skeletal electrons among the skeletal atoms implies that these skeletal atoms have a greater than average share of the skeletal bonding electrons, i.e., the skeletal atoms of lowest coordination number are negatively charged relative to the remainder, whereas atoms of high coordination number are relatively positively charged. These conclusions are consistent with those arrived at by other approaches, e.g., using MO calculations (*100*, *145*, *164*).

Yet other factors influence the interatomic distances in *nido*- and *arachno*-boranes, for example whether the polyhedron edges border the open face of the polyhedral fragment, and if so whether they are "sewn up" by B--H---B links, when some lengthening of the B----B distance is observed. Nevertheless, for polyhedron edges not subject to such factors, a reasonable consistency of B—B distances can be discerned for species formally based on the same polyhedron. For example, compare the B—B distance in $B_6H_6^{2-}$ (169 pm) with the apical-basal B—B distance of 169 pm in B_5H_9 (*42*, *67*, *120*) and with the unique short unbridged B—B link in B_4H_{10} (172 pm) (*169*) (Fig. 31). This last link

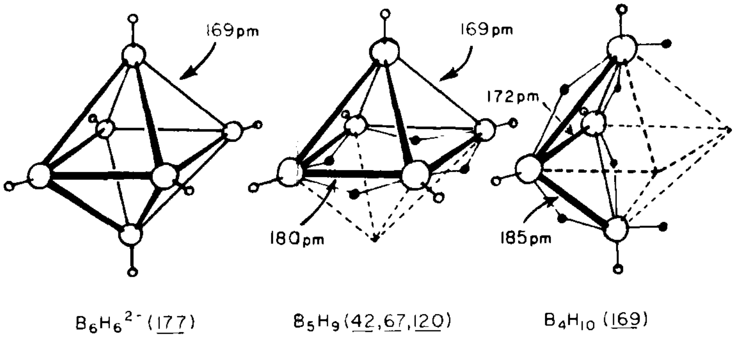


FIG. 31. Boron–boron interatomic distances in boranes with skeletons based on an octahedron: *closo*-$B_6H_6^{2-}$, *nido*-B_5H_9, and *arachno*-B_4H_{10}.

incidentally is treated as a bond of order 1 in the usual localized bond treatment (Fig. 4). Assuming similar relationships hold for the closo, nido, and arachno series of boranes based on a pentagonal bipyramid, $B_7H_7^{2-}$, B_6H_{10} (*172*), and B_5H_{11}, one would predict the following B—B interatomic distances in $B_7H_7^{2-}$: approx 167 pm (equatorial-equatorial) and 175 pm (axial-equatorial). Again, comparing $B_{11}H_{11}^{2-}$ with $B_{10}H_{14}$ (*145*) leads to the edge lengths predicted in Table VIII for $B_{11}H_{11}^{2-}$.

TABLE IX

CARBON–CARBON BOND DISTANCES IN CARBORANES, METAL–ACETYLENE π COMPLEXES, AND METAL–CYCLOBUTADIENYL AND –CYCLOPENTADIENYL π COMPLEXES

No. of vertices on fundamental polyhedron	Structure type	Coordination No. of carbon atoms	C—C distance (pm)	Compound	Ref.
5	Nido	4	135	$Ph_2C_2Ni_2(C_5H_5)_2$	*160*
5	Closo	4, 5	141	$Ph_2C_2Fe_3(CO)_9$	*19*
6	Closo	5	144	$Et_2C_2Co_4(CO)_{10}$	*50*
6	Nido	4	145	$Ph_4C_4Co(C_5H_4CN)$	*197*
6	Closo	5	154	$C_2B_4H_6$	*13*
7	Nido	4	141	$C_2B_3H_7Fe(CO)_3$	*26*
7	Nido	4	142	$(HO)_2Me_2C_4Fe_2(CO)_6$	*112*
7	Nido	4	143	$C_2B_4H_8$	*20*
7	Nido	4	143[a]	$C_5H_5MX_n$	*41*
7	Nido	4	143	$C_4B_2H_6$	*168*
7	Closo	5	145	$Ph_4C_4Fe_3(CO)_8$	*58*
7	Closo	5	147	$C_2B_4H_6GaMe$	*98*
10	Nido	5	155	$C_2B_7H_9Me_2$	*121*
12	Closo	6	165[a]	$C_2B_{10}H_{12-n}R_n$	*21*

[a] Average values for compounds of these general formulas.

The C—C and C—B interatomic distances in carboranes can also be related to the coordination numbers of the skeletal atoms. Two factors tend to make these distances shorter than the B—B distances in comparable boranes: the preference of the carbon atoms for sites of low coordination number and the greater electronegativity of carbon than boron, which increases the electron density in the region of the carbon atoms and so strengthens the bonds that they form. Table IX lists some C—C distances for *closo*- and *nido*-carboranes (*13*, *20*, *21*, *26*, *98*, *121*, *168*) and metal–acetylene (*50*, *58*, *112*) complexes, relating them to the coordination numbers of the atoms concerned. Although it is usual to treat the C—C links of metal–acetylene complexes as triple bonds reduced somewhat in strength by coordination, and the C—C links of carboranes as probably of order less than 1, the data in Table IX show that the formal bond order for both categories of compound lies between 1 and 2 [cf. the bond order in complexes of C_nH_n rings (*197*)].

