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Metal cluster topology

XV *. Rafting from the triangle to the octahedron in osmium carbonyl cluster chemistry

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Abstract

Osmium carbonyl clusters $Os_m(CO)_c$ containing from three to seven osmium atoms, each using nine-orbital spherical sp^3d^5 manifolds can be constructed from networks of osmium triangles with b edge-localized Os–Os bonds where $c = 5m - b$. Homologous series of such networks can be generated from a simple Os_3 triangle by the following processes: (1) bridging an edge of a triangle with a new vertex to give *rafts* of the general stoichiometry $Os_m(CO)_{3m+3}$, such as the known $Os_4(CO)_{15}$, $Os_5(CO)_{18}$ and $Os_6(CO)_{21}$ in which adjacent triangles share edges; (2) bridging a vertex of a triangle with a new edge to give *bow ties* of the general stoichiometry $Os_{2k+1}(CO)_{7k+5}$, such as the known $Os_5(CO)_{19}$ in which adjacent triangles share vertices; (3) capping a triangular face with a new vertex to give chains of tetrahedra of the general stoichiometry $Os_m(CO)_{2m+6}$, such as the known $Os_5(CO)_{16}$ and $Os_6(CO)_{18}$ in which adjacent tetrahedra share faces. Members of each of these homologous series can be represented by their *dualist graphs* which have vertices in the centers of each triangle in the case of rafts and bow ties, and vertices in the centers of each tetrahedron in the case of chains of tetrahedra, with pairs of vertices connected by an edge if the corresponding triangles share edges or vertices or if the corresponding tetrahedra share faces, respectively. The dualist graphs of the rafts and bow ties have a one-to-one correspondence with various types of planar sp^2 carbon networks, whereas the dualist graphs of the chains of tetrahedra have a one-to-one correspondence with acyclic saturated aliphatic hydrocarbons C_nH_{2n+2}. A periodic table of neutral binary osmium carbonyl clusters can be constructed in which possible stoichiometries are listed in an array in which one dimension is the number of metal atoms and the other dimension the number of metal–metal bonds. Replacement of an osmium atom with a spherical sp^3d^5 manifold by a platinum atom with a toroidal sp^2d^5 manifold in a stable metal cluster carbonyl results in the reduction of the number of carbonyl groups by two for each such substitution as exemplified by the pairs of stable compounds $Os_3(CO)_{12}/Os_2Pt(CO)_{10}$ and $Os_5(CO)_{18}/Os_3Pt_2(CO)_{14}$.

Key words: Topology; Cluster; Osmium; Platinum

1. Introduction

During the past two decades the research group headed by Johnson and Lewis has discovered an extensive series of osmium carbonyl clusters and has determined their structures by X-ray diffraction methods. In 1986, the author [2] used osmium cluster carbonyl chemistry to illustrate graph-theory derived methods for the study of structure and bonding in metal clusters with a particular emphasis on structures constructed from delocalized Os_6 octahedra. Since that time, further advances in osmium cluster carbonyl chemistry by the group of Johnson and Lewis as well as the group of Pomeroy have resulted in the discovery of numerous osmium cluster carbonyls constructed from networks of Os_3 triangles. This article examines the properties of such networks of Os_3 triangles using ideas at least distantly related to those developed by Dias [3] for the networks of C_6 hexagons found in benzenoid hydrocarbons. Of particular interest is the examination of 'growth' sequences leading from a simple Os_3 triangle such as that found in the binary carbonyl $Os_3(CO)_{12}$ through networks of such triangles including the raft-

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like planar cluster $Os_6(CO)_{21}$ to larger osmium clusters containing delocalized octahedral cavities. This paper will also discuss the effect of substituting platinum for osmium in some mixed platinum–osmium carbonyl clusters studied by Adams and coworkers.

