CHAPTER 5

\textit{mno Rule for Condensed Boranes versus Mingos’ Rule for Condensed Transition Metal Clusters: The Missing Link}

\begin{align*}
\text{SEP} &= m + n + o \\
\text{TEC} &= (A) + (B) - (\Delta c)
\end{align*}

\[ 6n - 3(m - 1) \]
Abstract

The correlation between the electron count for the polyhedral boranes (Wade’s $n + 1$ rule) and for the transition metal clusters (PSEPT, $7n + 1$ rule) can be understood from the isolobal analogy between BH and transition metal fragments. The relationship between the electron count of poly-condensed polyhedral boranes ($mno$ rule) and poly-condensed transition metal clusters (Mingos’ rule) is not straightforward. Here, a total valence electron count for the condensed transition metal clusters was proposed, which establishes the missing link between the electron count for condensed boranes ($mno$ rule) and transition metal clusters (Mingos’ rule). According to this rule, $m + n + o + 6n - 3(m - 1) = 7n - 2m + o + 3$ ($n =$ number of vertices, $m =$ number of polyhedra, $o =$ number of single vertex sharing) number of electron pairs are necessary for the stability of $closo$ polycondensed transition metal clusters. The additional electron pairs required for $nido$ and $arachno$ polyhedra, one and two respectively, are to be added separately. Comparison of this electron count with Mingos’ rule gives a relation between $n_s$ (number of shared vertices), $y$ (number of bonds between the shared atoms) and $m$ (number of polyhedra) as $y = 2n_s - 3(m - 1) + o$. Two possible ways of dividing the total electron count into skeletal and non-skeletal bonding electron pairs were discussed. The rule is also extended as $m + n + o + p + 6x - x_s/n_s\{3(m - 1)\}$, (where $x =$ number of transition metals, $x_s =$ number of shared transition metals and $n_s =$ number of shared atoms) to incorporate the electron counts of the metallaboranes. This rule gives $mno$ rule ($x = x_s = 0$) for
condensed boranes and $7n - 2m + o + 3$ rule ($x = n, x_s = n_s$) for condensed transition metal clusters.
[5.1] Introduction

Electron-counting rules\textsuperscript{1-11} are efficient tools to predict qualitatively the structure, stability and bonding of molecules and clusters. The octet rule\textsuperscript{1} for main group molecules, the 18-electron rule\textsuperscript{2} for transition metal complexes, Hückel $4n + 2$ rule\textsuperscript{3} for aromatic planar cyclic systems, Lipscomb’s styx rule\textsuperscript{4} for boranes and CVMO\textsuperscript{8,9} for transition metal clusters are some of the well known examples. Electron counts based on graph theoretical approaches\textsuperscript{10} are occasionally used for boranes and transition metal clusters. Contributions of Wade\textsuperscript{5} and Mingos\textsuperscript{11} in formulating the electronic requirement for boranes and transition metal clusters especially stand out. Wade’s $n + 1$ rule\textsuperscript{5} is not only helpful in rationalizing the known cage structures of polyhedral boranes, but also in suggesting the probable structures of unknown polyhedral boranes. Wade\textsuperscript{5a} and Mingos\textsuperscript{11a} recognized a common structural and electronic relationship between main group and transition metal polyhedral clusters in the early 1970’s. This lead to the development of PSEPT,\textsuperscript{11b} according to which stable \textit{closo} boranes require $n + 1$ skeletal electron pairs respectively, $(n$ is the number of vertices) whereas, the electronic requirement for isostructural \textit{closo} polyhedral transition metal clusters is $7n + 1$ total valence electron pairs. One and two additional electron pairs are required for \textit{nido} and \textit{arachno} polyhedra.

The difference between the skeletal electron pairs in boranes and total valence electron pairs in transition metal clusters is therefore $6n$, which corresponds to metal-ligand exohedral bonding electrons and non-bonding metal electrons (Figure 5.1, top). This can be rationalized by isolobal analogy,\textsuperscript{12} according to which
BH fragments in boranes and $d^5\text{ML}_3$ fragments [e.g. Ru(CO)$_3$, CoCp] in transition metal clusters contribute three orbitals and two electrons for the skeletal bonding. For example, the two ‘$e_g$’ electrons of Ru(CO)$_3$ would correspond to two valence electrons in the BH group. The ‘$t_{2g}$’ (6 electrons) and 3 CO groups (6 electrons) contribute 6 additional electron pairs for Ru(CO)$_3$ fragment. Accordingly, the skeletal electron pairs for octahedral B$_6$H$_6$$^2$ is 7 ($n = 6$) and the total valence electron pairs for octahedral Ru$_6$(CO)$_{18}$$^2$ is 43 ($n = 6$). The difference between the two electron counts is 36 ($= 6n$) electron pairs (Figure 5.1, top).

Mingos’ proposed another rule to explain the condensation of polyhedral transition metal complexes.$^{11c,d}$ This rule states that “the total electron count in a condensed cluster is equal to the sum of the electron counts for the parent polyhedra (A) and (B) minus the electron count ($\Delta c$) characteristic of the shared unit (atom, pair of atoms etc.)”. If polyhedron (A) is characterized by ‘$a$’ number of valence electrons and polyhedron (B) by ‘$b$’ number of valence electrons, then the condensed cluster (C) will have a total of ‘$a + b - \Delta c$’ valence electrons. The characteristic electron count ($\Delta c$) for vertex sharing is 18, edge sharing is 34 and triangular face sharing is 48 (or 50, when (A) and (B) are deltahedra with number of vertices $\geq 6$).$^{11c,d}$ A generalized skeletal electron counting rule, the $mno$ rule,$^6$ for polycondensed polyhedral boranes has been introduced by Jemmis and coworkers. According to this rule, $m + n + o$ skeletal electron pairs are necessary for a closed macro-polyhedral system to be stable. Here, $m$ is the number of condensed polyhedra; $n$ is the number of vertices and $o$ is the number of single-atom sharing between two polyhedra. Wade’s $n + 1$ rule is a special case of $m + n + o$ rule, where
$m = 1$ and $o = 0.6$. However, unlike Wade’s $n + 1$ rule for boranes and $7n + 1$ rule for non-condensed transition metal clusters, the relation between $mno$ rule and Mingos’ rule for poly-condensed systems is not obvious.

![Figure 5.1](image)

**Figure 5.1:** Schematic representation of the correlation among the electron count rules for mono cage and condensed polyhedral boranes and transition metal clusters. SEP is number of skeletal electron pairs and TVEP is number of total valence electron pairs.