Despite the resemblance between the shapes of borane clusters and metal clusters, this does not imply that the bond orders in metal clusters are as low as those given in Table VIII for borane anions. Whereas for the borane anions the number of electrons available for skeletal bonding is relatively clear-cut, in metal clusters the assignment of certain electrons to a nonbonding role, as outlined in Section IV, was a convenient device by which to stress their relationship to boranes. As was pointed out in connection with the various 86-electron octahedral clusters such as $H_2Ru_6(CO)_{18}$, these contain just 2 electrons too many to allow their bonding to be described in terms of 12 two-center electron pair bonds along the octahedron edges, and the metal–metal bond order in these clusters is likely to be rather higher than the boron–boron bond order in $B_6H_6^{2-}$. Microcalorimetric studies on the rhodium carbonyl clusters $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ (*29a*, *42a*) have nevertheless shown their metal–metal bonds to be weak (less than 30 kcal·mol^{-1}, i.e., about two-thirds of the strength of their metal–carbon bonds).

VIII. Some General Reactions

So far, in this survey, attention has been focused on the shapes and sizes of cluster species, their preparation and reactions having been mentioned only in passing. However, the close link between the shapes of borane-type clusters and the numbers of bonding electrons they contain makes it possible to predict the likely outcome of reactions that may change these numbers.

For example, opening of the cluster skeleton from closo to nido to arachno will accompany the addition of electron pairs, whether by reduction reactions or by addition of Lewis base molecules that do not dislodge other Lewis bases. Cluster closing is expected to accompany the removal of electron pairs, whether by oxidation or by loss of a substituent together with the electron pair by which it was formally bound to the cluster:

$$\textit{closo} \xrightleftharpoons[-2\text{ electrons}]{+2\text{ electrons}} \textit{nido} \xrightleftharpoons[-2\text{ electrons}]{+2\text{ electrons}} \textit{arachno}$$

For example, reductive cage opening, closo → nido, is the first step normally used in Hawthorne's polyhedral expansion reactions of carboranes (*63–71*, *77–80*):

$$\underset{closo\text{-}}{C_2B_{n-2}H_n} \xrightarrow{\text{Na/naphthalene}} \underset{nido\text{-}}{C_2B_{n-2}H_n{}^{2-}} \xrightarrow{\text{CpCo}^{2+}} \underset{closo\text{-}}{C_2B_{n-2}H_nCoCp}$$

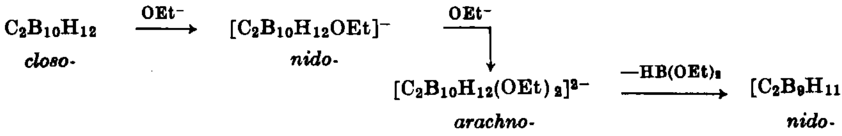
Reduction of *closo*-dicarbaboranes, $C_2B_{n-2}H_n$, to the dianionic nido species, $C_2B_{n-2}H_n{}^{2-}$, which are more susceptible to rearrangement reactions, also provides a route to isomers of the starting materials in which the carbon atoms have moved to different polyhedron vertices, e.g. (*185*, *186*),

$$\underset{closo\text{-}}{1,2\text{-}C_2B_{10}H_{12}} \xrightarrow[(+2e^-)]{2Na} \underset{nido\text{-}}{C_2B_{10}H_{12}{}^{2-}} \xrightarrow[(-2e^-)]{H_2O} \underset{closo\text{-}}{1,2\text{-}, 1,7\text{-}, \text{and } 1,12\text{-}C_2B_{10}H_{12}}$$

Similar reactions applied to transition metal–acetylene complexes appear capable of separating the 2 carbon atoms originally linked by the acetylenic triple bond (*18*). Thermal isomerization of metal–acetylene complexes may achieve the same result, showing how metal clusters can catalyze scrambling reactions of acetylenes, e.g.,

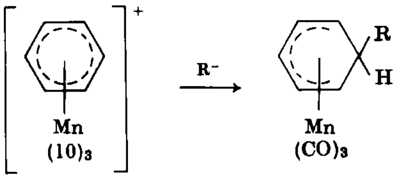
$$R^1C{:}CR^1 + R^2C{:}CR^2 \xrightarrow{\text{metal cluster}} 2R^1C{:}CR^2$$