2. Background

The topology of chemical bonding can be represented by a graph in which the vertices correspond to atoms (molecular graph) or orbitals (orbital network graph) participating in the bonding and the edges correspond to bonding relationships. The eigenvalues x_k of the adjacency matrix of such a graph are related to the Hückel theory molecular orbital energies E_k and the Hückel parameters α and β by the following equation [4,5]:

$$E_k = \frac{\alpha + x_k\beta}{1 + x_k S} \qquad (1)$$

Positive and negative eigenvalues x thus correspond to bonding and antibonding orbitals, respectively.

The two extreme types of chemical bonding in metal clusters may be called *edge-localized* and *globally-delocalized*. An edge-localized polyhedron has two-electron two-center bonds along each edges of the polyhedron and is favored when the numbers of internal orbitals of the vertex atoms match the vertex degrees where the *degree* of a vertex is defined as the number of edges meeting at that vertex. Structures constructed from Os_3 triangles without any octahedral cavities have such edge-localized bonding. A globally delocalized polyhedron has a multicenter core bond in the center of the polyhedron and is favored when the numbers of internal orbitals do not match the vertex degrees. The octahedron, which has all vertices of degree four, is the smallest polyhedron which can exhibit globally delocalized bonding.

Consider an $Os_m(CO)_c$ cluster in which the metal network has b Os–Os bonds. The minimum number of Os–Os bonds is $m - 1$ corresponding to an Os_m chain with no Os_n rings ($n \leq m$). The minimum number of Os–Os bonds for a cyclic structure is m corresponding to an Os_m polygon. The maximum number of Os–Os bonds is $b = 3m - 6$ corresponding to a deltahedron with m vertices where a *deltahedron* is a polyhedron in which all faces are triangles. Since each osmium atom needs a total of 10 electrons to attain the favored 18-electron noble gas configuration, the number of CO groups c in a cluster of stoichiometry $Os_m(CO)_c$ is $5m - b$.

The effect of substituting one or more osmium atoms by platinum atoms in a mixed metal carbonyl cluster is non-trivial since platinum vertices use a toroidal sp^2d^5 bonding orbital manifold in contrast to the spherical sp^3d^5 bonding orbital manifold used by osmium in all of its metal carbonyl clusters. This relates to the observation by Nyholm [6] as early as 1961 that one or two of the outer p orbitals in the late transition metals, including platinum, are shifted to such high energies that they no longer participate in the chemical bonding and the accessible spd valence orbital manifold is no longer spherical (isotropic). If one p orbital is so shifted to become antibonding, then the accessible spd orbital manifold contains only eight orbitals (sp^2d^5) and has the geometry of a torus or doughnut (Fig. 1). The 'missing' p orbital is responsible for the hole in the doughnut. This toroidal sp^2d^5 manifold can bond only in the two dimensions of the plane of the ring of the torus. Filling this sp^2d^5 manifold of eight orbitals with electrons leads to the 16-electron configuration found in square planar complexes of the d^8 transition metals such as Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II} and Au^{III}. The locations of the four ligands in these square planar complexes can be considered to be points on the surface of the torus (Fig. 1) corresponding to the sp^2d^5 manifold. The toroidal sp^2d^5 manifold can also lead to trigonal planar and pentagonal planar coordination for three- and five-coordinate complexes, respectively (Fig. 1). The x, y and z axes for a toroidal sp^2d^5 manifold are conventionally chosen so that the missing p orbital is the p_z orbital. Platinum atoms in metal carbonyl clusters, including those discussed in this paper, often use a toroidal sp^2d^5 manifold.

3. Homologous series of triangulated networks

The following three homologous series of triangulated networks can be generated from a simple triangle:

(1) Bridging an edge of a triangle with a new vertex to give *rafts* in which adjacent triangles share edges

Toroidal Trigonal Planar

Toroidal Square Planar

Toroidal Pentagonal Planar

Fig. 1. Trigonal planar, square planar and pentagonal planar bonding of toroidal bonding orbital manifolds such as those of platinum vertices in mixed osmium–platinum carbonyls.

