



A Unique Bypass to the Carbonyl Cluster 'Nucleus' Using the 14n Rule

ENOS MASHEIJA KIREMIRE

Department of Chemistry and Biochemistry,
University of Namibia, Private Bag 13301, Windhoek, Namibia.

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ABSTRACT

This paper introduces a method of classifying clusters of the transition metal carbonyls based on the 14n rule. It was derived from close analysis of the relationship between the number of skeletal atoms, valence electrons and eighteen electron rule in the case of transition elements, and the known bonds or linkages of simple clusters. The analysis reveals that there is an infinite range of carbonyl clusters. These clusters occur in an orderly manner forming definite series. In addition to the categorization of clusters, tentative assignment of geometries in particular those of simple ones can be predicted. Furthermore, the method is able to identify the possible INNER CORE NUCLEAR CLUSTER of some large carbonyl clusters. This paper presents a highly refined and simplified new method of classifying carbonyl clusters.

Key words: Bypass, Nucleus, Cluster, Inner core.

INTRODUCTION

Transition metal carbonyl clusters have stimulated immense interest for several decades largely due to their intriguing structural architecture, numerous potential industrial applications and challenging bonding properties. In this regard, the work by Wade and Mingos¹⁻⁶ as well as Jemmis⁷⁻⁸ has contributed tremendously towards the understanding of clusters. Subsequently, other research groups such as those headed by King, Teo, Zanello, and Slovokhotov⁹⁻¹³ have expanded the knowledge especially on the large carbonyl clusters. The polyhedral skeletal electron pair theory (PSEPT) which uses mainly the 4n, 5n and 6n rules

has classified clusters as closo, nido, arachno, hypho and some klapo. However on closer scrutiny of the structures and formulas of the simple boranes, hydrocarbons, carboranes and transition metal carbonyl clusters reveals that these clusters both simple and complex ones belong to a wide range of an infinite series. The series are formed according to definite numerical sequences reminiscent of the atomic number of elements.

Classification of Transition Metal Carbonyl Clusters Using the 14n Rule

The transition metal carbonyl clusters have been classified into closo, nido, arachno and hypho using Wade-Mingos rules for more than

fifty years¹. On closer analysis of the molecular structures of the clusters, it has been found that the transition metal carbonyl clusters form series based on 14n rule where n is the number of skeletal atoms that obey the 18 electron rule. A portion of the series is presented in Table 1 which will be used as a

reference for classification purposes. Consequently, using the 14n rule as a BASIS, a given formula of a transition metal carbonyl cluster can readily be categorized. Some selected carbonyls have been used as illustrations of this simple and short method for categorizing carbonyl clusters.

Table 1: Portion of Cluster Series for Main Group Elements and Transition Metal Carbonyl Clusters

| Transition metal carbonyl cluster series(14n) | Main group cluster Series(4n) | k Series | Remarks |
|---|-------------------------------|----------|---------------------------------------|
| 14n-10 | 4n-10 | 2n+5 | Hexacapped Series(C ⁶ C) |
| 14n-8 | 4n-8 | 2n+4 | Pentacapped Series (C ⁵ C) |
| 14n-6 | 4n-6 | 2n+3 | Tetracapped Series(C ⁴ C) |
| 14n-4 | 4n-4 | 2n+2 | Tricapped Series(C ³ C) |
| 14n-2 | 4n-2 | 2n+1 | Bicapped Series (C ² C) |
| 14n | 4n | 2n | Monocapped Series(C ¹ C) |
| 14n +2 | 4n+2 | 2n-1 | Closo Series(C) |
| 14n +4 | 4n+4 | 2n-2 | Nido Series(N) |
| 14n +6 | 4n+6 | 2n-3 | Arachno Series(A) |
| 14n +8 | 4n+8 | 2n-4 | Hypho Series(H) |
| 14n +10 | 4n+10 | 2n-5 | Klapo Series(H-1) |

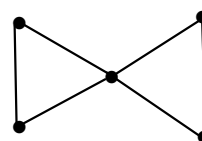
Hypho series(14n+8)

