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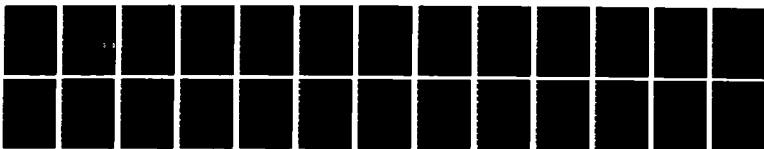
GRAPH THEORY IN THE STUDY OF METAL CLUSTER BONDING
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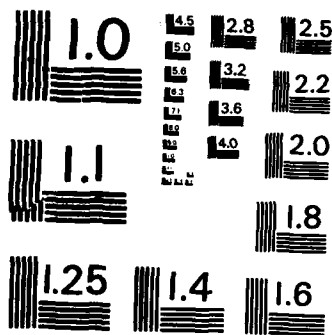
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two electrons for a multicenter core bond as well as 2v electrons for pairwise surface bonding. A problem of particular interest is how metal cluster polyhedra can fuse together leading ultimately to the infinite structures of the bulk metals. As a model for such processes the fusion of rhodium carbonyl octahedra is examined using graph theory derived methods. These lead to reasonable electron-precise models for the bonding topologies in the "biphenyl analogue" $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$, the "naphthalene analogue" $[\text{Rh}_9(\text{CO})_{19}]^{3-}$, the "anthracene analogue" $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$, and the "perinaphthene analogue" $[\text{Rh}_{11}(\text{CO})_{23}]^{3-}$. Similar models can also be developed for clusters based on centered larger rhodium polyhedra as exemplified by the centered cuboctahedral clusters of the type $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-q}]^q$ ($q = 2, 3, 4$) representing a fragment of the hexagonal close packed metal structure.

C. J. B. 16270

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TECHNICAL REPORT NO. 20

Graph Theory in the Study of Metal Cluster Bonding Topology:

Applications to Metal Clusters having Fused Polyhedra

by

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Abstract

The energy levels in a delocalized two- or three-dimensional chemical structure are related to the eigenvalues of the graph representing the corresponding bonding topology. Such relatively crude but computationally undemanding graph theory derived models provide a clear demonstration of the close relationship between two-dimensional aromatic systems such as benzene and three-dimensional aromatic systems such as deltahedral boranes, carboranes, and metal clusters. The basic building blocks for the three dimensional aromatic systems are deltahedra having no degree 3 vertices. Delocalized bonding in such systems having v vertices requires two electrons for a multicenter core bond as well as $2v$ electrons for pairwise surface bonding. A problem of particular interest is how metal cluster polyhedra can fuse together leading ultimately to the infinite structures of the bulk metals. As a model for such processes the fusion of rhodium carbonyl octahedra is examined using graph theory derived methods. These lead to reasonable electron-precise models for the bonding topologies in the ("biphenyl analogue") $(\text{Rh}_{12}(\text{CO})_{30})^{2-}$, the ("naphthalene analogue") $(\text{Rh}_9(\text{CO})_{19})^{3-}$, the ("anthracene analogue") $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$, and the ("perinaphthene analogue") $(\text{Rh}_{11}(\text{CO})_{23})^{3-}$. Similar models can also be developed for clusters based on centered larger rhodium polyhedra as exemplified by the centered cuboctahedral clusters of the type $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_{5-q}]^q$ ($q = 2, 3, 4$) representing a fragment of the hexagonal close packed metal structure.

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Introduction

The systematics of the fusion of metal cluster polyhedra are important in understanding the structural relationships between discrete metal clusters and bulk metals. Topologically the fusion of metal cluster polyhedra to give bulk metals can be regarded as a three-dimensional analogue of the two-dimensional problem of fusion of benzene rings to give graphite. This paper summarizes some key aspects of our graph-theory derived approach to metal cluster bonding topology^{1,2,3} and shows how it can be extended to the treatment of the fusion of metal cluster polyhedra using several fused rhodium carbonyl cluster polyhedra as examples. A more comprehensive discussion of graph-theory derived models of the bonding topology in fused rhodium carbonyl cluster polyhedra is presented elsewhere.⁴ Another recent paper⁵ compares the essential aspects of our graph-theory derived approach to metal cluster bonding topology with other approaches to metal cluster bonding such as the original Wade-Mingos skeletal electron pair method,^{6,7,8} the extended Hückel calculations of Lauher,⁹ the perturbed spherical shell theory of Stone,^{10,11} and the topological electron counting method of Teo.^{12,13,14,15} Strengths of our graph-theory derived method include the following:

- (1) The ability to deduce important information about the electron counts and shapes of diverse metal clusters using a minimum of computation.
- (2) The ability to generate reasonable electron-precise bonding models for metal clusters, such as platinum carbonyl clusters,^{16,17} that appear intractable by other methods not requiring heavy computation.
- (3) Information concerning the distribution of total cluster electron counts between skeletal bonding within the cluster polyhedron and bonding to external ligands.
- (4) Ability to distinguish between localized and delocalized bonding in cluster

polyhedra.

