

Unusual underground Capping Carbonyl Clusters of Palladium

Enos Masheija Rwantale Kiremire

Correspondence: Enos Masheija Rwantale Kiremire, Department of Chemistry and Biochemistry, University of Namibia, Private Bag 13301, Windhoek, Namibia. E-mail:kiremire15@yahoo.com

Received: December 29, 2015 Accepted: January 11, 2016 Online Published: January 21, 2016

doi:10.5539/ijc.v8n1p145

URL: <http://dx.doi.org/10.5539/ijc.v8n1p145>

Abstract

Transition metal carbonyls form unlike boranes a wide range of clusters. High nuclearity carbonyl clusters have a tendency to form capped clusters. Using the method of series explained in this paper, many capped carbonyl clusters have been identified for group 7, 8, 9 and 10 transition metals such as rhenium, osmium, rhodium and palladium. The series have discovered that palladium form exclusively capped carbonyl clusters. Furthermore, it has been discovered that some of the capped clusters have negative nuclear closo function. Such carbonyls have been regarded as capping underground. This paper presents the unique characteristic of high nuclearity capping carbonyl clusters of palladium.

Keywords: polyhedral skeletal electron pair theory, palladium capping series, underground capping clusters, clusters of high nuclearity, carbonyls of rhenium, osmium, rhodium, and palladium, hoffmann and isolobal series.

1. Introduction

The polyhedral skeletal electron pair theory (PSEPT) has been exceedingly useful in categorizing clusters especially boranes and carbonyls for many years (Mingos, 1972; Wade, 1976; Cox, 1981; Mingos, 1984; Lee, et al, 1989; Jemmis, et al, 1984; Jemmis et al, 2001; 2002; 2003; Balakrishnarajan and Hoffmann, 2004; Jemmis, 2005; 2005; Wales, 2005; Jemmis, et al., 2008; Welch, 2013). In our previous extensive work on clusters we found that the $4n$ and $14n$ rules could also be utilized to categorize the clusters and predict the shapes carbonyl cluster series (Kiremire, 2014; Kiremire, 2015a; Kiremire, 2015b) especially those of small to medium size level. Furthermore, we found that using $4n$ series cluster molecular formulas could be decomposed into fragments from which cluster series can be derived and their geometrical shapes predicted (Kiremire, E. M. R., 2015c). Unlike the PSEPT which was derived from molecular orbital theory, the $14n \pm q$ and $4n \pm q$ (where q is an integer) rules were empirically derived by analysis of carbonyl, hydrocarbons and borane cluster formulas and known shapes.

1.1 Authenticity of the $4n$ And $14n$ Series

Since the use of series categorize clusters is not well known, it is extremely important to explain this approach to cluster analysis. Recently, it has been found that Hoffmann's isolobal fragments (Hoffmann, 1982) could assigned series (Kiremire, 2015d). For a given cluster formula, skeletal elements of the cluster are identified. The formula is then decomposed into suitable mono-skeletal fragments. If a selected skeletal element is a main group element of the periodic table, then the $4n$ rule is applied, if it is a transition metal, the $14n$ rule is applied. For example, if carbon (C) is taken as a fragment, it has [4] valence electrons. According to the series approach used in this paper, it will be classified as belonging to $4n(n = 1)$ series. If the fragment is [CH], then the electron content will be [4+1] and this will be categorized as being a member of $4n+1$ series. A phosphorus atom P with a valence electron content of five will be categorized in the same way. That is, [5] = [4+1] = $4n+1$. Thus, the four electrons must be separated first to form the backbone of the series and the rest will be used in the categorization of the series and the cluster. The fragment [BH] = [3+1] = [4] will belong to $4n + 0$ series. In the case of transition metal carbonyl clusters, the classification is based upon $14n$ rule. Take the case of the fragment $F = [\text{Os}(\text{CO})_3]$, the valence electron content is $[8+3 \times 2] = [14]$. This means we can classify the fragment as belonging to $14n+0$ series. It has been found that the $14n$ is isolobal to $4n$. Therefore it is easier to use $4n$ instead of $14n$ for classification. If we get a fragment $F = [\text{Os}(\text{CO})_4]$, then the valence content is [16], then we can split this into $[14+2] = 14n+2$ series. This is the same as $4n+2$ due to isolobal relationship. In case of the fragment $F = [\text{Rh}(\text{CO})_3]$, the valence content is $[9+3 \times 2] = [15] = [14+1]$. This means we can classify the fragment as belonging to $14n+1$ series or to $4n+1$ due to isolobal relationship. If a fragment has less than 14, then its valence content can be transformed into a form consistent with $14n$ series. For instance, the fragment, such as $F = [\text{Pd}(\text{CO})]$ has [10+2] valence electron content. This is then transformed into $[10+2] = [14-2] = 14n - 2$ which equivalent to $4n-2$ due to isolobal relationship. In fact, the fragment $F = [\text{Pd}(\text{CO})]$ is equivalent to $F = \text{Os}(\text{CO})_2$ fragment. The isolobal relationship may simply be represented as given here $14n \pm q$ is isolobal to or simply $14n \pm q = 4n \pm q$.

