Generating Formulas of Transition Metal Carbonyl Clusters of Osmium, Rhodium and Rhenium

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Abstract

The series for carbonyl clusters of transition metals have been developed. They may be considered to be formed with a fragment centered around the 14 electron valence content. The capping series are based on the fragment of 12 electron valence content. The formulas of clusters can be decomposed into series from which the shapes of clusters may be predicted. The electron counting numbers of carbonyl clusters can be identified.

Keywords: Carbonyl and borane clusters, fragments, isolobal principle, numerical sequence of fragments, building blocks, cluster series, 14n and 4n rules, valence electron content, cluster number

1. Introduction

The discovery of the first mono-skeletal transition metal carbonyl $Ni(CO)_4$ one hundred and twenty five years ago (Mond, et al, 1890), opened a wide gate for the synthesis of hundreds of metal carbonyl complexes. The structure of the nickel carbonyl $Ni(CO)_4$ at the time was proposed to be as shown in Figure 1(F-1) in which the nickel atom exerted a valence of 2 while the valence of carbon and oxygen were 4 and 2 respectively. But the correct shape as we know it today is tetrahedral, Figure 1(F-2).
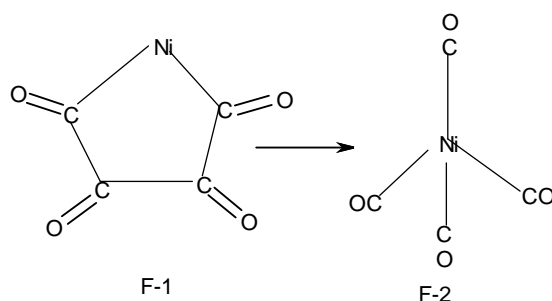

Figure 1. Historical Shapes of $Ni(CO)_4$

Other carbonyls such as $Fe(CO)_5$(Mond, et al, 1891), $Fe_2(CO)_9$(1905), $Re_2(CO)_{10}$(Hieber and Fuchs, 1941) and many others were discovered later. A good number of metal carbonyls and other related metal complexes have been applied in a good number of major industrial processes such as oxo-process, Monsanto process, Wacker oxidation process and Wilkinson catalyst in hydrogenation processes (Roth,1975;Ojima, et al, 2000;Grubbs, et al,2012; Wilkinson, et al, 1965; Tolman,1972). Many more carbonyl complexes of higher nuclearity skeletal metal atoms were synthesized (Dahl, et al, 2010). With emergency of borane chemistry (Stock, 1933; Longuet-Higgins , 1943; Lipscomb, 1963; Mingos, 1972; Lipscomb, 1976; Wade, 1976, Rudolph, 1976; Hoffmann, 1982; Mingos, 1984; King, 1986;Greenwood and Earnshaw,1998; Shriver and Atkins, 1999;Jemmis et al, 2001; 2002; 2003; Balakrishnarajan and Hoffmann, 2004; Jemmis, 2005; Housecroft and Sharpe, 2005; Jemmis, et al., 2008; Welch, 2013), it was found that the structures of carbonyl clusters could be explained using Polyhedral Skeletal Electron Pair Theory (PSEPT) or Wade-Mingos rules (Wade, 1971;Mingos, 1972).). It was also discovered that the structures of NIDO, ARACHNO, HYPHO and KLAPO clusters could be regarded as being successive derived from respective CLOSO clusters (Rudolph,1976). Transition metal carbonyl clusters and Zintyl ion clusters and others were found to be related to the borane clusters and their analogues (Crabtree, 2005; Miessler, et al, 2014). It became a great challenge to scientists to explain the intriguing

geometrical shapes and bonding of the clusters let alone their chemical reactivity (Rudolph, 1976;King,2002). Due to their unique chemical reactivity, special synthetic techniques and handling them were invented (Stock, 1933). New clusters comprising of borane, main group elements and transition metal fragments were synthesized and these provoked the creation of ISOLOBAL PRINCIPLE which linked up the various fields of chemistry (Hoffmann, et all, 1976; Hoffmann,1982; Mingos, 1991, Shriver, et al, 1999).

It has taken the author some time in searching for simple formulas to teach undergraduate chemistry the Lewis shapes of molecules and clusters of boranes and transition metal carbonyls (Kiremire, 2008; Kiremire, et al, 2014; Kiremire, 2015a). This has resulted in the creation of series discussed in this paper, the introduction of the proposed cluster number (k), the capping symbol (C^nC) and generating functions of cluster fragments and molecules of the series(Kiremire,2014a; 2014b;Kiremire,2015b) also to be discussed in this paper. The ISOLOBAL SERIES of chemical fragments unifies all the clusters such as boranes, heteroboranes, metalloboranes, metallacarboranes, metallocenes, transition metal carbonyl clusters, Zintyl ion clusters as well as other clusters of main group elements'(Hoffman, 1982;Kiremire, 2015c).

A close scrutiny of the formulas of the clusters revealed that the transition metal carbonyl clusters can be categorized by 14n rule (Kiremire,2015c). In addition, it has recently been found that not only can they be categorized according to 14n but can also be generated using the same. The Wade-Mingos rules(Wade, 1971, 1976, Mingos, 1984, 1991, Welch, 2013) point to the existence of series through the n+1, n+2, n+3 or electron counting 4n+0(14n+0), 4n+2(14n+2) and so on based on their Molecular Orbital Theory calculations (Mingos, 1972; Mingos, 1984) . This paper presents a simple technique of the deriving the cluster formulas using the 14n(4n) series.

2. Results and Discussion

2.1 Formation of Cluster Series Using the 14n+0 as a Base

During the study of osmium carbonyl clusters(Kiremire,2015c, 2015d) it was found that $Os(CO)_3$ fragment which carries 14 electron valence content can be utilized as a fulcrum to generate as many hypothetical osmium carbonyl clusters as possible. With this fragment a range of multiples of the fragment can be produced. For instance, doubling the fragment, $2[Os(CO)_3]$ we produce $Os_2(CO)_6$ fragment. Tripling the fragment, we get $Os_3(CO)_9$. Other multiples are $Os_4(CO)_{12}$, $Os_5(CO)_{15}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, $Os_8(CO)_{24}$, $Os_9(CO)_{27}$ and $Os_{10}(CO)_{30}$ and so on. These are shown in one of the columns of Table 1. If we divide each formula by the coefficient of osmium in that formula (or simply dividing the formula by the multiplier of the initial fragment) we just obtain a constant of $Os(CO)_3$ in each case. For instance, ½ $[Os_2(CO)_6] = Os(CO)_3$, ⅓ $[Os_3(CO)_9] = Os(CO)_3$, ⅕ $[Os_5(CO)_{15}]= Os(CO)_3$, ¹⁄10 $[Os_{10}(CO)_{30}] = Os(CO)_3$ and so on. Since the fragment $Os(CO)_3$ is the starting point of the column and its valence content is 14, it was deemed fit to label this column 14n or 14n+0 series. It is important to note that this result was previously obtained from molecular orbital calculations(Mingos,1991).When a CO ligand is added to $Os(CO)_3$,that is, $Os(CO)_3+CO$, we get a new fragment $Os(CO)_4$. The addition of the CO increases the valence electron content by 2. Therefore, we can regard $Os(CO)_4$ fragment as being the first member of the series S = 14n+2 since $Os(CO)_3$ fragment was considered to be the first member of the series S = 14n+0. Other fragments can be transformed in the same way. For example, $Os_2(CO)_6+CO \rightarrow Os_2(CO)_7$ and $Os_9(CO)_{27} +CO \rightarrow Os_9(CO)_{28}$. Indeed if n =1 is substituted into the series S = 14n+2 of the fragment $Os(CO)_4$ we get S = 14x1+2 = 16 which is the same as the valence content of $Os(CO)_4$. If we continue the process and add another CO to $Os(CO)_4$ we get $Os(CO)_5$. This means that we have added a total of 4 electrons to $Os(CO)_3$ fragment. Therefore the fragment $Os(CO)_5$ can be considered to be the first member of the series S =14n+4. If we substitute n = 1 into S =14n+4, we get 18. This means that $Os(CO)_5$ complex obeys the 18 electron rule. Thus, by adding a CO to each member of the S = 14n+0 series in Table 1, we generate members of 14n+2 series. Similarly, by adding a CO to each member of the 14n+2 we get the clusters of S = 14n+4 series. Some of these are given in Table 2 which is simply an extension of Table 1. Again starting with the 14 electron valence fragment of osmium, $Os(CO)_3$ and removing one CO ligand, we get a 12 valence electron fragment $Os(CO)_2$. The removal of the CO ligand means the loss of 2 electrons. Therefore the fragment $Os(CO)_2$ can be considered to be the first member of 14n-2 series of osmium carbonyl clusters. If we remove a CO ligand from every member of the 14n+0 members, then the members of the series S = 14n-2 are produced. Some of these are shown in Table 2. Further removal of a CO ligand from $Os(CO)_2$ we get a 10 electron valence fragment $Os(CO)$ which can be regarded as the first member of the S = 14n-4 series. The removal of CO from the members of S = 14n-2 can be extended to generate the clusters or fragments of 14n-4 series. The carbonyl clusters have been categorized as 14n+0(4n+0) mono-capped closo, 14n+2(4n+2) as closo, 14n+4(4n+4) as nido, 14n-2(4n-2) as bi-capped closo, 14n-4(4n-4) tri-capped closo and so on. This classification has been expanded and is given in Table 3. What this means is that if we take the 14n+0 as the middle column, moving to the right successively adding CO ligands we create series with positive integers after 14n(4n) whereas moving to the left of the 14n+0 series successively removing the CO ligand we create negative integers after (14n(4n). A good number of the known osmium carbonyl clusters** are given in Table 4. A good number of the clusters in the table are the same or electronically equivalent to

those generated in Table 3.These include, $Os_2(CO)_9$, $Os_3(CO)_{12}$, $Os_4(CO)_{14}$, $Os_5(CO)_{16}$, $OS_6(CO)_{18}$, $Os_6(CO)_{19}$ which equivalent to $Os_6(CO)_{18}^{2-}$, and $Os_7(CO)_{21}$, $Os_7(CO)_{22}$, $Os_8(CO)_{23}$,$Os_9(CO)_{25}$(disguised as $Os_9(CO)_{24}^{2-}$), and $Os_{10}(C)(CO)_{24}^{2-}$.The derivation of the known carbonyl clusters using series underpins the great significance of the same. Table 2 can be extended as needed.   A sketch of how the osmium carbonyl clusters can readily be generated and is shown in Figure 1 for 14n+0. It is quite clear that the movement along a column from one fragment to the next the difference is equivalent to $Os(CO)_3$ fragment which equivalent to 14 valence electrons. A sketch showing the derivation of uncapping series (those with 14n followed by positive even integers)is given such as S = 14n+2, 14n+4, 14n+6, and so on which are obtained by successive addition of CO on the right of 4n+0 series and the capping series (those with negative even integers after 14n) obtained by successive removing the CO from the 14n+0 series is given in Figure 2. The 14n series represent mono-capped series. The formation of carbonyl clusters of a given type of series is similar is similar to the formation of compounds between two elements one of which is exerting a fixed valence while the other portrays variable valence or oxidation states. For instance chromium(Cr) and fluorine(F) form the compounds CrF_2, CrF_3, CrF_4, CrF_5 and CrF_6. In these compounds, fluorine exerts a fixed valence of one while the chromium exerts the oxidation states (valencies) of 2,3, 4, 5 and 6. Likewise, for a fixed cluster series say 4n+2, the variation of n = 1, 2, 3, 4, 5 and so on to generate different clusters is similar to the variation of the chromium oxidation state. Now let us consider the osmium carbonyl clusters of 14n+2 (CLOSO) series. As we know, the building bloc fragment for osmium carbonyl clusters is $[Os(CO)_3]$. The building block has14 valence electrons. When n = 1, we generate F = 14n+2 = $[Os(CO)_3](1)+CO = Os(CO)_4$ fragment. While n = 2, we produce, F =$[Os(CO)_3](2)+CO = Os_2(CO)_6+CO = Os_2(CO)_7$ and for n values 3,4,5,and 6 we get $Os_3(CO)_{10}$,$Os_4(CO)_{13}$,$Os_5(CO)_{16}$,and $Os_6(CO)_{19}$ (disguised as $Os_6(CO)_{18}^{2-}$). Thus, n behaves as a variable valence similar to that in transition metals or main group elements. For example, in the case of compounds such as ClF, ClF_3, ClF_5 the fluorine atom can be regarded as exerting a valence of = 1, while Cl is portraying the valences 1, 3, and 5 or in SF_4 and SF_6 compounds the sulphur atom is using the valences V= 4 and 6. But when sulphur combines with oxygen which exerts a valence of 2, it can form compounds SO_2 and SO_3. The change of combination of sulphur with F to combination with O to produce different compounds is similar to changing of n values when generating cluster fragments when the series changes from CLOSO 4n+2 to NIDO 4n+4. In order to elaborate this point, let us consider the closo series S = 14n+2 and nido series S = 14n+4 for rhodium carbonyl clusters. The buiding bloc for rhodium may be taken as $[Rh(H)(CO)_2]$. This is a fragment loaded with 14 valence electrons. When n = 6, the corresponding cluster carbonyl formulas are F= 14n+2 = $[Rh(H)(CO)_2](6)+CO = Rh_6H_6(CO)_{12}+CO = Rh_6(CO)_3(CO)_{12}+CO = Rh_6(CO)_{15}+CO =Rh_6(CO)_{16}$. Therefore the corresponding nido (S = 14n+4 is when n = 6 is simply obtained by adding a CO ligand to rhodium cluster $Rh_6(CO)_{16}$. That is, $Rh_6(CO)_{16} +CO = Rh_6(CO)_{17}$. Let us compare the complexes generated when n = 4 for the same transition metal element rhodium. The closo complex F = 14n+2 = $[Rh(H)(CO)_2](4)+CO = Rh_4H_4(CO)_8+CO = Rh_4(CO)_2(CO)_8+CO= Rh_4(CO)_{10} +CO = Rh_4(CO)_{11}$. The corresponding nido cluster will be obtained by just adding a CO to the closo cluster $Rh_4(CO)_{11} +CO = Rh_4(CO)_{12}$. In this way, both $Rh_6(CO)_{16}$ and $Rh_4(CO)_{11}$ belong to the same closo series S = 14n+2 while $Rh_6(CO)_{17}$ and $Rh_4(CO)_{12}$ clusters belong to the nido series S = 14n+4.