TABLE 1. Homologous series of triangulated networks in osmium carbonyl chemistry

Homologous series	General formula	CO groups/ additional Os	Known examples
Rafts	$Os_k(CO)_{3k+3}$	3	$Os_4(CO)_{15}$, $Os_5(CO)_{18}$, $Os_6(CO)_{21}$
Bow ties	$Os_{2k+1}(CO)_{7k+5}$	3.5	$Os_5(CO)_{19}$
Chains of Tetrahedra	$Os_k(CO)_{2k+6}$	2	$Os_4(CO)_{14}$, $Os_5(CO)_{16}$, $Os_6(CO)_{18}$

(2) Bridging a vertex of a triangle with a new edge to give *bow ties* in which adjacent triangles share vertices
(3) Capping a triangular face with a new vertex to give chains of tetrahedra in which adjacent tetrahedra share faces.

Some of the important features of these three homologous series are depicted in Table 1.

3.1. Rafts (Fig. 2)

Planar *rafts* can be constructed by bridging an edge of a triangle by a new vertex (Fig. 2). A type of *dualist graph* for a raft has a vertex in the center of each triangle of the raft; two vertices of the dualist graph are connected by an edge if and only if the corresponding triangles share an edge (Fig. 2). Rafts can be classified as linear or branched depending upon whether their dualist graphs are straight or branched chains. The concept of a dualist graph relates rafts to *acyclic* networks of sp^2-hybridized carbon atoms such as those studied by the author more than 15 years ago [7,8]. The following points are of interest concerning the binary osmium cluster carbonyl rafts depicted in Fig. 2:

(1) The formulas of the osmium carbonyl rafts are $Os_k(CO)_{3k+3}$.

(2) The first possibility of isomerism of linear versus branched rafts occurs with an Os_6 cluster. Branched rafts appear to be preferred as exemplified by the structures of $Os_6(CO)_{21}$ and its substitution products.

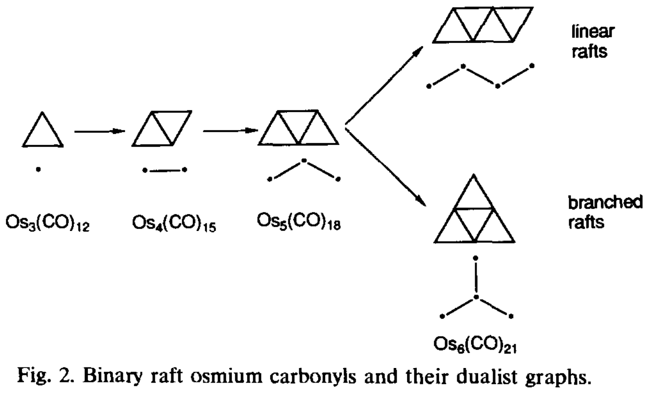

Fig. 2. Binary raft osmium carbonyls and their dualist graphs.

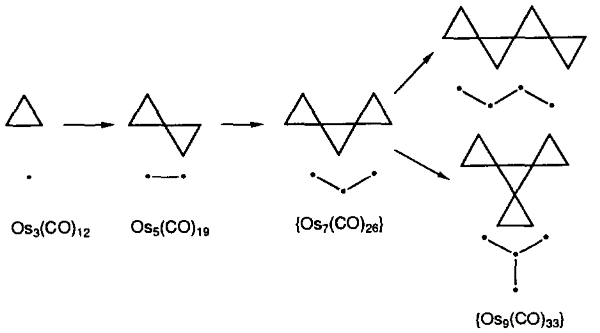

Fig. 3. Binary bow tie osmium carbonyl clusters and their dualist graphs. The formulas of unknown bow tie osmium carbonyl derivatives are enclosed in braces { }.

3.2. Bow ties (Fig. 3)

Bow ties can be constructed by bridging a vertex of a triangle by a new edge (Fig. 3). A type of *dualist graph* for a bow tie can be defined in a manner analogous to that of a raft (see above) (Fig. 3). Dualist graphs of bow ties, like those of rafts, have a one-to-one correspondence with networks of sp^2-hybridized carbon atoms not containing three-membered rings. Bow ties can be classified as linear, branched or cyclic depending upon whether their dualist graphs are straight chains, branched chains or contain cycles. The following points are of interest concerning the binary osmium cluster carbonyl rafts depicted in Fig. 3:

(1) All bow ties have an odd number of vertices.