2. Results and Discussion

Using the series approach, a large number of known carbonyl clusters have been categorized and the results came out precisely as the ones obtained from literature (Hughes and Wade, 2000). These findings are given in Table 1. Using the same method, a good collection of different 19 examples have been analyzed using fragments and series and the results are given in the following section so as to expose the reader to a variety of applying series for categorization of clusters.

2.1 Capping Clusters

In our earlier work (Kiremire, 2015a, Kiremire 2015b), a capping symbol C^nC ($n = 1, 2, 3, \dots$) was proposed. The capping symbol of clusters has been covered in previous work. But will briefly be repeated here for the purpose of getting readers be more familiar with it. For mono-capped closo, series $S = 14n+0$, the capping symbol C^1C , n has a value of 1 signifying one cap. In the case of bi-capped cluster, $S = 14n-2$, the capping symbol is $Cp = C^2C$ ($n = 2$). This means, if $S = 14n-2 = 14n+1(-2)$, then the capping is $Cp = C^1+C^1 = C^2C$. The first C^1 comes from the $14n$ component of the series as it implies a mono-cap. The second C^1 comes from $1(-2)$ component of the series. According to the series, for every negative integer of two (-2), there is an additional capping. Thus, $S = 14n-4 = 14n+2(-2)$, the capping symbol is $Cp = C^1+C^2 = C^3C$ (tri-capped). Similarly, for $S = 14n-6 = 14n+3(-2)$, the capping symbol is $Cp = C^1+C^3 = C^4C$ (tetra-capped). Some of the capped carbonyl clusters are given in Table 1. They include among others, $Re_4H_4(CO)_{12}$, $S = 14n$, $C^1C[M-3]$; $Os_6(CO)_{18}$, $S = 14n$, $C^1C[M-5]$; $Os_7(CO)_{21}$, $S = 14n$, $C^1C[M-6]$; and $Os_8(CO)_{22}^{2-}$, $S = 14n-2$, $C^2C[M-6]$. If we analyze $Re_4H_4(CO)_{12}$, $S = 14n$, $C^1C[M-3]$ cluster system closely, C^1 means that one skeletal atom is capping on three others which constitute an inner core closo cluster that obeys the $14n+2$ or simply $4n+2$ rule. The building block of the rhenium cluster must have a content of [14] electrons according to the series while the capping cluster must have a valence electron content of [12]. The suitable fragments of rhenium will be $[Re(H)(CO)_3]$ and $[Re(H)(CO)_2]$ respectively. The [M-3] symbol means that the inner core cluster is a member of $S = 4n+2$ series and $n = 3$. We can construct the formula of the inner core as follows: $F = 4n+2 = [Re(H)(CO)_3] (3)+CO = Re_3(H)_3(CO)_9 + CO = Re_3(H)_3(CO)_{10}$. This is the inner closo cluster. In order to derive the entire cluster formula, we must add the mono-cap, that is, $Re_3(H)_3(CO)_{10} + [Re(H)(CO)_2] = Re_4(H)_4(CO)_{12}$. Let us discuss a few more examples to illustrate how fragments are utilized to generate series. Consider $Os_4(CO)_{16}$ cluster. There are 4 skeletal osmium atoms. Hence, we can decompose this into $4[Os(CO)_3]$ fragments and 4CO ligands. The valence electron content of $[Os(CO)_3]$ fragment = $8+3 \times 2 = 14$. In using the series method, it makes the work easier to create fragments whose valence electron content are [14] for transition metals or [5] for main group elements. If not the values must be close to these values less or above. The fragment $F = [Os(CO)_3]$ belongs to $14n$ series. Therefore, $4 [14n] = 14n$ just as carbon fragment [C] fragment $S = 4n+0$ series ($n = 1$) and $C_4 = 4[C] = 4[4n] = S = 4n+0$ series ($n = 4$). Each of the CO ligand donates 2 valence electrons and therefore 4CO ligands will contribute 8 valence electrons. Therefore the net cluster series $S = (14n+0)+8 = 14n+8$. This cluster belongs to the HYPHO series. Since $14n$ is isolobal to $4n$, then the series can be regarded to be the same as $S = 4n+8$. The simplicity of working with $4n$ rather than $14n$, makes $4n$ more user friendly. Take another example, $Os_9(CO)_{24}^{2-}$ cluster. This cluster has 9 skeletal osmium atoms. It is easier to aim to decompose the cluster into nine [14] valence electron fragments. This is done as follows, $Os_9(CO)_{24}^{2-} = 9[Os(CO)_3]-3CO+2$. This gives us 27CO ligands. Since we have only 24CO ligands in the cluster, we need to subtract 3CO ligands to balance the ligands. This gives rise to subtracting $3 \times 2 = 6$ valence electrons. The cluster has a charge, q of -2. This means that q also supplies 2 more electrons to the valence electron content. To sum up, $9[Os(CO)_3] = 9[14] = 9[14n] = 14n+0$ which is the same as $4n+0$. We need to remove the valence electrons of 3CO and add 2 electrons from the charge. This gives us $S = (4n+0)-(6)+(2) = 4n-6+2 = 4n-4$. That is, $S = 4n-4 = 14n+2(-2)$, $Cp = C^1+C^2 = C^3C[M-6]$. This is a tri-capped cluster. This means that three of the nine osmium atoms are capped and the 6 comprise of nuclear octahedral closo cluster. The complex is a tri-capped octahedral cluster. The symbol {M-6} means this belongs to $14n+2$ or $4n+2$ series. We can generate the formula of this inner cluster using the electron building block [14] of the carbonyl clusters and the $n=6$ value of the closo cluster as follows $F = [Os(CO)_3] (6)+2 = Os_6(CO)_{18}^{2-}$. We could also have used CO ligand instead of converting +2 into a charge of (2-). The complex $Os_6(CO)_{18}^{2-}$ as is found is indeed an octahedral closo complex (Cotton and Wilkinson, 1980). Let us consider a few members of $S = 14n+0$ series starting with $Os(CO)_3$ fragment. Since $F = Os(CO)_3$ then $S = 4n+0$ and $Cp = C^1C[M-0]$. According to series, the building block of the series is based upon the [14] valence electron content. The capping fragment is based upon the [12] valence electron content. The capping is centered upon the closo inner nucleus. This means $[M-0] = 4n+2$ and $F = 4n+2 = [Os(CO)_3(0)+CO]$ since $n = 0$. This gives $F = CO$ for the first member of $14n+2$ or $4n+2$ series. In order to get the formula of the $14n$ or $4n$ series we have to add the value of the inner core [M-0] to the value of the capping fragment. That is, $F = [M-0] + C^1$. The value of $C^1 = [Os(CO)_2]$. Hence, $F = CO + [Os(CO)_2] = Os(CO)_3$. This means that CO is the closo nucleus of $Os(CO)_3$ while $Os(CO)_2$ is the capping component of $Os(CO)_3$. The combination of the two generates the first member of the fragment of the $4n$ series. The fragment $Os_2(CO)_6$ is the second member of $S = 4n+0$ series. This means that it is also a mono-capped cluster. That is, $Cp = C^1C[M-1]$ meaning that there is one skeletal capping atom while the other forms the inner closo