For example, the skeletal electron pairs for edge shared biocahedral $\text{B}_{10}\text{H}_{8}^2$ is 12 (by $mno$ rule, where $m = 2$, $n = 10$ and $o = 0$) (Figure 5.1, bottom). The total valence electron pairs (TVEP) for isostructural edge shared metal cluster $\text{Ru}_{10}\text{C}_{2}\text{(CO)}_{24}^2$ is 69 (by Mingos’ rule, where ‘a’ = ‘b’ = 43 electron pairs, $\Delta c = 17$
electron pairs). For mono-cage polyhedra, the difference between the electron count of boranes and transition metal cluster is $6n$ (Figure 5.1, top). However, the difference between the electron counts of isostructural condensed transition metal cluster $\text{Ru}_{10}C_2(\text{CO})_{24}^-$ and borane $\text{B}_{10}\text{H}_8^-2$ is 57 electron pairs ($= 69 - 12$, Figure 5.1, bottom), which is less than $6n = 60$ electron pairs ($n = 10$). Analysis of a large number of experimentally known condensed transition metal clusters (Table 5.1) shows that addition of $6n$ to the skeletal electron pair of isostructural condensed boranes ($mno$ rule) does not give TVEP for isostructural transition metal clusters (Mingos’ rule), as it does for Wade’s $n + 1$ and $7n + 1$ rules (PSEPT). In that scenario, what is the relationship between $mno$ rule and Mingos’ rule for poly-condensed clusters? The $mno$ rule for condensed boranes and Mingos’ rule for transition metal clusters are based on two entirely different sets of parameters and thus one to one correspondence between these two rules is missing. In our attempt to determine this missing link between these two electron counting rules, the electron count for the condensed transition metal clusters is revised in terms of parameters $m$, $n$ and $o$. This has been done by analyzing a series of the crystal structures of the condensed polyhedral transition metal clusters (Table 5.1).

[5.2] Total Valence Electron Pair (TVEP) Count for Transition Metal Clusters: $7n - 2m + o + 3$

The total valence electron pairs for the closo condensed transition metal clusters can be expressed in terms of the number of vertices ($n$), the number of polyhedra ($m$) and the number of single vertex sharing ($o$) as $m + n + o + 6n - 3(m - 1) = 7n - 2m + o + 3$. For nido and arachno metal clusters, one and two additional
pairs of electrons are required \((7n - 2m + o + 3 + p; \ p = 1 \text{ for } nido \text{ and } p = 2 \text{ for arachno})\). According to this electron count, the number of TVEP required for the stability of edge sharing octahedral cluster \(\text{Ru}_{10}\text{C}_2(\text{CO})_{24}^{2-}\) (Figure 5.1, bottom) is \(7n - 2m + o + 3 + p = 69\) \((m = 2, n = 10, o = 0 \text{ and } p = 0)\). This number is same as predicted by Mingos’ rule (Figure 5.1, bottom). When number of polyhedra \((m)\) is one, the TVEP count \(7n - 2m + o + 3\) becomes \(7n + 1\) \((o = 0)\) electron pairs, which is equal to the total valence electron pairs obtained by the PSEPT for closo systems. Therefore, our revised rule gives a generic electron count for condensed and non-condensed transition metal clusters. Applications of this electron count rule for a large number of condensed clusters are discussed in section 5.5.

The difference between the \(mno\) count in boranes and total valence electron count in condensed transition metal clusters is \(6n - 3(m - 1)\). What does this difference ‘\(6n - 3(m - 1)\)’ signify? In the condensed boranes, assignment of the skeletal and exohedral electron pairs is straightforward. The terminal BH fragment donates two electrons and shared boron atom, which does not have any exohedral bond, donates three electrons to the cluster bonding. However, this kind of assignment of the total electron count for condensed transition metal clusters is not practical due to the presence of closely spaced d orbitals. Thus, the simple argument of one to one mapping using isolobal analogy of BH and transition metal fragment is not sufficient to classify the TVEP of transition metal clusters into skeletal and non-skeletal electron pairs. On the other hand, the number of electrons donated by the shared metal fragment to the cluster bonding depends on the number of ligands attached to the metal. Since the connectivity of the terminal vertices does not change upon condensation, they would contribute equal numbers of electrons in
non-condensed as well as in condensed clusters. Therefore, it is apparent that the variable numbers of orbitals donated by shared metals are responsible for this difference in the electron count.

\[ 7n - 2m + o + 3 \]

Chart 5.1

The TVEP count \( 7n - 2m + o + 3 \) can be empirically divided into two ways – (a) \( \{m + n + o - 3(m - 1)\} + \{6n\} \) and (b) \( \{m + n + o\} + \{6n - 3(m - 1)\} \) – to account for the skeletal and non-skeletal electron pairs for the condensed transition metal clusters. In chart 5.1a, it is assumed that the skeletal electron count for the condensed transition metal clusters is \( m + n + o - 3(m - 1) \). It is observed that the number of ligands attached to the shared metals in condensed transition metal clusters commonly vary from one to three, which is less than the number of ligands attached to terminal vertices. The number of electrons contributed by these metal fragments for cluster bonding can be understood from secondary isolobal analogy.\(^{12}\)

The analysis of the frontier orbitals of the ML\(_3\) fragment indicates presence of three orbitals in the frontier region (Figure 5.2a). The prime consequence of removing two ligands along the z-axis from a ML\(_4\) fragment is the stabilization of the metal
$dz^2$ orbital (Figure 5.2b). Similarly, when four ligands from the ML$_5$ fragment is removed, $dz^2$ and $dx^2-y^2$ orbitals become stabilized (Figure 5.2c).

\[ \text{Figure 5.2: Frontier orbitals of metal ligand fragments (a) ML}_3 \text{ (b) ML}_2 \text{ obtained by removing two ligands from ML}_4 \text{ and (c) ML obtained by removing four ligands from ML}_5. \]

According to the above-mentioned argument, the d$^8$ML$_2$ and d$^{10}$ML fragments would not contribute any electron to the cluster bonding and d$^8$ML$_3$ (isolobal to BH fragment) would donate two electrons. This also holds true for other metal fragments as well. Therefore, in contrast to the shared B atoms in the condensed boranes, which donate three electrons as compared to terminal BH groups, all the transition metal fragments in the shared positions would donate less number of electrons for the skeletal bonding as compared to the terminal metal fragments. This accounts for the decrease in the number of skeletal electron pairs for the condensed transition metal clusters.
However, one can argue that a constant number of skeletal electrons are necessary for the stability of any particular topology. Therefore, division of the TVEP in the above-mentioned fashion implies different skeletal electrons for similar topology of boranes and transition metal clusters. This contradiction suggests the second way of dividing the TVEP into skeletal and non-skeletal components i.e. \( \{ m + n + o \} + \{ 6n - 3(m - 1) \} \) (Chart 5.1b). In this case, it is assumed that the skeletal electron pairs remain invariant for both condensed transition metal clusters and boranes of identical topology. It implies additional participation of \( 3(m - 1) \) number of non-bonding electron pairs by the shared metal fragments as compared to non-shared metal fragments.

The electronic requirement of transition metal clusters depends upon the types of condensation as well as the nature of the shared metal fragments and number of ligands attached to it. Therefore, the TVEP count is considered the best way to describe condensed transition metal clusters rather than skeletal electron count.