Consider the hypho cluster $\text{Os}_4(\text{CO})_{16}^{14}$; n = 4, $14n = 14 \times 4 = 56$, the total valence electrons(V) = $8 \times 4 + 16 \times 2 = 64$. The difference between V = 64 and $14n = 56$ is $64 - 56 = 8$. Hence, we must add 8 to the value of 14n to have the same value of valence electrons. Therefore the series for this cluster may be written as $T = 14n + 8$ (T = series symbol). Looking at Table 1, this cluster belongs to hypho series (H). The cluster number k is given by $2n-4$ when n = number of skeletal atoms in the cluster. In this case, $k = 2n-4 = 2 \times 4 - 4 = 4$. For small clusters k also represents the number of linkages or bonds of the cluster atoms. Hence, this represents a square shown in S-9 of Scheme 1 tabulated below. The scheme shows common shapes found for two (M-2) to ten (M-10) transition metal skeletal elements in carbonyl clusters.

Take another cluster, $\text{Os}_5(\text{CO})_{19}$; n = 5, $14n = 14 \times 5 = 70$, and the total valence electrons V = $5 \times 8 + 19 \times 2 = 78$. We need to add 8 to the value of 14n in order to reach the value of 78. Therefore the cluster series can be expressed as $T = 14n + 8 = V$. This means that $\text{Os}_5(\text{CO})_{19}$ belongs to the same cluster

series as $\text{Os}_4(\text{CO})_{16}$. The k value for $\text{Os}_5(\text{CO})_{19}$ is given by $k = 2n-4 = 2 \times 5 - 4 = 6$. It should be pointed out that from our previous work that the k value can be obtained¹⁵⁻¹⁶ from $k = \frac{1}{2}(E-V)$, where $E = 5 \times 18 = 90$ (sum of 18 electrons on the skeletal atoms assuming that each is surrounded by 18 electrons) and $V = 78$ and thus $k = \frac{1}{2}(90-78) = 6$. This implies the 5 skeletal elements having 6 linkages which are found to be two triangles joined together at one of their corners as shown in the following sketch.

k = 6



As can be seen the change in k value between the two clusters is $6-4 = 2$ and the change in valence values is $78-64 = 14$. Let us take examples from rhenium clusters. The case of $\text{Re}_4\text{H}_4(\text{CO})_{15}^{2-}$ cluster, n = 4, $14n = 56$, $V = 7 \times 4 + 4 + 15 \times 2 + 2 = 64$. This is similar to $\text{Os}_4(\text{CO})_{16}$ case. Hence, $T = 14n + 8$. This means the cluster belongs to hypho series and

$k = 4$. This cluster was found to have a shape of a triangle with an extended arm indicated in S-10 in scheme 1. On the other hand, its isoelectronic analogue $\text{Re}_4\text{H}_4(\text{CO})_{16}$ has a square geometry (S-9) similar to that of $\text{Os}_4(\text{CO})_{16}$ cluster. This means that in carbonyl clusters as in hydrocarbon clusters, there is some extent of k isomerism.

Arachno series(14n+6)

The $14n$ rule is being applied mainly to known cases of clusters so the readership can verify that it readily gives the same results as those obtained by the well established methods. Let us illustrate it on $\text{Os}_2(\text{CO})_8^{2-}$ cluster; $n = 2$, $14n = 14 \times 2 = 28$, $V = 8 \times 2 + 8 \times 2 + 2 = 34$. Hence, $T = 14n + 6 = 34$. This means the cluster belongs to the arachno series (see Table 1). The cluster k value is given by $k = 2n - 3 = 2 \times 2 - 3 = 1$. This corresponds to the single bond that links the two osmium atoms (S-1). Take another cluster $\text{Os}_3(\text{CO})_{12}$; $n = 3$, $14n = 14 \times 3 = 42$ and $V = 8 \times 3 + 12 \times 2 = 48$. The cluster series $T = 14n + 6 = 48$. This places $\text{Os}_3(\text{CO})_{12}$ cluster as a member of arachno series with $k = 2n - 3 = 2 \times 3 - 3 = 3$. This means that the osmium atoms form a triangle (S-5). One of the next member in the series is $\text{Os}_4(\text{CO})_{15}$; $n = 4$, $14n = 14 \times 4 = 56$ and $V = 8 \times 4 + 15 \times 2 = 62$. Therefore $T = 14n + 6 = 62$. Again, $\text{Os}_4(\text{CO})_{15}$ is a member of the arachno series with $k = 2n - 3 = 2 \times 4 - 3 = 5$. This corresponds to five linkages of the four osmium atoms (S-11). The shape resembles a square with a diagonal. Let us take a cluster with six skeletal atoms, $\text{Os}_6(\text{CO})_{17}\text{L}_4$ [$\text{L} = \text{P}(\text{OMe})_3$]. In this case $n = 6$, $14n = 14 \times 6 = 84$ and $V = 8 \times 6 + 17 \times 2 + 4 \times 2 = 90$. The cluster series will be given by $T = 14n + 6 = 90 = V$. Therefore the cluster is a member of arachno series (see Table 1) with k value of $2n - 3 = 2 \times 6 - 3 = 9$. Indeed the six osmium atoms form three linked triangles (S-21). If we use M to represent a skeletal atom, then the series go from $M-2$ to $M-3$, $M-4$, $M-5$, $M-6$ and so on. The corresponding change in M , k and V may be represented as $M-2-1-34$! $M-3-3-48$! $M-4-5-62$! $M-5-7-76$! $M-6-9-90$. The series can go on and on. The numerical change from one code to the next is simply (1, 2, 14). If we assume that M = osmium and all the ligands are CO, then the change from one cluster to the next is equivalent to adding an ' $\text{Os}(\text{CO})_3$ ' fragment. This fragment is loaded with $8 + 3 \times 3 = 14$ electron units. This also implies if we start with a given $M-2$ cluster in a series, we can construct an infinite number of hypothetical members that series.