In connection with understanding the fusion of cluster polyhedra an important development was the observation by Teo¹⁸ that the Hume-Rothery rule¹⁹ for electron counting in brasses can be extended to close packed high nuclearity metal clusters. Other aspects of the fusion of cluster polyhedra have been treated by Mingos^{20,21} and by Slovokhotov and Struchkov.²²

Background

Chemical bonding relationships can be represented by a graph in which the vertices correspond to the atoms participating in the bonding and the edges correspond to bonding relationships. The adjacency matrix of a graph, such as a graph representing chemical bonding, can be defined as follows

$$A_{ij} = \begin{cases} 0 & \text{if } i = j \\ 1 & \text{if } i \text{ and } j \text{ are connected by an edge} \\ 0 & \text{if } i \text{ and } j \text{ are not connected by an edge} \end{cases} \quad (1)$$

The eigenvalues of the adjacency matrix are obtained from the following determinantal equation:

$$|A - xI| = 0 \quad (2)$$

in which I is the unit matrix ($I_{ii} = 1$ and $I_{ij} = 0$ for $i \neq j$.)

The eigenvalues of the adjacency matrix of the graph representing the relevant chemical bonding are closely related to the energy levels as determined by Hückel theory.^{23,24,25,26} Thus Hückel theory uses the secular equation

$$|H - ES| = 0 \quad (3)$$

in which the energy matrix H and overlap matrix S can be resolved into the unit matrix I and the adjacency matrix A as follows:

$$H = \alpha I + \beta A \quad (4a)$$

$$S = I + \lambda A \quad (4b)$$

The energy levels of the system are related to the eigenvalues x of the adjacency matrix A (equation 2) as follows:

$$E = \frac{\alpha + x\beta}{1 + x\lambda} \quad (5)$$

Thus a positive eigenvalue x of A corresponds to a bonding orbital and a negative eigenvalue x corresponds to an antibonding orbital in the corresponding chemical system. In this simple way graph theory can be used to determine the number of bonding and antibonding orbitals for a bonding topology represented by a given adjacency matrix A . Such information, although very limited compared with information obtainable at least in principle by more sophisticated methods which are more complicated computationally, is sufficient to determine favored electron counts for different molecular shapes which are of considerable importance in metal cluster chemistry.

In this paper we apply such bonding models to the study of such metal clusters. The vertex atoms in such clusters may be classified as light atoms or heavy atoms depending on whether they use d orbitals as well as s and p orbitals for their chemical bonding. Furthermore, vertex atoms may be classified as normal or anomalous

vertex atoms depending upon whether or not they use precisely three of the four (for light atoms) or nine (for heavy atoms) valence orbitals for intrapolygonal or intrapolyhedral chemical bonding; these three orbitals are called internal orbitals and the remaining one (for light atoms) or six (for heavy atoms) valence orbitals are called external orbitals.

The two extreme types of chemical bonding in metal clusters may be called edge-localized and globally delocalized.^{1,3} An edge-localized polyhedron has two electron two-center bonds along each edge of the polyhedron. A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and may be regarded as a three-dimensional "aromatic" system.²⁷ A complicated metal cluster system consisting of fused and/or capped polyhedra can have globally delocalized bonding in some polyhedral regions and edge-localized bonding in other polyhedral regions.

One of the major triumphs of the graph-theory derived approach to the bonding topology in globally delocalized systems is the demonstration of the close analogy between the bonding in two-dimensional planar polygonal aromatic systems such as benzene and in three-dimensional deltahedral boranes and carboranes,¹ where a deltahedron is a polyhedron in which all faces are triangles. The latter three-dimensional structures are topologically equivalent to metal cluster structures through ideas first presented by Wade in 1971²⁸ and subsequently developed extensively by Hoffmann as isolobality.²⁹

Consider a globally delocalized polygonal or deltahedral system with v normal vertices. In such a system the three internal orbitals on each normal vertex atom are divided into two twin internal orbitals (called "tangential" in some treatments) and a unique internal orbital (called "radial" in some treatments). Pairwise overlap between the $2v$ twin internal orbitals is responsible for the formation of the polygonal or deltahedral framework and leads to the splitting of the $2v$ orbitals into

v bonding and v antibonding orbitals. The dimensionality of this bonding of the twin internal orbitals is one less than the dimensionality of the globally delocalized system. Thus in the case of the two-dimensional planar polygonal systems such as benzene the pairwise overlap of the $2v$ twin internal orbitals leads to the σ -bonding network which may be regarded as a collection of v one-dimensional bonds along the perimeter of the polygon involving adjacent pairs of polygonal vertices. The v bonding orbitals and v antibonding orbitals correspond to the σ bonding and σ^* antibonding orbitals, respectively. In the case of the three-dimensional deltahedral systems the pairwise overlap of the $2v$ twin internal orbitals results in bonding over the two-dimensional surface of the deltahedron, which may be regarded as (topologically) homeomorphic to the sphere.