(2) The formulas of the osmium carbonyl bow ties are $Os_{2k+1}(CO)_{7k+5}$.

(3) The first possibility of isomerism of linear versus branched bow ties occurs with an Os_9 cluster.

Osmium carbonyl bow ties appear to be less stable than rafts because of the smaller number of edges and resulting higher CO/Os ratio. Thus, the only known osmium carbonyl bow tie is $Os_5(CO)_{19}$.

3.3. Chains of tetrahedra (Fig. 4)

The final fundamental type of homologous series of triangle networks is the chain of tetrahedra of which the tetrahedron, trigonal bipyramid, and bicapped tetrahedron are the first members (Fig. 4). A type of *dualist graph* for a chain of tetrahedra has a vertex in the center of each tetrahedron of the chain; two vertices of the dualist graph are connected by an edge if and only if the corresponding tetrahedra share a face (Fig. 4). A dualist graph of a chain of tetrahedra can have vertices of degree 4 corresponding to four caps on

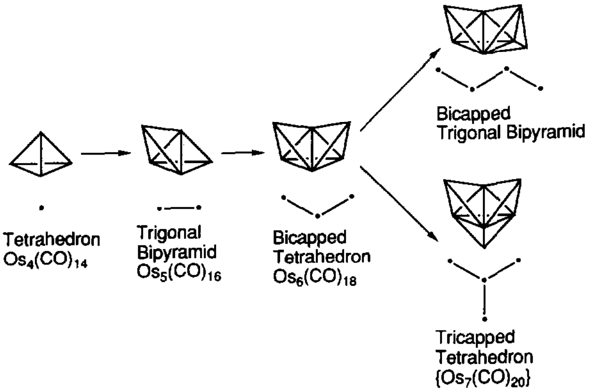

Fig. 4. Chains of tetrahedra in binary osmium carbonyl clusters and their dualist graphs. The formulas of unknown neutral binary osmium carbonyl chains of tetrahedra are enclosed in braces { }.

a single tetrahedron, so that the dualist graphs of chains of tetrahedra have a one-to-one correspondence with the saturated aliphatic hydrocarbons C_nH_{2n+2}. Tetrahedral chain osmium carbonyls have the general formula $Os_k(CO)_{2k+6}$.

3.4. Decarbonylation sequences

The CO/Os ratios in the three homologous series of triangulated network osmium carbonyl clusters depicted in Figs. 2, 3 and 4 decrease in the sequence bow ties > rafts > tetrahedral chains, with a concurrent increase in the numbers of Os–Os bonds. This is illustrated especially well with the series of Os_5 derivatives $Os_5(CO)_{19}$ (bow tie) → $Os_5(CO)_{18}$(raft) → $Os_5(CO)_{16}$ (tetrahedral chain). Thus decarbonylation of osmium carbonyl clusters with concurrent metal–metal bond formation first converts all Os_n polygons larger than triangles into triangles with square → butterfly conversions (Fig. 5) as the final stage of such processes. Subsequent decarbonylation of the resulting network of Os_3 triangles occurs in the sequence bow ties → rafts → chains of tetrahedra. Some fundamental processes for increasing the number of edges in osmium carbonyl cluster networks through decarbonylation sequences are illustrated in Fig. 5.

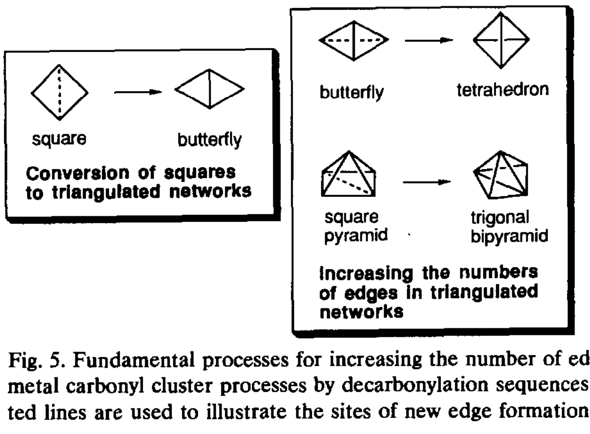

Fig. 5. Fundamental processes for increasing the number of edges in metal carbonyl cluster processes by decarbonylation sequences. Dotted lines are used to illustrate the sites of new edge formation.