[5.3] Correlation between Mingos’ Rule and TVEP Count for Poly-Condensed Transition Metal Clusters

In most of the cases, the TVEP count \((7n - 2m + o + 3)\) gives the same electrons as predicted by Mingos’ rule (Table 5.1, section 5.5). This indicates the existence of a one to one relationship between these two rules. The difference \(\Delta c\) in Mingos’ rule can be expressed as \(9n_s - y\) number of electron pairs, where \(n_s = \) number of shared atoms and \(y = \) number of bonds between the shared atoms.
Chapter 5

Mingos’ Rule:

\[ a + b - (9n_s - y) \] electron pairs

For condensation of two polyhedra, the required number of electron pairs

\[ = a + b - (9n_s - y) \]
\[ = (7n_a + 1) + (7n_b + 1) - (9n_s - y) \]
\[ = (1 + 1) + 7(n_a + n_b - n_s) - (2n_s - y) \]
\[ = 2 + 7n - (2n_s - y) \]
\[ = m + 7n - (2n_s - y) \]

For condensation of three polyhedra, the required number of electron pairs

\[ = a + b + c - (9n_s - y) \]
\[ = (7n_a + 1) + (7n_b + 1) + (7n_c + 1) - (9n_s - y) \]
\[ = (1 + 1 + 1) + 7(n_a + n_b + n_c - n_s) - (2n_s - y) \]
\[ = 3 + 7n - (2n_s - y) \]
\[ = m + 7n - (2n_s - y) \]

Hence, in general Mingos’ electron count can be expressed as

\[ = m + 7n - (2n_s - y) \] electron pairs (5.1)

\[ n_s = \text{number of shared vertices} \]
\[ y = \text{number of bonds between the shared atoms} \]
\[ n_a = \text{number of vertices in polyhedra A} \]
\[ n_b = \text{number of vertices in polyhedra B} \]
\[ n = \text{number of vertices in the condensed polyhedra} \]
\[ m = \text{number of polyhedra} \]

TVEP Count:

\[ m + 7n + a - 3(m - 1) \] electron pairs (5.2)

Comparing Mingos’ Rule (5.1) and TVEP count (5.2) we get,

\[ 2n_s - y = 3(m - 1) - o \]

OR, \[ y = 2n_s - 3(m - 1) + o \] (5.3)

This transforms the electron count by Mingos’ rule as \( a + b - (9n_s - y) \) electron pairs, where ‘a’ and ‘b’ are number of total valence electron pairs of the parent polyhedra. According to the PSEPT theory, \( 7n + 1 \) (\( n = \text{number of vertices of the polyhedra} \)) number of electron pairs are required for closo non-condensed polyhedra.\(^{11a,b}\) Applying the PSEPT theory to the Mingos’ rule, we get the TVEP count for the poly-condensed transition metal clusters as \((7n_a + 1) + (7n_b + 1) - (9n_s - \)
Mingos’ rule versus Mingos’ rule

\[ m + 7n - (2n_s - y) \]

where \( n_a \) and \( n_b \) are the number of vertices of the polyhedra A and B (Chart 5.2). From chart 5.2, it is clear that Mingos’ rule for the condensed transition metal clusters can be written as \( m + 7n - (2n_s - y) \), and the number of bonds formed between the shared atoms \( (y) \) depend upon the number of shared atoms \( (n_s) \), the number of polyhedra \( (m) \) and number of single vertex sharing. For \textit{nido} and \textit{arachno} polyhedra one and two additional electron pairs is to be added in both eq. 5.1 and 5.2 (Chart 5.2).

[5.4] Extension of TVEP Count for Condensed Metallaboranes and Metallacarboranes

The electronic requirement for the condensed metallaboranes and metallacarboranes can be explained by the \textit{mno} rule,\(^6\) where the exohedral electrons are not involved in the skeletal bonding. However, sometimes it is difficult to understand the number of electrons donated by the metal fragments for skeletal bonding in a metallaboranes. This difficulty is more predominant for the poly-condensed transition metal clusters due to great influence of the exohedral ligands on the number of electrons participating in the skeletal bonding. Therefore, the skeletal electrons for the main group elements and total valence electrons for the transition metal fragments are considered for metallaboranes.

As discussed earlier, the difference in the electron counts for boranes by \textit{mno} rule and transition metal clusters by TVEP count arises from the atoms in the shared positions. Therefore, the terminal transition metal fragment would donate \( 6x \) \((x = \text{number of metal atom})\) number of electron pairs, in comparison with 1 electron pair
donated by terminal B-H. Hence, the TVEP count for the condensed metallaboranes, where the metal occupies the terminal position, will be \( m + n + o + 6x \).

A similar argument can be invoked when the transition metal fragments occupy the shared positions. The shared transition metal fragments in transition metal clusters contain less number of ligands and as a result donate less number of electrons as compared to the terminal transition metal fragments. These difference is manifested by “3\((m - 1)\)” in our electron count for the condensed transition metal clusters. This implies that all the metal fragments in the shared position together will contribute “3\((m - 1)\)” electron pairs less in comparison with the terminal transition metal fragments irrespective of the mode of condensation. Thus, “3\((m - 1)\)” electron pairs is to be subtracted from the total valence electron pairs if all the shared positions are occupied by transition metal fragments. This gives an electron count of \( m + n + o + 6x - 3(m - 1) \) electron pairs for this type of condensed metallaboranes.

The metallaboranes where both boron and transition metal fragment are present in the shared position are also reported. For these metallaboranes, the aforementioned electron count cannot be used. Here, “\( x_s/n_s\{3(m - 1)\} \)” number of electron pairs is to be subtracted from the total valence electron pairs, \( m + n + o + 6x \), where \( n_s \) is the total number of shared atoms and \( x_s \) is the number of shared metal atoms. For example, if one of the shared position of an edge shared metallaborane is occupied by a transition metal fragment, then the subtraction parameter in electron count will be “1/2 \{3(m - 1)\}”. Similarly, for a face shared metallaborane, where one
shared position is occupied by a transition metal fragment, the reduction in the
electron count will be “1/3\{3(m - 1)\}”. Thus, in order to incorporate all these
factors we propose one electron count that can explain the electronic requirement of
the condensed boranes, metallaboranes as well as transition metal clusters; \( m + n + o + 6x - x_s/n_s\{3(m - 1)\} \). Here \( m \) is the number of polyhedra, \( n \) is the total number of
vertices, \( o \) is the number of single atom sharing, \( x \) is the number of metal atoms, \( n_s \) is
the number of shared vertices and \( x_s \) is the number of shared metal atoms. One
additional electron pair is to be added for each missing vertex in terms of the
variable \( p \). For condensed boranes, \( x \) and \( x_s \) is 0; then, the electron count \( m + n + o + 6x - x_s/n_s\{3(m - 1)\} \) is equivalent to \( m + n + o \). If three is no metal atom in the
shared position of metallaboranes, then, \( x_s = 0 \) and the electron count becomes \( m + n + o + 6x\). For transition metal clusters, \( x = n \) and \( x_s = n_s \) then the electron count becomes, \( m + n + o + 6n - n_s/n_s\{3(m - 1)\} = m + n + o + 6n - 3(m - 1) \). Thus, this electron count can be in principle applicable to the
condensed boranes, metallaboranes and transition metal clusters. In case of boranes,
this electron count reduces to % rule and in case of transition metal clusters it
equals \( m + n + o + 6n - 3(m - 1) \). It has to be noted that for those condensed
metallaboranes, where isolobal analogy can be used for the transition metal
fragments, % rule can be applied directly. For metallaboranes, where % rule is
difficult to apply, this rule for the mixed cluster might be useful (Table 5.2, Figure
5.4, Section 5.5).
[5.5] Illustrations of TVEP Count