Although we are discussing carbonyl clusters in this article, the boranes which obey the 4n rule, behave in the same manner. For instance S = 4n+2 closo series, we know that no neutral boranes are known and the building fragment in this case is [BH]. Hence to generate the charged closo boranes, we must leave the integer 2 to represent the charge. Thus, for n =4, F = 4n+2 = $[BH](4)+2 = B_4H_4^{2-}$,n= 5, F =$[BH](5)+2 = B_5H_5^{2-}$,n=6, F=$[BH](6)+2 = B_6H_6^{2-}$, and n =12, F=$[BH](12)+2 = B_{12}H_{12}^{2-}$. The exception appears to be n = 1, F =$[BH](1)+2H = BH_3$. Let us generate more boranes with S = 4n+4(nido) series. When n = 1, F = $[BH](1) +4H = BH_5$, n= 2, F = $[BH](2)+4H = B_2H_6$, n= 3, F =$[BH](3)+4H = B_3H_7$,n= 4, F = $[BH](4)+4H =B_4H_8$,n = 5, F =$[BH](5)+4H = B_5H_9$, and n= 6, F= $[BH](6)+4H = B_6H_{10}$.

In the discussion above, the rhodium fragment $[Rh(H)(CO)_2]$ was utilized to produce four hypothetical clusters. The fragment can be used to generate many more clusters. This has been done and the results are given in Tables 5. A good number of known rhodium carbonyls or their equivalents(Greenwood and Earnshaw,1998) can be identified in the Table 6. The examples include $Rh_4(CO)_{12}$ disguised as $Rh_4H_4(CO)_{10}$, $Rh_6(CO)_{16}$ which is disguised as $Rh_6(H)_6(CO)_{13}$, $Rh_7(CO)_{16}^{3-}$disguised as $Rh_7H_7(CO)_{14}$, $Rh_{10}(CO)_{21}^{2-}$disguised as $Rh_{10}H_{10}(CO)_{17}$and $Rh_{11}(CO)_{23}^{3-}$disguised as $Rh_{11}H_{11}(CO)_{19}$. Clearly, the hypothesis of a 14 electron valence fragment with plus or minus CO to generate cluster series is still valid for rhodium carbonyls. Many other known carbonyls of rhodium(Greenwood and Earnshaw,1998) can be identified in the hypothetically derived Table 5. A diagram for deriving rhodium carbonyl clusters are shown in Figure 3.

The utilization of 14 valence electron mono-skeletal carbonyl fragment was also tested on rhenium (Re) element. Since rhenium has 7 valence electrons, we need to add some suitable number of carbonyl ligands to constitute 14 electrons. In this regard, an appropriate fragment $[Re(H)(CO)_3]$ was selected. The presence of (H) in the fragment is to accompany Re which has an odd number of valence electrons and CO ligand has an even number of valence electrons and the required

fragment is an even number of 14 electrons. Thus the selected fragment has $[7+1+3x2 = 14]$electrons. This became the first member of the S = 14+0 series of rhenium. The mono-capped series of rhenium were derived starting with $[Re(H)(CO)_3]$ fragment and ending at $Re_{20}H_{20}(CO)_{60}$. The hypothetically derived rhenium carbonyl clusters are given in Table 7. A good number of known rhenium carbonyl clusters or their equivalents (Greenwood and Earnshaw,1998)were identified in the Table 8. Among these include, $Re_2H_2(CO)_8$, $Re_3H_3(CO)_{10}^{2-}$,$Re_4H_4(CO)_{12}$, $Re_4(CO)_{16}^{2-}$, $Re_5(C)(CO)_{16}(H)^{2-}$,$Re_6(C)(CO)_{19}^{2-}$, and $Re_7(C)(CO)_{21}^{3-}$. The principle of utilizing the 14n+0 mono-skeletal fragment and CO ligand for generating the members of 14n series appears to be applicable to a number of transition metal elements. A sketch for deriving rhenium carbonyl clusters is shown in Figure 4.

2.2 The Capping Series based on the Closo Series S = 4n+2

Using the example of osmium carbonyl series, we can identify the capping series which are lie on the diagonal fragments in the Table 2. For example, the $Os_6(CO)_{18}^{2-}[Os_6(CO)_{19}]$is a member of the closo series S = 14n+2 has the capping clusters with formulas $Os_7(CO)_{21}$[mono-capped O_h](Mingos,1991), $Os_8(CO)_{23}$ [bi-capped O_h](Hughes and Wade, 2000), $Os_9(CO)_{25}$[tri-capped O_h], and $Os_{10}(CO)_{27}$ [tetra-capped O_h]. But $Os_8(CO)_{23}$ occurs as $Os_8(CO)_{22}^{2-}$,while $Os_9(CO)_{25}$ and $Os_{10}(CO)_{27}$ occur as $Os_9(CO)_{24}^{2-}$ and $Os_{10}(CO)_{26}^{2-}$ respectively. $Os_5(CO)_{16}$ has the capping clusters with formulas $Os_6(CO)_{18}$(mono-capped)(, $Os_7(CO)_{20}$(bi-capped), $Os_8(CO)_{22}$(tri-capped), $Os_9(CO)_{24}$(tetra-capped) and $Os_{10}(CO)_{26}$(penta-capped). The $Os_6(CO)_{18}$ has been reported earlier as a mono-capped trigonal bipyramid (D_{3h}) complex(Hughes and Wade, 2000).Thus, the capping clusters that have been encountered are based upon the CLOSO systems S = 14n+0(4n+0). If we use the generated osmium carbonyl clusters in Table 2 as examples, apart from the capping series of closo $Os_5(CO)_{16}$ and $Os_6(CO)_{19}$ already mentioned, the other capping series based on the closo clusters S = 14n+0 are as follows: for $Os(CO)_4 \rightarrow Os_2(CO)_6 \rightarrow Os_3(CO)_8 \rightarrow Os_4(CO)_{10} \rightarrow Os_5(CO)_{12} \rightarrow Os_6(CO)_{14}$; for $Os_2(CO)_7 \rightarrow Os_3(CO)_9 \rightarrow Os_4(CO)_{11} \rightarrow Os_5(CO)_{13} \rightarrow Os_6(CO)_{15} \rightarrow Os_7(CO)_{17}$; for $Os_3(CO)_{10} \rightarrow Os_4(CO)_{12} \rightarrow Os_5(CO)_{14} \rightarrow Os_6(CO)_{16} \rightarrow Os_7(CO)_{18} \rightarrow Os_8(CO)_{20}$; for $Os_7(CO)_{22} \rightarrow Os_8(CO)_{24} \rightarrow Os_9(CO)_{26} \rightarrow Os_{10}(CO)_{28}$; for $Os_8(CO)_{25} \rightarrow Os_9(CO)_{27} \rightarrow Os_{10}(CO)_{29}$;and for $Os_9(CO)_{28} \rightarrow Os_{10}(CO)_{30}$. In all these capping series examples, we can identify a very important capping fragment of formula $Os(CO)_2$. This fragment carries 12 valence electrons and is the first member of bi-capping series 14n-2 or 4n-2.

2.3 Symbol for capping Cp = C^nC

In our earlier work, a symbol for capping was introduced (Kiremire,2015a). The proposed symbol is $Cp = C^nC$. Since for the series S = 4n+0 (14n+0) represents mono-capped series, a symbol $Cp = C^1C$ was introduced. The series S = 4n-2 represented bi-capped series and S = 4n-4 tri-capped series, and S = 4n-6 tetra-capped series, and so on. This means that for every addition of (-2) integer after 4n or 14n represents an additional capping, then for S= 4n-2 = S = 4n+(-2), and Cp $= C^1C+C^1C = C^2C$. This is because 14n implies a single capping C^1C and +(-2) after it is another cap C^1C and so we get a total of two caps C^2C. Also, S = 4n-4 = 4n+2(-2), and Cp $= C^1C+C^2C = C^3C$. Therefore, for S = 4n-6 = 4n+3(-2), Cp = $C^1C+C^3C = C^4C$. Let us take the case of osmium again, $Os_6(CO)_{18}^{2-}$, S = 4n+2 (14n+2) this is an octahedral complex [M-6] where the symbol [M-6](F-1) represents a closo cluster comprising of 6 atoms. The cluster $Os_7(CO)_{21}$, S = 4n+0(14n+0) is referred to as a mono-capped octahedral cluster(F-2). The capping symbol for this will be Cp = C^1C[M-6], a mono-capped closo octahedral complex. The complex $Os_8(CO)_{23}$, S = 4n-2 will be Cp = C^2C[M-6], that is, bi-capped closo octahedral complex(F-3). The capping on the octahedral geometry (O_h) can go on to form giant clusters. For example, $Ni_{38}Pt_6(CO)_{48}(H)^{5-}$, S= 4n-74; Cp = $C^{38}C$[M-6]. This means the cluster of 44 skeletal atoms has six of them which constitute an octahedral closo cluster as a nucleus. This has been found to be the case(Zanello, P.,2011).

2.4 Derivation of Carbonyl Cluster Formulas Using Series

It has been found that the building bloc of the carbonyl series has a valence electron content of 14. This number then forms the backbone for generating series. Let us create a closo [14n+2] cluster of osmium carbonyl comprising of six skeletal atoms. This means that the value of n = 6 and the osmium building bloc will be $Os(CO)_3$, V = 8+3x2 = 14. Therefore the cluster formula F = 14n+2 = $[Os(CO)_3]$(6)+CO = $Os_6(CO)_{18}$+CO = $Os_6(CO)_{19}$. But since we know that in case of osmium the cluster a negative charge of 2 is present. Hence we can derive the formula as F =$[Os(CO)_3]$(6)+2 = $Os_6(CO)_{18}^{2-}$. Let us take the example of rhenium. A possible backbone fragment for this element would be $[Re(H)(CO)_3]$,V = 7+1+3x2 = 14. Therefore the hypothetical closo cluster when n =6, will be $[Re(H)(CO)_3]$(6)+ CO = $[Re_6(H)_6(CO)_{18}]$+CO = $[Re_6(CO)_3(CO)_{18}]$+CO = $[Re_6(CO)_{22}]$. The known octahedral closo clusters include $Re_6(C)(CO)_{19}^{2-}$ which is electronically equivalent to $Re_6(CO)_2(CO)_{19}(CO) = Re_6(CO)_{22}$ in terms of valence electrons. In principle, we can derive hypothetical carbonyl cluster for a metal such as nickel. In this case, the backbone fragment will be $[Ni(CO)_2]$, V = 10+2x2 = 14. Hence, the hypothetical closo cluster when n = 6 will have the formula F= 14n+2 = $[Ni(CO)_2]$(6)+2 = $[Ni_6(CO)_{12}]^{2-}$ or $[Ni_6(CO)_{12}]$+CO = $Ni_6(CO)_{13}$]. The complex$[Ni_6(CO)_{12}]^{2-}$ is known(Greenwood and Earnshaw,1998).

$$Os = Os(CO)_3$$

Os

Os-Os

Os-Os-Os

Os-Os-Os-Os

Os-Os-Os-Os-Os

Os-Os-Os-Os-Os-Os

Os-Os-Os-Os-Os-Os-Os

Os-Os-Os-Os-Os-Os-Os-Os
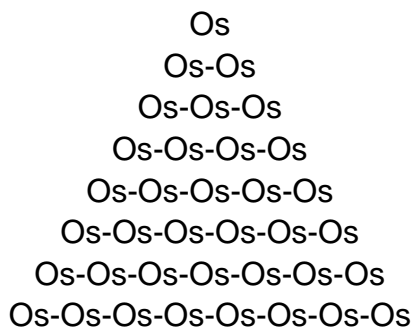
Figure 2a. Sketch representing the process of forming members of 14n+0 series

$$
S = 4n-q \quad \xleftarrow{\text{-CO}} \quad
\begin{array}{c}
Os(CO)_3 \\
Os_2(CO)_6 \\
Os_3(CO)_3 \\
Os_4(CO)_{12} \\
Os_5(CO)_{15} \\
Os(CO)_{18} \\
Os_7(CO)_{21} \\
Os_8(CO)_{24} \\
Os_9(CO)_{27} \\
Os_{10}(CO)_{30}
\end{array}
\quad \xrightarrow{\text{+ CO}} \quad S = 4n+q
$$

