Metal Cluster Topology.
4. Rhodium Carbonyl Clusters having Fused Polyhedra*

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Abstract

Previously discussed topological models of metal cluster bonding are now extended to the treatment of anionic rhodium carbonyl clusters having structures consisting of fused polyhedra. Examples of such rhodium carbonyl clusters built from fused octahedra include the 'biphenyl analogue' $[Rh_{12}(CO)_{30}]^{-2}$, the 'face-sharing naphthalene analogue' $[Rh_9(CO)_{19}]^{3-}$, and the 'perinaphthene analogue', $[Rh_{11}(CO)_{23}]^{3-}$. More complicated anionic rhodium carbonyl clusters treated in this paper include the $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ anions ($q = 2, 3, 4$) having an Rh_{13} centered cuboctahedron, the $[Rh_{14}(CO)_{25}H_{4-q}]^{q-}$ ($q = 3, 4$) and $[Rh_{14}(CO)_{26}]^{2-}$ anions based on a centered pentacapped cube, the $[Rh_{15}(CO)_{30}]^{3-}$ anion having an Rh_{15} centered 14-vertex deltahedron, the $[Rh_{15}(CO)_{27}]^{3-}$ anion having a tricapped centered 11-vertex polyhedron, the $[Rh_{17}(CO)_{30}]^{3-}$ anion having a tetracapped centered cuboctahedron, and the $[Rh_{22}(CO)_{37}]^{4-}$ anion having a hexacapped centered cuboctahedron fused to an octahedron so that the octahedron and the cuboctahedron share a triangular face. Analyses of the bonding topologies in $[Rh_9(CO)_{19}]^{3-}$, $[Rh_{17}(CO)_{30}]^{3-}$, and $[Rh_{22}(CO)_{37}]^{4-}$ indicate that a polyhedral network containing several fused globally delocalized polyhedral chambers will not necessarily have a multicenter core bond in the center of each such polyhedral chamber. This observation is of potential importance in extending topological models of metal cluster bonding to bulk metals.

1. Introduction

Since Wade's seminal paper in 1971 [2], the problem of the structure and bonding in discrete polyhedral metal clusters has been studied in considerable detail by diverse theoretical methods [3–9]. However, this extensive work still has relatively little to say about the relationship of metal cluster structures to the structures of bulk metals. In recent years this question has become very significant in view of the connection between homogeneous catalysis using metal clusters and heterogeneous catalysis on metal surfaces [10–12].

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. Naturally the third dimension increases considerably the complexity of the metal cluster → bulk metal fusion problem relative to the benzene → graphite problem. A major objective of the present paper is the interpretation of observations on large rhodium carbonyl clusters in ways that provide some insight into the much more complicated systematics of the fusion of discrete metal polyhedra into bulk metal structures.

Recently the systematics of the fusion of metal polyhedra has received attention from some of the prominent workers in the field. Perhaps the most striking of these recent discussions on the relationship between discrete metal clusters and bulk metal structures is the observation by Teo [13] that the Hume–Rothery rule [14] for electron-counting in brasses can be extended to the close packed high nuclearity metal clusters including the rhodium carbonyl derivatives discussed in this paper. This observation supports the idea that the bonding within discrete metal cluster polyhedra has similar essential features to the bonding in bulk metals. The present paper goes beyond the work of Teo [13] in providing topological interpretations for the electron counts in the large rhodium carbonyl clusters. Other workers who have recently discussed the problem of fusion of metal polyhedra include Mingos [15], and Slovokhotov and Struchkov [16].

The choice of rhodium carbonyl clusters as the objects of the present investigation relates to the following points:

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*For part 3 of this series, see ref. 1.

(1) The variety of known rhodium carbonyl clusters exhibiting structures having centered and/or fused metal polyhedra is greater than that of any other metal.

(2) All rhodium vertices in all rhodium carbonyl clusters use a spherical 18-electron sp^3d^5 bonding orbital manifold rather than the toroidal 16-electron sp^2d^5 and cylindrical 14-electron spd^5 bonding orbital manifolds used by the vertex atoms in many gold [17–19] clusters. This eliminates an important degree of freedom in the problem of metal cluster bonding thereby facilitating the development of meaningful bonding models.

2. Topological Considerations

There are two fundamentally different types of chemical bonding in metal clusters, namely edge-localized and globally delocalized bonding [5, 20]. 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 [21]. 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.