Table 5.1 illustrates the application of TVEP count on experimentally known transition metal clusters.\textsuperscript{13-15} The Mingos’ electron count (TVEC) for all the structures is also given. The detailed description of some selected structures is presented in figure 5.3. The description of structures starts with the planar clusters followed by clusters having tetrahedral, and octahedral skeletal units. Unless specified, all the clusters obey Mingos’ electron count rule. The extension of the TVEP count for the polycondensed metallaboranes are illustrated in table 5.2 and figure 5.4. Nevertheless, there are other structures which obey this TVEP count.\textsuperscript{13}

[5.5.1] Application to Transition Metal Clusters

[5.5.1.1] Clusters Based on Planar Skeleton (Structures 1-3)

The structures of this class of cluster are based on triangular units. The smallest triangular cluster Os\textsubscript{3}(CO)\textsubscript{12} (1) has three Os(CO)\textsubscript{4} metal fragments. The metal fragment Os(CO)\textsubscript{4} (d\textsuperscript{8}ML\textsubscript{4}) utilizes one electron pair for the skeletal bonding (Figure 5.2) and the corresponding isolobal main group fragment is CH\textsubscript{2}. Apparently this molecule can be viewed as an \textit{arachno} system derived from a trigonal bipyramid, where two of the apical vertices are removed. Hence, number of polyhedra, $m = 1$, number of vertices, $n = 3$, number of single atom sharing, $o = 0$ and number of missing vertices, $p = 2$. Therefore, according to the rule total valence electron pairs required for the molecule is $(7\times3 - 2\times1 + 0 + 3 + 2) = 24$. The 3 Os atoms contribute 12 electron pairs and 12 CO groups together also contribute 12 electron pairs.
### Table 5.1: TVEP count for transition metal clusters by $7n - 2m + o + 3 + p$ rule and Mingos’ rule are given. It is compared with the number of electron pairs provided by the constituent metal fragments.

<table>
<thead>
<tr>
<th>St. No.</th>
<th>Molecular formula</th>
<th>$m$</th>
<th>$n$</th>
<th>$o$</th>
<th>$p$</th>
<th>calc. $TVEP_{16}$</th>
<th>obs. $TVEP$</th>
<th>$c$</th>
<th>Mingos’ Count</th>
<th>Ref</th>
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<td>1.</td>
<td>Os$<em>8$(CO)$</em>{12}$</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>24</td>
<td>24</td>
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<td>24</td>
<td>8</td>
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<td>Os$<em>5$(CO)$</em>{19}$</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>4</td>
<td>39</td>
<td>39</td>
<td>0</td>
<td>39</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Os$<em>6$(CO)$</em>{21}$</td>
<td>4</td>
<td>6</td>
<td>0</td>
<td>8</td>
<td>45</td>
<td>45</td>
<td>0</td>
<td>45</td>
<td>8</td>
</tr>
<tr>
<td>4.</td>
<td>Ir$<em>4$(CO)$</em>{11}$CN(bu)</td>
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<td>4</td>
<td>0</td>
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<td>30</td>
<td>30</td>
<td>0</td>
<td>30</td>
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<td>2</td>
<td>51</td>
<td>51</td>
<td>0</td>
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<td>0</td>
<td>43</td>
<td>43</td>
<td>0</td>
<td>43</td>
<td>15d</td>
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<td>7</td>
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<td>1</td>
<td>49</td>
<td>49</td>
<td>0</td>
<td>49</td>
<td>15d</td>
</tr>
<tr>
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<td>Ru$_{12}$C$<em>2$(CO)$</em>{24}$</td>
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<td>-2</td>
<td>69</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>61</td>
<td>14k,n</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>61</td>
<td>14m</td>
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<td>12.</td>
<td>[Ir$_{12}$($\mu$-CO)$<em>6$(CO)$</em>{18}$]</td>
<td>3</td>
<td>12</td>
<td>0</td>
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<td>-2</td>
<td>79</td>
<td>14j</td>
</tr>
<tr>
<td>13.</td>
<td>[Rh$_6$Pt$_3$(CO)$_3$($\mu_3$-CO)$_3$($\mu_3$-CO)$_3$]</td>
<td>2</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>62</td>
<td>60</td>
<td>-4(-2)</td>
<td>61</td>
<td>14g</td>
</tr>
<tr>
<td>14.</td>
<td>Rh$<em>{11}$(CO)$</em>{23}$</td>
<td>3</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>74</td>
<td>72.5</td>
<td>-3</td>
<td>72.5</td>
<td>15c</td>
</tr>
<tr>
<td>15.</td>
<td>Os$_6$Pt$<em>3$(CO)$</em>{16}$(COD)$_2$</td>
<td>3</td>
<td>8</td>
<td>0</td>
<td>2</td>
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<td>54</td>
<td>-2(0)</td>
<td>55</td>
<td>15e,f</td>
</tr>
<tr>
<td>16.</td>
<td>Os$<em>7$(CO)$</em>{19}$Au$_2$(dppm)</td>
<td>4</td>
<td>9</td>
<td>0</td>
<td>2</td>
<td>60</td>
<td>60</td>
<td>0</td>
<td>60</td>
<td>15b</td>
</tr>
<tr>
<td>17.</td>
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<td>10</td>
<td>0</td>
<td>2</td>
<td>67</td>
<td>66</td>
<td>-2(0)</td>
<td>50</td>
<td>14o</td>
</tr>
<tr>
<td>18.</td>
<td>[Ir$_6$($\mu$-CO)$<em>3$(CO)$</em>{21}$H]</td>
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<td>0</td>
<td>0</td>
<td>62</td>
<td>60</td>
<td>-4</td>
<td>60</td>
<td>14b</td>
</tr>
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<td>0</td>
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<td>62</td>
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</tr>
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<td>68</td>
<td>14f</td>
</tr>
<tr>
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<td>9</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>61</td>
<td>14k,n</td>
</tr>
<tr>
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<td>9</td>
<td>0</td>
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<td>62</td>
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<td>0</td>
<td>61</td>
<td>14m</td>
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<td>9</td>
<td>0</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>61</td>
<td>14p</td>
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<td>[Ru$_6$Pt$<em>3$(CO)$</em>{21}$($\mu_3$-HgI)H]</td>
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<td>-1</td>
<td>61</td>
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<td>0</td>
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<td>62</td>
<td>0</td>
<td>61</td>
<td>14d</td>
</tr>
<tr>
<td>26.</td>
<td>[Os$<em>7$(CO)$</em>{21}$]</td>
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<td>10</td>
<td>0</td>
<td>4</td>
<td>67</td>
<td>66</td>
<td>-2</td>
<td>67</td>
<td>14a</td>
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<td>0</td>
<td>0</td>
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<td>-1</td>
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<td>66</td>
<td>-2(0)</td>
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<td>29.</td>
<td>Ru$_6$Pt$<em>3$(CO)$</em>{19}$(SMc$_2$)($\mu_3$-Ph$_2$C$_2$)$_2$H$_2$</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
<td>62</td>
<td>62</td>
<td>0</td>
<td>62</td>
<td>14d,e</td>
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<td>31.</td>
<td>[Rh$_6$Pt$_3$(CO)$_3$($\mu_2$-CO)$_3$($\mu_3$-CO)$_3$]</td>
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<td>0</td>
<td>0</td>
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<td>59.5</td>
<td>-5(-3)</td>
<td>61</td>
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<tr>
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<td>10</td>
<td>0</td>
<td>0</td>
<td>67</td>
<td>66</td>
<td>-2</td>
<td>67</td>
<td>14h</td>
</tr>
<tr>
<td>33.</td>
<td>Ru$_6$Pt$<em>3$(CO)$</em>{16}$($\mu_4$-$\eta^6$-PhC$_2$H$_4$Ph)$_4$</td>
<td>2</td>
<td>9</td>
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<td>62</td>
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<td>0</td>
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</tr>
<tr>
<td>34.</td>
<td>Ru$_6$Pt$<em>3$(CO)$</em>{18}$($\eta^6$-TolC$_2$H$_4$Tol)$_4$</td>
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<td>9</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>62</td>
<td>14l</td>
</tr>
<tr>
<td>35.</td>
<td>Ru$_6$Pt$<em>3$(CO)$</em>{21}$[$\mu$-PhCC(H)Ph]H</td>
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<td>9</td>
<td>0</td>
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<td>62</td>
<td>62</td>
<td>0</td>
<td>62</td>
<td>14n</td>
</tr>
<tr>
<td>36.</td>
<td>Os$_6$Pt$<em>3$(CO)$</em>{21}$[COD]</td>
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<td>0</td>
<td>2</td>
<td>55</td>
<td>55</td>
<td>0</td>
<td>55</td>
<td>15e,f</td>
</tr>
<tr>
<td>37.</td>
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<td>0</td>
<td>2</td>
<td>55</td>
<td>54</td>
<td>-2</td>
<td>55</td>
<td>15d</td>
</tr>
</tbody>
</table>