Nido series(14n +4)

Let us consider the following osmium clusters¹⁴, $\text{Os}_3\text{H}_2(\text{CO})_{10}$; $n = 3$, $14n = 14 \times 3 = 42$, $V = 8 \times 3 + 2 + 10 \times 2 = 46$. Therefore $T = 14n + 4$. This tells us, the cluster belongs to the nido series (see Table 1) and $k = 2n - 2 = 2 \times 3 - 2 = 4$. This could imply a triangular shape with a delocalized bond (-8). If we take a next cluster of the series with four skeletal atoms such $\text{Os}_4(\text{CO})_{14}$; $n = 4$, $14n = 14 \times 4 = 56$ and $V = 60$, Then the cluster series becomes $T = 14n + 4$ which belongs to the nido family. The k value will be $2n - 2 = 2 \times 4 - 2 = 6$. This gives us a tetrahedral shape (S-12).

Closo Series (14n+2)

This is a type of clusters that follow the $14n+2$ series in case of transition metal carbonyls while the main group elements obey the $4n+2$ rule. However in this illustration we will focus only on the $14n+2$ series. Let us consider the cluster $\text{Os}_5(\text{CO})_{16}$; $n = 5$, $14n = 14 \times 5 = 70$ and $V = 8 \times 5 + 16 \times 2 = 72$. Hence, $T = 14n + 2$ (see Table 1) and $k = 2n - 1 = 2 \times 5 - 1 = 9$. This value corresponds to the linkages observed in a trigonal bipyramid geometry (S-13). In actual fact, the skeletal shape of this cluster is a trigonal bipyramid¹⁴. It is also interesting to see that a similar result pertains in $\text{B}_5\text{H}_5^{2-}$ when subjected to $4n$ rule. Thus, for $\text{B}_5\text{H}_5^{2-}$ cluster; $n = 5$, $4n = 4 \times 5 = 20$ and $V = 3 \times 5 + 5 + 2 = 22$. Hence, $T = 4n + 2$ and $k = 2n - 1 = 2 \times 5 - 1 = 9$. The closo borane cluster $\text{B}_5\text{H}_5^{2-}$ has a well known trigonal bipyramid shape¹⁵. In the case of the $\text{Os}_6(\text{CO})_{18}^{2-}$ an established octahedral geometry⁹ is well documented (S-19). Applying the $14n$ rule to the cluster, $n = 6$, $14n = 14 \times 6 = 84$ and $V = 8 \times 6 + 18 \times 2 + 2 = 86$. The cluster is clearly a member of the $14n+2$ series. Accordingly, its cluster k value is $2n - 1 = 2 \times 6 - 1 = 11$. The rhodium cluster, $\text{Rh}_6(\text{CO})_{16}$ and $\text{Re}_6(\text{C})(\text{CO})_{19}^{2-}$ which are known to have octahedral shape¹¹ with $V = 86$ all belong to the $14n+2$ series and have k value of 11. Corresponding to the $14n+2$ series is the $4n+2$ series of the main group elements. The closo borane cluster $\text{B}_6\text{H}_6^{2-}$ with a regular octahedral geometry¹⁷ belongs to the $4n+2$ series with $k = 2n - 1 = 2 \times 6 - 1 = 11$. This brings about a departure from correlating the k value with the number of connections or linkages of skeletal atoms. Thus, the k value may simply be regarded as a characteristic of a given cluster of particular series. In this case, for transition metal carbonyl clusters with six skeletal elements