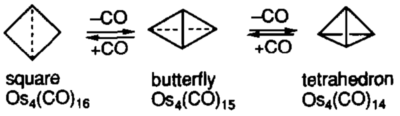

Fig. 6. Metal frameworks of the osmium carbonyl clusters with four metal atoms. The site of the next edge to be added upon decarbonylation is indicated by a dotted line.

4. Applications to osmium carbonyl cluster chemistry

4.1. Clusters with four osmium atoms (Fig. 6)

The chemistry of binary osmium carbonyl clusters with four osmium atoms has been reviewed by Pomeroy [9]. The tetranuclear osmium carbonyl with the highest CO/Os ratio is yellow–orange square $Os_4(CO)_{16}$ which can be obtained by treatment of the butterfly $Os_4(CO)_{15}$ with CO at 0°C as depicted in Fig. 6 [10]. The cluster $Os_4(CO)_{16}$ is unstable at room temperature, both with respect to decarbonylation to regenerate $Os_4(CO)_{15}$ as well as rupture of the four-membered ring to generate ultimately $Os_3(CO)_{12}$. The dark red butterfly cluster $Os_4(CO)_{15}$ can be made by addition of $Os(CO)_5$ to the reactive $Os_3(CO)_{10}$ fragment obtained from $Os_3(CO)_{10}$ (cyclooctene)$_2$ [11]. In a formal sense, this process consists of bridging an edge of an Os_3 triangle to give an Os_4 butterfly. Heating $Os_4(CO)_{15}$ to ~ 80°C in hexane solution results in decarbonylation to give tetrahedral $Os_4(CO)_{14}$ (Fig. 6) [12].

4.2. Clusters with five osmium atoms (Fig. 7)

Planar pentagonal $Os_5(CO)_{20}$ does not appear to be stable, in accord with the low observed stability of square $Os_4(CO)_{16}$. The Os_5 cluster with the highest CO/Os ratio which has been isolated is the orange bow tie cluster $Os_5(CO)_{19}$, which can be obtained by cleavage of one osmium atom from $Os_6(CO)_{18}$ by treatment with CO at 160°C/90 atm [13]. The planar Os_5 raft cluster $Os_5(CO)_{18}$ is obtained by reaction of $(MeCN)_2Os_3(CO)_{10}$ with $H_2Os_3(CO)_{10}$ at room temperature [14]. The end product of the decarbonylation of $Os_5(CO)_{19}$ and $Os_5(CO)_{18}$ is the trigonal bipyramidal cluster $Os_5(CO)_{16}$ (Fig. 7), which was first isolated in low yield from the pyrolysis of $Os_3(CO)_{12}$ [15]. The binary neutral carbonyl $Os_5(CO)_{17}$ appears to be unknown, but the isoelectronic dihydride $H_2Os_5(CO)_{16}$, a minor pyrolysis product of $Os_3(CO)_{12}$ in the presence of traces of water, has been shown by X-ray diffraction to have the edge-bridged tetrahedron structure indicated in Fig. 7 [16].

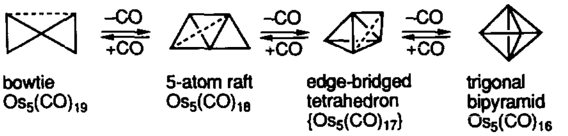

Fig. 7. Metal frameworks of the osmium carbonyl clusters with five metal atoms. The site of the next edge to be added upon decarbonylation is indicated by a dotted line.