The details of the graph-theoretical model of the bonding in globally delocalized clusters have been presented elsewhere [5, 20, 22]. The metal vertices in such cluster polyhedra use three internal orbitals for the cluster bonding. Two of these internal orbitals, the twin internal orbitals, are used to form two-center surface bonds by overlapping with the twin internal orbitals of adjacent metal vertices. The third internal orbital, the unique internal orbital, forms a single n-center core bond by overlap at the center of the polyhedron with the unique internal orbitals of the metal atoms at the other vertices of the polyhedron. In a globally delocalized deltahedron (polyhedron having all triangular faces) the n two-center surface bonds require $2n$ skeletal electrons and the single n-center core bond requires 2 skeletal electrons thereby leading to the $2n + 2$ skeletal electron rule for globally delocalized deltahedral systems [2, 3, 5, 10, 22].

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 determines whether or not the bonding in the polyhedral cluster is edge-localized or globally delocalized [20]. 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 atoms [20] use three internal orbitals as noted above, 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 building three-dimensional delocalized metal clusters and bulk metals as planar carbon hexagons have in building fused planar aromatic systems including graphite. Therefore, a portion of this paper will deal with various ways of fusing rhodium octahedra.

A major focus of this paper is the development of viable schemes for counting ('bookkeeping') electrons in complicated rhodium carbonyl clusters. In these specific systems the following two electron-counting rules appear to be inviolate:

(1) Vertex rhodium atoms in these clusters always have the 18-electron configuration of the next rare gas, *i.e.*, they always use a 9-orbital spherical sp^3d^5 manifold rather than 8-orbital toroidal sp^2d^5 or 7-orbital cylindrical spd^5 manifolds [19].

(2) All carbonyl groups are two-electron donors regardless of whether they are terminal, edge-bridging, or face-bridging. Carbonyl groups donating four or six electrons are not found in rhodium carbonyl chemistry.

The apparent inviolability of these two rules facilitates the use of rhodium carbonyl clusters for developing the systematics of complicated metal cluster systems.

Many of the rhodium carbonyl clusters of interest have interstitial atoms or groups located in the center of the polyhedron. Most frequently such interstitial atoms are rhodium or carbon. An interstitial rhodium atom functions as a donor of nine skeletal electrons since all nine orbitals of its spherical sp^3d^5 bonding orbital manifold function as internal orbitals. Similarly, an interstitial carbon atom functions as a donor of four skeletal electrons since all four orbitals of its spherical sp^3 bonding orbital manifold function as internal orbitals. An interstitial RhS_2 group as found in $[Rh_{16}(CO)_{32}(RhS_2)]^{3-}$ [23] can be assumed to have two Rh–S single bonds which use four electrons from the three interstitial atoms. Since a neutral rhodium atom has nine valence electrons and a neutral sulfur atom has six valence electrons, an interstitial RhS_2 group is a donor of $(1)(9) + (2)(6) - (2)(2) = 17$ skeletal electrons.

Interstitial atoms have certain volume requirements for the surrounding polyhedron [24]. Thus an interstitial carbon atom cannot fit into a tetrahedron but fits into an octahedron as exemplified by $Ru_6(CO)_{17}C$ [25]. An interstitial transition metal such as rhodium cannot fit into an octahedron but fits into a twelve-vertex polyhedron. The volume of a poly-

hedron 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 [26–28]. For example, rupture of six edges in this manner from an icosahedron can give a cuboctahedron [26]. An n-vertex non-deltahedron derived from an n-vertex deltahedron by volume expansion through edge rupture in this manner and containing an interstitial atom may function as a globally delocalized $2n + 2$ skeletal electron system like the n-vertex deltahedron of the polyhedron. Most frequently an interstitial atom may function as a globally delocalized $2n + 2$ skeletal electron system like the n-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 [20, 22, 29]; such polyhedra generate nido and arachno systems in the boron hydrides [3, 5, 30]. In a centered pseudodeltahedron the interstitial atom in the center may be regarded as plugging up the surface holes arising from the non-triangular faces so that globally delocalized bonding is possible. The effect of an interstitial (central) atom in converting a deltahedron into a pseudodeltahedron is potentially important in understanding the differences between the polyhedra found in isolated molecular clusters and the polyhedra found in infinite lattices such as metallic structures. The best example of this is the 12-vertex case where a single interstitial transition metal such as rhodium in $[Rh_{12}(CO)_{24}H_3(Rh)]^{2-}$ [31] can distort the icosahedron found in uncentered clusters (a deltahedron, e.g. $B_{12}H_{12}{}^{2-}$) into a cuboctahedron (a pseudodeltahedron) through six parallel diamond-square processes. This destroys the fivefold rotation axis of the icosahedron although the resulting cuboctahedron has relatively high octahedral symmetry. This destruction of the fivefold axis of the iscosahedron upon introduction of an interstitial atom is suggestive of the inability to pack identical objects having a fivefold rotation axis into an infinite lattice [32].