The alkaline degradation of *closo*-carboranes, used to prepare smaller carboranes from icosahedral starting materials, also occurs by closo- to nido-, possibly even arachno-, cage opening, e.g. (*107*),



$$\underset{closo\text{-}}{C_2B_{10}H_{12}} \xrightarrow{OEt^-} \underset{nido\text{-}}{[C_2B_{10}H_{12}OEt]^-} \xrightarrow{OEt^-} \underset{arachno\text{-}}{[C_2B_{10}H_{12}(OEt)_2]^{2-}} \xrightarrow{-HB(OEt)_2} \underset{nido\text{-}}{[C_2B_9H_{11}]^{2-}}$$

Examples of reductive cluster-opening and oxidative cluster-closing reactions are common in the chemistry of metal–hydrocarbon π complexes. For example, bases convert *nido*- (hexa-hapto)arene–manganese tricarbonyl complexes into *arachno*(pentahapto)-π-cyclohexadienyl complexes (*129*, *130*, *217*):



This exemplifies a quite general reaction in organometallic chemistry, the cluster-opening conversion of an n-hapto ligand into an $(n-1)$-hapto ligand by addition of a nucleophile X^-. The converse, cluster-closing conversion accompanies removal of X^-.

Reference to Tables II and III shows that cluster expansion reactions are in principle possible if neutral units such as BH, $Fe(CO)_3$, $Co(C_5H_5)$, or $Ni(PR_3)_2$ can be incorporated in an existing polyhedral cluster:

$$\text{An } n\text{-atom cluster} \quad \left\{\begin{matrix}\text{closo}\\ \text{nido}\\ \text{arachno}\end{matrix}\right. \xrightarrow{ML_x} \left.\begin{matrix}\text{closo}\\ \text{nido}\\ \text{arachno}\end{matrix}\right\} \quad \text{An } (n+1)\text{-atom cluster}$$

where $ML_x =$ BH, $Fe(CO)_3$, $Co(C_5H_5)$, $Ni(PR_3)_2$, etc., units that can furnish 1 skeletal atom and 1 skeletal bond pair. It has already been noted that Hawthorne's polyhedral expansion procedure incorporates $Co(C_5H_5)$ units in carborane polyhedra in two stages [reduction to the nido dianion $C_2B_{n-2}H_n{}^{2-}$ followed by addition of $Co(C_5H_5)^{2+}$] *(68–71, 77–80, 82)*. Alternatively, separate stages may not be necessary, as in the formation of the 10-atom clusters $(C_5H_5)_2Co_2C_2B_8H_{10}$ (six isomers) by thermal decomposition of $(C_5H_5)CoC_2B_8H_{10}$ *(81)*, and in the synthesis of the icosahedral metallocarborane $Me_2C_2B_9H_9Pt(PEt_3)_2$ from *closo*-$Me_2C_2B_9H_9$ and the complex $Pt(PEt_3)_3$, from which one phosphine ligand is readily dislodged *(90, 91, 154)*:

$$\textit{closo}\text{-}Me_2C_2B_9H_9 + Pt(PEt_3)_3 \xrightarrow{-Et_3P} \textit{closo-}\ Me_2C_2B_9H_9Pt(PEt_3)_2$$

In related reactions, units, such as $Cr(CO)_3$, $Mn(CO)_3{}^+$, $Fe(CO)_3{}^{2+}$, $Co(C_5H_5)^{2+}$, Me_3N, Be^{2+}, or Tl^+, that can supply 1 skeletal atom and three *vacant* AO's (no skeletal electrons) for cluster bonding can be used to fill in the vacant vertices of nido or arachno species, thereby converting them into closo or nido species, e.g. *(184, 194)*,

$$\begin{array}{llcl}
C_6H_6 & + M(CO)_6 & \xrightarrow{-3CO} & (C_6H_6)M(CO)_3 (M = Cr, Mo, \text{ or } W)\\
(\textit{arachno-}) & & & (\textit{nido-})\\[1ex]
C_2B_9H_{12}{}^- & + Tl^+ & \longrightarrow & [TlC_2B_9H_{11}]^- + H^+\\
(\textit{nido-}) & & & (\textit{closo-})\\[1ex]
2C_6H_6 & + Cr & \longrightarrow & (C_6H_6)_2Cr\\
(\textit{arachno-}) & & & (\textit{nido-})
\end{array}$$

The exchange of 1 skeletal atom by another is exemplified by the common "ligand exchange" reactions of metal–hydrocarbon π complexes, e.g. (*88*)

$$\underset{(\textit{nido-})}{(Ph_4C_4PdBr_2)_2} \xrightarrow{Fe(CO)_5} \underset{(\textit{nido-})}{Ph_4C_4Fe(CO)_3}$$

by the use of the *closo*-thallium species $Tl_2C_2R_2B_9H_9$ in the synthesis of other icosahedral metallocarboranes (*184*) and by the preparation of the nido-ferraborane $B_4H_8Fe(CO)_3$ from B_5H_9 and $Fe(CO)_5$ (*94*).

For further examples of the ways in which the reactions of boranes (and related clusters) can be rationalized in terms of changes in their skeletal electron numbers and distribution, see Ref. (*173a*).