The equal numbers of bonding and antibonding orbitals formed by pairwise overlap of the twin internal orbitals are supplemented by additional bonding and antibonding molecular orbitals formed by global mutual overlap of the v unique internal orbitals. This overlap can be represented by a graph G in which the vertices correspond to the vertex atoms or (equivalently) their unique internal orbitals and the edges represent pairs of overlapping unique internal orbitals. The relative energies of the additional molecular orbitals arising from such overlap of the unique internal orbitals are determined from the eigenvalues x of the adjacency matrix A of the graph G (see equations 2 and 5 above). In the case of benzene the graph G is the C_6 graph (hexagon) which has three positive and three negative eigenvalues corresponding to the three π bonding and three π^* antibonding orbitals, respectively. In the case of a globally delocalized deltahedron having v vertices such as found in the deltahedral boranes $B_vH_v^{2-}$ and carboranes $C_2B_{v-2}H_v$ ($6 \leq v \leq 12$) as well as most octahedral metal clusters ($v = 6$), the graph G is the complete graph K_v in which each of the vertices has an edge going to every other vertex leading to a total of $v(v-1)/2$ edges. This corresponds to a v -center bond

at the center (core) of the deltahedron formed by overlap of each unique internal orbital with every other unique internal orbital. The complete graph K_v has one positive eigenvalue and $v-1$ negative eigenvalues regardless of the value of v indicating that the v -center core bond in a globally delocalized deltahedral cluster leads to only one new bonding molecular orbital. The sum of the v bonding orbitals arising from the surface bonding of the twin internal orbitals and the single bonding orbital arising from the v -center core bonding of the unique internal orbitals gives a total of $v + 1$ bonding orbitals for globally delocalized deltahedra having v vertices. Filling these $v + 1$ bonding orbitals with electron pairs in the usual way gives a total of $2v + 2$ bonding electrons in accord with the observed number of skeletal electrons required to form stable globally delocalized deltahedral boranes, carboranes, and metal clusters. Further details of this bonding model are presented elsewhere.^{1,2,3}

The relationship between the number of edges meeting at a vertex (the vertex degree) and the number of internal orbitals used by the atom at the vertex in question determines whether or not the bonding in the polyhedral cluster is edge-localized or globally delocalized.³ Thus edge-localized bonding requires that all vertex degrees match the numbers of internal orbitals used by the corresponding vertex atoms. Conversely, delocalization occurs when there is a mismatch between the vertex degrees of the polyhedron and the numbers of internal orbitals provided by the corresponding vertex atoms. Since normal vertex atoms³ use three internal orbitals, the smallest globally delocalized polyhedron is the regular octahedron, which is the smallest polyhedron having no vertices of degree 3. Delocalized metal octahedra have a similar prototypical role in constructing three-dimensional delocalized metal clusters and bulk metals as planar carbon hexagons have in constructing fused planar aromatic systems ("polyhexes") including graphite. This paper thus considers fusion of rhodium octahedra as a model for important stages

in the generation of bulk metal structures by fusion of individual metal polyhedra.

Many interesting higher nuclearity metal clusters have interstitial atoms or groups located in the center of the polyhedra. In such interstitial atoms all valence orbitals (four in the case of a light atom and nine in the case of a heavy atom) contribute to the skeletal bonding so that all of the valence electrons of the interstitial atom are available for the skeletal bonding. For example, interstitial carbon and rhodium atoms contribute four and nine electrons to the skeletal bonding, respectively. Such interstitial atoms require the surrounding polyhedron to have a certain minimum volume.³⁰ Thus an interstitial carbon atom cannot fit into a tetrahedron but fits into an octahedron as exemplified by $\text{Ru}_6(\text{CO})_{17}\text{C}$.³¹ An interstitial transition metal such as rhodium cannot fit into an octahedron but fits into a twelve-vertex polyhedron. In this connection the volume of a polyhedron containing an interstitial atom can be increased by decreasing the number of edges. In the case of a deltahedron this can be done by converting pairs of triangular faces sharing an edge into single quadrilateral faces by rupture of the edge shared by the two triangular faces. This process is similar to the "diamond-square" portion of the diamond-square-diamond process involved in polyhedral rearrangements.^{32,33,34} For example, rupture of six edges in this manner form an icosahedron can give a cuboctahedron.³² A v -vertex non-deltahedron derived from a v -vertex deltahedron by volume expansion through edge rupture in this manner and containing an interstitial atom may function as a globally delocalized $2v + 2$ skeletal electron system like the v -vertex deltahedron from which it is derived. Such non-deltahedra can conveniently be called pseudodeltahedra; they have only triangular and quadrilateral faces with only a limited number of the latter. In an uncentered polyhedron having some faces with more than three edges, these faces may be regarded as holes in the otherwise closed polyhedral surface.^{2,3,35} Such polyhedra are found in electron-rich clusters having more