core. We need to define what [M-1] means in terms of the series. The closo symbol $[M-1] = 4n+2 = [\text{Os}(\text{CO})_3(1)+\text{CO} = \text{Os}(\text{CO})_3 + \text{CO} = \text{Os}(\text{CO})_4$. Let us recall that for osmium, $C^1 = \text{Os}(\text{CO})_2$. Hence, $F = C^1 + [M-1] = \text{Os}(\text{CO})_2 + \text{Os}(\text{CO})_4 = \text{Os}_2(\text{CO})_6$. It is quite clear that the series easily explain why $\text{Os}(\text{CO})_3$ and $\text{Os}_2(\text{CO})_6$ are members of the first mono-capping series. The third member of the $4n$ series is $\text{Os}_3(\text{CO})_9$. The corresponding capping symbol for this is $C_p = C^1C[M-2]$. The symbol, [M-2] represents $4n+2$ content $= [\text{Os}(\text{CO})_3(2)+\text{CO} = \text{Os}_2(\text{CO})_6+\text{CO} = [\text{Os}_2(\text{CO})_7]$. Therefore the cluster formula is generated by adding the capping fragment to the closo nuclear component $C^1 + [M-2] = [\text{Os}(\text{CO})_2] + [\text{Os}_2(\text{CO})_7] = \text{Os}_3(\text{CO})_9$. In the same manner, it can easily be shown that $\text{Os}_4(\text{CO})_{16}$ is a member of $S = 4n$ series and $C_p = C^1C[M-3]$ where $C^1 = \text{Os}(\text{CO})_2$ and $[M-3] = \text{Os}_3(\text{CO})_{10}$. The clusters, $\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_7(\text{CO})_{21}$ which are also members of the C^1C series have already been discussed.