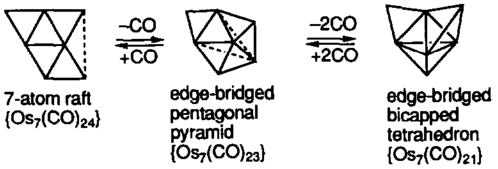

Fig. 9. A hypothetical decarbonylation sequence of the seven-vertex osmium raft cluster $Os_7(CO)_{24}$.

4.3. *Clusters with six osmium atoms (Fig. 8)*

Neutral binary osmium carbonyl clusters with six osmium atoms are of interest since the globally delocalized Os_6 octahedron is not found among their structures. The predicted neutral hexanuclear osmium carbonyl with the highest CO/Os ratio is the presently unknown $Os_6(CO)_{22}$ with a combination bow tie/butterfly structure (Fig. 8). The hexanuclear osmium carbonyl cluster with the highest CO/Os ratio which has been isolated is the blue–purple raft cluster $Os_6(CO)_{21}$, which can be obtained in nearly quantitative yield by reaction of solid $Os_6(CO)_{18}$ with carbon monoxide under pressure [17]. Numerous derivatives of $Os_6(CO)_{21}$ of the type $Os_6(CO)_{21-x}L_x$ have also been prepared [18,19].

Pyrolysis of $Os_3(CO)_{12}$ under relatively vigorous conditions (*e.g.* in a sealed tube at 195–200°C) gives a complicated mixture of products [20], from which brown $Os_6(CO)_{18}$ can be isolated. As expected from the vigorous reaction conditions under which it is formed, $Os_6(CO)_{18}$ has the lowest CO/Os ratio of any hexanuclear osmium carbonyls which have been isolated. The early observation (1973) by X-ray diffraction [21] that the Os_6 framework in $Os_6(CO)_{18}$ is a bicapped tetrahedron (Fig. 8) rather than an octahedron was the initial indication that non-trivial principles governed the structures of osmium carbonyl clusters. Note that in a hypothetical octahedral $Os_6(CO)_{18}$ *with edge-localized bonding* in which each vertex has degree 4, each osmium vertex has the favored 18-electron rare gas configuration so that there is nothing wrong electronically with an edge-localized octahedral $Os_6(CO)_{18}$. However, the delocalization energy of globally delocalized octahedral clusters makes them generally more stable than edge-localized octahedral clusters. In addition, note that a globally delocalized *neutral* $Os_6(CO)_{18}$ has only 12 skeletal electrons, which is two less than the $2n + 2 = 14$ skeletal electrons for $n = 6$ for a globally delocalized octahedron. In this connection, the binary octahedral dianion $Os_6(CO)_{18}^{2-}$ *dianion* and the hydridohexaosmium monoanion $HOs_6(CO)_{18}^{-}$ have been shown [22] to contain octahedral Os_6 units in accord with their 14 skeletal electrons.

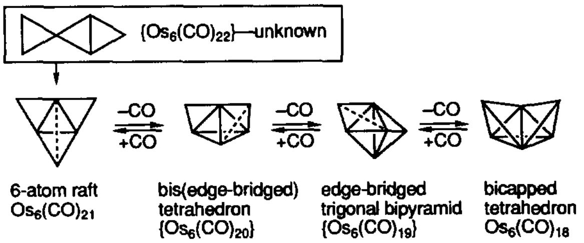

Fig. 8. Metal frameworks of the osmium carbonyl clusters with six metal atoms. The site of the next edge to be added upon decarbonylation is indicated by a dotted line.

4.4. *Clusters with seven osmium atoms*

Figure 9 shows a possible decarbonylation sequence for a hypothetical seven-vertex osmium raft cluster $Os_7(CO)_{24}$. Note that the addition of the seventh osmium atom to the raft structure makes a pair of osmium atoms in the Os_7 unit relatively close together to form a new Os–Os bond, as indicated by a dotted line in the seven-atom raft in Fig. 9. Formation of such a new Os–Os bond can be followed by bending of the coplanar raft structure leading to an edge-bridged pentagonal pyramid in the hypothetical $Os_7(CO)_{23}$. Subsequent formation of two Os–Os bonds in the pentagonal face of the pentagonal pyramid can lead to an edge-bridged bicapped tetrahedron in a hypothetical $Os_7(CO)_{21}$ (Fig. 9).