than $2v + 2$ skeletal electrons as exemplified by the $2v + 4$ skeletal electron nido boron hydrides having one nontriangular face and the $2v + 6$ skeletal electron arachno boron hydrides having two non-triangular faces or one large non-triangular face (e.g., $B_{10}H_{14}$).^{1,36,37} However, an interstitial atom at the center of such a polyhedron may be regarded as plugging up the surface holes arising from the non-triangular faces so that globally delocalized bonding is now possible.

Electron-poor v -vertex metal clusters having less than $2v + 2$ apparent skeletal electrons have structures based on a central deltahedron having one or more capped (triangular) faces to generate a tetrahedral chamber for each such capping relationship.^{1,3} If the central deltahedron is an octahedron or other deltahedron having no degree three vertices, then the tetrahedral chambers are regions of edge-localized bonding attached to a globally delocalized central polyhedron. Thus a capped octahedron is an example of a metal cluster polyhedron having globally delocalized bonding in some regions (i.e., the cavity of the octahedron) and edge-localized bonding in other regions (i.e., the tetrahedral chamber formed by the cap).

Let us now consider in more detail the general effects of face capping on the required number of skeletal electrons. An edge-localized tetrahedral chamber formed by capping a triangular face requires 12 skeletal electrons corresponding to two-electron bonds along each of the six edges of the tetrahedron. However, six of these skeletal electrons are the same as the six skeletal electrons of three surface bonds involving the vertex atoms of the face being capped. Thus capping a triangular face requires six additional skeletal electrons to generate the total of 12 skeletal electrons required for the resulting tetrahedral chamber. These additional six skeletal electrons from capping a triangular face can be viewed as forming three two-center edge-localized bonds along the three edges connecting the cap with the three vertices of the triangular face being capped. Note that

each of the three atoms of the triangular face being capped needs an extra internal orbital beyond the three internal orbitals for the skeletal bonding for the central polyhedron. In general these "new" internal orbitals will come from previously non-bonding external orbitals already containing the electron pair required for the two-center bond to the capping atom. This is the basis for the statement in earlier papers^{1,3} that capping a triangular face contributes skeletal electrons to a central polyhedron without contributing any new bonding orbitals; such a statement summarizes the net result of this process without considering the details. In treating capped triangular faces we can thus regard the three atoms of the face being capped either falsely as using three internal orbitals so that such capping generates no new bonding orbitals or more accurately as using four internal orbitals so that such capping generates the three new bonding orbitals of the three two-center bonds to the cap but concurrently the six electrons required to fill these new bonding orbitals. Both approaches lead to equivalent electron counts.

A polyhedron with a single cap may alternatively be regarded as a pair of fused polyhedra having the capped face in common. Thus a deltahedron having a capped (triangular) face can be regarded as a tetrahedron fused to the deltahedron so that a triangular face is shared by both polyhedra. Thus capped polyhedra may be regarded as special types of fused polyhedra. Furthermore note that the vertices of a face shared by two fused polyhedra also belong to the two polyhedra. In general, the larger the number of polyhedra to which a given metal vertex belongs, the larger the number of internal orbitals required for its skeletal bonding. In the face-sharing fused octahedral rhodium carbonyl derivatives discussed in this paper electron-precise bonding models can be devised in which rhodium vertices belonging to one, two, and three octahedra use three, four, and five internal orbitals, respectively; such $\text{Rh}(\text{CO})_2$ vertices donate one, three, and five skeletal electrons, respectively. Similar relationships do not necessarily hold for edge-sharing fused

metal octahedra such as $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$ (ref. 4).

Application to Rhodium Carbonyl Clusters Having Fused Polyhedra

The general ideas outlined in the previous section are illustrated in this section for selected fused polyhedral rhodium carbonyl clusters which are potential models for understanding the fusion of discrete metal clusters to extended bulk metal structures. First the properties of rhodium carbonyl clusters based on a single polyhedron are listed below:

(1) $\text{Rh}_4(\text{CO})_{12}$ and substitution products³⁸: These clusters form edge-localized tetrahedra having the required 12 skeletal electrons since each $\text{Rh}(\text{CO})_3$ vertex contributes three skeletal electrons.