(M-6) and 86 valence electrons usually adopt an octahedral geometry and has a characteristic k value of 11. If we extrapolate below and above the k value of 11 for closo series, we will have the numbers such as 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, ... and so on. As can be seen, a movement across the same series from one cluster to another, the k value changes by 2. This observation is found in all series. It is interesting to note that for the series from closo to nido, arachno, hypho downwards, the value of valence electrons (V) is greater than that of $14n$ ($V > 14n$), while for the mono-capped series ($V = 14n$) and for the closo capped series ($V < 14n$).

Monocapped Series(14n)

This series ($14n$) is quite interesting in that when the number of the skeletal elements in the cluster in question are multiplied by 14, the resultant value is numerically the same as the number of valence electrons (V) of the cluster. Falling in this category is $\text{Os}_6(\text{CO})_{18}$, $n = 6$, $14n = 14 \times 6 = 84$, and $V = 8 \times 6 + 18 \times 2 = 84$. Thus $14n = V$ in value. Therefore, the cluster belongs to a series represented by $T = 14n$ and it has a k value of $2n = 2 \times 6 = 12$. It is important to note that for this cluster, the k -value corresponds to the number of cluster linkages. It has been found convenient to symbolize monocap with C^1 and closo with C . Hence, the symbol for mono-capped series may be written as C^1C . Since 'monocap' implies one of the skeletal atoms is being used for capping purposes, the rest of the atoms become the 'inner' closo system. In this case of $\text{Os}_6(\text{CO})_{18}$ cluster, the capping is being done on the remaining 5 atoms which constitute a closo system presumably with a trigonal bipyramid geometry as has been observed⁹. We may also use the symbol $C^1C[M-5]$ to represent a mono-capping on a trigonal bipyramid geometry (S-18). Since capping involves a stepwise change of 12 valence electrons, if we remove them from 84 we will remain with 72 for the inner core. This corresponds to the equivalent presence of $\text{Os}_5(\text{CO})_{16}$ inner core cluster. The inner core ' $\text{Os}_5(\text{CO})_{16}$ ' belongs to the close series $14n+2$. This also corresponds to the $4n+2$ of the main group elements. Furthermore, if we subtract the equivalent of $10n$ from $14n+2$, the balance will be $4n+2$ equivalent to a closo system of the main group element. That is to say, from 72 electrons of the inner core [M-5] of $\text{Os}_6(\text{CO})_{18}$ cluster, if we deduct equivalent of $10n$ ($10 \times 5 = 50$) from 72 we will remain