2.2 Palladium Underground Capping Carbonyl Clusters

From the discussion presented above, it is quite clear that series are have the power to analyze clusters of all types based on fragments and series derived from them using the valence electron content. An analysis on palladium carbonyl clusters was made on a large collection of carbonyl clusters using series. The results are given in Table 2. A large number of these palladium carbonyls have been produced by Dahl research team (Mednikov, Dahl, 2010). It is quite amazing that palladium forms a wide range of capped carbonyl clusters. They range from closo [M-11] to closo [M⁻⁷⁶]. What was found interesting according to series is that for palladium there are clusters which cap using negative closo nuclear clusters. It is proposed that such capping clusters with negative closo values such as [M⁻⁷⁶] be regarded as undergoing clapping underground. This is similar to highways which are constructed for underground traffic travel. Consider capping at [M-0]. This means capping at base level highway. The symbol [M-0] for palladium carbonyl means $[M-0] = 4n+2 = [\text{Pd}(\text{CO})_2(0)+\text{CO} = \text{CO}$. That is, the cluster has a closo nucleus with no skeletal atom ($n = 0$) and the skeletal building block is based on [14] valence electrons. In the case of palladium a suitable fragment is $F = [\text{Pd}(\text{CO})_2]$ and a capping fragment of twelve valence electrons [12], [is $F = \text{Pd}(\text{CO})$]. The integer (+2) means two valence electrons added to $14n$ or $4n$ series. Likewise, capping at [M⁻¹] means $= 4n+2 = [\text{Pd}(\text{CO})_2(-1)+\text{CO} = -\text{Pd}(\text{CO})_2+\text{CO} = -\text{Pd}(\text{CO})$. That is, capping at underground highway level $n = -1$. The negative sign means that closo value function will have a negative value since $n = -1$. This negative value must be added to the value of the capping function to generate the cluster molecular formula. Since [M⁻¹] has a negative power, $n = -1$, as in the case of $\text{Pd}_{54}(\text{CO})_{40}\text{L}_{14}$, $C^{55}C[M^{-1}]$ cluster. The capping fragment $F = [\text{Pd}(\text{CO})]$ and hence $C^{55} = 55[\text{Pd}(\text{CO})] = \text{Pd}_{55}(\text{CO})_{55}$ and $M^{-1} = -[\text{Pd}(\text{CO})]$. Therefore the molecular formula is obtained by adding the two functions as $F = \text{Pd}_{55}(\text{CO})_{55} - [\text{Pd}(\text{CO})] = \text{Pd}_{54}(\text{CO})_{54}$. This cluster is equivalent to $\text{Pd}_{54}(\text{CO})_{40}\text{L}_{14}$ in terms of valence electron content as CO and L each donate two electrons.

2.3 Capping carbonyl Clusters above the Ground and Underground

An X-Y type of axis has been designed to explain the impression derived from the capping cluster carbonyls of palladium. This is shown in Figure 1. As can be seen from Table 2, there are clusters whose closo nucleus starts from [M-0] to [M-11]. The closo [M-0] may be regarded as the beginning of being above the ground and those below the [M-0] similar to the X-axis may be taken as capping below the ground (underground). Those capping above the ground include [M-0], osmium cluster $\text{Os}_{20}(\text{CO})_{40}^{2-}$, $C^{20}C[M-0]$ is used as a reference, [M-1] closo carbonyl, $\text{Pd}_{34}(\text{CO})_{24}\text{L}_{12}$, $C^{33}[M-1]$. This closo is based on the first highway above the ground. On the other hand the [M-2] series, C^1 , C^{30} , C^{33} , and C^{35} are based on the highway level 2 above the ground. Other examples include the [M-5] series C^3 , C^9 , C^{11} , and C^{25} . The [M-6] series are C^{17} , C^{23} , C^{24} , and C^{36} . Members of [M-7] series are C^3 , C^{25} and C^{29} . The last series to include is the [M-9], C^3 and C^8 . The capping image here is similar to that of athletics where runners in lanes compete in jumping series of huddles. In the example of [M-6] lane or highway, one cluster is at C^{17} huddle or series, another at C^{23} , another at C^{24} , and the last at C^{36} . From the capping symbol of a cluster, its molecular formula may be derived. The palladium cluster with a capping code $C^{36}C[M-6]$ is $\text{Pd}_{33}\text{Ni}_9(\text{CO})_{41}\text{L}_6^{4-}$ and this can be readily be converted into its equivalent cluster. The capping fragment has an electron content of [12] and in the case of palladium carbonyl clusters this corresponds to $[\text{Pd}(\text{CO})]$ and in for skeletal building block contains [14] skeletal electrons. Therefore, $C^{36} = 36[\text{Pd}(\text{CO})] = \text{Pd}_{36}(\text{CO})_{36}$. The closo inner core $[M-6] = 4n+2 = [\text{Pd}(\text{CO})_2(6)+\text{CO} = \text{Pd}_6(\text{CO})_{12}+\text{CO} = \text{Pd}_6(\text{CO})_{13}$. The formula of the cluster will be the sum of the capping value and that of the inner core cluster $\text{Pd}_{36}(\text{CO})_{36} + \text{Pd}_6(\text{CO})_{13} = \text{Pd}_{42}(\text{CO})_{49}$. In the cluster $\text{Pd}_{33}\text{Ni}_9(\text{CO})_{41}\text{L}_6^{4-}$, Pd = Ni in terms of valence electron content. Also the ligand CO = L in terms of electron content. The charge of (-4) has electron content of 2CO ligands. Hence, the cluster $\text{Pd}_{33}\text{Ni}_9(\text{CO})_{41}\text{L}_6^{4-} = 33\text{Pd} + 9\text{Ni} + 41\text{CO} + 6\text{CO} + 2\text{CO} = \text{Pd}_{42}(\text{CO})_{49}$. The underground capping cluster is also readily identified by the series. Take the case of $\text{Pd}_{59}(\text{CO})_{36}\text{L}_{14}$, $S = 4n-136$, $C_p = C^{69}C[M^{10}]$. According to the series the symbol, C^{69} means that there 69 capping fragments each of 12 electrons. That is, $C^{69} = 69[\text{Pd}(\text{CO})] = \text{Pd}_{69}(\text{CO})_{69}$. The closo inner core [M¹⁰] cluster means that it belongs to the closo series $S = 4n+2$. Therefore $[M^{10}] = 4n+2 = [\text{Pd}(\text{CO})_2(-10)+\text{CO} = -\text{Pd}_{10}(\text{CO})_{20}+\text{CO} = -\text{Pd}_{10}(\text{CO})_{19}$. In terms of the series, this means that in order to generate the observed cluster formula of the carbonyl complex, we must the value of the inner core from the value of the capping function. This leads us to the following formula of the complex $F = \text{Pd}_{69}(\text{CO})_{69} - \text{Pd}_{10}(\text{CO})_{19} = \text{Pd}_{59}(\text{CO})_{50}$. In terms of valence electron content $\text{Pd}_{59}(\text{CO})_{36}\text{L}_{14}$, L = CO and hence the cluster is