None of the indicated Os_7 carbonyl derivatives in the hypothetical decarbonylation sequence depicted in Fig. 9 has been isolated. The difficulty with this decarbonylation sequence may arise from the fact that the edge-capped bicapped tetrahedron end product, $Os_7(CO)_{21}$, has the correct number of apparent skeletal electrons, namely 14, for a more stable structure consisting of a globally delocalized octahedron in which one of the eight faces has been capped with a seventh vertex in accord with the structure established by X-ray diffraction [23] for $Os_7(CO)_{21}$. Thus a seven-vertex osmium carbonyl cluster appears to be the smallest *neutral* osmium carbonyl cluster that can contain a globally delocalized octahedral Os_6 cavity.

4.5. A periodic table of neutral binary osmium carbonyl clusters

Dias [3] has introduced the concept of a periodic table for polycyclic benzenoid aromatic hydrocarbons consisting of networks of fused hexagons, in which the formulas of possible benzenoid hydrocarbons are entered into a two-dimensional array with one dimension representing the number of internal vertices of degree 3 and the other dimension relating in a somewhat complicated manner to the properties of the internal edges. The neutral binary osmium carbonyl networks containing Os_3 triangles can be placed in a similar periodic table in which one dimension is the number of metal atoms and the other dimension is the number of metal–metal bonds (Table 2). This periodic table of binary osmium carbonyls lists the nine known binary neutral osmium carbonyl clusters ranging in complexity from the triangular $Os_3(CO)_{12}$ to the capped octahedral $Os_7(CO)_{21}$ with a number of the intermediate structures such as those of $Os_4(CO)_{15}$, $Os_5(CO)_{18}$ and $Os_6(CO)_{21}$ being rafts (Fig. 2). The periodic table depicted in Table 2 thus describes "rafting from the triangle to the (capped) octahedron in osmium carbonyl cluster chemistry".

The periodic table of binary osmium carbonyl clusters (Table 2) suggests the formulas of eight feasible but currently unknown neutral binary osmium carbonyl compositions based on networks of Os_3 triangles containing from five to seven osmium atoms of which the $Os_5(CO)_{17}$ currently being sought by Lewis and coworkers [13] is the simplest species. Some of these currently unknown binary osmium carbonyl derivatives may be sufficiently stable to be prepared by suitably chosen synthetic methods under sufficiently mild conditions.

4.6. Mixed osmium–platinum carbonyl clusters

A platinum atom has two more valence electrons than osmium. For this reason, replacement of an osmium atom with a platinum atom in a mixed metal carbonyl cluster might be expected to give a stable metal cluster with one less carbonyl group for each platinum atom. However, this is the case only if the platinum atom uses a spherical sp^3d^5 valence orbital manifold like the osmium atom which it replaces. More frequently, platinum atoms in platinum carbonyl derivatives have toroidal sp^2d^5 valence orbital manifolds with one non-bonding p orbital and thus a favored 16-electron configuration rather than the 18-electron configuration of the next noble gas. Thus, each replacement of a spherical sp^3d^5 osmium atom with a toroidal sp^2d^5 platinum atom reduces the number of carbonyl groups by two, namely one carbonyl group as a result of the extra two platinum valence electrons and a second carbonyl group as a result of the empty p orbital of the toroidal platinum atom.

This point is best illustrated by a comparison of the stoichiometries of the triangular clusters $Os_3(CO)_{12}$ and $Os_2Pt(CO)_{10}$ and those of the five atom raft clusters $Os_5(CO)_{18}$ and $Os_3Pt_2(CO)_{14}$ (Fig. 10) [24]. In both cases, the number of carbonyl groups is reduced by two for each osmium atom replaced by a platinum atom. The platinum atoms have the planar coordination expected for a toroidal platinum atom, being distorted tetragonal planar for the Pt atom in $Os_3Pt_2(CO)_{14}$ (Fig. 10), and pentagonal planar for the inner Pt atom in $Os_3Pt_2(CO)_{14}$.