with 22 electrons. Indeed this is the electron count of $\text{B}_5\text{H}_5^{2-}$ (22) which has a trigonal bipyramid geometry. The trigonal bipyramid geometry can be regarded as a capping on a tetrahedral geometry which in turn can be viewed as a capping on a trigonal planar shape. It is not surprising therefore that $\text{Os}_6(\text{CO})_{18}$ cluster is regarded as a doubly capped tetrahedral shape⁹. Although the closo capping series start at $T = 14n$, the capping series can be extended to series such as nido and arachno. For instance start with $\text{Os}_3(\text{CO})_{12}$, we can construct capping series by adding successive fragments of ' $\text{Os}(\text{CO})_2$ ' as follows, $\text{Os}_3(\text{CO})_{12}$! $\text{Os}_4(\text{CO})_{14}$! $\text{Os}_5(\text{CO})_{16}$! $\text{Os}_6(\text{CO})_{18}$! $\text{Os}_7(\text{CO})_{20}$! $\text{Os}_8(\text{CO})_{22}$ and so on ($k = 3$). Hence, $\text{Os}_6(\text{CO})_{18}$ is one member of the whole chain of (diagonal or vertical depending on how they are written) capping series. The next member of capping in this (horizontal) series ($k = 2$) of osmium clusters is $\text{Os}_7(\text{CO})_{21}$ [change involves $\text{Os}(\text{CO})_3$ fragment] where $n = 7$, $14n = 14 \times 7 = 98$ and $V = 8 \times 7 + 21 \times 2 = 98$. Therefore, $\text{Os}_7(\text{CO})_{21}$ is a member of mono-capped series with $k = 2n = 2 \times 7 = 14$. $\text{Os}_7(\text{CO})_{21}$ cluster may be viewed as a derivative of $\text{Os}_6(\text{CO})_{18}$ by adding ' $\text{Os}(\text{CO})_3$ ' fragment. Since one of the skeletal atoms is utilized for capping, the 'inner core' of six is presumed to form a closo octahedral system. If we remove a capping fragment ' $\text{Os}(\text{CO})_2$ ' from $\text{Os}_7(\text{CO})_{21}$ we will be left with ' $\text{Os}_6(\text{CO})_{19}$ '. These chemical species are isoelectronic with the known $\text{Os}_6(\text{CO})_{18}^{2-}$ octahedral complex. Thus, $\text{Os}_7(\text{CO})_{21}$ cluster is found to be a mono-capped octahedral complex¹⁴(S-23). The symbol $C^1C[M-6]$ may be used to represent this-meaning it is a mono-capped octahedral closo system. The cluster $\text{Re}_7(\text{C})(\text{CO})_{21}^{3-}$ may be treated in the same way as $\text{Os}_7(\text{CO})_{21}$ and it has a mono-capped octahedral geometry¹¹.

Bi-capped series (14n-2)

It has been observed that in bi-capped series and higher series, the value of $14n$ is numerically greater than that of the valence electrons. That is, $14n > V$ for clusters symbolized as C^nC where $n = 2, 3, 4, 5, \dots$). In the case of closo, nido, arachno, hypho and lower series, $V > 14n$. The borderline is reached at mono-capped series (C^1C) where $V = 14n$. In the bi-capped series, let us consider $\text{Re}_8(\text{C})(\text{CO})_{24}^{2-}$; $n = 8$, $14n = 14 \times 8 = 112$, $V = 7 \times 8 + 4 + 24 \times 2 + 2 = 110$. Therefore the series will be given by $T = 14n - 2 = V$. In this series, the value of

14n exceeds that of valence electrons(V) by 2. This series will be in a higher row after the mono-capped series and a second row after the closo series row. Since 14n symbolizes a mono-capped (1 cap) series, any numerical multiple of (-2) will symbolize additional cap. Hence, the symbol 14n+1(-2) will correspond to a single cap C¹ from the symbol 14n and an additional single cap C¹ from 1(-2). Hence, the series T = 14n -2 will correspond to double-capped series C²C. In conclusion, the cluster Re₈(C)(CO)₂₄²⁻ is a member of a bi-capped series T = 14n-2 with k=2n+1 = 2.6-1 = 17. Since two of the atoms are involved in capping, the remaining 6 will be the 'inner core' of an octahedral system [M-6]. Thus, the eight skeletal atom (M-8) bi-capped cluster may be given the symbol C²C[M-6] and this means the Re₈(C)(CO)₂₄²⁻ cluster will be a bi-capped octahedron as is found experimentally¹¹. The osmium cluster, Os₈(CO)₂₂²⁻; n = 8, 14n = 112, V = 8x8+22x2+2 = 110. Hence, T = 14n-2. Again, this cluster is expected to be a bi-capped series based on an octahedral geometry as is observed⁹. Following the same approach, the clusters Ru₈H₂(CO)₂₁²⁻¹⁸, Os₈H(CO)₂₁⁻⁹, and Os₈(C)(CO)₂₁ belong to the bi-capped series(14n-2) based on an octahedral inner core and may be considered to have a similar structure. A possible bi-capped octahedral shape is shown in S-27 and S-28.