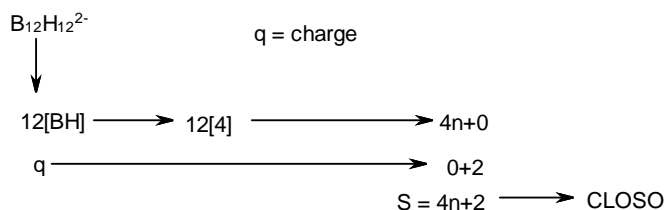
the same as $\text{Pd}_{59}(\text{CO})_{36}(\text{CO})_{14} = \text{Pd}_{59}(\text{CO})_{50}$. Just as in developed nations complex road system, this cluster could be viewed as having been formed (capping) along the high way 10 $[\text{M}^{-10}]$ underground. Let us consider the next underground capping cluster $\text{Pd}_{69}(\text{CO})_{36}\text{L}_{18}$, $4n-168$, and $\text{Cp} = \text{C}^{85}\text{C}[\text{M}^{-16}]$. The capping formula can be utilized to recreate the cluster formula of the carbonyl complex. Following the same procedure as in the above example, $\text{C}^{85} = 85[\text{Pd}(\text{CO})] = \text{Pd}_{85}(\text{CO})_{85}$. The closo inner core $[\text{M}^{-16}] = 4n+2 = [\text{Pd}(\text{CO})_2](-16)+\text{CO} = -\text{Pd}_{16}(\text{CO})_{32}+\text{CO} = -\text{Pd}_{16}(\text{CO})_{31}$. In order to get the formula of the cluster complex we have to subtract the inner core from the capping function. This gives us $\text{F} = \text{Pd}_{85}(\text{CO})_{85} - \text{Pd}_{16}(\text{CO})_{31} = \text{Pd}_{69}(\text{CO})_{54}$. The cluster $\text{Pd}_{69}(\text{CO})_{36}\text{L}_{18}$ has the same valence electron content as $\text{Pd}_{69}(\text{CO})_{54}$. Consider the cluster $\text{Pd}_{165}(\text{CO})_{60}\text{L}_{30}$, $S = 4n-480$, $\text{Cp} = \text{C}^{241}\text{C}[\text{M}^{-76}]$. The capping function, $\text{C}^{241} = 241[\text{Pd}(\text{CO})] = \text{Pd}_{241}(\text{CO})_{241}$. The closo function, $[\text{M}^{-76}] = 4n+2 = [\text{Pd}(\text{CO})_2](-76)+\text{CO} = -\text{Pd}_{76}(\text{CO})_{151}$. The molecular formula is $\text{Pd}_{241}(\text{CO})_{241} - \text{Pd}_{76}(\text{CO})_{151} = \text{Pd}_{165}(\text{CO})_{90}$. This is the same as $\text{Pd}_{165}(\text{CO})_{60}\text{L}_{30}$. The cluster series formula such as $4n-480$ can also be used to calculate the molar mass. If we put $n = 241$ into the series, we get $S = 4(165)-480 = 180$. Since $14n$ is isolobal to $4n$, then the difference is $10n$. This means for transition metal we must add $10n$ electrons we will get the value of valence electron cluster of the palladium cluster. That is, to the $165 \times 10 = 1650$ we must add $180 = 1830$. The valence electron content of the cluster $\text{Pd}_{165}(\text{CO})_{60}\text{L}_{30}$ is $165 \times 10 + 90 \times 2 = 1860$. What is fascinating is the discovery by use of series that the cluster, $\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}(\text{H})^5$, $S = 4n-74$; $\text{Cp} = \text{C}^{38}\text{C}[\text{M}-6]$ has an octahedral closo nuclear cluster comprising of six platinum atoms (Rossi, 2011) at the centre of a large cluster. The rhodium cluster (Hughes and Wade, 2000), $\text{Rh}_{22}(\text{CO})_{37}^4$, $S = 4n-38$, $\text{Cp} = \text{C}^{20}\text{C}[\text{M}-2]$, has two atoms in the centre of the cluster of 22 skeletal atoms. For the cluster (Hughes and Wade, 2000), $\text{Os}_{17}(\text{CO})_{36}^2$, $S = 4n-28$, $\text{Cp} = \text{C}^{15}\text{C}[\text{M}-2]$. According to the series, this cluster has 2 atoms at the centre of a cluster of 17 skeletal elements. Thus, both the rhodium and osmium clusters are placed on $[\text{M}-2]$ highway above the ground. The osmium is at 'city' number 15 along the $[\text{M}-2]$ highway while the rhodium is at city number 20 (C^{20}) along the $[\text{M}-2]$ highway above the ground. Clearly, the palladium element mainly form unique carbonyl clusters, those which do capping above the ground and those which cap underground.