CAPPING SERIES   UNCAPPING SERIES
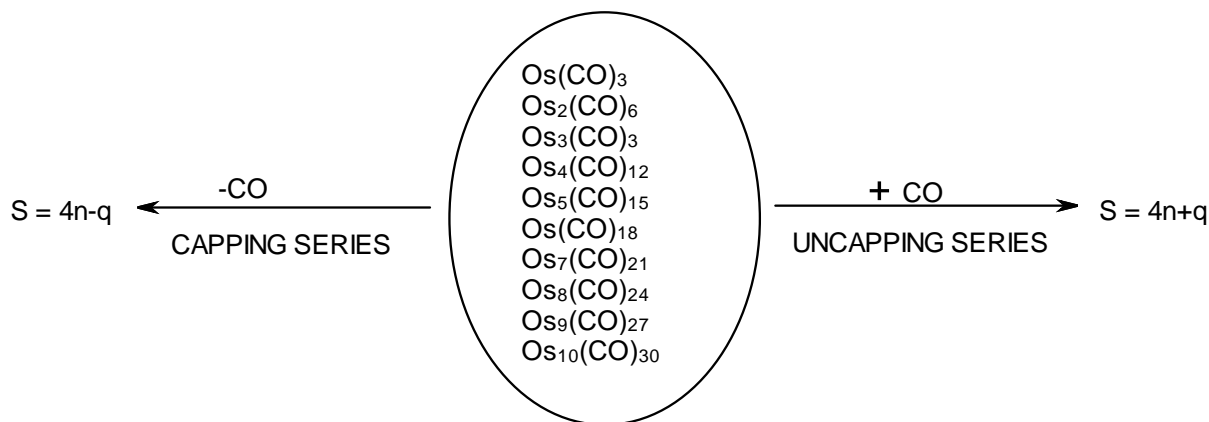
Figure 2b. Generating Capping and Decapping Series of Osmium carbonyls

Table 1. Derivation of 14n+0 series

14n	n	V	V/n	
$Os(CO)_3$	1	14	14	$Os(CO)_3$
$Os_2(CO)_6$	2	28	14	$Os(CO)_3$
$Os_3(CO)_9$	3	42	14	$Os(CO)_3$
$Os_4(CO)_{12}$	4	56	14	$Os(CO)_3$
$Os_5(CO)_{15}$	5	70	14	$Os(CO)_3$
$Os_6(CO)_{18}$	6	84	14	$Os(CO)_3$
$Os_7(CO)_{21}$	7	98	14	$Os(CO)_3$
$Os_8(CO)_{24}$	8	112	14	$Os(CO)_3$
$Os_9(CO)_{27}$	9	126	14	$Os(CO)_3$
$Os_{10}(CO)_{30}$	10	140	14	$Os(CO)_3$

Table 2. Hypothetically derived osmium carbonyl clusters

C^5C 14n-8	C^4C 14n-6	C^3C 14n-4	C^2C 14n-2	C^1C 14n+0	CLOSO 14n+2	NIDO 14n+4	ARACHNO 14n+6
	Os	$Os(CO)_1$	$Os(CO)_2$	$Os(CO)_3$	$Os(CO)_4$	$Os(CO)_5$	
$Os_2(CO)_2$	$Os_2(CO)_3$	$Os_2(CO)_4$	$Os_2(CO)_5$	$Os_2(CO)_6$	$Os_2(CO)_7$	$Os_2(CO)_8$	$Os_2(CO)_9$
$Os_3(CO)_5$	$Os_3(CO)_6$	$Os_3(CO)_7$	$Os_3(CO)_8$	$Os_3(CO)_9$	$Os_3(CO)_{10}$	$Os_3(CO)_{11}$	$Os_3(CO)_{12}$
$Os_4(CO)_8$	$Os_4(CO)_9$	$Os_4(CO)_{10}$	$Os_4(CO)_{11}$	$Os_4(CO)_{12}$	$Os_4(CO)_{13}$	$Os_4(CO)_{14}$	$Os_4(CO)_{15}$
$Os_5(CO)_{11}$	$Os_5(CO)_{12}$	$Os_5(CO)_{13}$	$Os_5(CO)_{14}$	$Os_5(CO)_{15}$	$Os_5(CO)_{16}$	$Os_5(CO)_{17}$	$Os_5(CO)_{18}$
$Os_6(CO)_{14}$	$Os_6(CO)_{15}$	$Os_6(CO)_{16}$	$Os_6(CO)_{17}$	$Os_6(CO)_{18}$	$Os_6(CO)_{19}$	$Os_6(CO)_{20}$	$Os_6(CO)_{21}$
$Os_7(CO)_{17}$	$Os_7(CO)_{18}$	$Os_7(CO)_{19}$	$Os_7(CO)_{20}$	$Os_7(CO)_{21}$	$Os_7(CO)_{22}$	$Os_7(CO)_{23}$	$Os_7(CO)_{24}$
$Os_8(CO)_{20}$	$Os_8(CO)_{21}$	$Os_8(CO)_{22}$	$Os_8(CO)_{23}$	$Os_8(CO)_{24}$	$Os_8(CO)_{25}$	$Os_8(CO)_{26}$	$Os_8(CO)_{27}$
$Os_9(CO)_{23}$	$Os_9(CO)_{24}$	$Os_9(CO)_{25}$	$Os_9(CO)_{26}$	$Os_9(CO)_{27}$	$Os_9(CO)_{28}$	$Os_9(CO)_{29}$	$Os_9(CO)_{30}$
$Os_{10}(CO)_{26}$	$Os_{10}(CO)_{27}$	$Os_{10}(CO)_{28}$	$Os_{10}(CO)_{29}$	$Os_{10}(CO)_{30}$	$Os_{10}(CO)_{31}$	$Os_{10}(CO)_{32}$	$Os_{10}(CO)_{33}$

Table 3. Classication of Clusters

		PROPOSED SYMBOL	NAME
$14n+10$	$4n+10$		KLAPO
$14+8$	$4n+8$		HYPHO
$14n+6$	$4n+6$		ARACHNO
$14n+4$	$4n+4$		NIDO
$14n+2$	$4n+2$		CLOSO
$14n+0$	$4n+0$	C^1C	MONOCAP
$14n-2$	$4n-2$	C^2C	BICAP
$14n-4$	$4n-4$	C^3C	TRICAP
$14n-6$	$4n-6$	C^4C	TETRACAP
$14n-8$	$4n-8$	C^5C	PENTACAP
$14n-10$	$4n-10$	C^6C	HEXACAP
$14n-12$	$4n-12$	C^7C	HEPTACAP
$14n-14$	$4n-14$	C^8C	OCTACAP
$14n-16$	$4n-16$	C^9C	
$14n-18$	$4n-18$	$C^{10}C$	
$14n-20$	$14n-20$	$C^{11}C$	

Table 4. Some known osmium carbonyl clusters

CLUSTER	SERIES	CLUSTER	SERIES	CLUSTER	SERIES
$Os_{20}(CO)_{40}^{2-}$	$4n-38$	$Os_7(CO)_{21}$	$4n+0$	$Os_5(H)(CO)_{15}^{-}$	$4n+2$
$Os_{17}(CO)_{36}^{2-}$	$4n-20$	$Os_7(H)(CO)_{21}^{-}$	$4n+2$	$Os_4(H)_4(CO)_{12}$	$4n+4$
$Os_{10}(C)(CO)_{24}$	$4n-8$	$Os_7(H)_2(C)(CO)_{19}$	$4n+2$	$Os_4(CO)_{15}$	$4n+6$
$Os_{10}(CO)_{26}^{2-}$	$4n-14$	$Os_6(CO)_{18}^{2-}$	$4n+2$	$Os_4(CO)_{16}$	$4n+8$
$Os_{10}(C)(CO)_{24}^{2-}$	$4n-14$	$Os_6(H)(CO)_{18}^{-}$	$4n+2$		
$Os_{10}(C)(CO)_{24}^{4-}$	$4n-12$	$Os_6(P)(CO)_{18}Cl$	$4n+6$		
$Os_{10}(H)(C)(CO)_{24}^{-}$	$4n-6$	$Os_6(H)_2(CO)_{19}$	$4n+4$		
$Os_{10}(H)_4(CO)_{24}^{2-}$	$4n-6$	$Os_6(CO)_{18}$	$4n+0$	$Os_4(H)_2(CO)_{12}^{2-}$	$4n+4$
$Os_{10}(H)_2(C)(CO)_{24}$	$4n-6$	$Os_6(CO)_{17}L_4$	$4n+6$	$Os_4(H)_2(CO)_{13}$	$4n+4$
$Os_9(CO)_{24}^{2-}$	$4n-4$	$L=P(OMe)_3$		$Os_4(CO)_{14}$	$4n+4$
$Os_9(H)(CO)_{24}^{-}$	$4n-4$	$Os_5(CO)_{19}$	$4n+8$	$Os_3(CO)_{12}$	$4n+6$
$Os_8(CO)_{23}$	$4n-2$	$Os_5(CO)_{16}$	$4n+2$	$Os_2(CO)_9$	$4n+6$
$Os_8(CO)_{22}^{2-}$	$4n-2$	$Os_5(H)_2(CO)_{16}$	$4n+4$		
$Os_8(CO)_{12}$	$4n-24$	$Os_5(CO)_{18}$	$4n+6$		

$$S = 4n-q \xleftarrow[\text{CAPPING SERIES}]{-CO}$$

$Rh(H)(CO)_2$
$Rh_2(H)_2(CO)_4$
$Rh_3(H)_3(CO)_6$
$Rh_4(H)_4(CO)_8$
$Rh_5(H)_5(CO)_{10}$
$Rh_6(H)_6(CO)_{12}$
$Rh_7(H)_7(CO)_{14}$
$Rh_8(H)_8(CO)_{16}$
$Rh_9(H)_9(CO)_{18}$
$Rh_{10}(H)_{10}(CO)_{20}$

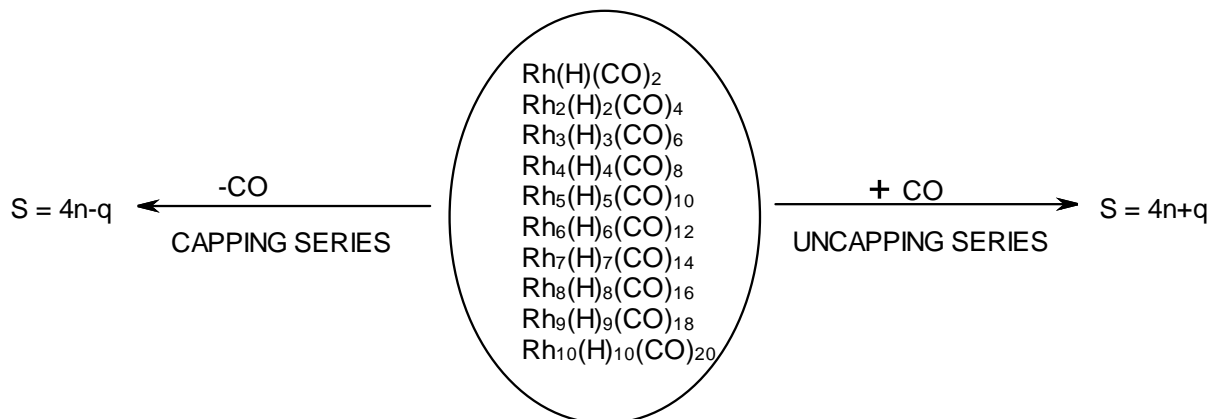$$\xrightarrow[\text{UNCAPPING SERIES}]{+CO} S = 4n+q$$

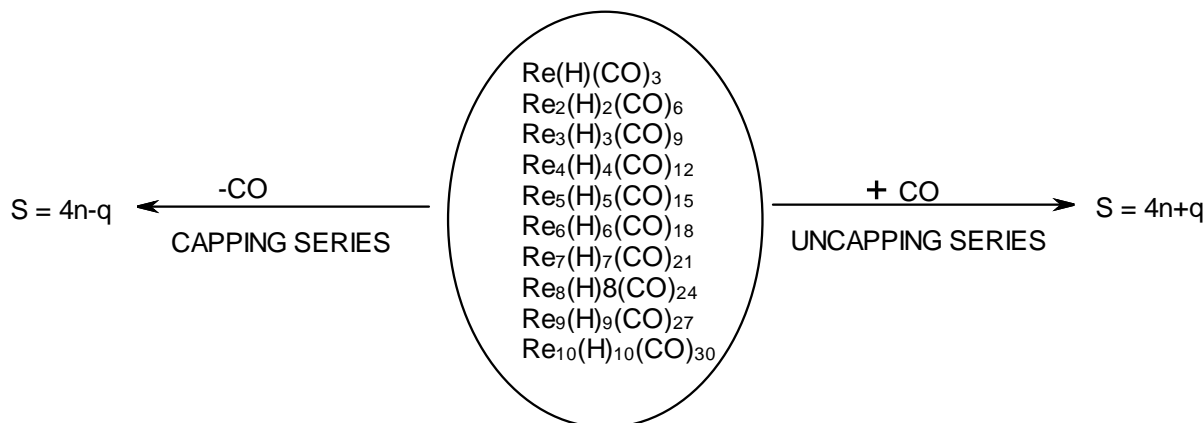Figure 3. Generating Capping and Decapping Series of Rhodium carbonyls