Previous papers [5, 20] have discussed capping one or more (triangular) faces of a central deltahedron to generate an n-vertex electron-poor polyhedral cluster having less than $2n + 2$ apparent skeletal electrons. If the central deltahedron is an octahedron or other deltahedron having no degree three vertices, than 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 polyhedral regions (*i.e.*, the tetrahedral chamber formed by the cap).

Centered pseudodeltahedral clusters having quadrilateral faces can have caps on one or more of these faces. Such a cap is a vertex of degree four and generates a tetragonal pyramidal chamber. Such a chamber exhibits globally delocalized bonding including a five-center core bond provided that the capping atom uses the normal three internal orbitals for the skeletal bonding. The globally delocalized bonding in the tetragonal pyramidal chamber formed by capping a quadrilateral face contrasts with the edge-localized bonding in the tetrahedral chamber formed by capping a triangular face. Furthermore, consideration later in this paper of specific centered pseudodeltahedral rhodium carbonyl clusters having several capped quadrilateral faces shows that the globally delocalized bonding in the tetragonal pyramidal chambers can destroy the core bond of the central pseudodeltahedron if the unique internal orbitals of too many of its vertex atoms are needed for the core bonds of the tetragonal pyramidal chambers.

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. 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 to the central polyhedron. Since we are considering only 18-electron complexes in which all nine orbitals of the sp^3d^5 bonding orbital manifold contain electron pairs from some source, 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 paper [5, 20] that capping a triangular face contributes skeletal electrons to a central polyhedron without contributing any new bonding orbitals; such a statement summarizes the
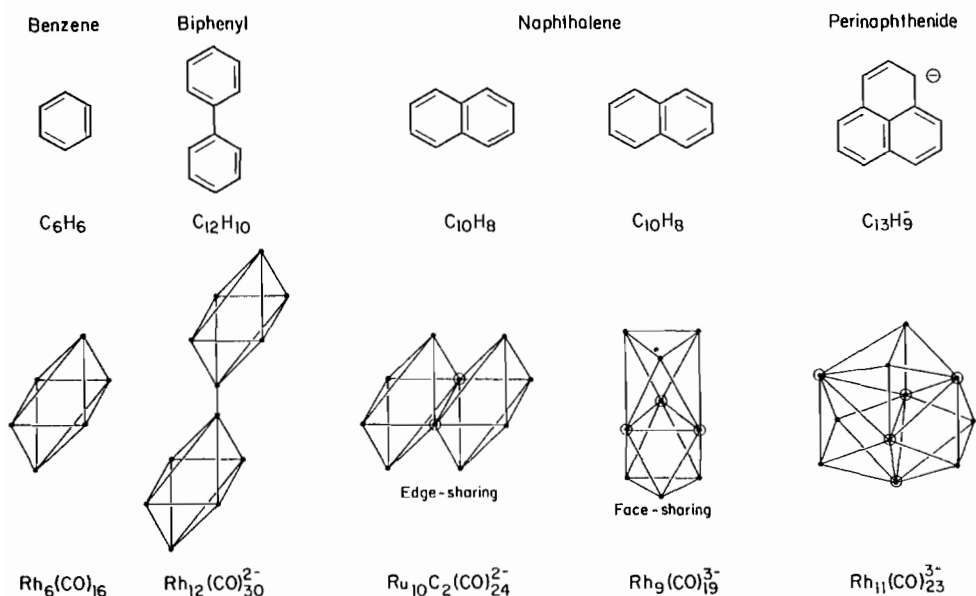
Fig. 1. Analogies between the fusion of Rh_6 octahedra in rhodium carbonyl clusters and the fusion of benzene rings in planar polycyclic aromatic hydrocarbons.

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. Either way the final result is the same.