Tri-capped series(14n-4)

This is a series of clusters where the value of 14n exceeds that of the valence electrons (V) by 4. Take the example of Os₉(CO)₂₄²⁻; n = 9, 14n = 14x9 = 126, V = 8x9+24x2+2 = 122. This gives us the series T= 14n-4 = V. The k value for this cluster will be 2n+2 = 2x9+2 = 20. To identify the capping, we can re-write the series as T= 14n+2(-2). If we use the symbol C_p to represent the capping, then in this case, C_p = C¹ (implied from 14n) + C² (implied from 2(-2)). Thus, the overall capping can be represented as C_p = C³C. In this way, the symbol implies that 3 of the 9 skeletal atoms are being utilized for capping leaving the remaining six forming an octahedral 'inner core'. Indeed, the Os₉(CO)₂₄²⁻ cluster is a tri-capped octahedron¹⁴ (S-29). Similar clusters such as Os₉H(CO)₂₄⁻¹⁴, Rh₉(CO)₁₉³⁻²¹ and PtRh₈(CO)₁₉²⁻²⁰ can be analyzed in the same way and predicted as being tri-capped based on an octahedral inner core. In the case of capping, the value of k changes by 3 units. Since

we are considering capping based on an octahedral unit (k = 11), the mono-cap (C¹C) will have k = 11+3 = 14, bi-cap(C²C) k = 11+3+3 = 17, and tri-cap(C³C) k = 11+3+3+3 = 20 and tetracap (C⁴C), k = 11+4x3 = 23.

Tetra-capped Series(14n-6)

Let us illustrate this starting with the cluster Ru₁₀(C)(CO)₂₄²⁻; n = 10, 14n = 140 and V = 134. Hence, T = 14n-6 and may be written as T = 14n + 3(-2). The k value is given by k= 2n+3 = 2x10+3 = 23. In terms of capping, this will correspond to C_p = C¹ + C³ = C⁴C. This implies that 4 atoms out of 10 skeletal atoms are engaged in capping while the remaining six form the inner core of an octahedral geometry. This complex may be regarded to possess a tetra-capped octahedral geometry symbolized as C⁴C[M-6] and this has been observed¹¹. This is sketched in S-30. By this approach of analysis the clusters Os₁₀(CO)₂₆²⁻¹⁴, Os₁₀(C)(CO)₂₄²⁻¹¹, Os₁₀H₄(CO)₂₄²⁻¹⁴, and Rh₁₀(CO)₂₁²⁻ are expected to have a tetra-capped geometry based on an octahedral inner core. Furthermore, the k value of 23 can also be deduced from 11+3+3+3+3=23.

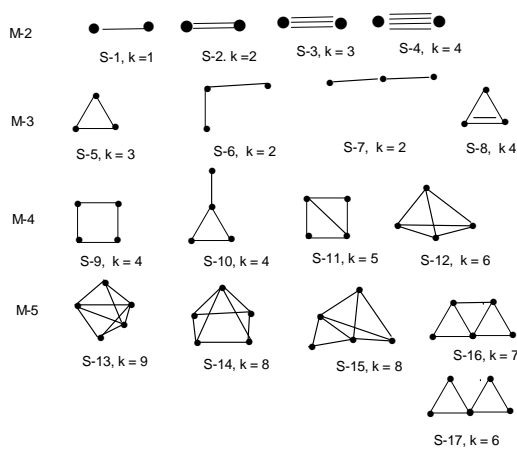
Selected higher capped series based on [M-6] inner core

Consider the cluster the palladium ruthenium carbonyl cluster¹⁹, Pd₆Ru₆(CO)₂₄²⁻. For this cluster n = 12, 14n = 14x12 = 168, V = 10x6+8x6+24x2+2 = 158. Hence, T = 14n-10 = 14n +5(-2). Therefore, this cluster belongs to the capping series C_p = C¹+ C⁵ = C⁶C. This implies that this is a hexa-capped complex based on an octahedral inner core C⁶C [M-6] as is reported^{12,19}. What is fascinating in this cluster, is the fact that the inner octahedral core comprises of the heavier Pd atoms. This is sketched in S-31. The cluster number k is given by 2n+5 = 2x12+5 = 29(11+6x3). Since an octahedral geometry has 8 triangular faces, in principle, all of them could be capped. This is what is implied by the cluster, Os₁₀(C)(CO)₂₄Au(AuL)₃, L = PPh₃; where n = 14, 14n = 14x14 = 196 and V = 8x10+4+24x2+11+(11+2)x3 = 182. The cluster series for the cluster will be T = 14n-14 = 14n+7(-2). The cluster will have a capping series C_p = C¹ + C⁷ = C⁸C. This implies the cluster comprising of 14 skeletal atoms has 8 of them taking up capping positions while the remaining 6 constitute the inner