$m$ = number of polyhedra; $n$ = number of vertices; $o$ = number of single vertex bridge; $p$ = number of missing vertices; $c$ = charge of the molecule obtained by TVEP count and actual charge is given in parenthesis. Last column gives the references to experimental structures.

* indicates structures that do not obey the electron count $7n - 2m + o + 3 + p$ and $^b$ indicates structures where Mingos’ count does not match the electron count.
Thus, the charge of the molecule is zero. PSEPT \((7n + 1 + p)\) also gives the same electron count. On the other hand, \(\text{Os}_3(\text{CO})_{12}\) is considered equivalent to saturated cyclic hydrocarbon (cyclo-propane).\(^\text{11}\) Hence, it cannot be considered as an arachno fragment of trigonal bipyramid geometry. The ideal arachno fragment of a trigonal bipyramid geometry of borane is \(\text{B}_3\text{H}_3\).\(^\text{6}\) Hence, the corresponding metal cluster is
Os\textsubscript{5}(CO)\textsubscript{19}\textsuperscript{-6}, where each vertex Os(CO)\textsubscript{3} is isolobal to BH. These three additional electron pairs are provided by three CO ligands in Os\textsubscript{5}(CO)\textsubscript{12}.

The molecule Os\textsubscript{5}(CO)\textsubscript{19} (2) shows a vertex sharing between two triangular metal clusters. The total electron count for this cluster is 39 \([m = 2, n = 5, o = 1, p = 4]\). The electron pairs contributed by 5 Os atoms and 19 CO groups are 20 and 19 respectively and thus it is neutral. This cluster can also be considered as an equivalent to the saturated hydrocarbon system. The molecule Os\textsubscript{6}(CO)\textsubscript{21} (3) exhibits face sharing among four triangular metal clusters, where all the three edges of the central triangle is shared. According to \(7n - 2m + o + 3 + p\) electron count, it should have 45 total valence electron pairs \([m = 4, n = 6, p = 8]\). The 6 Os atoms and 21 CO groups donate the 24 and 21 electron pairs respectively and this makes the molecule neutral. As mentioned above, this molecule can be considered equivalent to the saturated cyclic hydrocarbon rather than fragment of polyhedral clusters. According to Mingos’ rule, the electronic requirement of planar Os\textsubscript{3}(CO)\textsubscript{12}, Os\textsubscript{5}(CO)\textsubscript{19} and Os\textsubscript{6}(CO)\textsubscript{21} are 24, 39 and 45 electron pairs respectively, which is same as obtained from \(7n - 2m + o + 3 + p\) electron count.\textsuperscript{11}

[5.5.1.2] Clusters Based on Tetrahedral Skeleton (Structures 4-5)

This class of structures can be considered as a \textit{nido} fragment of trigonal bipyramidal cluster. The number of total valence electron count for the non-condensed tetrahedral cluster Ir\textsubscript{4}(CO)\textsubscript{11}CN(tbu) (4) is \(7n - 2m + o + 3 + p = 30\) electron pairs \((m = 1, n = 4, p = 1)\). Each Ir atom contributes 4.5 electron pairs, 11
CO groups and one CN(tbu) group contribute 12 electron pairs. Hence this cluster is neutral.

The vertex shared cluster Os$_6$Pt(CO)$_{18}$H$_8$ (5) has number of polyhedra, $m = 2$, number of vertices, $n = 7$, number of single vertex sharing, $o = 1$ and number of missing vertices, $p = 2$. Thus according to the total electron count ($7n - 2m + o + 3 + p$) the number of electron pairs required for its stability is 51. The six Os(CO)$_3$ vertices donate 42 electron pairs, Pt atom donates 5 electron pairs and 8 hydrogen atoms give 4 electron pairs. This results a neutral cluster.

[5.5.1.3] Clusters Based on Octahedral Skeleton (Structures 6-13)

Os$_6$(CO)$_{18}$H$_2$ (6) is an example for non-condensed clusters based on octahedral skeleton. In this cluster $m = 1$, $n = 6$, and $o = 0$. Hence, the number of total valence electron pairs is 43 [$7n - 2m + o + 3 + p = 43$]. The six Os atoms donate 48 electrons, each CO group contributes 2 electrons to the valence electron count and two hydrogen atoms donate 2 electrons. Hence, the cluster is neutral according to this electron count rule.