The seemingly different process of capping a quadrilateral face of a centered pseudodeltahedron thereby adding a delocalized tetragonal pyramidal chamber also has the net result of requiring six additional skeletal electrons for each such cap. A tetragonal pyramid is a nido polyhedron requiring $2n + 4 = (2)(5) + 4 = 14$ skeletal electrons since n, the number of vertices, is 5. In this case the surface bonding of the central centered pseudodeltahedron already accounts for eight of these electrons in the four surface bonds involving the four vertex atoms of the face being capped. This leaves $14 - 8 = 6$ additional skeletal electrons required for each capped quadilateral face. Remember, however, that capping a quadrilateral face in contrast to capping a triangular face may disturb the core bonding of the centered pseudodeltahedron so that the net effect on electron counting can be considerably more complicated as illustrated by $[Rh_{17}(CO)_{30}]^{3-}$ discussed later.

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 tetra-

hedron fused to the deltahedron so that a triangular face is shared by both polyhedra. Similarly, a centered pseudodeltahedron having a capped quadrilateral face can be regarded as a tetragonal pyramid fused to the centered pseudodeltahedron so that the quadrilateral face is shared by both polyhedra. Thus the capped polyhedra discussed in this as well as in previous papers [5, 20] may be regarded as specific types of fused polyhedra.

Many planar aromatic hydrocarbons consist of fused planar hexagonal benzene rings, e.g., naphthalene, phenanthrene, and perinaphthenide. Similarly, the regular octahedron can be a building block for a variety of three-dimensional clusters, some of which can be viewed as analogues of naphthalene or perinaphthenide (Fig. 1). Note, however, the possibilities for varied structures for fusing two delocalized octahedra are richer than those obtained by fusing two planar hexagonal rings. Thus the only way of fusing two benzene rings involves edge sharing (*i.e.*, naphthalene), whereas two octahedra can be fused to share a vertex, edge, or face (Fig. 1).

3. 'Simple' Rhodium Carbonyl Clusters

Before treating the rhodium carbonyl clusters containing fused and/or centered polyhedra that are the main object of this paper, it is instructive to review the 'simple' rhodium carbonyl clusters based on a single uncentered polyhedron. In this connection the following fundamental systems are of interest:

(1) $Rh_4(CO)_{12}$ and Substitution Products [33]

These clusters form edge-localized tetrahedra having the required 12 skeletal electrons since each $Rh(CO)_3$ vertex contributes three skeletal electrons.

(2) $[Rh_5(CO)_{15}]^-$ [34]

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 [20]. Note that an $Rh(CO)_3$ 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) $Rh_6(CO)_{16}$ and Substitution Products [35]

These clusters form globally delocalized octahedra having the required 14 skeletal electrons. The prototype $Rh_6(CO)_{16}$ was the first octahedral cluster metal carbonyl to be identified structurally [36].

(4) $[Rh_7(CO)_{16}]^{3-}$ [37]

This cluster forms a capped octahedron receiving 7 skeletal electrons from seven $Rh(CO)_2$ units, 4 more skeletal electrons from the two 'extra' carbonyl groups, and three more skeletal electrons from the -3 charge on the anion to give the 14 skeletal electrons required by the globally delocalized center octahedron.

4. Rhodium Carbonyl Clusters Having Fused Octahedra

The modes of fusion of rhodium (and, in at least one case, ruthenium) carbonyl octahedra can conveniently be classified by the trivial name of the polycyclic benzenoid hydrocarbon having a similar configuration of its planar hexagon building blocks. A limitation, however, of this crude classification system is that the topological variety of the (three-dimensional) fusion of octahedra is much richer than that of the (two-dimensional) fusion of hexagons so that additional descriptors become necessary in some cases.

The following metal carbonyl clusters exemplify different ways of fusing octahedra and the applicable electron-counting procedures. These systems are illustrated schematically in Fig. 1. Mingos [15] has a different, but equivalent scheme for counting electrons in some of these systems. However, application of his rules is somewhat obscure for $[Rh_9-(CO)_{19}]^{3-}$ and difficult for $[Rh_{11}(CO)_{23}]^{3-}$.