2.4 The Generating Function of the Palladium Carbonyl Clusters

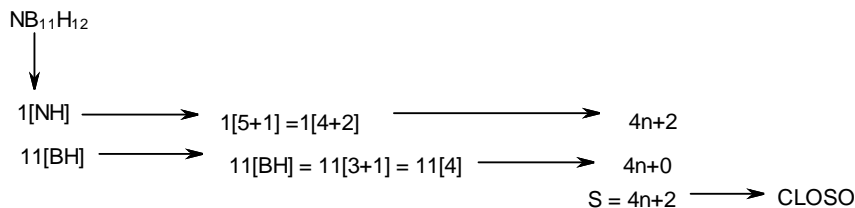
It has been found that one of the best way of generating the molecular formulas of known and unknown carbonyl clusters is to use the $[4]$ or $[14]$ function and multiples. That is, the multiples of $4n$ or $14n$ series generate the backbone of the series. The addition of CO ligands to the backbone members gives the clusters series with positive integers such as $4n+2$ closo, $4n+4$ nido, and $4n+6$ arachno. The capping clusters begin with digit zero (0) after $4n$, that is, $S = 4n+0$ (mono-capped), the next capping has the series $S = 4n-2$ (bi-capped), $4n-6$ (tri-capped) and so on. These have negative integers after $4n$. Using $4n$ instead of $14n$ is much easier and faster. This is the approach that has been used to categorize the clusters from main group and transition metals. Since palladium forms exclusively capping clusters, generating functions that give capping clusters have been designed for palladium. A selected number of these clusters and fragments have been created and are given in Table 3. A number of known and hypothetical clusters were identified in the table. Among others, these include $\text{Pd}_{12}(\text{CO})_{15}\text{L}_7$, $\text{Pd}_{10}(\text{CO})_{14}\text{L}_4$, $\text{Pd}_3(\text{CO})_3\text{L}$, $\text{Pd}_8(\text{CO})_{14}$, $\text{Pd}_{10}(\text{CO})_{16}$, $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$, and $\text{Pd}_{16}(\text{CO})_{13}\text{L}_9$.

Table 1. Comparison of Categorization of Clusters Using 4n Series and the known Literature results

	SERIES	SERIES	LITERATURE*	CAP SYMBOL
$\text{Os}_2(\text{CO})_{10}$	4n+8	HYPHO	HYPHO	
$\text{Re}_3(\text{H})(\text{CO})_{14}$	4n+8	HYPHO	HYPHO	
$\text{Os}_4(\text{CO})_{16}$	4n+8	HYPHO	HYPHO	
$\text{Re}_4(\text{H})_4(\text{CO})_{16}$	4n+8	HYPHO	HYPHO	
$\text{Os}_5(\text{CO})_{19}$	4n+8	HYPHO	HYPHO	
$\text{Re}_2(\text{CO})_{10}$	4n+6	ARACHNO	ARACHNO	
$\text{Os}_2(\text{CO})_8^{2-}$	4n+6	ARACHNO	ARACHNO	
$\text{Re}_3(\text{H})_3(\text{CO})_{12}$	4n+6	ARACHNO	ARACHNO	
$\text{Os}_4(\text{CO})_{12}$	4n+6	ARACHNO	ARACHNO	
$\text{Re}_4(\text{CO})_{16}^{2-}$	4n+6	ARACHNO	ARACHNO	
$\text{Os}_5(\text{CO})_{18}$	4n+6	ARACHNO	ARACHNO	
$\text{Os}_6(\text{CO})_{21}$	4n+6	ARACHNO	ARACHNO	
$\text{Re}_2(\text{H})_2(\text{CO})_{10}$	4n+4	NIDO	NIDO	
$\text{Re}_3(\text{H})_3(\text{CO})_{10}^{2-}$	4n+4	NIDO	NIDO	
$\text{Os}_3(\text{H})_2(\text{CO})_{12}$	4n+4	NIDO	NIDO	
$\text{Os}_4(\text{CO})_{14}$	4n+4	NIDO	NIDO	
$\text{Re}_4(\text{H})_6(\text{CO})_{12}^{2-}$	4n+4	NIDO	NIDO	
$\text{Os}_5(\text{H})_2(\text{CO})_{16}$	4n+4	NIDO	NIDO	
$\text{Re}_5(\text{C})(\text{H})(\text{CO})_{16}^{2-}$	4n+4	NIDO	NIDO	
$\text{Re}_6(\text{H})_8(\text{CO})_{18}^{2-}$	4n+4	NIDO	NIDO	
$\text{Os}_6(\text{H})_2(\text{CO})_{19}$	4n+4	NIDO	NIDO	
$\text{Os}_7(\text{H})_2(\text{CO})_{22}$	4n+4	NIDO	NIDO	
$\text{Re}_4(\text{H})_5(\text{CO})_{12}^-$	4n+2	CLOSO	CLOSO	
$\text{Os}_5(\text{CO})_{16}$	4n+2	CLOSO	CLOSO	
$\text{Re}_6(\text{C})(\text{CO})_{19}^{2-}$	4n+2	CLOSO	CLOSO	
$\text{Os}_6(\text{CO})_{18}^{2-}$	4n+2	CLOSO	CLOSO	
$\text{Re}_4(\text{H})_4(\text{CO})_{12}$	4n+0	MONOCP	MONOCP	$\text{C}^1\text{C}[\text{M}-3]$
$\text{Os}_6(\text{CO})_{18}$	4n+0	MONOCP	MONOCP	$\text{C}^1\text{C}[\text{M}-5]$
$\text{Os}_7(\text{CO})_{21}$	4n+0	MONOCP	MONOCP	$\text{C}^1\text{C}[\text{M}-6]$
$\text{Re}_7(\text{C})(\text{CO})_{21}^{-3}$	4n+0	MONOCP	MONOCP	$\text{C}^1\text{C}[\text{M}-6]$
$\text{Re}_8(\text{C})(\text{CO})_{24}^{2-}$	4n-2	BICP	BICP	$\text{C}^2\text{C}[\text{M}-6]$
$\text{Os}_8(\text{CO})_{22}^{2-}$	4n-2	BICP	BICP	$\text{C}^2\text{C}[\text{M}-6]$
$\text{Os}_9(\text{CO})_{24}^{2-}$	4n-4	TRICP	TRICP	$\text{C}^3\text{C}[\text{M}-6]$
$\text{Pd}_6\text{Ru}_6(\text{CO})_{24}^{2-}$	4n-10	HEXACP	HEXACP	$\text{C}^6\text{C}[\text{M}-6]$

