

❖ Total Electron Count (TEC)

The simple 18-electron rule has been proven of great significance in the case of structural rationalization of low nuclearity carbonyl clusters. However, if the number of metal centers per cluster is equal or greater than five; then the conventional approach is not significant, and does not provide any satisfactory results. For example, the 18-electron count for $\text{Rh}_6(\text{CO})_{16}$ is $6 \times 9 + 16 \times 2 = 86$; which means that eleven metal-metal bonds ($108 - 86 = 22$) are needed to fulfil the requirement of six metal centres. But the actual structure of $\text{Rh}_6(\text{CO})_{16}$ is consisted of an octahedral Rh_6 core with twelve metal-metal bonds. Moreover, simple 18-electron treatment for high nuclearity carbonyl clusters (HNCC) does not provide any information regarding the overall geometry. The situation also becomes more and more complex if some encapsulated heteroatom like carbon is also present. Therefore, because of the lacking of any rational solution for the electronic structure of high nuclearity carbonyl clusters, most of the efforts have been devoted to find a correlation between their structure and the number of electrons available for cluster binding. It is worthy to mention that high-nuclearity carbonyl clusters are also considered as electron-deficient compounds; which is obviously due to the inadequate number of electrons to allow the assignment of all bonds as 2-centre 2-electron in nature.

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➤ **Isolobal Analogy Between $M(\text{CO})_3$ And BH Fragments**

A British chemist, Kenneth Wade, solved the unexplained problem of structure and bonding predictions in high nuclearity carbonyl clusters by developing a new scheme of electron counting, total electron count (TEC). This new proposal was actually the extension of his previously used scheme for boranes and carboranes, in which he had correlated the structure of boranes and their derivatives with the number of electrons involved in the skeletal framework. The idea behind this extension was that the $M(\text{CO})_3$ unit is actually isolobal with the BH unit. This can be better explained by taking the example of $\text{Ru}(\text{CO})_3$ fragment.

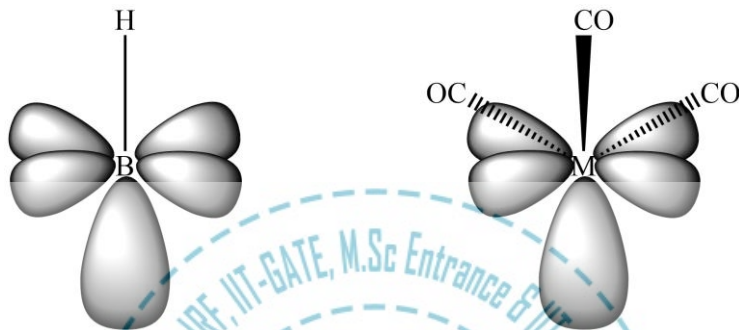


Figure 35. Structures and bonding in the isolobal pair of BH and $\text{Ru}(\text{CO})_3$.

The BH unit uses one of four valence orbitals of boron and two electrons, one from boron and one from hydrogen. Hence, the spare valence orbitals and corresponding electrons left on boron are three and two respectively. These spare orbitals and electrons are then used in cluster bonding. Similarly, the $\text{Ru}(\text{CO})_3$ unit uses six of nine valence orbitals of ruthenium and twelve electrons, six from ruthenium and six from three carbonyl ligands. Therefore, the spare valence orbitals and corresponding electrons left on ruthenium are three and two respectively.

Therefore, $3n$ valence orbitals and $2n$ electrons should be available in any B_nH_n cluster system. The overlap of $2n$ valence orbitals oriented towards the surface of the polyhedron generates n bonding and n antibonding molecular orbitals. The overlap of n valence orbitals oriented towards the core of the polyhedron generates 1 strongly bonding and $n-1$ weakly bonding, nonbonding or antibonding molecular orbitals. Thus we can say that a total of $n+1$ bonding molecular orbitals are generated in the process of cluster formation, and the number of electrons required to fill these bonding molecular orbitals is $2n+2$. However, in n BH units of B_nH_n cluster can supply only $2n$ electron, explain why $\text{B}_n\text{H}_n^{2-}$ or cluster is more stable than simple B_nH_n . The same argument holds true about $\text{Ru}_n(\text{CO})_{3n}$ cluster system, i.e. $2n+2$ electrons are needed to fill all the bonding molecular orbitals. Hence, $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ anion would be more stable than $\text{Ru}_6(\text{CO})_{18}$ cluster system.