(1) Biphenyl Analogue, $[Rh_{12}(CO)_{30}]^{2-}$ [38]

The following electron counting scheme generates the 26 skeletal electrons suggestive of a regular icosahedron analogous to $B_{12}H_{12}^{2-}$ [39]:

12 $Rh(CO)_2$ vertices: (12)(1)	= 12 electrons
6 'extra' CO groups: (6)(2)	= 12 electrons
-2 charge	= 2 electrons
Total skeletal electrons	= 26 electrons

However, two octahedra joined by a rhodium—rhodium bond require 28 skeletal electrons, namely 14 for each octahedron. The interoctahedral rhodium—rhodium bond effectively makes one extra skeletal electron available for each Rh_6 octahedron. The rhodium atoms forming this two-center bond each use an extra internal orbital and therefore together generate four 'extra' bonding electrons from two previously non-bonding electron pairs. However, only two of these four new bonding electrons are required for the interoctahedral rhodium—rhodium bond thereby generating two extra skeletal electrons for the two Rh_6 octahedra, *i.e.* one extra skeletal electron for each Rh_6 octahedron as noted above.

(2) Edge-sharing Naphthalene Analogue, $[Ru_{10}C_2-(CO)_{24}]^{2-}$ [39]

This ruthenium carbonyl cluster consists of two globally delocalized octahedra sharing an edge and with a carbon atom in the center of each octahedron. The two ruthenium atoms of the shared edge use five internal orbitals whereas the other eight ruthenium atoms use the normal three internal orbitals. The electron counting scheme for $[Ru_{10}C_2(CO)_{24}]^{2-}$ can be represented as follows:

(a) Source of skeletal electrons:

8 $Ru(CO)_2$ groups using 3 internal orbitals	= 0 electrons
2 $Ru(CO)_2$ groups using 5 internal orbitals: (2)(4)	= 8 electrons
4 'extra' CO groups: (4)(2)	= 8 electrons
2 interstitial carbon atoms: (2)(4)	= 8 electrons
Total available skeletal electrons	= 24 electrons

(b) Use of skeletal electrons:

10 Ru—Ru surface bonds	20 electrons
2 6-center (K_6) core bonds	4 electrons
Total skeletal electrons required	24 electrons

(3) Face-sharing Naphthalene Analogue, $[Rh_9-(CO)_{19}]^{3-}$ [40]

A face-sharing pair of octahedra (Fig. 1) is closely related to the 4,4,4-tricapped trigonal prism, which is the standard nine-vertex deltahedron [22, 41].
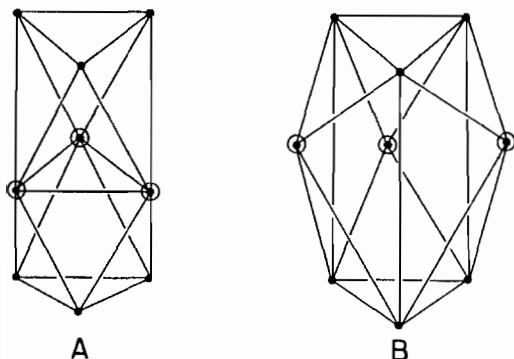
Fig. 2. Relationship between the face-sharing pair of octahedra found in $[Rh_9(CO)_{19}]^{3-}$ (A: circled vertices are those in the face common to both octahedra) and the 4,4,4-tricapped trigonal prism (B: the circled vertices are the three caps).

Both have 9 vertices, 21 edges, and 14 faces (Fig. 2). In the 4,4,4-tricapped trigonal prism (B in Fig. 2), three of the edges connect directly a vertex on the top triangle with one on the bottom triangle and there are no edges connecting pairs of capping vertices. Six vertices have degree 5 and the three capping vertices have degree 4. However, in a face-sharing pair of octahedra (A in Fig. 2) there are no edges directly connecting vertices on the 'top' triangle with vertices on the 'bottom' triangle but formation of the 'middle' triangle (*i.e.*, the face shared by both octahedra) involves three additional edges not found in the 4,4,4-tricapped trigonal prism. Six vertices have degree 4 and the three vertices common to both octahedra have degree 6.

Because of the close relationship of the face-sharing pair of octahedra to the 4,4,4-tricapped trigonal prism (Fig. 2), the electron counting schemes are similar except that the three vertex atoms of the face common to both octahedra use four rather than the normal three internal orbitals. Topologically a face-sharing octahedral pair can be regarded as homeomorphic to a pinched sphere.