The situation is more complicated for the six-vertex mixed osmium–platinum raft clusters [25] $Os_4Pt_2(CO)_{18}$, which has three rather than four carbonyl groups less than the $Os_6(CO)_{21}$ raft cluster as well as

TABLE 2. A 'periodic table' of the neutral binary osmium carbonyl triangulated clusters [a] $Os_m(CO)_c$

$b \rightarrow$ $m \downarrow$	3	4	5	6	7	8	9	10	11	12	13	14	15
3	$\boxed{12}$												
4		$\boxed{15}$ r	$\boxed{14}$ d										
5				$\boxed{19}$ t	$\boxed{18}$ r	17	$\boxed{16}$ d						
6						22	$\boxed{21}$ r	20	19	$\boxed{18}$ d			
7							26t		24	23	22	$\boxed{21}$ [b]	20 [b]

[a] The entries in the table are the values of c for $Os_m(CO)_c$ for a species with b Os–Os bonds. Known compounds are indicated in boxes $\boxed{}$. Raft structures are indicated by r, bow tie structures by t and deltahedral structures by d.

[b] The stoichiometry $Os_7(CO)_{20}$ is the hypothetical stoichiometry for a neutral binary seven-vertex osmium carbonyl cluster with an edge-localized deltahedron, namely a tricapped tetrahedron or a bicapped trigonal bipyramid (Fig. 4). However, the stoichiometry $Os_7(CO)_{21}$ is the stoichiometry actually observed for the deltahedral seven-vertex neutral binary osmium carbonyl cluster, since the observed deltahedron in the seven-vertex osmium carbonyl cluster system is the capped octahedron with a globally delocalized octahedral Os_6 cavity. Thus $Os_7(CO)_{21}$ appears to be the smallest stable neutral binary osmium carbonyl $Os_m(CO)_c$ that can obtain an octahedral Os_6 cavity.

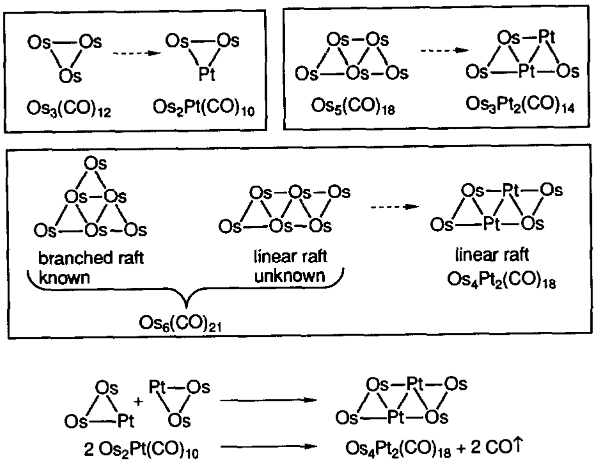

Fig. 10. Relationship of the metal frameworks of osmium carbonyl clusters to mixed osmium–platinum carbonyl clusters.

the linear raft structure rather than the branched raft structure of $Os_6(CO)_{21}$ (Fig. 10). The stoichiometry of $Os_4Pt_2(CO)_{18}$ arises from the fact that one of the two platinum atoms has a spherical sp^3d^5 manifold whereas the other platinum atom has a toroidal sp^3d^5 manifold. The linear shape of $Os_4Pt_2(CO)_{18}$ can be a consequence of its synthesis [25] based on the dimerization of $Os_2Pt(CO)_{10}$ under mild conditions (Fig. 11). This is an excellent illustration of the use of a rational method to synthesize a metal cluster with a specific shape.

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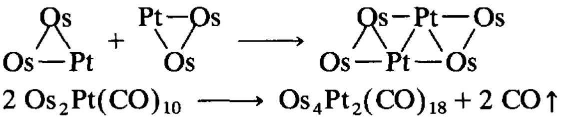

Fig. 11. Conversion of $Os_2Pt(CO)_{10}$ to $Os_4Pt_2(CO)_{18}$.

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