IX. Other Cluster Systems

A. BISMUTH CLUSTERS

Various cationic bismuth clusters, Bi_n^{x+}, have been prepared by Corbett and his co-workers (*43*, *44*, *86*, *111*) who have pointed out the close relationship between these species and borane clusters. For example, reduction of bismuth(III) chloride by bismuth affords a crystalline product of empirical formula Bi_6Cl_7. An X-ray crystallographic study (*111*) has shown this to contain cations Bi_9^{5+} and anions $BiCl_5^{2-}$ and $Bi_2Cl_8^{2-}$. The cations have tricapped trigonal prism shapes, although very distorted, in a manner suggesting they might be regarded as nido structures based on a bicapped Archimedean antiprism with 1 vacant vertex (assuming there is 1 "lone pair" on each metal atom, a cation Bi_9^{5+} contains 11 skeletal bond pairs). However, the distortion from the ideal D_{3h} symmetry of a tricapped trigonal prism may well be caused by interactions in crystalline "Bi_6Cl_7" between the cations and the adjacent anions, because the same cations, although hardly distorted from D_{3h} symmetry, have been found by X-ray crystallography in bismuth hafnium chloride $Bi^+ \; Bi_9^{5+} \; (HfCl_6^{2-})_3$ (*86*) (prepared from Bi, $BiCl_3$, and $HfCl_4$).

Different bismuth clusters are apparently formed in reactions between bismuth and bismuth trichloride–aluminum trichloride mixtures, from which the salts $(Bi_5)^{3+} \; (AlCl_4^-)_3$, and $(Bi_8)^{2+} \; (AlCl_4^-)_2$ have been isolated (*43*). A trigonal-bipyramidal structure was predicted for Bi_5^{3+} (a closo 6 skeletal bond pair system; cf. $C_2B_3H_5$), and a square antiprismatic structure for Bi_8^{2+}, as appropriate for an arachno 8-atom, 11 skeletal bond pair cluster. Similar polyhedral shapes appear likely for other clusters not only of bismuth but also of other heavy main group metals (the anion Pb_9^{4-}, for example, is isoelectronic with Bi_9^{5+}).

B. SOME METAL HALIDE CLUSTERS

The octahedral metal clusters that have long been familiar features of the lower halide chemistry of niobium, tantalum, molybdenum, and tungsten represent a category of cluster different from those so far considered in that their metal–metal bonding is best treated as involving *four* AO's on each metal (*49*, *133*, *144*, *165*, *178*).

There are two important structural types, containing M_6X_8 and M_6X_{12} units, respectively (Fig. 32). The former, typified by $Mo_6Cl_8^{4+}$, have a triply bridging halogen atom X, located over the center of each of the eight octahedral faces. The latter, typified by $Nb_6Cl_{12}^{2+}$, have 12 doubly bridging halogen atoms located over the centers of the twelve octahedral edges. Both types have an effectively square-planar arrangement of halogen atoms about each metal, which contributes four appropriate (e.g., dsp^2 hybrid) orbitals. One further metal orbital (e.g., a *pd* hybrid) pointing radially outward from the center of the cluster is available for bonding to the exo ligands usually associated with these clusters. This leaves four remaining AO's that point toward the other metals or toward the cluster center. The number of bonding MO's they generate (12 for $Mo_6Cl_8^{4+}$, 8 for $Nb_6Cl_{12}^{2+}$) reflects their orientation (*49*) which, in turn, reflects the orientation of the square-planar MX_4 units with respect to the fourfold axes of the octahedra (Fig. 32). An electron count for the units Mo_6^{12+} and Nb_6^{14+}, which formally constitute the cores of these clusters, shows them to contain 12 and 8 skeletal bond pairs, respectively, as appropriate for closed-shell configurations.

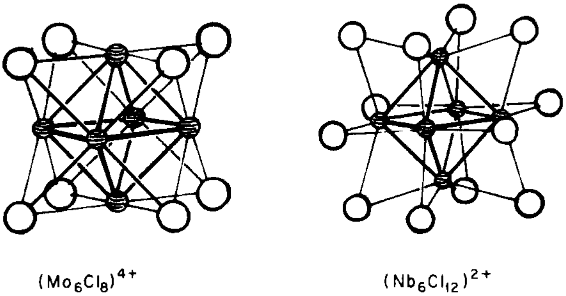


FIG. 32. Structures of the octahedral metal–halide clusters $(Mo_6Cl_8)^{4+}$ and $(Nb_6Cl_{12})^{2+}$ (*49*, *133*, *144*, *165*, *178*).