Figure 4. Generating Capping and Decapping Series of Rhenium carbonyls

Table 5. Hypothetically derived rhodium carbonyl clusters

14n-6	14n-4	14n-2	14n+0	14n+2	14n+4	14n+6
	$Rh(H)$	$Rh(H)(CO)_1$	$Rh(H)(CO)_2$	$Rh(H)(CO)_3$	$Rh(H)(CO)_4$	$Rh(H)(CO)_5$
$Rh_2(H)_2(CO)_1$	$Rh_2(H)_2(CO)_2$	$Rh_2(H)_2(CO)_3$	$Rh_2(H)_2(CO)_4$	$Rh_2(H)_2(CO)_5$	$Rh_2(H)_2(CO)_6$	$Rh_2(H)_2(CO)_7$
$Rh_3(H)_3(CO)_3$	$Rh_3(H)_3(CO)_4$	$Rh_3(H)_3(CO)_5$	$Rh_3(H)_3(CO)_6$	$Rh_3(H)_3(CO)_7$	$Rh_3(H)_3(CO)_8$	$Rh_3(H)_3(CO)_9$
$Rh_4(H)_4(CO)_5$	$Rh_4(H)_4(CO)_6$	$Rh_4(H)_4(CO)_7$	$Rh_4(H)_4(CO)_8$	$Rh_4(H)_4(CO)_9$	$Rh_4(H)_4(CO)_{10}$	$Rh_4(H)_4(CO)_{11}$
$Rh_5(H)_5(CO)_7$	$Rh_5(H)_5(CO)_8$	$Rh_5(H)_5(CO)_9$	$Rh_5(H)_5(CO)_{10}$	$Rh_5(H)_5(CO)_{11}$	$Rh_5(H)_5(CO)_{12}$	$Rh_5(H)_5(CO)_{13}$
$Rh_6(H)_6(CO)_9$	$Rh_6(H)_6(CO)_{10}$	$Rh_6(H)_6(CO)_{11}$	$Rh_6(H)_6(CO)_{12}$	$Rh_6(H)_6(CO)_{13}$	$Rh_6(H)_6(CO)_{14}$	$Rh_6(H)_6(CO)_{15}$
$Rh_7(H)_7(CO)_{11}$	$Rh_7(H)_7(CO)_{12}$	$Rh_7(H)_7(CO)_{13}$	$Rh_7(H)_7(CO)_{14}$	$Rh_7(H)_7(CO)_{15}$	$Rh_7(H)_7(CO)_{16}$	$Rh_7(H)_7(CO)_{17}$
$Rh_8(H)_8(CO)_{13}$	$Rh_8(H)_8(CO)_{14}$	$Rh_8(H)_8(CO)_{15}$	$Rh_8(H)_8(CO)_{16}$	$Rh_8(H)_8(CO)_{17}$	$Rh_8(H)_8(CO)_{18}$	$Rh_8(H)_8(CO)_{19}$
$Rh_9(H)_9(CO)_{15}$	$Rh_9(H)_9(CO)_{16}$	$Rh_9(H)_9(CO)_{17}$	$Rh_9(H)_9(CO)_{18}$	$Rh_9(H)_9(CO)_{19}$	$Rh_9(H)_9(CO)_{20}$	$Rh_9(H)_9(CO)_{21}$
$Rh_{10}(H)_{10}(CO)_{17}$	$Rh_{10}(H)_{10}(CO)_{18}$	$Rh_{10}(H)_{10}(CO)_{19}$	$Rh_{10}(H)_{10}(CO)_{20}$	$Rh_{10}(H)_{10}(CO)_{21}$	$Rh_{10}(H)_{10}(CO)_{22}$	$Rh_{10}(H)_{10}(CO)_{23}$
$Rh_{11}(H)_{11}(CO)_{19}$	$Rh_{11}(H)_{11}(CO)_{20}$	$Rh_{11}(H)_{11}(CO)_{21}$	$Rh_{11}(H)_{11}(CO)_{22}$	$Rh_{11}(H)_{11}(CO)_{23}$	$Rh_{11}(H)_{11}(CO)_{24}$	$Rh_{11}(H)_{11}(CO)_{25}$
$Rh_{12}(H)_{12}(CO)_{21}$	$Rh_{12}(H)_{12}(CO)_{22}$	$Rh_{12}(H)_{12}(CO)_{23}$	$Rh_{12}(H)_{12}(CO)_{24}$	$Rh_{12}(H)_{12}(CO)_{25}$	$Rh_{12}(H)_{12}(CO)_{26}$	$Rh_{12}(H)_{12}(CO)_{27}$
$Rh_{13}(H)_{13}(CO)_{23}$	$Rh_{13}(H)_{13}(CO)_{24}$	$Rh_{13}(H)_{13}(CO)_{25}$	$Rh_{13}(H)_{13}(CO)_{26}$	$Rh_{13}(H)_{13}(CO)_{27}$	$Rh_{13}(H)_{13}(CO)_{28}$	$Rh_{13}(H)_{13}(CO)_{29}$
$Rh_{14}(H)_{14}(CO)_{25}$	$Rh_{14}(H)_{14}(CO)_{26}$	$Rh_{14}(H)_{14}(CO)_{27}$	$Rh_{14}(H)_{14}(CO)_{28}$	$Rh_{14}(H)_{14}(CO)_{29}$	$Rh_{14}(H)_{14}(CO)_{30}$	$Rh_{14}(H)_{14}(CO)_{31}$

4n-6	4n-4	4n-2	4n	4n+2	4n+4
$Rh_{14}(H)_{14}(CO)_{25}$	$Rh_{14}(H)_{14}(CO)_{26}$	$Rh_{14}(H)_{14}(CO)_{27}$	$Rh_{14}(H)_{14}(CO)_{28}$	$Rh_{14}(H)_{14}(CO)_{29}$	$Rh_{14}(H)_{14}(CO)_{30}$
$Rh_{15}(H)_{15}(CO)_{27}$	$Rh_{15}(H)_{15}(CO)_{28}$	$Rh_{15}(H)_{15}(CO)_{29}$	$Rh_{15}(H)_{15}(CO)_{30}$	$Rh_{15}(H)_{15}(CO)_{31}$	$Rh_{15}(H)_{15}(CO)_{32}$
$Rh_{16}(H)_{16}(CO)_{29}$	$Rh_{16}(H)_{16}(CO)_{30}$	$Rh_{16}(H)_{16}(CO)_{31}$	$Rh_{16}(H)_{16}(CO)_{32}$	$Rh_{16}(H)_{16}(CO)_{33}$	$Rh_{16}(H)_{16}(CO)_{34}$
$Rh_{17}(H)_{17}(CO)_{31}$	$Rh_{17}(H)_{17}(CO)_{32}$	$Rh_{17}(H)_{17}(CO)_{33}$	$Rh_{17}(H)_{17}(CO)_{34}$	$Rh_{17}(H)_{17}(CO)_{35}$	$Rh_{17}(H)_{17}(CO)_{36}$
$Rh_{18}(H)_{18}(CO)_{33}$	$Rh_{18}(H)_{18}(CO)_{34}$	$Rh_{18}(H)_{18}(CO)_{35}$	$Rh_{18}(H)_{18}(CO)_{36}$	$Rh_{18}(H)_{18}(CO)_{37}$	$Rh_{18}(H)_{18}(CO)_{38}$
$Rh_{19}(H)_{19}(CO)_{35}$	$Rh_{19}(H)_{19}(CO)_{36}$	$Rh_{19}(H)_{19}(CO)_{37}$	$Rh_{19}(H)_{19}(CO)_{38}$	$Rh_{19}(H)_{19}(CO)_{39}$	$Rh_{19}(H)_{19}(CO)_{40}$
$Rh_{20}(H)_{20}(CO)_{37}$	$Rh_{20}(H)_{20}(CO)_{38}$	$Rh_{20}(H)_{20}(CO)_{39}$	$Rh_{20}(H)_{20}(CO)_{40}$	$Rh_{20}(H)_{20}(CO)_{41}$	$Rh_{20}(H)_{20}(CO)_{42}$
$Rh_{21}(H)_{21}(CO)_{39}$	$Rh_{21}(H)_{21}(CO)_{40}$	$Rh_{21}(H)_{21}(CO)_{41}$	$Rh_{21}(H)_{21}(CO)_{42}$	$Rh_{21}(H)_{21}(CO)_{43}$	$Rh_{21}(H)_{21}(CO)_{44}$
$Rh_{22}(H)_{22}(CO)_{41}$	$Rh_{22}(H)_{22}(CO)_{42}$	$Rh_{22}(H)_{22}(CO)_{43}$	$Rh_{22}(H)_{22}(CO)_{44}$	$Rh_{22}(H)_{22}(CO)_{45}$	$Rh_{22}(H)_{22}(CO)_{46}$
$Rh_{23}(H)_{23}(CO)_{43}$	$Rh_{23}(H)_{23}(CO)_{44}$	$Rh_{23}(H)_{23}(CO)_{45}$	$Rh_{23}(H)_{23}(CO)_{46}$	$Rh_{23}(H)_{23}(CO)_{47}$	$Rh_{23}(H)_{23}(CO)_{48}$
$Rh_{24}(H)_{24}(CO)_{45}$	$Rh_{24}(H)_{24}(CO)_{46}$	$Rh_{24}(H)_{24}(CO)_{47}$	$Rh_{24}(H)_{24}(CO)_{48}$	$Rh_{24}(H)_{24}(CO)_{49}$	$Rh_{24}(H)_{24}(CO)_{50}$
$Rh_{25}(H)_{25}(CO)_{47}$	$Rh_{25}(H)_{25}(CO)_{48}$	$Rh_{25}(H)_{25}(CO)_{49}$	$Rh_{25}(H)_{25}(CO)_{50}$	$Rh_{25}(H)_{25}(CO)_{51}$	$Rh_{25}(H)_{25}(CO)_{52}$
$Rh_{26}(H)_{26}(CO)_{49}$	$Rh_{26}(H)_{26}(CO)_{50}$	$Rh_{26}(H)_{26}(CO)_{51}$	$Rh_{26}(H)_{26}(CO)_{52}$	$Rh_{26}(H)_{26}(CO)_{53}$	$Rh_{26}(H)_{26}(CO)_{54}$
$Rh_{27}(H)_{27}(CO)_{51}$	$Rh_{27}(H)_{27}(CO)_{52}$	$Rh_{27}(H)_{27}(CO)_{53}$	$Rh_{27}(H)_{27}(CO)_{54}$	$Rh_{27}(H)_{27}(CO)_{55}$	$Rh_{27}(H)_{27}(CO)_{56}$
$Rh_{28}(H)_{28}(CO)_{53}$	$Rh_{28}(H)_{28}(CO)_{54}$	$Rh_{28}(H)_{28}(CO)_{55}$	$Rh_{28}(H)_{28}(CO)_{56}$	$Rh_{28}(H)_{28}(CO)_{57}$	$Rh_{28}(H)_{28}(CO)_{58}$
$Rh_{29}(H)_{29}(CO)_{55}$	$Rh_{29}(H)_{29}(CO)_{56}$	$Rh_{29}(H)_{29}(CO)_{57}$	$Rh_{29}(H)_{29}(CO)_{58}$	$Rh_{29}(H)_{29}(CO)_{59}$	$Rh_{29}(H)_{29}(CO)_{60}$
$Rh_{30}(H)_{30}(CO)_{57}$	$Rh_{30}(H)_{30}(CO)_{58}$	$Rh_{30}(H)_{30}(CO)_{59}$	$Rh_{30}(H)_{30}(CO)_{60}$	$Rh_{30}(H)_{30}(CO)_{61}$	$Rh_{30}(H)_{30}(CO)_{62}$