(2) $[\text{Rh}_5(\text{CO})_{15}]^-$ (ref. 39): This cluster forms an elongated trigonal bipyramid in which the equatorial rhodium atoms use three internal orbitals but the axial rhodium atoms use only two internal orbitals thereby providing the vertex degree/internal orbital mismatch required for a globally delocalized trigonal bipyramid.³ Note that an $\text{Rh}(\text{CO})_3$ vertex contributes three skeletal electrons when it uses three internal orbitals but only one skeletal electron when it uses only two internal orbitals thereby corresponding to $(3)(3) + (2)(1) + 1 = 12$ skeletal electrons = $2n + 2$ for $n = 5$.

(3) $\text{Rh}_6(\text{CO})_{16}$ and substitution products⁴⁰: These clusters form globally delocalized octahedra having the required 14 skeletal electrons.

(4) $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ (ref. 41): This cluster is an example of an electron-poor cluster having only $2v$ apparent skeletal electrons (see above) for $v = 7$. Its structure is normally viewed as a capped octahedron but can be equivalently considered

as an octahedron fused to a tetrahedron with a (triangular) face in common. The seven $\text{Rh}(\text{CO})_2$ units contribute a total of seven skeletal electrons, the two "extra" carbonyl groups contribute $(2)(2) = 4$ skeletal electrons, and the -3 charge on the anion contributes an additional three skeletal electrons leading to the 14 skeletal electrons required by the globally delocalized center octahedron.

Now let us consider rhodium carbonyl clusters formed by the joining in various ways of rhodium carbonyl octahedra similar to the isolated Rh_6 octahedron in $\text{Rh}_6(\text{CO})_{16}$. Such combinations of rhodium octahedra can conveniently be classified by the trivial name of the polycyclic benzenoid hydrocarbon having an analogous configuration of its planar hexagon building blocks. In this connection fusion of two rhodium octahedra so that a triangular face is shared by both octahedra will be considered as analogous to the fusion of two carbon hexagons so that one edge is shared by both hexagons (e.g., naphthalene). Figure 1 depicts the fused rhodium carbonyl octahedra that will be considered in this paper as analogues of polycyclic aromatic hydrocarbons. The specific systems are discussed below:

(1) Biphenyl analogue, $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ (ref. 42): The structure of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ consists of two Rh_6 octahedra joined by a rhodium-rhodium bond analogous to biphenyl in which two C_6 hexagons are joined by a carbon-carbon bond. Such a combination of two octahedra requires 28 skeletal electrons, namely 14 for each octahedron ($2v + 2$ rule where $v = 6$). These 28 skeletal electrons can be obtained as follows:

12 $\text{Rh}(\text{CO})_2$ vertices: $(12)(1) =$	12 electrons
6 "extra" CO groups: $(6)(2) =$	12 electrons
Rh-Rh bond	2 electrons
-2 charge	<u>2 electrons</u>
Total skeletal electrons	28 electrons

(2) Naphthalene analogue, $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ (ref. 43): The structure of $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ consists of a pair of octahedra having a (triangular) face in common analogous to naphthalene which consists of two carbon hexagons with an edge in common. The face-sharing pair of octahedra has 9 vertices, 21 edges, and 14 faces like the 4,4,4-tricapped trigonal prism, which is the nine-vertex deltahedron found in systems with $2v + 2 = 20$ skeletal electrons ($v = 9$) so that a bonding scheme with a K_9 complete graph for the core bonding is reasonable for a fused pair of octahedra just as it is for the 4,4,4-tricapped trigonal prism. However, in the fused pair of octahedra the three rhodium vertices common to both octahedra use four internal orbitals whereas the six rhodium vertices belonging to only one of the octahedra use the normal three internal orbitals. This leads to the following electron-counting scheme for $[\text{Rh}_9(\text{CO})_{19}]^{3-}$:

(a) Source of skeletal electrons:

6 $\text{Rh}(\text{CO})_2$ groups present in only one octahedron and	
therefore using 3 internal orbitals: $(6)(1) =$	6 electrons
3 $\text{Rh}(\text{CO})_2$ groups common to both octahedra and	
therefore using 4 internal orbitals: $(3)(3) =$	9 electrons
1 "extra" CO group: $(1)(2) =$	2 electrons
-3 charge	<u>3 electrons</u>
Total available skeletal electrons	20 electrons

(b) Use of skeletal electrons:

9 Rh-Rh surface bonds:	18 electrons
1 9-center (K_9) core bond:	<u>2 electrons</u>
Total skeletal electrons required	20 electrons

(3) Anthracene analogue, $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$ (ref. 44): The structure of $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$

consists of a linear chain of three fused octahedra similar to the fusion of three benzene rings to form anthracene (Figure 1). In $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$ the distance between the three vertex atoms of the triangular face unique to the octahedron at one end of the chain and the three vertex atoms unique to the octahedron at the other end of the chain is too large for the core bonding to be represented by a single complete graph analogous to the K_9 graph used to represent the core bonding in the above naphthalene analogue $[\text{Rh}_9(\text{CO})_{19}]^{3-}$. Instead in $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$ the core bonding consists of two complete graphs, one associated with the octahedron at one end of the chain and the other associated with the octahedron at the other end of the chain. This leads to the following electron-counting scheme for $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$:

(a) Source of skeletal electrons:

6 $\text{Rh}(\text{CO})_2$ groups present in only one octahedron and therefore using 3 internal orbitals: $(6)(1) =$	6 electrons
6 $\text{Rh}(\text{CO})_2$ groups common to two octahedra and therefore using 4 internal orbitals: $(6)(3) =$	18 electrons
1 "extra" CO group: $(1)(2) =$	2 electrons
2 hydrogen atoms: $(2)(1) =$	<u>2 electrons</u>
Total available skeletal electrons	28 electrons

(b) Use of skeletal electrons:

12 Rh-Rh surface bonds:	24 electrons
2 core bonds	<u>4 electrons</u>
Total skeletal electrons required	28 electrons

The analysis of the bonding topologies in the naphthalene analogue $[\text{Rh}_9(\text{CO})_{19}]^{3-}$ and the anthracene analogue $\text{H}_2\text{Rh}_{12}(\text{CO})_{25}$ suggests that in a linear chain of

an odd number of face-sharing octahedra the core bonding occurs in alternate octahedra including the octahedra at both ends whereas in a linear chain of an even number of face-sharing octahedra the core bonding consists of a K_9 graph in the two octahedra at one end followed by core bonding in alternate octahedra along the remainder of the chain. Such ideas are potentially useful in the construction of one-dimensional chains of fused polyhedra having novel metallic properties.

(4) Perinaphthene analogue, $[Rh_{11}(CO)_{23}]^{3-}$ (ref. 45): The cluster $[Rh_{11}(CO)_{23}]^{3-}$ consists of three fused octahedra. The six rhodium atoms unique to a single octahedron are considered to use the normal three internal orbitals, the three rhodium atoms shared by two octahedra are considered to use four internal orbitals, and the two rhodium atoms shared by all three octahedra are considered to use five internal orbitals. Each of the three octahedral cavities contains a K_n multicenter core bond and in addition there is a "hidden" two-center two-electron bond between the two rhodium vertices common to all three octahedra. This leads to the following electron-counting scheme for $[Rh_{11}(CO)_{23}]^{3-}$:

(a) Source of skeletal electrons:

6 $Rh(CO)_2$ groups present in only one octahedron and therefore using 3 internal orbitals: $(6)(1) =$	6 electrons
3 $Rh(CO)_2$ common to two octahedra and therefore using 4 internal orbitals: $(3)(3) =$	9 electrons
2 $Rh(CO)_2$ groups common to all three octahedra and therefore using 5 internal orbitals: $(2)(5) =$	10 electrons
1 "extra" CO group: $(1)(2)$	2 electrons
-3 charge	<u>3 electrons</u>
Total available skeletal electrons	30 electrons

(b) Use of skeletal electrons:

11 Rh-Rh surface bonds:	22 electrons
3 core bonds in the three octahedral cavities: $(3)(2) =$	6 electrons
1 "hidden" two-center, two-electron bond between the two Rh vertices common to all three octahedra:	<u>2 electrons</u>
Total skeletal electrons required	30 electrons

Another interesting type of high nuclearity rhodium carbonyl cluster consists of a polyhedron having 12 or more rhodium atoms with an additional rhodium atom in the center. Many of these systems are particularly significant in representing fragments of body-centered cubic (bcc) or hexagonal close-packed (hcp) metal structures.⁴⁶ A frequently encountered feature of these systems is a Rh_{13} centered cuboctahedron (Figure 2) representing a fragment of the hcp metal structure.¹⁸ The prototypical systems of this type have the general formula $[Rh_{13}(CO)_{24}H_{5-q}]^q-$ ($q = 2, 3, 4$).^{47,48,49} These systems have the correct electron count for a globally delocalized Rh_{12} pseudodeltahedron having the thirteenth rhodium atom in the center as an interstitial atom. The electron counting for these systems illustrates the effect of an interstitial atom and can be summarized as follows:

(a) Source of skeletal electrons:

12 $Rh(CO)_2$ groups using 3 internal orbitals: $(12)(1) =$	12 electrons
Center (interstitial) Rh atom:	9 electrons
5-q hydrogen atoms and -q charge: $(5-q) + q =$	<u>5 electrons</u>
Total available skeletal electrons	26 electrons

(b) Use of skeletal electrons:

12 Rh-Rh surface bonds:	24 electrons
1 core bond: (1)(2) =	<u>2 electrons</u>
Total skeletal electrons required	26 electrons

A variety of more complicated centered rhodium carbonyl clusters are known.¹⁸
Their bonding topologies are discussed in some detail elsewhere.⁴