Since an octahedron has twelve edges and eight faces, it is possible to describe the metal–metal bonding in these species in terms of localized two- or three-center bonds, e.g., using twelve two-center octahedron edge bonds for $Mo_6Cl_8{}^{4+}$, and eight three-center octahedron face bonds for $Nb_6Cl_{12}{}^{2+}$. Although this may appear to imply much stronger skeletal bonding in the molybdenum cluster, if one takes account of the contribution to skeletal bonding made by the edge- or face-bridging chlorides of these species, then the two types, $Mo_6Cl_8{}^{4+}$ and $Nb_6Cl_{12}{}^{2+}$, are seen to be effectively isoelectronic: each contains 20 pairs of electrons associated with the metal–metal or metal–(bridging) halogen bonding, occupying MO's of symmetries A_{1g} (2), A_{2u}, E_g, T_{1u} (2), T_{2g} (2), and T_{2u} (*133*).

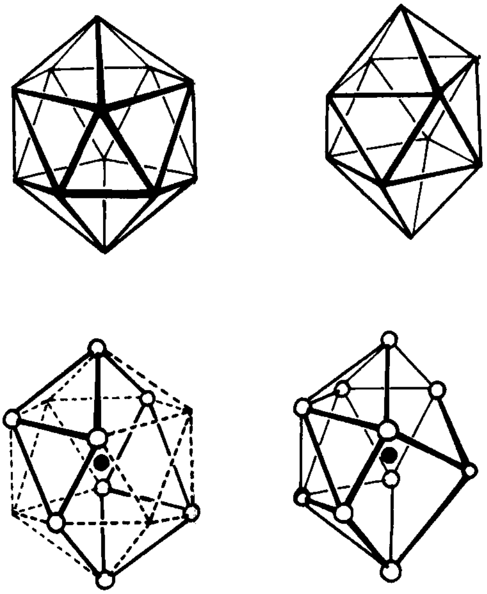
The platinum(II) halides, $PtCl_2$ and $PtBr_2$, adopt hexameric structures Pt_6X_{12} formally analogous to the M_6X_{12} cluster shown in Fig. 32, but with long metal–metal distances (approx. 336 pm). This is not surprising, since the $Pt_6{}^{12+}$ core on which these halides are formally based contains 24 electron pairs, enough to fill all the cluster antibonding, as well as the bonding orbitals (*200*).

C. GOLD CLUSTERS

Yet further examples of octahedral metal clusters are to be found in the chemistry of the coinage metals. Borohydride reduction of an ethanolic suspension of tris(*p*-tolyl)phosphinegold nitrate affords, among other products, the cationic cluster $[p\text{-tolyl}_3PAu]_6{}^{2+}$, which has been isolated as the tetraphenylborate (*16*) and shown by X-ray crystallography to have a slightly distorted octahedral Au_6 skeleton, the phosphine ligands occupying exo positions pointing radially outward. An electron count shows that the gold atoms can use all nine of their valence shell AO's if each atom uses one AO to bond the phosphine ligand, four AO's for nonbonding electron pairs, and the remaining four AO's for cluster bonding, for which 8 electron pairs will then be available. This treatment suggests a closer bonding relationship to clusters such as $Nb_6Cl_{12}{}^{2+}$ than to $B_6H_6{}^{2-}$, although a relationship to the latter has been argued (*16*).

A distorted octahedral arrangement of 6 copper atoms has been found in crystals of the 2-dimethylaminophenylcopper bromide, $[Cu(2\text{-}Me_2NC_6H_4)]_4(CuBr)_2 1.5C_6H_6$ (*101*), in which the bromine atoms bridge trans-equatorial edges, whereas the 2-dimethylaminophenyl ligands bridge four octahedron faces. Since both types of ligand perform a bridging role, and so furnish 3 electrons apiece, there are 84 electrons associated with the Cu_6 cluster, which formally has 12 electron pairs available for skeletal bonding if each metal atom uses four AO's for the purpose (cf. $Mo_6Cl_8{}^{4+}$).

More complicated structures are adopted by some other gold clusters of general formulas $[Au(AuL)_8]^{3+}$ (*15*, *16*) and $[Au(AuL)_{10}]^{3+}$ (*5*, *16*, *17*, *32*, *152*) (Fig. 33), where L is a 2-electron ligand [the Au_{11} clusters are actually most commonly obtained as neutral species $Au_{11}L_7X_3$, where L is a tertiary phosphine and X is a halogen or pseudohalogen (*32*)]. Both types have a central gold atom surrounded by AuL units at distance (260–290 pm) compatible with metal–metal bonding not only between the central gold atom and the surrounding gold atoms but also between



$[Au(AuL)_8]^{3+}$ (15) $[Au(AuL)_{10}]^{3+}$ (17)

FIG. 33. Skeletons of the gold clusters $(Au(AuL)_8]^{3+}$ and $[Au(AuL)_{10}]^{3+}$ compared with the icosahedron and the bicapped Archimedean antiprism. Central atoms are shaded; peripheral atoms are unshaded.

the surrounding atoms themselves. It, therefore, appears unrealistic to regard their skeletal bonding as involving only interactions between the central atoms and their neighbors, and an ingenious attempt has been made (*16*) to relate these clusters to the borane pattern. However, a simple convincing bonding rationale for these structures has yet to be found.