4n-16	4n-14	4n-12	4n-10	4n-8	4n-6
$Rh_{14}(H)_{14}(CO)_{20}$	$Rh_{14}(H)_{14}(CO)_{21}$	$Rh_{14}(H)_{14}(CO)_{22}$	$Rh_{14}(H)_{14}(CO)_{23}$	$Rh_{14}(H)_{14}(CO)_{24}$	$Rh_{14}(H)_{14}(CO)_{25}$
$Rh_{15}(H)_{15}(CO)_{22}$	$Rh_{15}(H)_{15}(CO)_{23}$	$Rh_{15}(H)_{15}(CO)_{24}$	$Rh_{15}(H)_{15}(CO)_{25}$	$Rh_{15}(H)_{15}(CO)_{26}$	$Rh_{15}(H)_{15}(CO)_{27}$
$Rh_{16}(H)_{16}(CO)_{24}$	$Rh_{16}(H)_{16}(CO)_{25}$	$Rh_{16}(H)_{16}(CO)_{26}$	$Rh_{16}(H)_{16}(CO)_{27}$	$Rh_{16}(H)_{16}(CO)_{28}$	$Rh_{16}(H)_{16}(CO)_{29}$
$Rh_{17}(H)_{17}(CO)_{26}$	$Rh_{17}(H)_{17}(CO)_{27}$	$Rh_{17}(H)_{17}(CO)_{28}$	$Rh_{17}(H)_{17}(CO)_{29}$	$Rh_{17}(H)_{17}(CO)_{30}$	$Rh_{17}(H)_{17}(CO)_{31}$
$Rh_{18}(H)_{18}(CO)_{28}$	$Rh_{18}(H)_{18}(CO)_{29}$	$Rh_{18}(H)_{18}(CO)_{30}$	$Rh_{18}(H)_{18}(CO)_{31}$	$Rh_{18}(H)_{18}(CO)_{32}$	$Rh_{18}(H)_{18}(CO)_{33}$
$Rh_{19}(H)_{19}(CO)_{30}$	$Rh_{19}(H)_{19}(CO)_{31}$	$Rh_{19}(H)_{19}(CO)_{32}$	$Rh_{19}(H)_{19}(CO)_{33}$	$Rh_{19}(H)_{19}(CO)_{34}$	$Rh_{19}(H)_{19}(CO)_{35}$
$Rh_{20}(H)_{20}(CO)_{32}$	$Rh_{20}(H)_{20}(CO)_{33}$	$Rh_{20}(H)_{20}(CO)_{34}$	$Rh_{20}(H)_{20}(CO)_{35}$	$Rh_{20}(H)_{20}(CO)_{36}$	$Rh_{20}(H)_{20}(CO)_{37}$
$Rh_{21}(H)_{21}(CO)_{34}$	$Rh_{21}(H)_{21}(CO)_{35}$	$Rh_{21}(H)_{21}(CO)_{36}$	$Rh_{21}(H)_{21}(CO)_{37}$	$Rh_{21}(H)_{21}(CO)_{38}$	$Rh_{21}(H)_{21}(CO)_{39}$
$Rh_{22}(H)_{22}(CO)_{36}$	$Rh_{22}(H)_{22}(CO)_{37}$	$Rh_{22}(H)_{22}(CO)_{38}$	$Rh_{22}(H)_{22}(CO)_{39}$	$Rh_{22}(H)_{22}(CO)_{40}$	$Rh_{22}(H)_{22}(CO)_{41}$
$Rh_{23}(H)_{23}(CO)_{38}$	$Rh_{23}(H)_{23}(CO)_{39}$	$Rh_{23}(H)_{23}(CO)_{40}$	$Rh_{23}(H)_{23}(CO)_{41}$	$Rh_{23}(H)_{23}(CO)_{42}$	$Rh_{23}(H)_{23}(CO)_{43}$
$Rh_{24}(H)_{24}(CO)_{40}$	$Rh_{24}(H)_{24}(CO)_{41}$	$Rh_{24}(H)_{24}(CO)_{42}$	$Rh_{24}(H)_{24}(CO)_{43}$	$Rh_{24}(H)_{24}(CO)_{44}$	$Rh_{24}(H)_{24}(CO)_{45}$
$Rh_{25}(H)_{25}(CO)_{42}$	$Rh_{25}(H)_{25}(CO)_{43}$	$Rh_{25}(H)_{25}(CO)_{44}$	$Rh_{25}(H)_{25}(CO)_{45}$	$Rh_{25}(H)_{25}(CO)_{46}$	$Rh_{25}(H)_{25}(CO)_{47}$
$Rh_{26}(H)_{26}(CO)_{44}$	$Rh_{26}(H)_{26}(CO)_{45}$	$Rh_{26}(H)_{26}(CO)_{46}$	$Rh_{26}(H)_{26}(CO)_{47}$	$Rh_{26}(H)_{26}(CO)_{48}$	$Rh_{26}(H)_{26}(CO)_{49}$
$Rh_{27}(H)_{27}(CO)_{46}$	$Rh_{27}(H)_{27}(CO)_{47}$	$Rh_{27}(H)_{27}(CO)_{48}$	$Rh_{27}(H)_{27}(CO)_{49}$	$Rh_{27}(H)_{27}(CO)_{50}$	$Rh_{27}(H)_{27}(CO)_{51}$
$Rh_{28}(H)_{28}(CO)_{48}$	$Rh_{28}(H)_{28}(CO)_{49}$	$Rh_{28}(H)_{28}(CO)_{50}$	$Rh_{28}(H)_{28}(CO)_{51}$	$Rh_{28}(H)_{28}(CO)_{52}$	$Rh_{28}(H)_{28}(CO)_{53}$
$Rh_{29}(H_{29}(CO)_{50}$	$Rh_{29}(H_{29}(CO)_{51}$	$Rh_{29}(H_{29}(CO)_{52}$	$Rh_{29}(H_{29}(CO)_{53}$	$Rh_{29}(H_{29}(CO)_{54}$	$Rh_{29}(H_{29}(CO)_{55}$
$Rh_{30}(H)_{30}(CO)_{52}$	$Rh_{30}(H)_{30}(CO)_{53}$	$Rh_{30}(H)_{30}(CO)_{54}$	$Rh_{30}(H)_{30}(CO)_{55}$	$Rh_{30}(H)_{30}(CO)_{56}$	$Rh_{30}(H)_{30}(CO)_{57}$

Table 6. Some known rhodium carbonyl clusters

$Rh_4(CO)_{12}$	4n+4	$Rh_{12}(CO)_{25}(H)_2$	4n-8
$Rh_4(CO)_{11}^-$	4n+4	$Rh_{13}(CO)_{12}(H)_2^{3-}$	4n-36
$Rh_5(CO)_{15}^-$	4n+6	$Rh_{13}(CO)_{24}(H)_2^{3-}$	4n-12
$Rh_5Pt(CO)_{15}^-$	4n+2	$Rh_{14}(CO)_{25}^{4-}$	4n-16
$Rh_6(CO)_{13}(C)^{2-}$	4n-2	$Rh_{14}(CO)_{25}(N)_2^{2-}$	4n-8
$Rh_6(CO)_{15}(N)^-$	4n+6	$Rh_{14}(CO)_{33}(C\,)_2^{2-}$	4n+6
$Rh_6(CO)_{15}(C)^{2-}$	4n+6	$Rh_{14}(CO)_{25}(H)^{3-}$	4n-16
$Rh_6(CO)_{14}(N)(H)^{2-}$	4n+6	$Rh_{14}(CO)_{25}^{4-}$	4n-16
$Rh_6(CO)_{16}$	4n+2	$Rh_{14}(CO)_{26}^{2-}$	4n-16
$Rh_7(CO)_{16}^{3-}$	4n+0	$Rh_{15}(CO)_{28}(C)_2^-$	4n-10
$Rh_7(CO)_{15}(N)^{2-}$	4n+2	$Rh_{15}(CO)_{25}^{3-}$	4n-22
$Rh_8(CO)_{19}(C)$	4n+2	$Rh_{15}(CO)_{28}(C)^{2-}$	4n-10
$Rh_9(CO)_{19}^{3-}$	4n-4	$Rh_{15}(CO)_{27}^{3-}$	4n-18
$Rh_9(CO)_{21}(P)^{2-}$	4n+4	$Rh_{17}(CO)_{30}^{3-}$	4n-22
$Rh_{10}(CO)_{22}(P)^{3-}$	4n+2	$Rh_{17}(CO)_{32}(S)_2^{3-}$	4n-6
$Rh_{10}(CO)_{21}^{2-}$	4n-6	$Rh_{22}(CO)_{35}(H)^{5-}$	4n-34
$Rh_{11}(CO)_{23}^{3-}$	4n-6	$Rh_{22}(CO)_{37}^{4-}$	4n-32
$Rh_{12}(CO)_{23}(N)_2(H)^{3-}$	4n+0	$Rh_{23}(CO)_{38}(N)_4^-$	4n-18
$Rh_{12}(CO)_{24}(C\,)_2^{2-}$	4n-2	$Rh_{28}(CO)_{41}(N)_4(H)_2^{4-}$	4n-32
$Rh_{12}(CO)_{23}(C)_2^{4-}$	4n-6		

Table 7. Hypothetically derived rhenium carbonyl clusters

4n-6	4n-4	4n-2	4n	4n+2	4n+4	4n+6
ReH	ReH(CO)	$ReH(CO)_2$	$ReH(CO)_3$	$ReH(CO)_4$	$ReH(CO)_5$	$ReH(CO)_6$
$Re_2H_2(CO)_3$	$Re_2H_2(CO)_4$	$Re_2H_2(CO)_5$	$Re_2H_2(CO)_6$	$Re_2H_2(CO)_7$	$Re_2H_2(CO)_8$	$Re_2H_2(CO)_9$
$Re_3H_3(CO)_6$	$Re_3H_3(CO)_7$	$Re_3H_3(CO)_8$	$Re_3H_3(CO)_9$	$Re_3H_3(CO)_{10}$	$Re_3H_3(CO)_{11}$	$Re_3H_3(CO)_{12}$
$Re_4H_4(CO)_9$	$Re_4H_4(CO)_{10}$	$Re_4H_4(CO)_{11}$	$Re_4H_4(CO)_{12}$	$Re_4H_4(CO)_{13}$	$Re_4H_4(CO)_{14}$	$Re_4H_4(CO)_{15}$
$Re_5H_5(CO)_{14}$	$Re_5H_5(CO)_{13}$	$Re_5H_5(CO)_{14}$	$Re_5H_5(CO)_{15}$	$Re_5H_5(CO)_{16}$	$Re_5H_5(CO)_{17}$	$Re_5H_5(CO)_{18}$
$Re_6H_6(CO)_{15}$	$Re_6H_6(CO)_{16}$	$Re_6H_6(CO)_{17}$	$Re_6H_6(CO)_{18}$	$Re_6H_6(CO)_{19}$	$Re_6H_6(CO)_{20}$	$Re_6H_6(CO)_{21}$
$Re_7H_7(CO)_{18}$	$Re_7H_7(CO)_{19}$	$Re_7H_7(CO)_{20}$	$Re_7H_7(CO)_{21}$	$Re_7H_7(CO)_{21}$	$Re_7H_7(CO)_{21}$	$Re_7H_7(CO)_{21}$
$Re_8H_8(CO)_{21}$	$Re_8H_8(CO)_{22}$	$Re_8H_8(CO)_{23}$	$Re_8H_8(CO)_{24}$	$Re_8H_8(CO)_{25}$	$Re_8H_8(CO)_{26}$	$Re_8H_8(CO)_{27}$
$Re_9H_9(CO)_{24}$	$Re_9H_9(CO)_{25}$	$Re_9H_9(CO)_{26}$	$Re_9H_9(CO)_{27}$	$Re_9H_9(CO)_{28}$	$Re_9H_9(CO)_{29}$	$Re_9H_9(CO)_{30}$
$Re_{10}H_{10}(CO)_{27}$	$Re_{10}H_{10}(CO)_{28}$	$Re_{10}H_{10}(CO)_{29}$	$Re_{10}H_{10}(CO)_{30}$	$Re_{10}H_{10}(CO)_{31}$	$Re_{10}H_{10}(CO)_{32}$	$Re_{10}H_{10}(CO)_{33}$
$Re_{11}H_{11}(CO)_{30}$	$Re_{11}H_{11}(CO)_{31}$	$Re_{11}H_{11}(CO)_{32}$	$Re_{11}H_{11}(CO)_{33}$	$Re_{11}H_{11}(CO)_{34}$	$Re_{11}H_{11}(CO)_{35}$	$Re_{11}H_{11}(CO)_{36}$
$Re_{12}H_{12}(CO)_{33}$	$Re_{12}H_{12}(CO)_{34}$	$Re_{12}H_{12}(CO)_{35}$	$Re_{12}H_{12}(CO)_{36}$	$Re_{12}H_{12}(CO)_{37}$	$Re_{12}H_{12}(CO)_{38}$	$Re_{12}H_{12}(CO)_{39}$
$Re_{13}H_{13}(CO)_{36}$	$Re_{13}H_{13}(CO)_{37}$	$Re_{13}H_{13}(CO)_{38}$	$Re_{13}H_{13}(CO)_{39}$	$Re_{13}H_{13}(CO)_{40}$	$Re_{13}H_{13}(CO)_{41}$	$Re_{13}H_{13}(CO)_{42}$
$Re_{14}H_{14}(CO)_{39}$	$Re_{14}H_{14}(CO)_{40}$	$Re_{14}H_{14}(CO)_{41}$	$Re_{14}H_{14}(CO)_{42}$	$Re_{14}H_{14}(CO)_{43}$	$Re_{14}H_{14}(CO)_{44}$	$Re_{14}H_{14}(CO)_{45}$
$Re_{15}H_{15}(CO)_{42}$	$Re_{15}H_{15}(CO)_{43}$	$Re_{15}H_{15}(CO)_{44}$	$Re_{15}H_{15}(CO)_{45}$	$Re_{15}H_{15}(CO)_{46}$	$Re_{15}H_{15}(CO)_{47}$	$Re_{15}H_{15}(CO)_{48}$
$Re_{16}H_{16}(CO)_{45}$	$Re_{16}H_{16}(CO)_{46}$	$Re_{16}H_{16}(CO)_{47}$	$Re_{16}H_{16}(CO)_{48}$	$Re_{15}H_{15}(CO)_{49}$	$Re_{15}H_{15}(CO)_{50}$	$Re_{15}H_{15}(CO)_{51}$
$Re_{17}H_{17}(CO)_{51}$	$Re_{17}H_{17}(CO)_{51}$	$Re_{17}H_{17}(CO)_{51}$	$Re_{17}H_{17}(CO)_{51}$	$Re_{15}H_{15}(CO)_{52}$	$Re_{15}H_{15}(CO)_{53}$	$Re_{15}H_{15}(CO)_{54}$
$Re_{18}H_{18}(CO)_{51}$	$Re_{18}H_{18}(CO)_{52}$	$Re_{18}H_{18}(CO)_{53}$	$Re_{18}H_{18}(CO)_{54}$	$Re_{15}H_{15}(CO)_{55}$	$Re_{15}H_{15}(CO)_{56}$	$Re_{15}H_{15}(CO)_{57}$
$Re_{19}H_{19}(CO)_{54}$	$Re_{19}H_{19}(CO)_{55}$	$Re_{19}H_{19}(CO)_{56}$	$Re_{19}H_{19}(CO)_{57}$	$Re_{15}H_{15}(CO)_{58}$	$Re_{15}H_{15}(CO)_{59}$	$Re_{15}H_{15}(CO)_{60}$
$Re_{20}H_{20}(CO)_{57}$	$Re_{20}H_{20}(CO)_{58}$	$Re_{20}H_{20}(CO)_{59}$	$Re_{20}H_{20}(CO)_{60}$	$Re_{15}H_{15}(CO)_{61}$	$Re_{15}H_{15}(CO)_{62}$	$Re_{15}H_{15}(CO)_{63}$