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Bibliography

- [1] R.B. King and D.H. Rouvray, *J. Am. Chem. Soc.* **99**, 7834 (1977).
- [2] R.B. King, *Inorg. Chim. Acta* **57**, 79 (1982).
- [3] R.B. King in "Chemical Applications of Topology and Graph Theory," R.B. King, Ed.; Elsevier: Amsterdam, 1983, pp. 99-123.
- [4] R.B. King, *Inorg. Chim. Acta* **00**, 000 (1986).
- [5] R.B. King, *Inorg. Chim. Acta* **00**, 000 (1986).
- [6] D.M.P. Mingos, *Nature (London), Phys. Sci.* **236**, 99 (1972).
- [7] K. Wade, *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
- [8] D.M.P. Mingos, *Accts. Chem. Res.* **17**, 311 (1984).
- [9] J.W. Lauher, *J. Am. Chem. Soc.* **100**, 5305 (1978).
- [10] A.J. Stone, *Inorg. Chem.* **20**, 563 (1981).
- [11] A.J. Stone, *Polyhedron* **3**, 1299 (1984).
- [12] B.K. Teo, *Inorg. Chem.* **23**, 1251 (1984).
- [13] B.K. Teo, G. Longoni, and F.R.K. Chung, *Inorg. Chem.* **23**, 1257 (1984).
- [14] B.K. Teo, *Inorg. Chem.* **24**, 115 (1985).
- [15] B.K. Teo, *Inorg. Chem.* **24**, 4209 (1985).
- [16] R.B. King in "The Applications of Mathematical Concepts to Chemistry," N. Trinajstić, Ed.; Ellis Horwood: Chichester, in press.
- [17] R.B. King, *Inorg. Chim. Acta* **00**, 000 (1986).
- [18] B.K. Teo, *Chem. Comm.* 1362 (1983).
- [19] W. Hume-Rothery, "The Metallic State"; Oxford University Press: New York, 1931, p. 328.
- [20] D.M.P. Mingos, *Chem. Comm.* 706 (1985).
- [21] D.M.P. Mingos, *Chem. Comm.* 1352 (1985).
- [22] Yu. L. Slovokhotov and Yu. T. Struchkov, *J. Organometal. Chem.* **258**, 47

(1983).

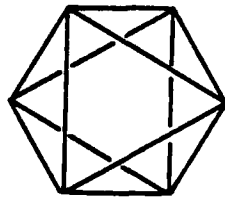
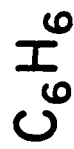
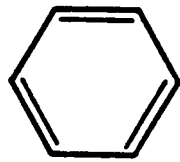
- [23] K. Ruedenberg, *J. Chem. Phys.* **22**, 1878 (1954).
- [24] H.H. Schmidtke, *Coord. Chem. Rev.* **2**, 3 (1967).
- [25] H.H. Schmidtke, *J. Chem. Phys.* **45**, 3920 (1966).
- [26] I. Gutman and N. Trinajstić, *Topics Curr. Chem.* **42**, 49 (1973).
- [27] J. Aihara, *J. Am. Chem. Soc.* **100**, 3339 (1978).
- [28] K. Wade, *Chem. Comm.* 792 (1971).
- [29] R. Hoffmann, *Angew. Chem. Int. Ed.* **21**, 711 (1982).
- [30] G. Ciani, L. Garlaschelli, A. Sironi, and S. Martinengo, *Chem. Comm.* 563 (1981).
- [31] A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Comm.* 596 (1969).
- [32] W.N. Lipscomb, *Science* **153**, 373 (1966).
- [33] R.B. King, *Inorg. Chim. Acta* **49**, 237 (1981).
- [34] R.B. King, *Theor. Chim. Acta* **64**, 439 (1984).
- [35] R.B. King, *J. Am. Chem. Soc.* **94**, 95 (1972).
- [36] R. Rudolph and W.R. Pretzer, *Inorg. Chem.* **11**, 1974 (1972).
- [37] R.N. Grimes, *Ann. N.Y. Acad. Sci.* **239**, 180 (1974).
- [38] F.H. Carré, F.A. Cotton, and B.A. Frenz, *Inorg. Chem.* **15**, 380 (1976).
- [39] A. Fumagalli, T.F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B.T. Heaton, *J. Am. Chem. Soc.* **102**, 1740 (1980).
- [40] P. Chini, G. Longoni, and V.G. Albano, *Adv. Organometal. Chem.* **14**, 285 (1976).
- [41] V.G. Albano, P.L. Bellon, and G.F. Ciani, *Chem. Comm.* 1024 (1969).
- [42] V.G. Albano and P.L. Bellon, *J. Organometal. Chem.* **19**, 405 (1969).
- [43] S. Martinengo, A. Fumagalli, R. Bonfichi, G. Ciani, and A. Sironi, *Chem. Comm.* 825 (1982).
- [44] G. Ciani, A. Sironi, and S. Martinengo, *Chem. Comm.* 1757 (1985).