D. FURTHER METAL–CARBONYL CLUSTERS

In addition to the metal–carbonyl clusters discussed in Sections IV and V, which conform to the borane pattern, there is an increasing number of metal–carbonyl clusters with shapes that have no counterparts in borane chemistry. For example, whereas the nickel–carbonyl dianion $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ has an essentially octahedral skeleton (*31*), as appropriate for a hexanuclear closo cluster formally related to $B_6H_6^{2-}$, its platinum analog has a trigonal prismatic skeleton (*31a*) (Fig. 34). Moreover, it is but one member of a homologous series of

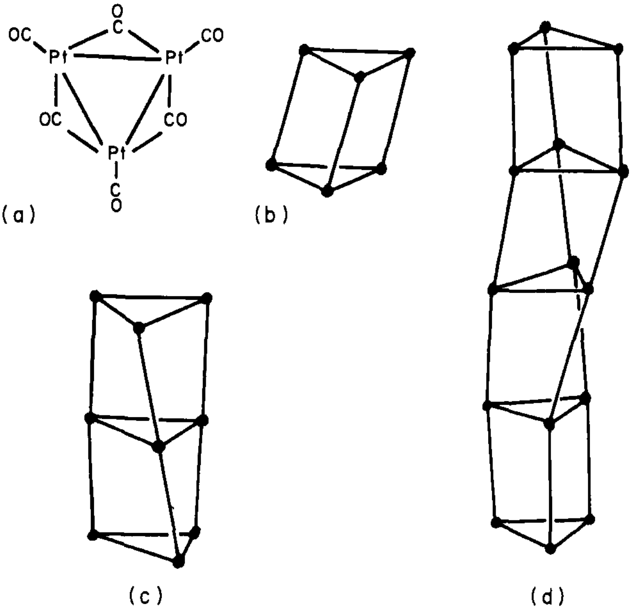
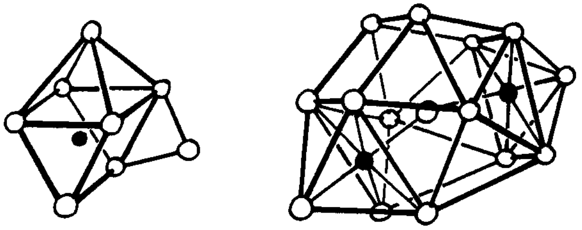


FIG. 34. Structures of the platinum–carbonyl anions $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ ($n = 2$, 3, and 5) (*31a*). (*a*) The triangular $Pt_3(CO)_3(\mu_2\text{-}CO)_3$ unit from which these anions are built up; (*b*) $[Pt_6(CO)_{12}]^{2-}$; (*c*) $[Pt_9(CO)_{18}]^{2-}$; (*d*) $[Pt_{15}(CO)_{30}]^{2-}$.

platinum–carbonyl anions of general formula $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ ($n = 2$, 3, 4, or 5) with column structures (Fig. 34) in which the triangular $Pt_3(CO)_3(\mu_2\text{-}CO)_3$ units are stacked in an eclipsed or nearly eclipsed configuration, forming slightly twisted trigonal prisms (*31a*). A trigonal prism is, in principle, one of several possible structures for a cluster of 6 units, each capable of forming three bonds, held together by 9 electron pairs, as in prismane (contrast the 10 skeletal bond pairs required for the *tricapped* trigonal-prismatic array of 9 skeletal atoms, as in $B_9H_9^{2-}$). That a trigonal prism should form the basis for the structure of $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_2^{2-}$ and its homologs is surprising since a cluster $Pt_6(CO)_{12}^{2-}$, counting electrons as outlined in Section V, A (Table III), formally contains only 7 skeletal bond pairs.



$Rh_8(CO)_{19}C$ $[Rh_{15}(CO)_{28}C_2]^-$

FIG. 35. Skeletal structures of the rhodium–carbonyl carbide complexes $Rh_8(CO)_{19}C$ and $[Rh_{15}(CO)_{28}C_2]^-$ (*7*).

Among other unusual structures are those of the rhodium–carbonyl carbide clusters $Rh_8(CO)_{19}C$ and $[Rh_{15}(CO)_{28}C_2]^-$ (7) (Fig. 35). The former, for which a closo-dodecahedral structure might have been expected, has a monocapped trigonal prism structure with a central carbon atom and with the remaining metal atom in an edge-bridging position. The latter has a centered tetracapped pentagonal prism structure in which the central metal atom not only has the highly metallic environment of 12 near neighbor metal atoms but also serves as the common vertex of two Rh_6 octahedra, each of which contains a central core carbon atom.