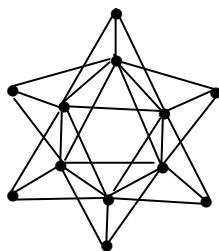
core of an octahedral geometry, C^8C [M-6]. Finally, let us consider the cluster $Ni_{38}Pt_6(CO)_{48}(H)^5$; $n = 44$, $14n = 14 \times 44 = 616$ and $V = 44 \times 10 + 48 \times 2 + 1 + 5 = 542$. This cluster belongs to the series $T = 14n - 74 = 14n + 37(-2)$. The capping series may be expressed as $C_p = C^1 + C^{37} = C^{38}C$. This implies that the cluster has 38 capping atoms based on an octahedral geometry of the inner core, $C^{38}C$ [M-6] and amazingly this is what is observed¹². What is even more exciting is the fact that all the six inner core atoms comprise of the heavier Pt atoms. It is as if the heavier atoms sink towards the nuclear centre or inner layer and the lighter ones move towards the outer layers. This observation is similar to the case of $Pd_6Ru_6(CO)_{24}^{2-}$ cluster discussed above. Furthermore, the capping atoms on the outside the nuclear inner core must be capping on top of one another.

Possible Use in Data Interpretation

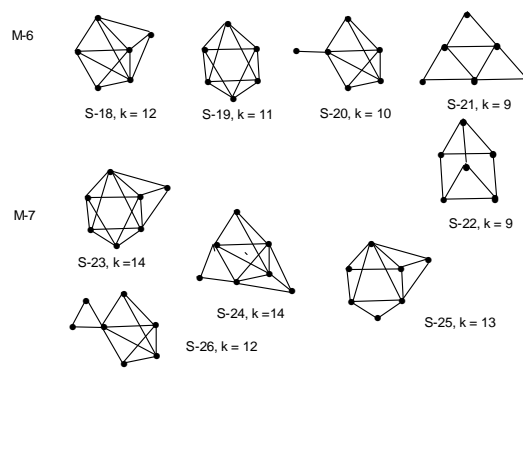
This method may also assist in the interpretation of some geometrical structures. For example, the set of clusters¹⁰, $Ni_5(CO)_{12}^{2-}$ ($T = 14n + 6$, $k = 7$), $Rh_5(CO)_{15}^{-}$ ($T = 14n + 6$, $k = 7$), $Rh_5(CO)_{14}I_2^{2-}$ ($T = 14n + 6$, $k = 7$), $Ni_3M_2(CO)_{16}^{2-}$ ($M = Cr, Mo, W$, $T = 14n + 6$, $k = 7$), $Ru_4(CO)_{15}^{2-}$ ($T = 14n + 6$, $k = 7$), and $PtRh_4(CO)_{14}^{2-}$ ($T = 14n + 6$, $k = 7$) were all reported to have elongated trigonal bipyramid structure whereas the second set of clusters¹⁰ $Os_5(CO)_{16}$ ($T = 14n + 2$, $k = 9$), and $Os_5(CO)_{15}^{2-}$ ($T = 14n + 2$, $k = 9$) were found to have a regular trigonal bipyramid shape. Clearly, the first set belong to the arachno series $T = 14n + 6$ with the characteristic cluster number $k = 7$ while the regular second set belong to the closo series $T = 14n + 2$ with $k = 9$. These are expected to have a similar geometry as that of closo