➤ **Electron Counting Scheme for High Nuclearity Carbonyl Clusters**

The isolobal analogy of $M(\text{CO})_3$ fragment with B–H (or C–H) unit inspired Kenneth Wade to explore this field further; and he of course then came with a new set of rules for electron counting in high nuclearity carbonyl cluster systems. He suggested that the total electron count of these clusters can be correlated to

skeletal electron count participating in the cluster bonding in a similar way adopted in boranes or carboranes. The total electron count can be calculated by adding the following contributions:

- i) The number of valence electrons of all metal-centers.
- ii) Two electrons for each carbonyl group irrespective of the fact whether it is terminal or bridged.
- iii) One electron for each unit of negative charge.
- iv) The number of valence electrons of each hetero or interstitial atoms like carbon or nitrogen.

This total electron count then can be used to predict the structure and bonding of carbonyl cluster systems by extracting the skeletal electron count. Now, as we know that $2n+2$, $2n+4$, $2n+6$ skeletal electrons are required for closo, nido and arachno boranes, respectively; the same is true for metal carbonyl clusters. However, in addition to the 2 valence electrons to be used in the skeletal framework, each $M(CO)_3$ also contains 12 non-skeletal electrons. The theoretical basis of this claim comes from the fact that each $M-CO$ bond contains 4 electrons; 2 σ -electrons donated by CO ligand to the metal, and 2 π -electrons donated by the metal back to the lowest unoccupied antibonding molecular orbital of CO ligand. This gives a total electron count for closo polyhedron as $12n + 2(n+1)$. Hence, the predictions of structure and bonding in high nuclearity carbonyl cluster with n vertexes can be summed up only after considering these twelve non-skeletal electrons.

Table 9. Total electron count (TEC) and predicted structure.

Total electron count	Name	Predicted structure
$12n + 2(n - 1)$	Bicapped closo	$n - 2$ vertex closo polyhedron with 2 capped faces
$12n + 2n$	Capped closo	$n - 1$ vertex closo polyhedron with 1 face capped
$12n + 2(n + 1)$	Closo	Closo polyhedron with n vertices
$12n + 2(n + 2)$	Nido	$n + 1$ vertex closo polyhedron with 1 missing vertex
$12n + 2(n + 3)$	Arachno	$n + 2$ vertex closo polyhedron with 2 missing vertex
$12n + 2(n + 4)$	Hypho	$n + 3$ vertex closo polyhedron with 3 missing vertex
$12n + 2(n + 5)$	Klado	$n + 4$ vertex closo polyhedron with 4 missing vertex

It should also be noted that Wade's predictions based on total electron count are also applicable to low nuclearity carbonyl cluster systems in which the number of metal centers present is three or four. For example, the total electron count for $Ir_4(CO)_{12}$ is $4 \times Ir + 12 \times CO = 4 \times 9 + 12 \times 2 = 60$. Since $n = 4$, $12n + 2(n + 2) = 60$, so the cluster is nido. Starting from a trigonal bipyramid, a vertex is removed. Similarly, the total electron count for $Fe_3(CO)_{12}$ is $3 \times Fe + 12 \times CO = 3 \times 8 + 12 \times 2 = 48$. Since $n = 3$, $12n + 2(n + 3) = 48$, so the cluster is arachno. Therefore, the structure prediction Starts from a trigonal bipyramid, and then two axially opposite vertexes are removed.

➤ **Structure and Bonding Profile of Some Typical High Nuclearity Carbonyl Clusters Using TEC**

As we have already discussed the fundamentals of structure and bonding in high nuclearity carbonyl clusters systems, now we will implement those ideas to explain some typical examples.

1. $M_6(CO)_{16}$ ($M = Co, Rh$): The total electron count for $Rh_6(CO)_{16}$ is $6 \times Rh + 16 \times CO = 6 \times 9 + 16 \times 2 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $Rh_6(CO)_{16}$ cluster system is shown below.

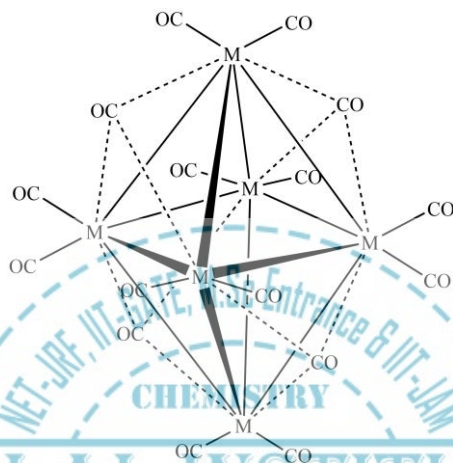


Figure 36. Structure of $M_6(CO)_{16}$ ($M = Co, Rh$).