A metal-*nitrosyl* cluster that apparently has no borane counterpart is the anion $[Fe_4S_3(NO)_7]^-$ present in "Roussin's black salt," $Cs^+[Fe_4S_3(NO)_7]^- \cdot H_2O$ (*124*). Its skeleton consists of a trigonal pyramid of iron atoms, the 3 sulfur atoms capping the three pyramid faces (Fig. 36). As a 7-atom cluster formally containing 9 skeletal bond pairs, it might have been expected to adopt a *nido* structure with its Fe_4S_3 skeleton defining all but one of the vertices of a dodecahedron, a structural type that, incidentally and possibly significantly, is missing from the series of *nido*-boranes (see Williams, this volume). This may be because the number of skeletal bond pairs appropriate for such a fragment

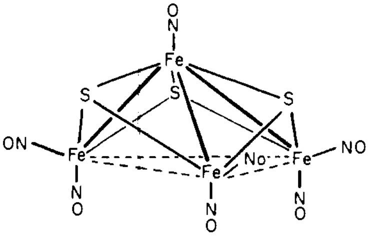


FIG. 36. Structure of anion $[Fe_4S_3(NO)_7]^-$ (*124*).

would not necessarily be the same as the number (9) appropriate for closo-dodecahedral species such as $B_8H_8^{2-}$ or $C_2B_6H_8$. The removal of 1 atom from a dodecahedral cluster would certainly change the symmetry more drastically than would the removal of 2 symmetry-related atoms. In short, closo, nido, arachno relationships are expected to break down when the nido or arachno fragment has a symmetry no longer appropriate to generate the same number of bonding MO's as the parent closo species (cf. the different skeletal bonding requirements of a tricapped trigonal prism—10 bond pairs—and what might be regarded as its hypho derivative a trigonal prism—9 bond pairs). Indeed, the difficulty of preserving the same number of bonding MO's when 3 polyhedron vertices are left vacant is probably one reason why few hypho species are known. Another factor is that, as the excess of electron pairs over skeletal atoms rises, it becomes less appropriate to regard each skeletal atom as contributing as many as three AO's to the cluster: if fewer than three AO's are involved in skeletal bonding, ring or chain structures result.

This last point may be illustrated by considering the bonding in the trinuclear triangular clusters $M_3(CO)_{12}$ (M = Fe, Ru, or Os) (Fig. 11). If one uses the electron-counting procedure summarized in Table III, and assumes that each metal atom uses three AO's for cluster bonding, these clusters formally contain 6 skeletal bond pairs. They can, thus, be regarded as arachno species, and their triangular shapes are, indeed, appropriate for structures based on a trigonal bipyramid with 2 vacant vertices. However, a skeletal *bonding* role cannot be found for all 6 electron pairs formally available, since these would fill more than half of the nine skeletal MO's generated from three AO's per metal. A more realistic treatment of the skeletal bonding is to regard each skeletal atom as using only *two* AO's for cluster bonding, when the number of skeletal bond pairs available (3) is the appropriate number to fill the three skeletal bonding MO's (effectively producing a two-center bond along each edge of the triangle).

E. SULFUR COMPOUNDS

Echoes of the borane pattern can be detected in the chemistry of sulfur and the heavier Group VI elements, although many of their relatively electron-rich ring and cage systems can be described quite satisfactorily in terms of localized two-center bonds. For example, tetrasulfur tetranitride, S_4N_4, has a structure (Fig. 37) based on a tetrahedral arrangement of its sulfur atoms, with the nitrogen atoms bridging four of the tetrahedron edges (*89*, *180*). If a lone pair is allocated to each sulfur and nitrogen atom, and a bond pair to each two center S—N link,

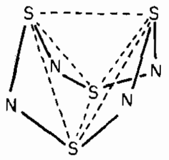


FIG. 37. Structure of tetrasulfur tetranitride, S_4N_4 (*89, 180*).

there remain 6 electron pairs for skeletal bonding in the S_4 tetrahedron, a number that is appropriate if each sulfur atom makes use of two *d* orbitals (*12, 204*). Elsewhere in sulfur chemistry, the relationship to borane-type clusters is less clear-cut (*12*), although the neighboring Group VI element, selenium, forms square-planar Se_4^{2+} ions (*30*) which may be regarded as tetranuclear arachno species (cf. $C_4H_4^{2-}$ or $B_4H_8^{2-}$).

F. HYDROCARBONS

Benzvalene, C_6H_6, and the carbo cations $C_5H_5^+$ and $C_6Me_6^{2+}$ have already been cited (Section VI) as hydrocarbons of the same structural type as boranes and carboranes, and we have also seen that such aromatic