These considerations suggest the following electron-counting scheme for $[Rh_9(CO)_{19}]^{3-}$:

(a) Source of skeletal electrons:

6 Rh(CO)$_2$ groups using 3 internal orbitals: (6)(1)	=	6 electrons
3 Rh(CO)$_2$ groups using 4 internal orbitals (3)(3)	=	9 electrons
1 'extra' CO group: (1)(2)	=	2 electrons
−3 charge	=	3 electrons
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	2 electrons
Total skeletal electrons required	20 electrons

Note that the face-sharing pair of octahedra found in $[Rh_9(CO)_{19}]^{3-}$ has only one core bond rather than two core bonds, one for each octahedron. This is the simplest illustration how fusion of two globally delocalized polyhedra can lead to fewer multicenter core bonds than those found in the individual polyhedra. More complicated examples of this phenomenon will be encountered later.

(4) Perinaphthene Analogue, $[Rh_{11}(CO)_{23}]^{3-}$ [42]

The cluster $[Rh_{11}(CO)_{23}]^{3-}$ consists of three fused octahedra sharing a total of five vertices represented by the following '[1,1,1]-propellane' graph (see also Fig. 1):
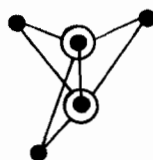
The two circled vertices of degree 4 in the above graph are shared by all three octahedra whereas the three uncircled vertices of degree 2 are shared by only two of the three octahedra. The edge connecting the two circled vertices is called the hidden edge [43] in $[Rh_{11}(CO)_{23}]^{3-}$ and represents a two-center bond in addition to the three core bonds at the centers of the three octahedra and the 11 surface bonds representing pairwise interactions along the surface of the cluster. The six rhodium atoms unique to a single octahedron are considered to use 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. Also note that Rh(CO)$_2$ vertices can be regarded as donors of 1, 3, or 5 skeletal electrons as they use 3, 4, or 5 internal orbitals, respectively. As usual each additional internal orbital adds an additional electron pair to the skeletal bonding.

These considerations suggest the following electron-counting scheme for $[Rh_{11}(CO)_{23}]^{3-}$:

(a) Source of skeletal electrons:

6 Rh(CO)$_2$ groups using 3 internal orbitals: (6)(1)	=	6 electrons
3 Rh(CO)$_2$ groups using 4 internal orbitals: (3)(3)	=	9 electrons
2 Rh(CO)$_2$ groups using 5 internal orbitals: (2)(5)	=	10 electrons
1 'extra' CO group: (1)(2)	=	2 electrons
−3 charge		3 electrons
Total available skeletal electrons		30 electrons

$[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ $[Rh_{14}(CO)_{26}]^{2-}$ $[Rh_{15}(CO)_{30}]^{3-}$

$[Rh_{15}(CO)_{27}]^{3-}$ $[Rh_{17}(CO)_{30}]^{3-}$ $[Rh_{22}(CO)_{37}]^{4-}$
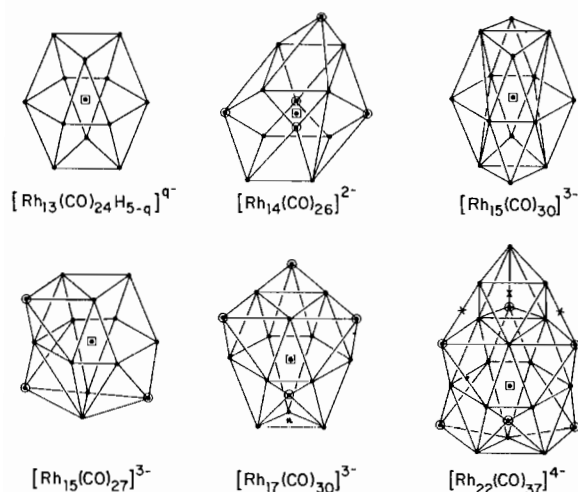
Fig. 3. Arrangements of the rhodium atoms in the centered rhodium carbonyl clusters discussed in this paper. The center rhodium atoms are enclosed in squares and the capping rhodium atoms are enclosed in circles.

(b) Use of skeletal electrons:

11 Rh–Rh surface bonds: (11)(2)	=	22 electrons
3 core bonds in the three octahedral cavities: (3)(2)	=	6 electrons
1 two-center bond along the 'hidden edge': (1)(2)	=	2 electrons
Total skeletal electrons required		**30 electrons**

5. Centered Rhodium Carbonyl Clusters

A variety of interesting clusters are known which consist 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 (b.c.c.) or hexagonal close-packed (h.c.p.) metal structures [44]. A frequently encountered feature of these systems is an Rh_{13} centered cuboctahedron. Some structures based on this unit discussed below are illustrated in Fig. 3.