- [45] A. Fumagalli, S. Martinengo, G. Ciani, and A. Sironi, Chem. Comm. 453 (1983).
- [46] W.B. Pearson, "The Crystal Chemistry and Physics of Metals and Alloys"; Wiley-Interscience: New York, 1972.
- [47] V.G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W.M. Anker, Chem. Comm. 859 (1975).
- [48] V.G. Albano, G. Ciani, S. Martinengo, and A. Sironi, J. Chem. Soc. Dalton, 978 (1979).
- [49] G. Ciani, A. Sironi, and S. Martinengo, J. Chem. Soc. Dalton 519 (1981).

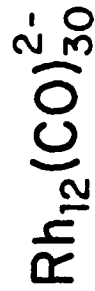
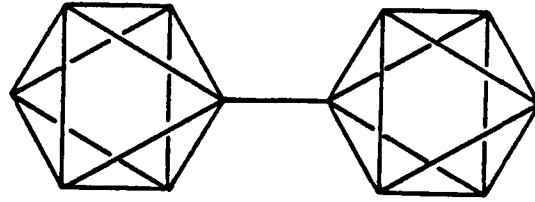
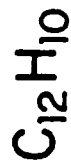
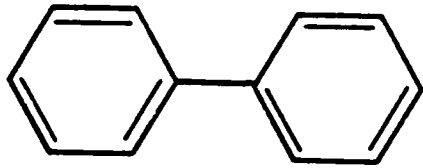
Figure 1: Analogies between the fusion of Rh_6 octahedra in rhodium carbonyl clusters and the fusion of benzene rings in planar polycyclic aromatic hydrocarbons.

Figure 2: The centered rhodium cuboctahedron found in the $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_5\text{-q}]^9-$ clusters; the center (interstitial) rhodium atom is enclosed in a square.

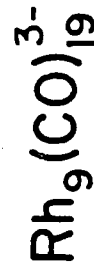
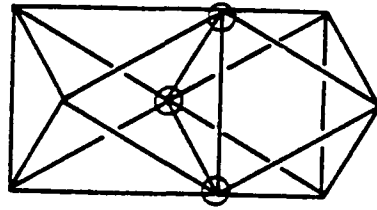
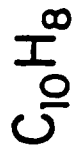
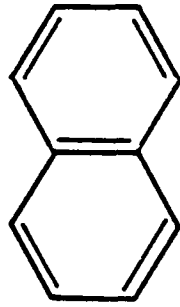
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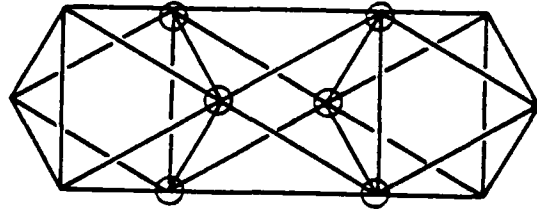
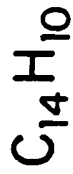
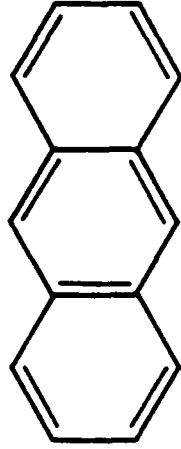
Biphenyl



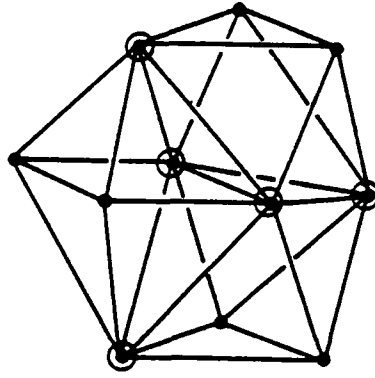
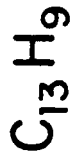
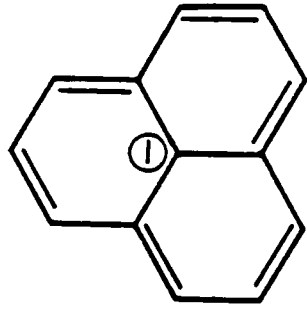
Naphthalene

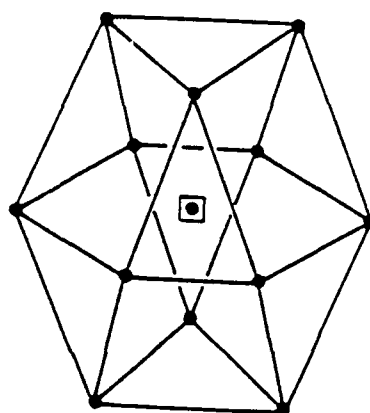


Anthracene



Perinaphthenide





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