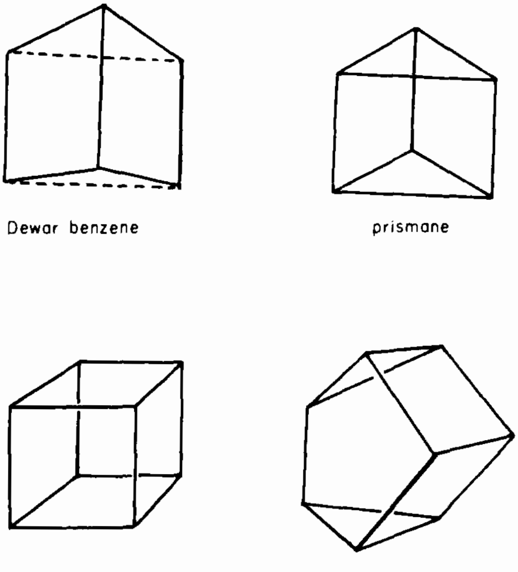
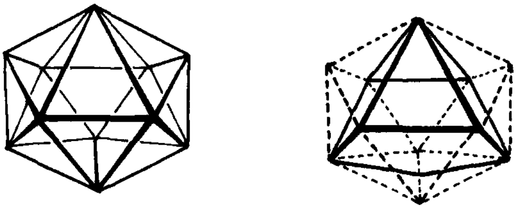

Dewar benzene
prismane
cubane
cuneane

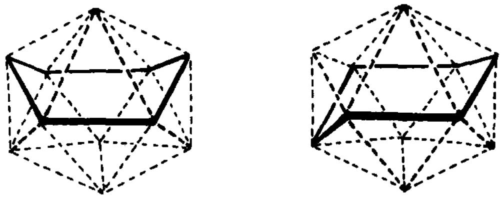
FIG. 38. Skeletons of Dewar benzene, prismane, cubane, and cuneane.

ring systems as benzene and the cycloheptatrienyl cation, $C_7H_7^+$, regarded as arachno systems, effectively extend the series of polyhedra on which borane-type clusters may be based. Quite apart from these, there are many other organic ring or cage systems that serve as models for further structural types, particularly for systems with a higher skeletal electron-to-atom ratio than is common in borane chemistry. They range in type from other benzene isomers such as Dewar benzene and prismane to cages such as cubane, C_8H_8, and its isomer cuneane (Fig. 38) and even more complicated structures. These and other hypothetical cluster shapes have been discussed by Lipscomb (*145*) and King (*137*), and the ways in which the skeletons of *electron-precise* species—species for which two-center bond descriptions are adequate—open up as more electron pairs are added have been discussed by Mingos (*161*).

Two systems, which it is tempting to relate to the 11-vertex octadecahedron of Fig. 1, are worth brief mention. One is the carbo cation $[C_8Me_8H]^+$ believed to have a structure (Fig. 39) formed by bringing a unit CH^+ up to the open face of the double bonds of octamethylnorbornadiene (*105, 132*). When compared with the octadecahedron, as in Fig. 39, this carbo cation has the CMe_2 unit in an edge-bridging position,



$(B_{11}H_{11})^{-2}$ $(C_8Me_8H)^+$ (105,132)



C_6H_{12} boat form C_6H_{12} chair form

Fig. 39. Skeletal structures of the carbo cation $(C_8Me_8H)^+$ and the boat and chair forms of cyclohexane compared with the octadecahedron of $(B_{11}H_{11})^{2-}$.

and 4 polyhedron vertices are left vacant. (As an octanuclear species with 12 skeletal bond pairs, $C_8Me_8H^+$ might, in principle, have been expected to adopt a hypho structure based on an octadecahedron, but with three vertices vacant.) Figure 39 also shows how the skeletal structures of both boat and chair forms of cyclohexane, C_6H_{12}, interestingly can be related to the octadecahedron, with, however, *5* vacant vertices. However, treating a ring of 6 methylene CH_2 units, each capable of forming *two* bonds and furnishing *2* electrons, as a cluster of the borane type, unnecessarily complicates rather than clarifies the bonding description, although it preserves the structural distinction between the axial (*endo*-) hydrogen and equatorial (*exo*-)hydrogen atoms of C_6H_{12} in its chair configuration.

X. Conclusion

The main object of this survey has been to demonstrate the wide range of substances which, like boranes and carboranes, may be regarded as clusters of n skeletal atoms, each providing three AO's for skeletal bonding, held together by from n to $(n + 3)$ bond pairs. Examples include metalloboranes and carboranes, metal–hydrocarbon π complexes, some hydrocarbons, and certain metal clusters. Their closo, nido, or arachno structures reflect their skeletal electron numbers in a manner that allows the structures of new compounds to be inferred, new syntheses to be devised, reactions to be predicted, and interatomic distances to be rationalized. Exceptions to the simple pattern are to be found in the case of some halogenated species (B_8Cl_8, $C_4H_4B_2F_2$, etc.) and certain metallo systems, in which extra electrons may simply expand rather than deform the skeleton. The existence of other cluster types, e.g., systems using four AO's per skeletal atom ($Mo_6Cl_8{}^{4+}$, $Nb_6Cl_{12}{}^{2+}$), or not obeying the inert gas rule (S_4N_4) has also been noted briefly. Although the shapes of some recently prepared metal clusters show that further structural patterns have yet to be recognized, these too may be expected to reflect the number of electrons present.

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