The following centered rhodium carbonyl clusters have been well characterized including structure determinations by X-ray diffraction methods.

(1) $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ (q = 2,3,4) [31, 45, 46]

These are the prototypical Rh_{13} centered cuboctahedral systems. These systems have the correct electron count for a globally delocalized Rh_{12} pseudodeltahedron having the thirteenth rhodium atom in the center. The electron counting for these systems can be summarized as follows:

(a) Source of skeletal electrons:

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

(b) Use of skeletal electrons:

12 surface bonds: (12)(2)	=	24 electrons
1 core bond: (1)(2)	=	2 electrons
Total skeletal electrons required		**26 electrons**

(2) $[Rh_{14}(CO)_{25}H_{4-q}]^{q-}$ (q = 3,4) [47–49] and $[Rh_{14}(CO)_{26}]^{2-}$ [50]

This isoelectronic series of Rh_{14} clusters is based on a centered pentacapped cube (Fig. 3). The volume requirement of the center rhodium atom swells the cube so that one edge-related pair of rhodium atoms is stretched beyond bonding distance (e.g., 3.697 Å in $[Rh_{14}(CO)_{25}H]^{3-}$) and two other edge-related rhodium pairs are stretched to relatively long bonding distances (e.g., 3.352 Å in $[Rh_{14}(CO)_{25}H]^{3-}$). Nevertheless, the 24 skeletal electrons required for edge-localized bonding in a cube can be obtained as follows for $[Rh_{14}(CO)_{26}]^{2-}$:

13 Rh(CO)$_2$ vertices using 3 internal orbitals: (13)(1)	=	13 electrons
Center Rh atom		9 electrons
−2 charge		2 electrons
Total skeletal electrons		**24 electrons**

A similar electron-counting scheme is possible for the isoelectronic systems $[Rh_{14}(CO)_{25}H_{4-q}]^{q-}$. Note that these systems are four skeletal electrons short of the 28 skeletal electrons required for a centered 13-vertex pseudodeltahedron thereby providing a crude rationalization of the unusual pentacapped cube structure.

(3) $[Rh_{15}(CO)_{30}]^{3-}$ [51]

This rhodium cluster has the 30 skeletal electrons required for the observed centered 14-vertex deltahedral geometry [51]. These electrons arise from the following sources:

14 Rh(CO)$_2$ vertices using 3 internal orbitals: (14)(1)	=	14 electrons
2 'extra' CO groups		4 electrons
Center Rh atom		9 electrons
−3 charge		3 electrons
Total skeletal electrons		**30 electrons**

(4) [Rh₁₅(CO)₂₇]³⁻ [52]

(4) [Rh_{15}(CO)_{27}]^{3-} [52]

This rhodium cluster has six electrons less than the $[Rh_{15}(CO)_{30}]^{3-}$ cluster discussed above. The structure of this cluster [52] can be interpreted as a centered tricapped 11-vertex 263 stack [53]. The eleven rhodium vertices of the 263 stack function as a pseudodeltahedron in that they participate in globally delocalized bonding. Metric evidence for this interpretation lies in the fact that eleven of the peripheral rhodium atoms are within 3.00 Å of the center rhodium atom but the remaining three peripheral rhodium atoms are further from the center rhodium atoms (3.38 Å, 3.52 Å, and 3.91 Å) [52] and therefore may be regarded as caps. The required 24 skeletal electrons for a tricapped centered 11-vertex pseudodeltahedron can be obtained in the following straightforward manner:

14 Rh(CO)₂ vertices using 3 internal orbitals: (14)(1)	14 electrons
'Missing' CO group	−2 electrons
Center Rh atom	9 electrons
−3 charge	3 electrons
Total skeletal electrons	24 electrons

(5) [Rh₁₇(CO)₃₀]³⁻ [54]

The structure of this rhodium cluster (Fig. 3) is a tetracapped centered cuboctahedron, *i.e.*, a tetracapped version of the $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ systems discussed above. The following electron counting scheme suggests that the cuboctahedron in $[Rh_{17}(CO)_{30}]^{3-}$ has only 24 skeletal electrons rather than the 26 skeletal electrons required for a globally delocalized 12-vertex pseudodeltahedron:

16 Rh(CO)₂ vertices using 3 internal orbitals: (16)(1)	16 electrons
2 'missing' CO groups	−4 electrons
Center Rh atom	9 electrons
−3 charge	3 electrons
Total skeletal electrons	24 electrons

This discrepancy can be rationalized by assuming that the multicenter core bond is absent in the cuboctahedron since 11 of its 12 vertex atoms can direct their unique internal orbitals towards the center of one of the four square pyramidal chambers formed by the four caps. This is a good example of how fusion of globally delocalized polyhedra (a cuboctahedron and four square pyramids in this case) can lead to systems having fewer multicenter core bonds than the number of individual globally delocalized polyhedra.

(6) [Rh₂₂(CO)₃₇]⁴⁻ [55]

The structure of this rhodium cluster, the largest rhodium carbonyl cluster which has been definitively characterized crystallographically, is a hexacapped centered cuboctahedron fused to an octahedron so that the octahedron and the cuboctahedron share a triangular face (Fig. 3). This configuration leads to three exopolyhedral rhodium–rhodium bonds (marked X in Fig. 3) connecting the three rhodium atoms of the octahedron which are not in the face shared with the cuboctahedron to the nearest rhodium atoms capping rectangular faces of the cuboctahedron. The six rhodium atoms forming these exopolyhedral rhodium–rhodium bonds use four internal orbitals. The three rhodium atoms in the triangular face shared by the cuboctahedron and the octahedron use five internal orbitals. The remaining 12 peripheral rhodium atoms use the three internal orbitals typical for vertex atoms of globally delocalized deltahedra and pseudodeltahedra.

These general considerations lead to the following electron counting scheme for $[Rh_{22}(CO)_{37}]^{4-}$:

(a) Source of skeletal electrons

12 Rh(CO)₂ vertices using 3 internal orbitals (12)(1)	12 electrons
6 Rh(CO)₂ vertices using 4 internal orbitals: (6)(3)	18 electrons
3 Rh(CO)₂ vertices using 5 internal orbitals: (3)(5)	15 electrons
Deficiency of 5 CO groups	−10 electrons
Center Rh atom	9 electrons
−4 charge	4 electrons
Total available skeletal electrons	48 electrons

(b) Use of skeletal electrons

15 bonds on the surface of the Rh₁₅ cuboctahedron–octahedron face-fused pair	30 electrons
3 exopolyhedral Rh–Rh bonds	6 electrons
6 multicenter core bonds	12 electrons
Total skeletal electrons required	48 electrons

Symmetry considerations suggest that the six multicenter core bonds in the above bonding model are located in the centers of the six tetragonal pyramidal chambers formed by the six caps on the quadrilateral faces of the cuboctahedron. The centers of the cuboctahedron and the octahedron therefore do not contain multicenter core bonds. The $[Rh_{22}(CO)_{37}]^{4-}$ system, like the $[Rh_9(CO)_{19}]^{3-}$ and $[Rh_{17}(CO)_{30}]^{3-}$ systems discussed above, represents an example of a system of fused globally delocalized polyhedra in which each such polyhedron does not contain a multicenter core bond.

Summary

The fused polyhedral rhodium carbonyl clusters discussed in this paper are important since they rep-

resent transitions between single discrete molecular cluster polyhedra and bulk metal structures. More specifically, analyses of the bonding topologies in $[Rh_9(CO)_{19}]^{3-}$ consisting of a face-sharing octahedral pair, $[Rh_{17}(CO)_{30}]^{3-}$ consisting of a centered tetracapped cuboctahedron, and $[Rh_{22}(CO)_{37}]^{4-}$ consisting of a octahedron sharing a face with a hexacapped cuboctahedron all indicate that a polyhedral network containing several fused globally delocalized polyhedral chambers will not necessarily have a multicenter core bond in the center of each such polyhedral chamber. This idea undoubtedly will prove crucial in extending topological models of metal cluster bonding to bulk metals. In addition, many of the most complicated fused rhodium carbonyl clusters discussed in this paper (Fig. 3) contain an Rh_{13} centered cuboctahedral structural unit which represents a fragment of the hexagonal close packed structure found in many bulk metals [44].

Acknowledgement

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