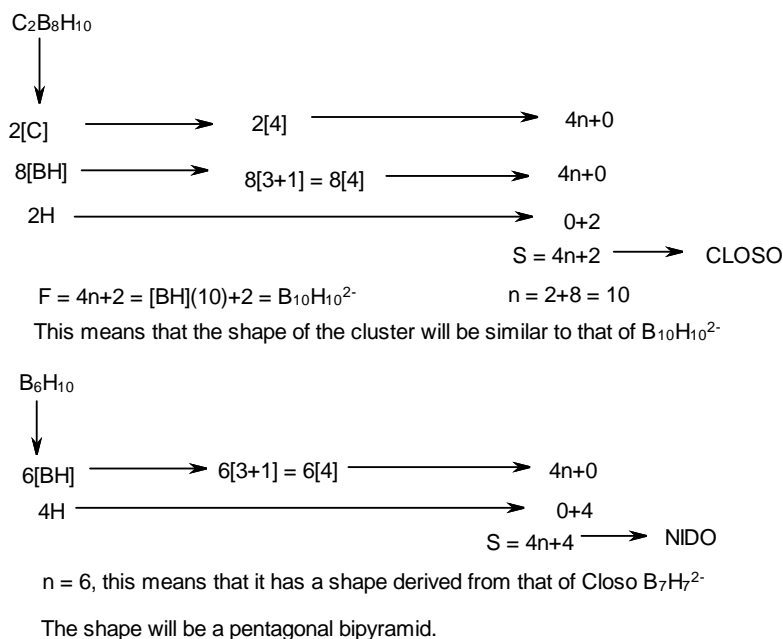
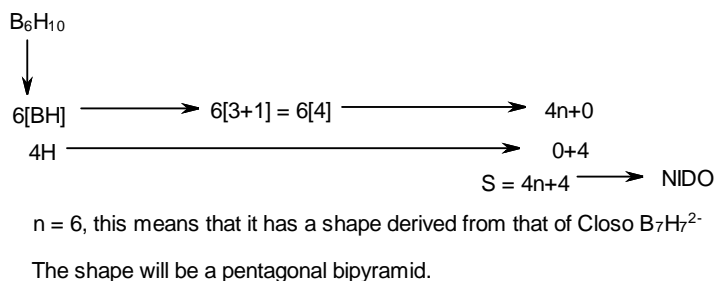
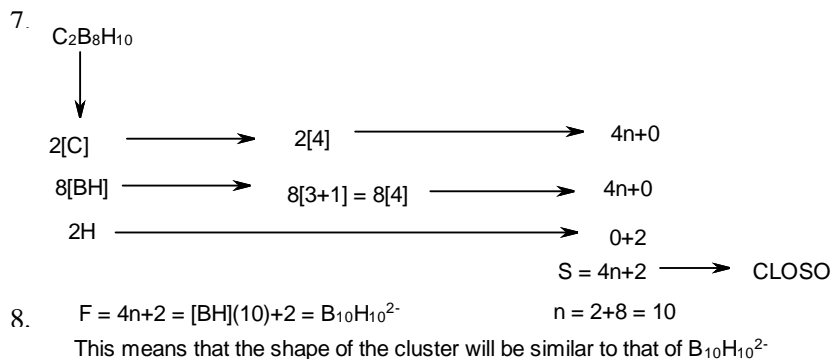
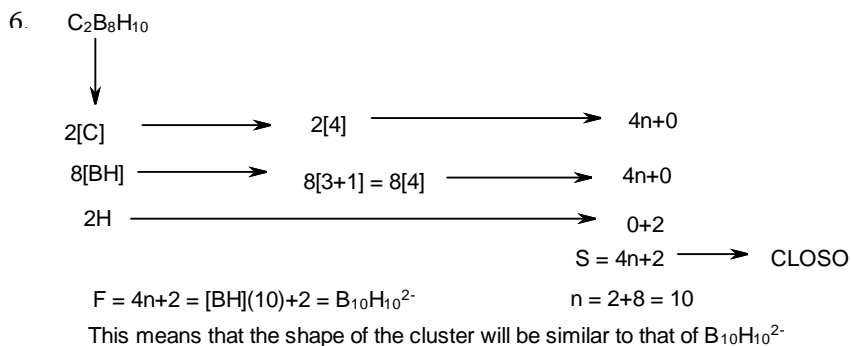