Table 8. Some known rhenium carbonyl clusters

	S=4n+q	k=2n-q/2	Category	Proposed Symbol
$Re_2(H)_2(CO)_8$	4n+4	2	nido	
$Re_2(H)_3(CO)_8^-$	4n+6	1	arachno	
$Re_2(CO)_{10}$	4n+6	1	arachno	
$Re_3(H)_3(CO)_{10}^{2-}$	4n+4	4	nido	
$Re_3(H)_4(CO)_{10}^-$	4n+4	4	nido	
$Re_3(H)(CO)_{12}^{2-}$	4n+6	3	arachno	
$Re_3(H)_2(CO)_{12}^-$	4n+6	3	arachno	
$Re_3(H)_3(CO)_{12}$	4n+6	3	arachno	
$Re_3(H)_2(CO)_{13}^-$	4n+8	2	hypho	
$Re_3(H)(CO)_{14}$	4n+8	2	hypho	
$Re_4(H)_4(CO)_{12}$	4n+0	8	monocapped	$C^1C[M-3]$
$Re_4(H)_5(CO)_{12}^-$	4n+2	7	closo	
$Re_4(H)_4(CO)_{13}^{2-}$	4n+4	6	nido	
$Re_4(H)_6(CO)_{12}^{2-}$	4n+4	6	nido	
$Re_4(CO)_{16}^{2-}$	4n+6	5	arachno	
$Re_4(H)_5(CO)_{14}^-$	4n+6	5	arachno	
$Re_4(H)_4(CO)_{15}^{2-}$	4n+8	4	hypho	
$Re_4(H)_4(CO)_{16}$	4n+8	4	hypho	
$Re_5(C)(H)(CO)_{12}^{2-}$	4n+4	8	nido	Square pyramid
$Re_6(C)(CO)_{19}^{2-}$	4n+2	11	closo	Octahedral, O_h
$Re_6(C)(H)(CO)_{19}^-$	4n+2	11	closo	Octahedral, O_h
$Re_6(H)(CO)_{18}^{3-}$	4n+2	11	closo	Octahedral, O_h
$Re_6(H)_2(CO)_{18}^{2-}$	4n+2	11	closo	Octahedral, O_h
$Re_6(H)_8(CO)_{18}^{2-}$	4n+4	10	nido	
$Re_6(H)_7(CO)_{18}^-$	4n+2	11	closo	Octahedral, O_h
$Re_7(C)(H)(CO)_{21}^{3-}$	4n+0	14	monocapped O_h	$C^1C[M-6]$
$Re_7(C)(H)(CO)_{21}^{2-}$	4n+0	14	monocapped O_h	$C^1C[M-6]$
$Re_7(C)(H)_2(CO)_{21}^-$	4n+4	12	nido	
$Re_7(C)(CO)_{22}^-$	4n+0	14	monocapped O_h	$C^1C[M-6]$
$Re_8(C)(CO)_{24}^{2-}$	4n-2	17	Bi-capped O_h	$C^2C[M-6]$

2.5 Applications of 4n Series to Classify Clusters and Predict Their Possible Shapes

We have been demonstrated that the formation of transition metal carbonyl clusters obeys the law of natural series. Also in earlier work, it was shown that chemical fragments and clusters can be categorized into series (Kiremire, 2015c).In addition, using series, we can readily concert cluster formulas into series from which their geometrical shapes may be deduced.

2.5.1 Procedure for Deriving Series and Predicting Symmetries of Clusters

According to this approach, suitable skeletal elements are identified in the cluster formula. The cluster formula is then fragmented into suitable mono-skeletal fragments. If a skeletal element is from the main group elements of the periodic table, then it is best to convert it into a fragment which has a content of four valence electrons say,[C], [BH], [BeH$_2$], [B$^-$], and [N$^+$]. Each of these fragments is regarded as being a member of S = 4n+0 series where n = 1 since we are focusing on one skeletal fragment. Since main group elements which obey the octet rule also tend to obey the 4n rule of the cluster series, if a mono-skeletal fragment has more than four valence electrons, the extra become important in categorization of the series. For example, [CH] fragment has five electrons which can be expressed as [4+1]. In such case, the series will be S = 4n+1 where n =1. For the fragment [N] which also has five valence electrons it will belong to the series S = 4n+1 while [O] with six electrons[4+2] will belong to S = 4n+2. Similarly, [CH$_2$] and [NH] fragments are also members of S= 4n+2 series. The [F] atom with seven valence electrons belongs to S = 4n+3. The 4n function may be considered to constitute the backbone of the main group element cluster series while the additional digits after 4n determine the type of series. For example, if S= 4n+(0)→mono-capped series, 4n+(2)→closo series, 4n+(4) →nido series, 4n+(6) →arachno series, 4n+(8) →hypho series and 4n+(10) →klapo series. The bicapped and higher series carry negative integers after 4n as in the case of 4n-2 or 4n-4. If a skeletal fragment is short of 4 backbone valence electrons, its series is still expressed according to 4n rule but reflecting the shortage of valence electrons. For instance, the fragment [B] has three valence electrons. So in terms of the series it is expressed as S =[4-1] = 4n-1 where n = 1, and [Be] = [4-2] →4n-2 series. In case of transition metal carbonyl clusters, it is assumed that the 18-electron rule is obeyed by the skeletal atoms. This means that the skeletal elements obey the 14n rule of the series. The same procedure as in the case of 4n for the main group elements is followed. That is, the carbonyl cluster formula is first decomposed into mono-skeletal fragments. The fragments are chosen in such a way that it conforms to 14 valence backbone configuration. Examples that fit this category are [Os(CO)$_3$],[Rh(H)(CO)$_2$], [ReH(CO)$_3$] ,[Ni(CO)$_2$], [C$_5$H$_5$Rh], [C$_5$H$_5$(CO)Re] and [C$_5$H$_5$Fe$^-$]. If a mono-skeletal fragment has a shortfall of 14, it is reflected in its series. For instance,

$[C_5H_5Os]$ has 13 valence electrons. Its series is expressed as $[14-1] = 14n-1$. Since $14n$ is isolobal to $4n$, we can also write and use $14n-1$ as $4n-1$. A transition metal atom if taken alone, its valence electrons may be expressed in the form of $14n$ series. For instance, $[Fe] \rightarrow [8] = [14-6] = S = 14n-6$ or $4n-6$. In clusters where a transition metal fragment is combined with hydrocarbon fragments such as $C_4H_4Fe(CO)_3$ or borane fragments such as $B_4H_8Ir_2(Cp^*)_2$, it is best to work with $4n$ series only. In these two examples, we can decompose the formulas as follows $C_4H_4Fe(CO)_3 \rightarrow 4[C]+4H+1[Fe(CO)_3] = 4[4]+4+1[8+3 \times 2] = 4[4n]+4+1[14n] = (4n)+4+(4n) = 4n+4$. That is, $S = 4n+4 \rightarrow$ nido cluster. The $14n$ has be utilized as $4n$ due to isolobal relationship. The 4 hydrogen atoms have contributed valence electrons to the cluster and are not regarded as skeletal elements. The value of $n = 4+1 = 5$. The cluster is regarded as having 5 skeletal elements. Using the series formula, we can derive a corresponding or an equivalent borane cluster as follows $F = 4n+4 = [BH](5)+4H = B_5H_5+4H = B_5H_9$. This borane cluster has a square pyramid shape missing one atom to have an octahedral closo shape of $B_6H_6^{2-}$. Let us consider the cluster $B_4H_8Ir_2(Cp^*)_2$. This formula can be decomposed into series as follows: $B_4H_8Ir_2(Cp^*)_2 \rightarrow S = 4[BH]+4H+2[IrCp^*] = 4[4]+4+2[9+5] = 4[4n]+4+2[14n] = 4[4n]+4+2[4n] = (4n)+4+(4n) = 4n+4$. This means the cluster belongs to the series $S = 4n+4 \rightarrow$ Nido cluster with $n = 4+2 = 6$. It is interesting to derive the equivalent borane cluster. This is given by the formula $F = [BH](6)+4H = B_6H_6+4H = B_6H_{10}$. This cluster has a pentagonal pyramid shape which a derivative of $B_7H_7^{2-}$ with a missing atom. Therefore the borane iridium cluster will have a shape similar to that of B_6H_{10}.

Summing up: Cluster Formula →Mono-skeletal fragments + other support ligands if needed →Series→ Possible geometry.

The following section gives selected examples to illustrate the application of series to categorize clusters and predict their possible shapes. Since the use of series to categorize clusters is not well known to many readers, it is best to give some highlights of the background information. One important discovery regarding series is that the series $S = 14n+q$ for the transition metal clusters is isolobal to $S = 4n+q$ of the main group elements. For instance, $14n \multimap 4n$, $14n+1 \multimap 4n+1$, $14n+2 \multimap 4n+2$, $14n+3 \multimap 4n+3$, $14n+4 \multimap 4n+4$, $14n-2 \multimap 4n-2$, and so on. This means that we can use $14n$ series or $4n$ series whichever is more convenient. In this paper, the $4n$ series will be used throughout. Some examples of isolobal series are shown below.

ISOLOBAL SERIES

$$S = 4n+q = 14n+q, \ 0,1,2,3,4,..... \qquad 4n+q \longleftrightarrow 14n+q$$

Examples:

$CH_2 \longleftrightarrow$ $SiH_2 \longleftrightarrow$ $BH_3 \longleftrightarrow$ $M(CO)_4, Fe, Ru, Os$

$S = [4+2] = 4n+2$ $\qquad S = 4n+2 \qquad S = [3+3] = [4+2]$ $\qquad S = [8+4 \times 2] = [16] = [14+2]$

$S = 4n+2$ $\qquad S = 14n+2$

$CH_3 \longleftrightarrow$ $\qquad BH_3^- \longleftrightarrow$ $\qquad Fe(CO)_5^+$

$S = [4+3] = 4n+3$ $\qquad S = [3+3+1] = [4+3] = 4n+3$ $\qquad S = [8+10-1] = [17] = [14+3]$

$S = 14n+3$

$C \longleftrightarrow$ $\qquad BH \longleftrightarrow$ $\qquad Fe(CO)_3$

$S = [4] = 4n$ $\qquad S = [3+1] = [4] = 4n$ $\qquad S = [8+3 \times 2] = [14]$

$S = 14n$
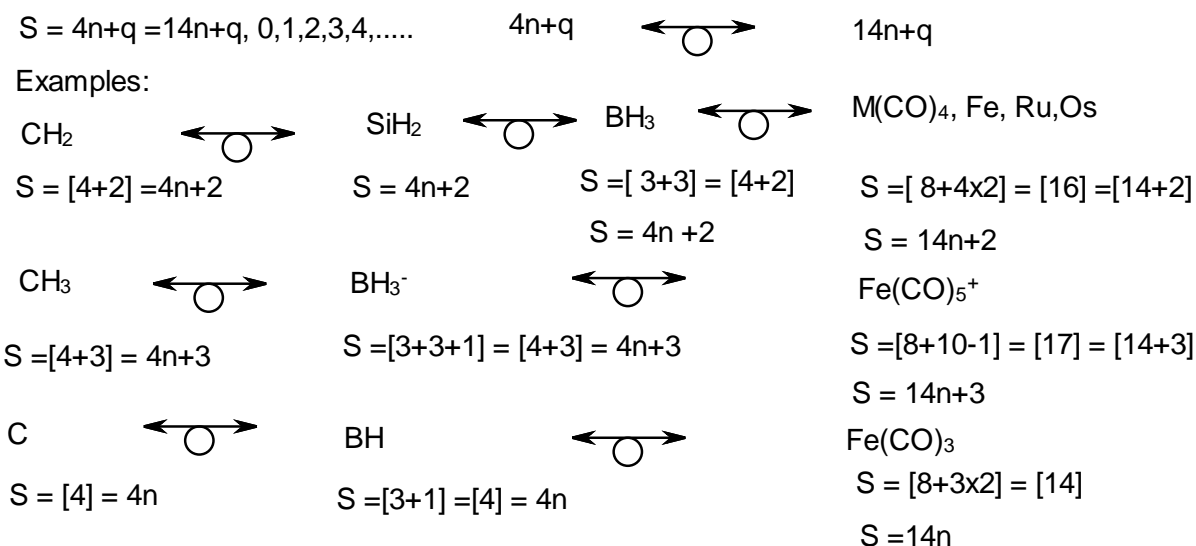
Scheme 1. Some examples of isolobal series

2.6 Cluster Number k = 2n-q/2 for Series S = 4n+q

Let us consider C_2H_6. The carbon atom $[C]$ fragment like the $[BH]$ fragment belongs to $4n+0$ series since it has 4 valence electrons. Therefore the fragment $[CH]$ of valence electron content of 5 will belong to $4n+1$ series. The other fragments $[CH_2]$ and $[CH_3]$ will be members of the series $4n+2$ and $4n+3$ respectively. When two $[CH_3]$ fragments are combined we get the C_2H_6 molecule. The corresponding series of the molecule will be given by $S = [4n+3] + [4n+3] = 2[4n+3] = 4n+6$. We can also derive the series of C_2H_6 by decomposing the molecule as follows; $C_2H_6 \rightarrow C_2 + 6H$, $C_2 \rightarrow 4n+0$ and $6H \rightarrow 6$ valence electrons. Hence, the C_2H_6 series is $S = (4n+0)+6 = 4n+6$. The number of carbon-carbon bonds in C_2H_6 are given by $k = 2n-6/2 = 2n-3$. Since there are two skeletal atoms, $n = 2$. Hence $k = 2(2)-3 = 1$. This means, there is only one bond joining the two carbon atoms together in C_2H_6. Let us consider another example, C_2H_4.