The simplest extension of octahedral cluster is Os$_7$(CO)$_{21}$ (7), where one of the triangular face of the octahedra is capped by Os(CO)$_3$ fragment. This structure demonstrates the validity of the electron count in the capped polyhedra. Here the number of polyhedron $m = 2$, the number of vertices $n = 7$, the number of single vertex sharing $o = 0$, and number of missing vertex $p = 1$ (considering the capped vertex as a nido fragment derived from trigonal bipyramid). The number of total electron pairs is 49 ($7n - 2m + o + 3 + p = 49$). The seven Os atoms and 21 CO
groups contribute 49 total valence electron pairs and hence the cluster is neutral. If the Os(CO)$_3$ is considered as a capped vertex, it would donate two valence electrons to the octahedral Os$_6$(CO)$_{18}^-$ and form a neutral cluster Os$_7$(CO)$_{21}$.

As per our knowledge, there is no example, until date, of the vertex shared octahedral metal cluster in the literature. The non-existence of these clusters is probably due to the non-bonded repulsive interaction between the ligands on the vertices adjacent to the shared atoms. An example of edge sharing between two octahedra is demonstrated by the molecule Ru$_{10}$C$_2$(CO)$_{24}^-$(8). The electron count $(7n - 2m + o + 3 + p)$ gives 69 total valence electron pairs ($m = 2$, $n = 10$, $o = 0$). The 10 Ru atoms donate 40 electron pairs, two carbon atoms donate 4 electron pairs and 24 CO groups contribute 24 electron pairs. Therefore, the metal cluster requires two negative charges to be stable and it is predicted to be a dianion.

Next example describes the validity of the electron count in a cluster Ru$_6$Pt$_3$(CO)$_{21}$H$_4$ (9), where two octahedra are fused by a face. Here, $m = 2$, $n = 9$, $o = 0$ and hence, this structure requires 62 valence electron pairs. The molecule has 6 Ru atoms contributing 24 electron pairs and 3 shared Pt atoms that contribute 15 electron pairs. The 21 CO groups and 4 bridging H atoms contribute 21 and 2 electron pairs respectively. This makes the molecule neutral. On the other hand, Mingos’ electron count gives different electron counts for the cluster (Table 5.1).$^{11c,d}$ According to Mingos’ the characteristic electron count ($\Delta c$) for the triangular face sharing is 50 when number of vertices of one or both deltahedral $\geq 6$. Therefore, it predicts 61 valence electron pairs as the required number of electron pairs for a stable face shared biocathedral cluster. The structures 10-13, 18-19, 21-25 have
similar skeleton where two or more octahedra are fused by face. In these structures CO ligands are replaced by other ligands like COD, \( \text{Ph}_2\text{C}_2 \), Tol\(_2\text{C}_2\) etc. They also obey the electron count and have appropriate charges and bridging H atoms to satisfy the electron count. The principle of capping is valid in this class of clusters also, as demonstrated by \( \text{Ru}_6\text{Pt}_3(\text{CO})_{21}[\text{Au}(\text{PEt}_3)]_2\text{H}_2 \) (10). This molecule has two capping vertices. Since \( m = 4 \), \( n = 11 \), \( o = 0 \) and \( p = 2 \), the structure requires 74 electron pairs for stability. The 6 Ru atoms, 3 Pt atoms, 21 CO groups and 2 bridging H atoms contribute 61 electron pairs for skeletal bonding. The 2 Au(PEt\(_3\)) groups contribute 13 electron pairs and thus the molecule is neutral. Similar structure (St. 22, Table 5.1) with one capping Au(PEt\(_3\)) group also obeys the total valence electron count. The cluster \( \text{Rh}_8\text{Pt}(\text{CO})_{19}^+ \) (13) is another example of face shared bioctahedra which requires 62 electron pairs \([m = 2, n = 9, o = 0]\). The 8 Rh atoms, 1 Pt atom and 19 CO groups contribute 60 electron pairs. The molecule needs 4 more electrons to satisfy the electron count and hence it is electron deficient. However, this molecule is observed as dianion and hence does not obey electron count rule. On the other hand, Mingos’ electron count predicts this cluster to be dianion (Table 5.1). Interestingly, it is found to decompose to smaller fragments under CO atmosphere.\(^{13g}\) The isoelectronic structure \( \text{Rh}_9(\text{CO})_{19}^- \) (St. 31, Table 5.1) also undergo decomposition in CO atmosphere,\(^{14c}\) which is also electron deficient by two electrons according to our electron count rule.

**[5.5.1.4] Some Special Cases**

\[ \text{Ru}_{11}(\text{CO})_{23}^- \] (14): This structure can be described as the condensation of three octahedra by four atoms. Here, \( m = 3 \), \( n = 11 \), \( o = 0 \) and hence it require 74
electron pairs to be stable. The 11 Rh atoms and 23 CO groups donate 49.5 and 23 electron pairs respectively. Hence, the cluster requires 1.5 electron pairs and thus exists as trianion. This structure also obeys Mingos’ electron count. The Mingos considered this cluster as a condensation of a butterfly unit between an octahedra and a component polyhedra which is formed by face sharing between two octahedron. The St. 32 (Table 5.1) also shows condensation between three polyhedra by four atoms and obeys the total valence electron count.

Os₆Pt₂(CO)₁₆(COD)₂ (15) : This molecule shows a relatively rare condensation of three polyhedra in which one trigonal bipyramid and one tetrahedron are fused by face and that fused polyhedra shares an edge with another tetrahedron. According to our electron count it requires 55 valence electron pairs \([m = 3, n = 8, p = 2]\). There are 6 Os atoms, 2 Pt atoms, 16 CO groups and 2 COD groups and together contribute 54 skeletal electron pairs. Thus, it is electron deficient by 2 electrons and also found to be converted to stable structure (St. 36, Table 5.1) in CO atmosphere. According to Mingos’ approach, it can be considered as an edge sharing between, a tetrahedron, and a bicapped tetrahedron. The Mingos’ electron count for this cluster is 55 total valence electron pairs, same as predicted by our rule.

Os₇(CO)₁₉Au₂(Ph₂PCH₂PPh₂) (16) : This complex is essentially a face fused system between two trigonal bipyramid having two capping vertices. Application of our total electron count to this system predicts an electron count of 60 skeletal electron pairs \((m = 4, n = 9, p = 2)\). The 28 electron pairs are provided by 7 Os atoms, 11 electron pairs by 2 Au atoms, 19 electron pairs by 19 CO groups and 2
electron pairs by Ph$_2$PCH$_2$PPh$_2$ ligand. As a result, the molecule is stable as a neutral species. Mingos’ electron count for this cluster is also the same.