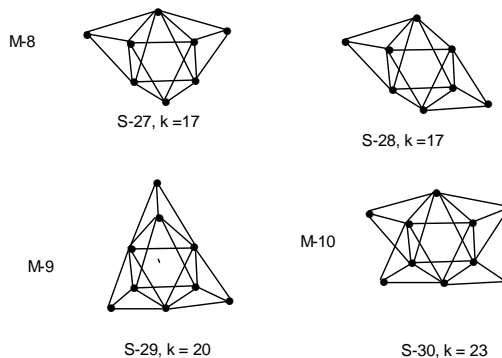
Scheme 1: Types of skeletal linkages



S-31. Skeletal shape of a hexacapped cluster



Scheme 1: Types of skeletal linkages continued

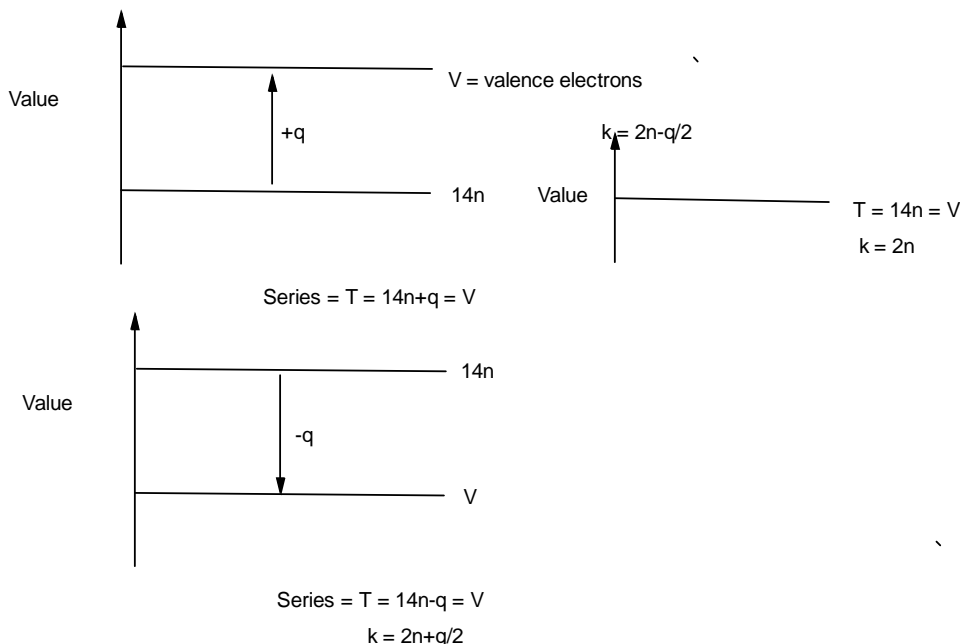


Scheme 1. Types of Skeletal Linkages continued

$B_5H_5^{2-}$ which has a well documented regular trigonal bipyramid¹⁷. Since these two sets of clusters belong to different series, it would probably be not possible to have identical characteristics.

In scheme 2(a), shows that $V > 14n$ for Closo, Nido, Arachno, Hypho and Klappo Series. But the value of $14n$ increases in clusters until it is

equal to V . This is shown in 2(b). That is, when $14n = V$, the value of valence electrons, mono capping series (C^1C) begin. In scheme 2(c), when the value of $14n$ becomes greater than V , that is $14n > V$, then more capping series are generated. It is also found that when $T = 14n + q$, then the corresponding value cluster number is given by $k = 2n - q/2$, while $T = 14n$, $k = 2n$ and for $T = 14n - q$, the k value is $2n + q/2$.



Scheme 2: Illustration of series derivation

CONCLUSION

The formation of transition metal carbonyl clusters occurs in an ordered manner resulting into numerous series. The movement across a given series the cluster number varies by two cluster number units ($k = 2$). In case of the osmium carbonyl clusters such change is equivalent to a formula change by $'Os(CO)_3'$ fragment containing 14 electron units. On the other hand capping series involves the change in k value by 3 units ($k = 3$). This is equivalent to a change in capping series by $'Os(CO)_2'$. This fragment carries 12 valence electrons. Although the evolution of cluster series was demonstrated for those clusters whose inner core or nucleus is based on an implied octahedral closo geometry [M-6], this could also be done with other nuclear clusters such as [M-5], [M-4], [M-8],

and others. Equipped with this information, the construction of hypothetical cluster series of carbonyls becomes quite easy. This method has been found to be reliable in the classification of carbonyl clusters in agreement with Wade-Mingos rules and it can also be used as a guide in predicting the geometries of wide range of small to medium type of clusters. With the concept of capping, this approach can give us a rough idea of how the cluster may geometrically appear to be based on its cluster molecular formula. The method involves deducing the cluster series of the complex from which the cluster number can be calculated and the type capping series based on the nuclear closo system. On reflecting on the capping, it appears to be a mechanism by which a cluster as it grows bigger and bigger a possible inner closo nuclear cluster may also be formed.

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Dedication

The paper is dedicated to Prof. Charles Alfred Coulson who briefly but inspiringly taught the author as a student at Makerere University, Uganda, Africa, 1969, Prof. Irving Langmuir and Prof Gilbert Newton Lewis for their powerful insights of 18 and 8 electron rules respectively which they formulated more than 90 years ago.

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