The ethylene molecule belongs to $S = 4n+4$ series which can easily be derived as was done for C_2H_6. The corresponding k value is given by $k = 2n-4/2$, $n = 2$ and hence $k = 2n-2 = 2(2) -2 = 2$. This means that there is a double bond C=C in C_2H_4. For the C_2H_2 molecule, it belongs to the series $S = 4n+2$ and $k = 2n-1 = 2(2)-1 = 3$. This corresponds to the C≡C triple bond. For C_2 molecule, it belongs to $S = 4n+0$, $k = 2n = 2(2) = 4$. This means that the C_2 molecule is linked by four bonds. These are shown in Figures 4 and 5. The structures of C_2H_6, C_2H_4 and C_2H_2 structures are well known. However, the case of C_2 having a quadruple bond caused shock waves in scientific community as it was always believed to have a double bond as deduced from molecular orbital theory(Douglas, McDaniel, Alexander, 1994). In actual fact, the isoelectronic species of C_2 including BN, CN^+, and CB^- were found to have quadruple bonds obtained from high level computations (Shaik, et al, 2012).

Empirical analysis of series and bonds linking skeletal elements which collectively obey the octet or 18 electron rule have the same formula for k value. Thus, when $S = 4n+q$ (main group elements) or $14n+q$ for transition metal carbonyl clusters, then $k = 2n+x$ where $x = q/2$ and $q = 0, \pm1, \pm2, \pm3, \pm4, \ldots$.For example, if $S = 4n+4$ or $S = 14n+4$, $k = 2n-2$ in each case. For many hydrocarbons and inorganic molecules and ions, the k-value is quite precise. For instance, N_2, $S = 4n+2$ and $k = 2n-2 = 3$. Thus N_2 has a triple bond, N≡N. In the case of S_8, $S = 4n+16$, $k = 2n-8 = 8$ whereas S_8^{2+}, $S = 4n+14$, $k = 2n-7 = 9$. Hence, 8 and 9 linkages are observed for these species respectively(Greenwood and Earnshaw,1998) The k value is so precise in predicting the number of carbon-carbon bonds especially in hydrocarbons. This is well demonstrated by the k-values in prismanes, C_6H_6, C_9H_6 and $C_{12}H_6$ and the sketches of the molecules are shown in
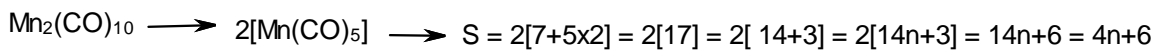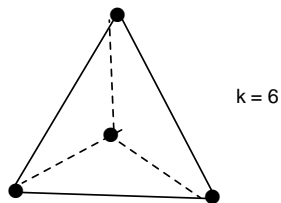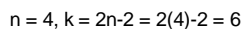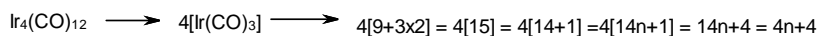
Figure 3.
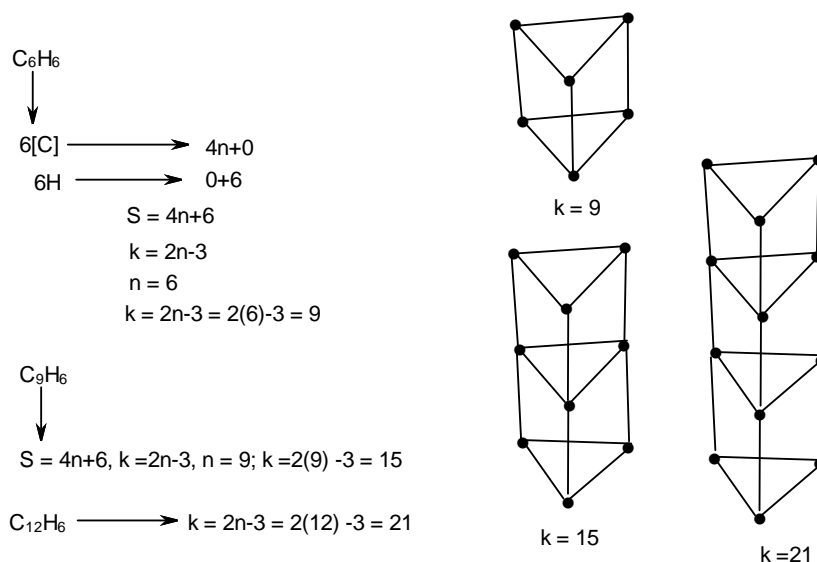
Figure 3 Sketches of prismanes C_6H_6, C_9H_6, $C_{12}H_6$
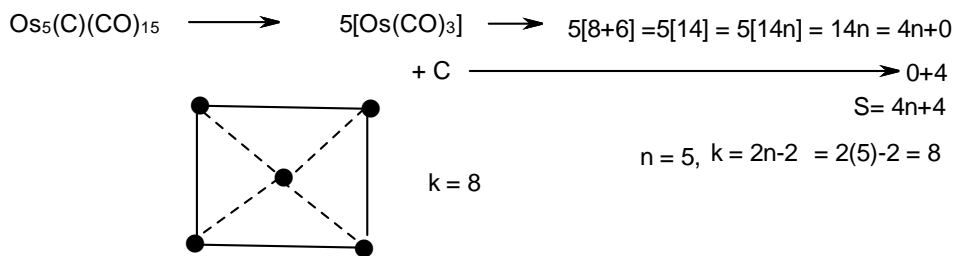
2.7 Rigid Polyhedral Shapes

In general, the shapes of borane clusters were found to be rigid polyhedral three diamensional shapes. The common closo boranes $(4n+2)$ have naturally standardized shapes which are well documented especially for $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$(Cotton and Wilkinson, 1980). For instance, closo $B_5H_5^{2-}$ has a trigonal bipyramid (D_{3h}) while the closo $B_6H_6^{2-}$ has an octahedral shape (O_h). The $B_7H_7^{2-}$ has pentagonal bipyramid (D_{5h}) shape. The other borane and related heteroboranes have shapes which are linked to the respective parent closo through the Rudolph decapping relationship. Selected examples to illustrate the use of series to predict the possible shape of a cluster are given below.
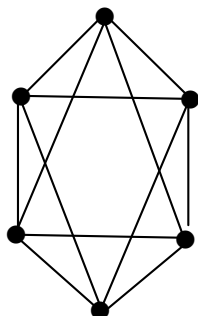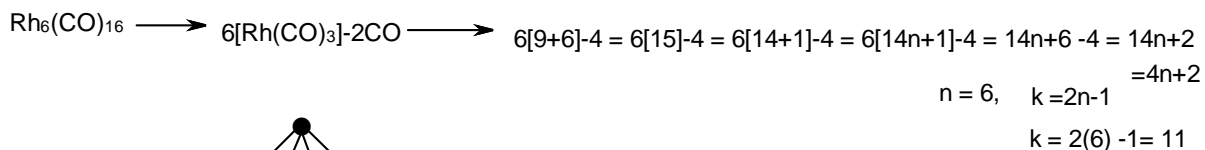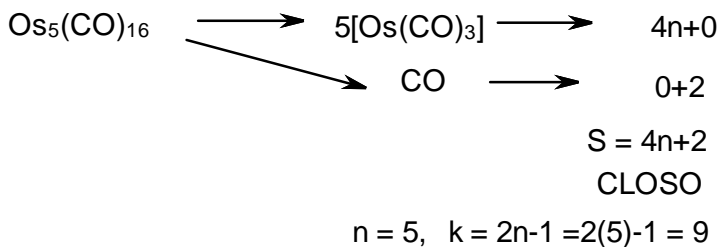
$Mn_2(CO)_{10}$ $\longrightarrow$ $2[Mn(CO)_5]$ $\longrightarrow$ S = 2[7+5x2] = 2[17] = 2[14+3] = 2[14n+3] = 14n+6 = 4n+6

n = 2, k = 2n-3 = 2(2)-3 =1

● = Mn

• = CO

k = 1

$Rh_2(CO)_2(Cp)_2$ $\longrightarrow$ $2[RhCp]+2CO$ $\longrightarrow$ 2[9+5] +2x2 = 2[14]+4 = 2[14n]+4 = 14n+4 = 4n+4

n = 2, k = 2n-2 = 2(2)-2 = 2

◯ = Cp

● = CO

● = Rh

k = 2

$Mo_2(CO)_4(Cp)_2$ $\longrightarrow$ $2[Mo(CO)_2(Cp)]$ = 2[6+2x2+5] =2[15] = 2[14+1] = 2[14n+1] = 14n+2]= 4n+2

n = = 2, k = 2n-1 = 2(2)-1 = 3

◯ = Cp

• = CO

● = Mo

k = 3

$Os_3(CO)_{12}$ $\longrightarrow$ $3[Os(CO)_3]$ +3CO $\longrightarrow$ 3[8+3x2]+3x2 = 3[14]+6 =3[14n] +6 = 14n+6 = 4n+6

n = 3, k = 2n-3 = 2(3)-3 = 3

k = 3

● = Os
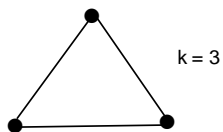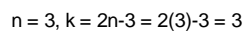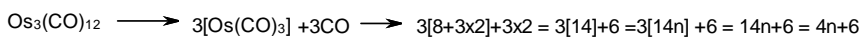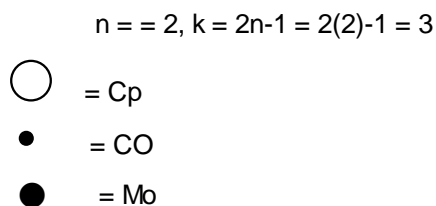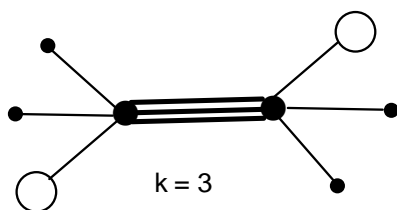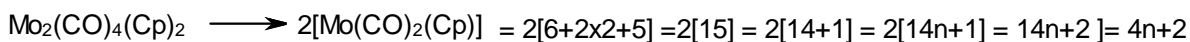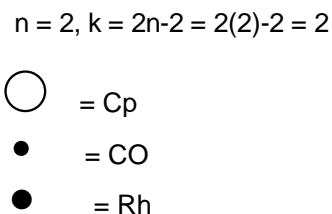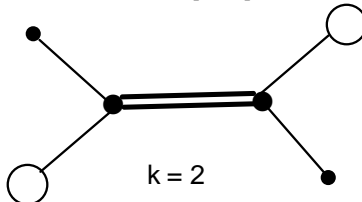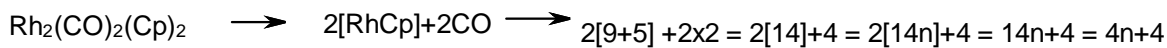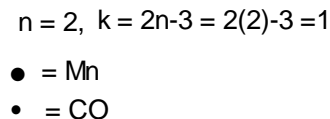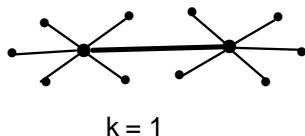
Skeletal shape of $Os_3(CO)_{12}$

$Ir_4(CO)_{12}$ $\longrightarrow$ $4[Ir(CO)_3]$ $\longrightarrow$ 4[9+3x2] = 4[15] = 4[14+1] =4[14n+1] = 14n+4 = 4n+4

n = 4, k = 2n-2 = 2(4)-2 = 6

k = 6

Projection map of Skeletal atoms of $Ir_4(CO)_{12}$

$Os_5(C)(CO)_{15} \longrightarrow 5[Os(CO)_3] \longrightarrow 5[8+6] = 5[14] = 5[14n] = 14n = 4n+0$

$+ C \longrightarrow 0+4$

$S = 4n+4$

$n = 5, \ k = 2n-2 = 2(5)-2 = 8$

$k = 8$

Projection map of skeletal elements of $Os_5(C)(CO)_{15}$

$Rh_6(CO)_{16} \longrightarrow 6[Rh(CO)_3]-2CO \longrightarrow 6[9+6]-4 = 6[15]-4 = 6[14+1]-4 = 6[14n+1]-4 = 14n+6 -4 = 14n+2$

$= 4n+2$

$n = 6, \quad k = 2n-1$

$k = 2(6) -1 = 11$

$k = 11$

Sketch of Octahedral skeletal geometry of $Rh_6(CO)_{16}$

$Os_5(CO)_{16} \longrightarrow 5[Os(CO)_3] \longrightarrow 4n+0$

$\longrightarrow CO \longrightarrow 0+2$

$S = 4n+2$

CLOSO

$n = 5, \ k = 2n-1 = 2(5)-1 = 9$

Shape, $F = 4n+2 = [BH](5) +2 = B_5H_5^{2-}$

Trigonal bipyramid, D_{3h}

$k = 9$

Trigonal bipyramid, D_{3h}

$C_2B_4H_6 \longrightarrow 2[CH] \longrightarrow 4n+2$

$\longrightarrow 4[BH] \longrightarrow 4n+0$

$n = 2+4 = 6 \quad S = 4n+2$
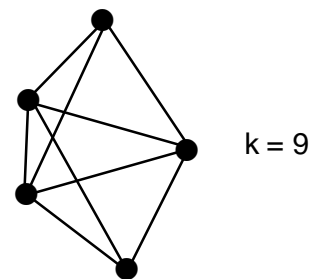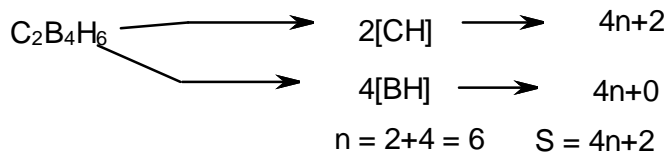
CLOSO