[5.5.2] Application to Metallaboranes

[5.5.2.1] Clusters where mno Rule can be Applied

The structures 38 is a triple decker sandwich compound and thus the number of polyhedra, $m = 3$. In this structure, the number of vertices ($n$) is 17 and there are two metal atoms in the vertex-shared position. Hence, $x$, $x_s$, $n_s$ and $o$ equals to 2. The Cp* ligand on Ru and Co can be considered as nido fragments derived from pentagonal bipyramid, which gives $p = 2$. Therefore, the electron count for this cluster according to \($m + n + o + p + 6x - x_s/n_s\{3(m - 1)\}$ is $3 + 17 + 2 + 2 + 6\times2 - 2/2\{3(3 - 1)\} = 30$ electron pairs. This structure contains 3 BH groups, 10 CMe groups and 2 CR groups. They contribute 21 electron pairs. The number of electron pairs contributed by Ru and Co are 4 and 4.5 electron pairs respectively. The H attached to Ru contributes 1 electron. Therefore, the total number of electron pairs in this metallaborane is $21 + 4 + 4.5 + 0.5 = 30$. The electron count for this cluster can also be obtained by applying mno rule ($m + n + o + p$; the $m$, $n$, $o$ and $p$ represents the same variables as described earlier), which predicts an electron count of $3 + 17 + 2 + 2 = 24$ electron pairs ($m = 3$, $n = 17$, $o = 2$ and $p = 2$). In this case, the skeletal electron pairs contributed by Ru and Co are 1 and 1.5 electron pairs respectively. It is also considered that the H attached to Ru will donate its electron for the cluster bonding. This makes the electron count by mno rule as 24 electron pairs (21 electron pairs contributed by CMe, CR and BH groups and 3 electron pairs contributed by Ru, Co and one negative charge).
Figure 5.4: Schematic representation of some experimentally known metallaboranes and metallacarboranes. A point at the vertex and a line drawn from the vertex represents the CH group and the CMe group respectively.
Table 5.2: The electron count of metallaboranes and carboranes according to \( mno \) \((m + n + o + p)\) and \( m + n + o + p + 6x - x_s/n_s\{3(m - 1)\}\) rules. It is compared with the number of electron pairs provided by the constituent fragments.

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<th>St. No.(^*)</th>
<th>(m)</th>
<th>(n)</th>
<th>(O)</th>
<th>(p)</th>
<th>(x)</th>
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</tbody>
</table>

\(m = \text{number of polyhedra}; n = \text{number of vertices}; o = \text{number of single vertex bridge}; p = \text{number of missing vertices}\). Last column gives the references to experimental structures. \(^a\) indicates the structures whose electron count does not obey \(mno\) rule but obey rule A and \(^b\) indicates where both the rule fails. *Molecular Formula of the structures are given below:

38 : RuCo(Cp*)\(_2\)B\(_3\)H\(_4\)C\(_2\)Et\(_2\); 39 : FeMe\(_3\)C\(_5\)B\(_7\)H\(_{12}\); 40 : Ir(PPh\(_3\))\(_3\)C\(_8\)B\(_8\)H\(_9\);
41 : Ru\(_2\)(CO)\(_6\)(PPhMe\(_2\))\(_2\)C\(_2\)B\(_9\)H\(_9\)Me\(_2\); 42 : Co\(_2\)(Cp*)\(_2\)Mo(CO)\(_2\)C\(_2\)B\(_8\)H\(_9\)Et\(_3\);
43 : Rh\(_2\)(Cp*)\(_2\)Ru(CO)\(_2\)C\(_2\)B\(_9\)H\(_9\)Et\(_3\); 44 : [C\(_8\)H\(_{20}\)N\(_1\)]\(^+\)[Ru(PPh\(_3\))\(_2\)C\(_2\)B\(_8\)H\(_9\)]\(^-\);
45 : Fe\(_2\)C\(_4\)B\(_7\)(Et)\(_2\); 46 : Os(PPh\(_3\))\(_2\)B\(_3\)H\(_3\)B(OMe)C(Ph)\(_3\); 47 : CpRu(PPh\(_3\))C\(_2\)B\(_9\)H\(_12\);
48 : Cp\(_3\)RuRhB\(_2\)C\(_6\)(Me)H\(_3\); 49 : Os\(_3\)(CO)\(_6\)B\(_3\)H\(_3\)C(NMe\(_3\))\(_2\); 50 : Ru\(_3\)(Cp*)\(_2\)B\(_8\)H\(_{20}\);

The complex 39 can be considered as a sandwich structure, where the Fe atom is shared between a carboranes unit and an arene ring. Here, number of polyhedra \(m = 2\), number of vertices \(n = 16\) and number of single atom sharing \(o = 1\). The arene ring can be considered as a \(nido\) fragment and thus \(p = 1\). Since, this structure has only one metal atom, which occupies the shared position, the value of \(x, x_s\) and \(n_s\) is 1. Thus, according to \(m + n + o + p + 6x - x_s/n_s\{3(m - 1)\}\) the total valence electron count of this transition metal cluster is \(2 + 16 + 1 + 1 + 6 - 2/2\{3(2 - 1)\} = 23\) electron pairs. There are 5 CH groups and 3 CMe groups, contributing 12 electron pairs and 7 BH groups contributing 7 electron pairs. The Fe atom
contributes 4 electron pairs. As a result, the total electron count for this cluster becomes $12 + 7 + 4 = 23$ electron pairs. The electronic requirement of this structure can be determined from mno rule in a similar fashion as described for the structure 38 (Table 5.2).

The structure 40 is a 10-vertex closo structure ($m = 1, n = 10, o = 0$ and $p = 0$), where one vertex is a transition metal fragment. Therefore, the electron count according to mno rule will be $m + n + o + p = 1 + 10 = 11$ electron pairs. According to the electron count for mixed cluster, the electronic requirement is $m + n + o + p + 6x = 1 + 10 + 6 \times 1 = 17$ electron pairs. This structure contains 7 BH groups, one CH and one BPh$_3$ groups. They will together contribute 10 electron pairs. The secondary isolobal analogy (Figure 5.2) predicts that the Ir(PPh$_3$)$_2$ group donates 1 electron for skeletal bonding. In addition, H also donates 1 electron to the cluster bonding. Therefore, the total skeletal electron pairs for this cluster are 11 electron pairs. Hence, this cluster obeys mno rule. The Ir(PPh$_3$)$_2$ fragment would contribute 6.5 electron pairs (4.5 by Ir atom and 2 by two PPh$_3$ groups) if we consider the electron count rule for the mixed cluster. As a result, the total number of electron will be equal to 17 electron pairs (10 electron pairs from 7 BH, 1 CH and 1 BPh$_3$; 6.5 electron pairs from Ir(PPh$_3$)$_2$ and 0.5 electron pair from H atom). Thus, this structure obeys both mno and the electron count for the mixed metallaboranes and carboranes.
[5.5.2.2] Clusters where mno Rule cannot be Applied

The structure 41 is a face shared polyhedra, where one icosahedron and one \textit{nido} square pyramid are condensed. One of the vertex of the shared face is metal atom and remaining two are B atoms. Here, $m = 2$, $n = 14$, $o = 0$ and $p = 1$. Therefore, the electron count according to mno rule $(m + n + o + p)$ will be $2 + 14 + 0 + 1 = 17$ electron pairs. The 7 BH, 2 CH groups and 2 B atoms of this cluster will contribute 7, 3 and 3 electron pairs respectively. The two Ru(CO)$_2$(PPhMe$_2$) groups also contributes 2 electron pairs and 2 H atoms will give 1 electron pair. According to the secondary isolobal analogy discussed earlier (Figure 5.2) the Ru(CO)$_2$ fragment will not donate any electron pair to the skeletal bonding. Hence, the total electron pairs for the skeletal bonding by mno rule are $7 + 3 + 3 + 2 + 1 = 16$ electron pairs. It implies that the cluster is electron deficient by 2 electrons, but, this cluster is neutral. If we apply the $m + n + o + p + 6x - x_{s}/n_{s}\{3(m - 1)\}$ electron count for this cluster, the electron count becomes $2 + 14 + 0 + 1 + 1 + 6x - x_{s}/n_{s}\{3(m - 1)\}$ = 34 electron pairs ($x = 1, x_{s} = 1$ and $n_{s} = 3$). The electron pairs donated by 7 BH groups, 2 CH groups, 2 B atoms and 2 H atoms will remain the same, but the total electron pairs donated by 3 Ru atoms, 5 CO groups and 2 (PPhMe$_2$) groups will be 12, 5 and 2 respectively. Thus, the total valence electron count for this cluster is $7 + 3 + 3 + 1 + 12 + 8 = 34$. This matches the electronic requirement for this cluster.