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2. $Os_5(CO)_{16}$: The total electron count for $Os_5(CO)_{16}$ is $5 \times Os + 16 \times CO = 5 \times 8 + 16 \times 2 = 72$. Since $n = 5$, $12n + 2(n + 1) = 72$, so the cluster is closo. Therefore, the structure prediction starts from an idealized trigonal bipyramid. The predicted structure for $Os_5(CO)_{16}$ cluster system is shown below.

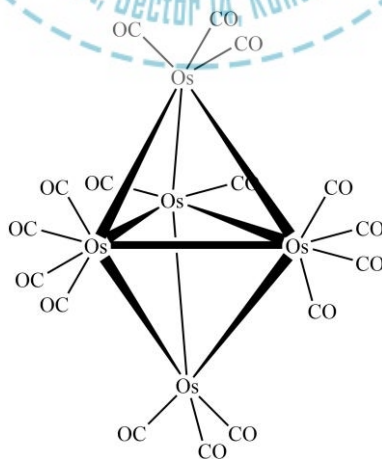


Figure 37. Structure of $Os_5(CO)_{16}$.

3. $[\text{Os}_6(\text{CO})_{18}]^{2-}$: The total electron count for $[\text{Os}_6(\text{CO})_{18}]^{2-}$ is $6 \times \text{Os} + 18 \times \text{CO} + 2$ (for negative charge) = $6 \times 8 + 18 \times 2 + 2 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $[\text{Os}_6(\text{CO})_{18}]^{2-}$ cluster system is shown below.

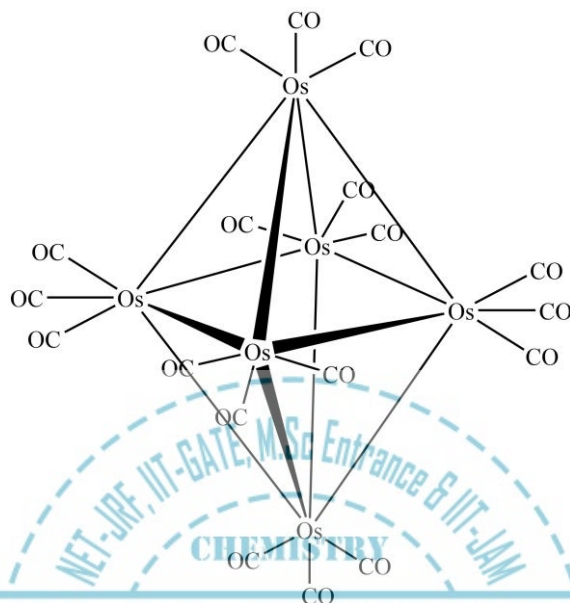


Figure 38. Structure of $[\text{Os}_6(\text{CO})_{18}]^{2-}$.

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4. $\text{Os}_5\text{C}(\text{CO})_{15}$: The total electron count for $\text{Os}_5\text{C}(\text{CO})_{15}$ is $5 \times \text{Os} + 15 \times \text{CO} + 1 \times \text{C} = 5 \times 8 + 15 \times 2 + 4 \times 1 = 74$. Since $n = 5$, $12n + 2(n + 2) = 74$, so the cluster is nido. Therefore, the structure prediction starts from an idealized octahedron, and then one vertex is removed. The predicted structure for $\text{Os}_5\text{C}(\text{CO})_{15}$ cluster system is shown below.

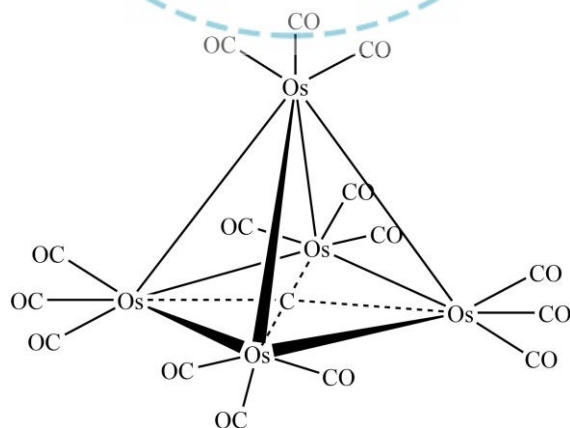


Figure 39. Structure of $\text{Os}_5\text{C}(\text{CO})_{15}$.