Shape , $F = 4n+2 = [BH](6)+2 = B_6H_6^{2-}$

Octahedral based

$TlSn_9^{3-} \longrightarrow 1[Tl^{3-}] \longrightarrow 1[3+3] = 1[4+2] = 4n+2$

$9[Sn] \longrightarrow 9[4] = 9[4n+0] = 4n+0$

$n = 1+9 = 10, \ S = 4n+2 \ \ CLOSO$

$Shape = F = 4n+2 = [BH](10)+2 = B_{10}H_{10}^{2-}$

$Shape \ similar \ to \ B_{10}H_{10}^{2-}$

$B_4H_6\{CoCp)_2 \longrightarrow 4[BH] \longrightarrow 4[4] = 4[4n] = 4n+0$

$2H \longrightarrow 0+2$

$2[CoCp] \longrightarrow 2[9+5] = 2[14] = 2[4n] = 4n+0$

$n = 4+2 = 6 \ \ S = 4n+2 \ \ \ CLOSO$

$Shape, \ F = 4n+2 = [BH](6)+2 = B_6H_6^{2-}$

$Shape \ similar \ to \ B_6H_6^{2-}$

$CB_9H_{10}CoCp^- \longrightarrow 1[CH] \longrightarrow 1[4+1+1] = 4n+2$

$9[BH] \longrightarrow 9[4] = 4n+0$

$1[CoCp] \longrightarrow 1[9+5] = 1[14] = 4n+0$

$n = 1+9+1 = 11, \ S = 4n+2, \ CLOSO$

$Shape, \ F = 4n+2 = [BH](11)+2 = B_{11}H_{11}^{2-}$

$Shape \ similar \ to \ B_{11}H_{11}^{2-}$

$C_2B_3H_7Fe(CO)_3 \longrightarrow 2[CH] \longrightarrow 2[4+1] = 2[4n+1] = 4n+2$

$3[BH] \longrightarrow 3[3+1] = 3[4] = 4n+0$

$2H \longrightarrow 0+2$

$1[Fe(CO)_3] \longrightarrow 1[8+3\times2] = 1[14] = 1[4] = 4n+0$

$n = 2+3+1 = 6 \ \ \ \ \ \ S = 4n+4, \ \ NIDO$

$Shape, \ F = 4n+4 = [BH](6) +4H = B_6H_6+4H = B_6H_{10}$

$Shape \ similar \ to \ B_6H_{10} \ \ \ Pentagonal \ pyramid. \ Its \ CLOSO \ derivative \ is \ B_7H_7^{2-}$

$Pd_6Ru_6(CO)_{24}^{2-}$

$\downarrow$

$6[Pd(CO)] \longrightarrow 6[10+2] = 6[14-2] = 6[4-2] = 6[4n-2] = 4n-12$

$6[Ru(CO)_3] \longrightarrow 6[8+6] = 6[14] = 6[4] = 6[4n] = 4n+0$

$q \longrightarrow 0+2$

$$S = (4n-12) + (4n+0) + (0+2) = 4n-10$$

$$S = 4n-10$$

$$Cp = C^1C + C^5C = C^6C[M-6]$$

Cluster is a hexa-capped cluster.

$Os_{17}(CO)_{36}^{2-}$

$\downarrow$

$17[Os(CO)_2] \longrightarrow 17[8+4] = 17[14-2] = 17[4-2] = 17[4n-2] = 4n-34$

$2CO \longrightarrow 0+4$

$q \longrightarrow 0+2$
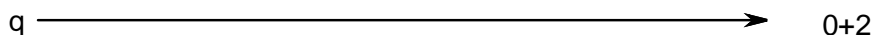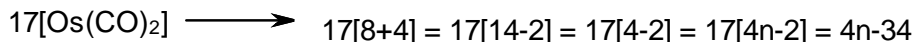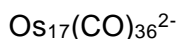
$$S = 4n-28$$

$$Cp = C^1C + C^{14}C = C^{15}C[M-2]$$

This means the cluster has two atoms at the nucleus being a closo member of 4n+2 series.

$Os_{20}(CO)_{40}^{2-}$

$\downarrow$

$20[Os(CO)_2] \longrightarrow 20[8+4] = 20[14-2] = 20[4-2] = 20[4n-2] = 4n-40$

$q \longrightarrow 0+2$
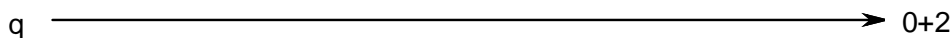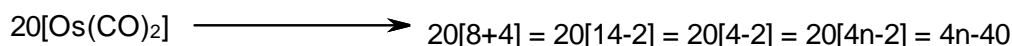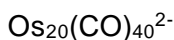
$$S = 4n-38$$

$$Cp = C^1C + C^{19}C = C^{20}C[M-0]$$

$$[M-0] = 4n+2 = [Os(CO)_3](0) + CO$$

$$[M-0] = 0 + CO = CO$$

$$Cp = C^1C + C^{19}C = C^{20}C[CO]$$

This means that the cluster series starts capping with a CO fragment.

$Cp^*IrB_3H_5Co_2(CO)_5$

↓

$1[Cp^*Ir]$ $=1[5+9]=1[14]$ ⟶ $4n+0$

$3[BH]=3[3+1]=3[4]$ ⟶ $4n+0$

$2H$ ⟶ $0+2$

$2[Co(CO)_3=2[9+6]=2[15]=2[14+1]=2[4+1]$ ⟶ $4n+2$

$F_B=$ $4n+2=[BH](6)+2=B_6H_6^{2-}$
-CO ⟶ $0-2$

$S=4n+2$ ⟶ CLOSO

$n=1+3+2=6$
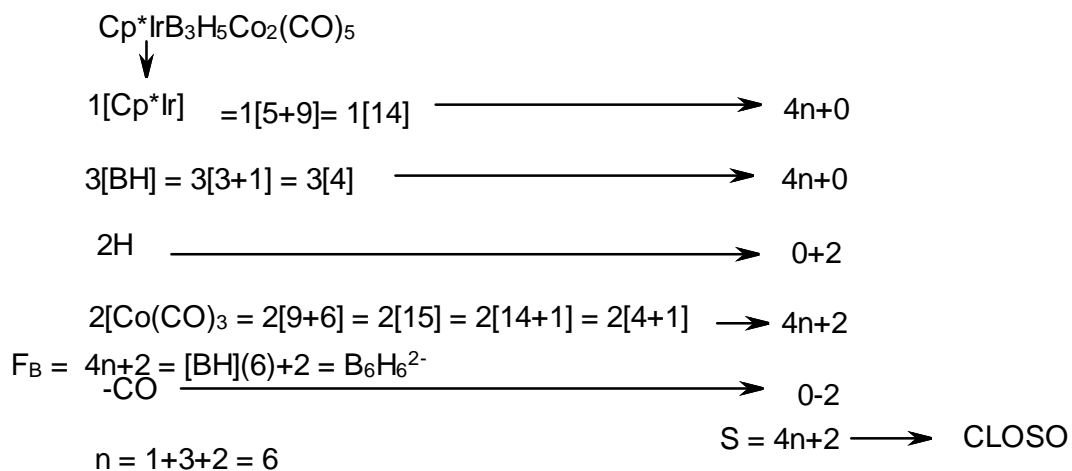
Shape similar to $B_6H_6^{2-}$ ⟶ Octahedral, O_h

● = Ir

● = Co

• = B

$C_5H_5Mn(CO)_3$

↓
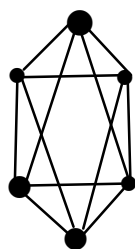
$5[C]$ ⟶ $4n+0$

$5H$ ⟶ $0+5$

$1[Mn(CO)_3]$ ⟶ $4n-1$

$=1[7+6]=1[14-1]=1[4-1]$

$n=5+1=6$

$S=4n+4$ ⟶ NIDO ⟶ Shape Derived ftom $B_7H_7^{2-}$

$k=2n-2=2(6)-2=10$

$F_B=4n+4=[BH](6)+4H=B_6H_6+4H=B_6H_{10}$

Shape similar to that of B_6H_{10}

• = CO

● = Mn

• = C

Ferrocene, $Fe(C_5H_5)_2$

Consider $CpFeC_5H_5$

$= Cp$

$= Fe$

$= C$

$1[FeCp(H)] \longrightarrow 1[8+5+1] = 1[14] = 1[4] \longrightarrow 4n+0$

$5[C] \longrightarrow 5[4] \longrightarrow 4n+0$

$4H \longrightarrow 0+4$

$n = 1+5 = 6$

$S = 4n+4 \longrightarrow$ NIDO

$F_B = 4n+4 = [BH](6) +4H = B_6H_6+4H = B_6H_{10}$

$k = 2n-2 = 2(6)-2 = 10$

Shape similar to that of B_6H_{10} Derived from $B_7H_7{}^{2-}$

Ferrocene, $Fe(C_5H_5)_2$

Consider $C_5H_5FeC_5H_5$

$= Fe$
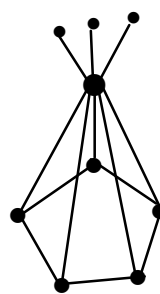
$= C$
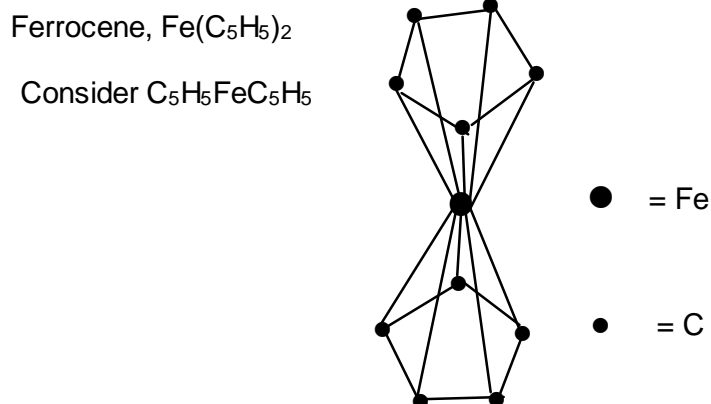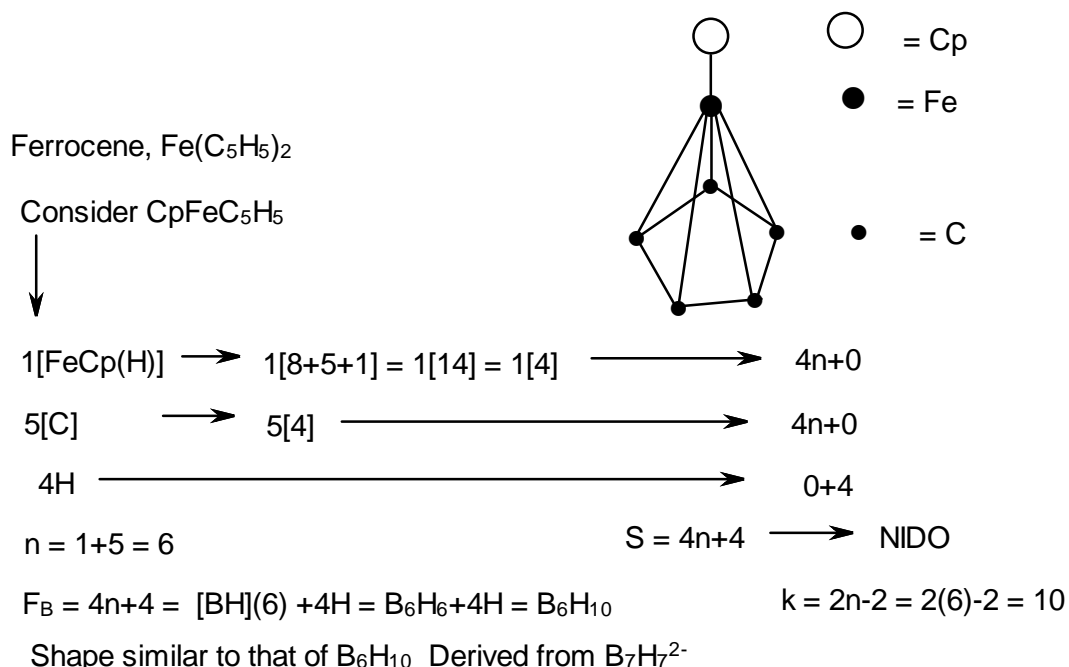
Shape will be two pentagonal pyramids joined through Fe atom

3. Conclusions

The transition metal carbonyl clusters are formed according to a numerical sequence centered on number 14. The 14n series can be generated by multiples of 14. The clusters that belong to $S = 14n+0$ constitute mono-capped closo series. The addition of two valence electrons on members of mono-capped series produces closo series $S = 14n+2$. Other series can be produced by successive addition of 2 extra valence electrons. The two electrons could be supplied by a CO ligand or in some cases two hydrogens or two negative charges. Successive subtraction of 2 valence electrons from the 14n series creates more capping series. Cluster fragments of a particular type of series say 14n+2 can be produced by changing the value of n and adding a CO for integer 2 and substituting a building block fragment with a valence electron content of 14. In case of osmium, the building bloc is $Os(CO)_3$, rhodium, $RhH(CO)_2$, rhenium, $ReH(CO)_3$, and palladium, $Pd(CO)_2$. A cluster formula can be decomposed into chemical fragments centered on mono-skeletal elements and other free atoms or molecules. From the decomposition products series can be derived. From the series a possible geometrical shape of the cluster may be predicted. The series are useful in predicting shapes of hydrocarbons, boranes, carboranes, and their complexes with metals, carbonyl clusters, zintyl ions and other clusters from simple to more complex ones.

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