The structure 42 exemplifies a tetra-decker mixed cluster of transition metal and carborane. The electron count for this cluster following the mno rule $(m + n + o + p)$ is $4 + 23 + 3 + 2 = 32$ ($m = 4$, $n = 23$, $o = 3$ and $p = 2$). It includes 6 BH, 10 CMe and 4 CEt groups. They contribute 6, 15 and 6 electron pairs to the cluster.
bonding respectively. The 2 Co atoms will contribute 3 electron pairs. The Mo(CO)₂ group will not contribute any electron pairs to the cluster bonding according to the secondary isolobal analogy (Figure 5.2). Thus, the total valence electron count is 6 + 15 + 6 + 3 = 30, which is less by 2 electron pairs than the electronic requirement provided by mno rule. However, this cluster is neutral and therefore does not obey mno rule. The values for \( x = x_s = n_s = 3 \), since his cluster has 3 transition metal fragments and all are in the vertex shared position. Therefore, the total valence electron pairs required for this cluster are 4 + 23 + 3 + 2 + 6 \times 3 - 3/3 \{3(4 - 1) = 41 \text{ electron pairs}. The 27 electron pairs are contributed by 6 BH, 10 CMe and 4 CEt groups. The total electron pairs donated by two Co atoms and one Mo atom are 9 and 3 electron pairs respectively. The 2 CO groups attached to the Mo donate 2 electron pairs. Thus, the total valence electron pairs for this cluster are 6 + 15 + 6 + 9 + 3 + 2 = 41, same as predicted by the electron count for the mixed cluster.

The last example (43) depicts condensation of 4 polyhedra \((m = 4)\) and it has 24 vertices \((n = 24)\). The triangular metal skeleton (2Rh and 1Ru) is considered as bis-nido trigonal bipyramid. The 2 Rh are shared by the Cp* ligand \((nido\) pentagonal bipyramid) and the Ru atom is shared by closo icosahedral carboranes. Therefore, the number of missing vertices \( p = 4 \) and the number of single vertex sharing \( o = 3 \). The mno rule \((m + n + o + p)\) predicts \(4 + 24 + 3 + 4 = 35\) skeletal electron pairs for this cluster. There are 9 BH groups, which contributes 9 electron pairs. The 10 CMe and 2 CH groups contribute 18 electron pairs. The 2 Rh atoms, 1 Ru atom and 4 bridging CO groups can be divided into 2 Rh(CO)₂ groups and one
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Ru atom so that the electron pairs contributed by the transition metal fragments become 2 (1 by Ru and 1 by 2 Rh(CO)₂, following the secondary isolobal analogy discussed in Figure 5.2). Thus, the skeletal electron pairs for this cluster are 9 + 15 + 3 + 1 + 1 = 29. This suggests that this cluster is electron deficient by 6 electron pairs, whereas the cluster is neutral. Application of the electron count for the mixed cluster to this structure gives the total electron count as 

\[ m + n + o + p + 6x - \frac{x_s}{n_s} \{3(m - 1)\} = 4 + 24 + 3 + 4 + 6 \times 3 - 3/3 \{3(4 - 1)\} = 44 \text{ electron pairs} \]  

(x = x_s = n_s = 3). The number of electron pairs donated by 9 BH, 10 CMe and 2 CH groups will remain the same. The total electron pairs donated by 2 Rh atoms, 1 Ru atom and 2 CO groups are 9, 4 and 4 respectively. Thus, the total valence electron pairs for this cluster are 9 + 15 + 3 + 9 + 4 + 4 = 44 electron pairs.

This new rule, however, has its limitations. Some of the exceptions to this are illustrated in the Table 5.2. This rule is useful for those metallaboranes, where the number of skeletal electron pairs donated by the transition metal fragments cannot be assigned appropriately.

[5.6] Concluding Remarks

The connection between the skeletal electron count in polycondensed boranes by mno rule and total valence electron pairs in polycondensed transition metal clusters by Mingos’ rule is established. The total electron count of the transition metal clusters can be expressed as 

\[ m + n + o + 6n - 3(m - 1) \]

where \( m \) = number of polyhedra, \( n \) = number of vertices and \( o \) = number of single vertex sharing. One and two additional pairs of electrons have to be added to the total
electron count for nido and arachno systems respectively. This rule indicates the difference between the electron count for condensed boranes (mno rule) and transition metal clusters as $6n - 3(m-1)$ and establishes the missing link between the electron count in boranes and transition metal clusters. According to this rule, $6n - 3(m - 1)$ numbers of electron pairs have to be added to the mno count of boranes to achieve the total valence electron pairs of an isostructural transition metal clusters. This rule gives a unifying electron count for the electron count of both condensed and non-condensed transition metal clusters. The $7n + 1$ rule for non-condensed transition metal cluster becomes a special case of this generalized rule, when $m = 1$. This can successfully explain the stability and charge of a large number of transition metal clusters. The variables in the Mingos’ rule is correlated with the variables in the mno rule by the relation $y = 2n_s - 3(m - 1) + a$, where $n_s =$ number of shared vertices, $y =$ number of bonds between the shared atoms and $m =$ number of polyhedra. It is not possible to identify the skeletal and non-skeletal electron pairs for the condensed transition metal clusters unambiguously. This is due to the difficulty in defining a sharp boundary for the skeletal electrons in case of condensed transition metal clusters. In the attempt to bridge the gap between the electron count rule in condensed boranes (mno rule) and transition metal clusters (Mingos’ rule) we have also formulated a counting rule to incorporate all the clusters ranging from boranes to metallaboranes to transition metal clusters under the same umbrella. This rule gives the total valence electron pairs of the condensed polyhedra as $m + n + o + p + 6x - x_s/n_s\{3(m - 1)\}$, where $x =$ number of transition metals, $x_s =$ number of shared transition metals and $n_s =$ number of shared atoms.
[5.7] References


**mn**o rule versus Mingos’ rule


16. While distributing the bridging ligands between the shared and terminal vertices, the shared vertices are assigned with less number of ligands.