5. $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$: The total electron count for $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ is $6 \times \text{Ru} + 16 \times \text{CO} + 1 \times \text{N} + 1$ (for negative charge) = $6 \times 8 + 16 \times 2 + 1 \times 5 + 1 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ cluster system is shown below.

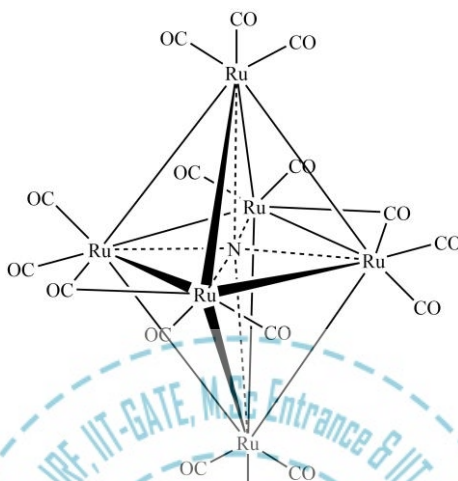


Figure 40. Structure of $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$.

6. $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$: The total electron count for $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ is $4 \times \text{Fe} + 12 \times \text{CO} + 1 \times \text{N} + 1$ (for negative charge) = $4 \times 8 + 12 \times 2 + 1 \times 5 + 1 = 62$. Since $n = 4$, $12n + 2(n + 3) = 62$, so the cluster is arachno. Therefore, the structure prediction starts from an idealized octahedron, then two adjacent vertexes are removed. The predicted structure for $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ cluster system is shown below.

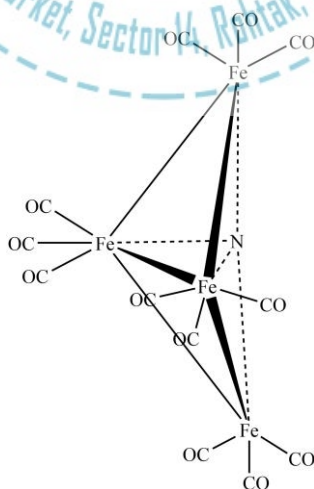


Figure 41. Structure of $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$.

➤ **Correlation Between TEC and SEP**

The implementation of the rules listed in 'Table 9' is more often carried out in reverse gear, i.e. 12 electrons for each metal center are subtracted from the total electron count. The number of electrons thus obtained is then divided by 2 to get skeletal electron pairs. The number of skeletal electron pairs (SEP) can be calculated using equation (23) as described below:

$$\text{SEP} = \frac{1}{2}(\text{TEC} - 12 \text{ electrons per metal center}) \quad (23)$$

Now the structure prediction of some common high nuclearity carbonyl cluster systems on the correlative basis of total electron count (TEC) and skeletal electron pairs (SEP) can be summed up as:

Table 10. Structure prediction of some common clusters on the correlative basis of TEC and SEP.

Carbonyl cluster	Total electron count (TEC)	Skeletal electron pairs (SEP)	Vertex in parent polyhedron	Predicted structure
$\text{Rh}_6(\text{CO})_{16}$	$(6 \times 9) + (16 \times 2) = 86$	$0.5 \times [86 - (6 \times 12)] = 7$	6	Closo
$\text{Os}_5(\text{CO})_{16}$	$(5 \times 8) + (16 \times 2) = 72$	$0.5 \times [72 - (5 \times 12)] = 6$	5	Closo
$\text{Os}_5\text{C}(\text{CO})_{15}$	$(5 \times 8) + (15 \times 2) + (4) = 74$	$0.5 \times [74 - (5 \times 12)] = 7$	5	Nido
$[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$	$(4 \times 8) + (12 \times 2) + (4) + (2) = 62$	$0.5 \times [62 - (4 \times 12)] = 7$	6	Arachno
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$	$(4 \times 8) + (12 \times 2) + (3) + (1) = 60$	$0.5 \times [60 - (4 \times 12)] = 6$	5	Nido
$[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$	$(5 \times 8) + (14 \times 2) + (5) + (1) = 74$	$0.5 \times [74 - (5 \times 12)] = 7$	7	Nido
$[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$	$(4 \times 8) + (12 \times 2) + (5) + (1) = 62$	$0.5 \times [62 - (4 \times 12)] = 7$	6	Arachno

Finally, it should also be noted that the total electron counting scheme is applicable to most of the high nuclearity carbonyl cluster systems, yet the exceptions like $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ do exist.

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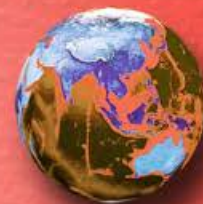
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