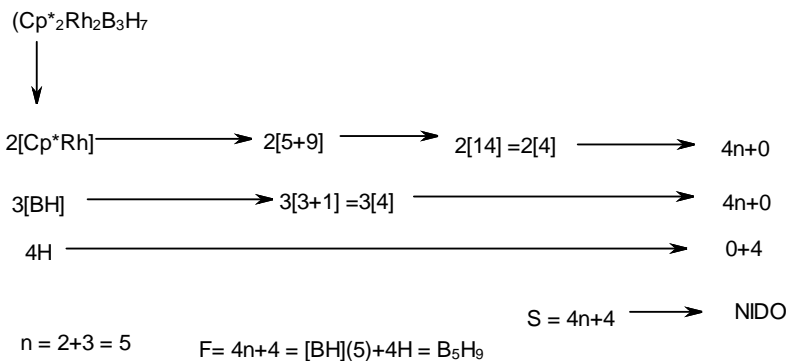
This closo cluster will have the well known standard shape of $\text{B}_{12}\text{H}_{12}^{2-}$



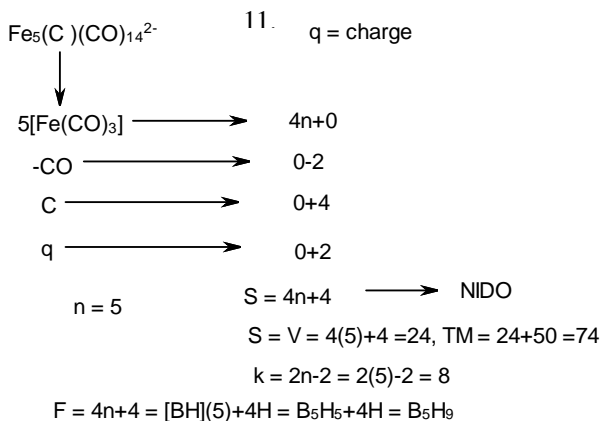
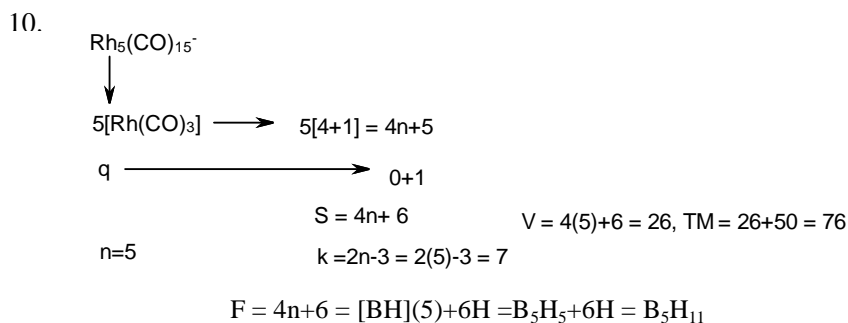
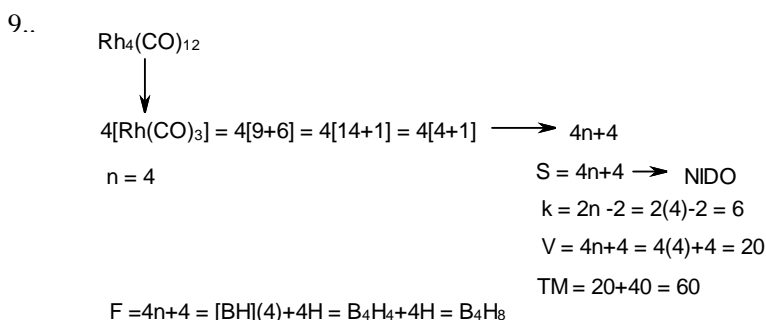
$$n = 1+11 = 12 \quad F = 4n+2 = [\text{BH}](12)+2 = \text{B}_{12}\text{H}_{12}^{2-}$$

This means that the cluster will adopt a shape similar to that of $\text{B}_{12}\text{H}_{12}^{2-}$.





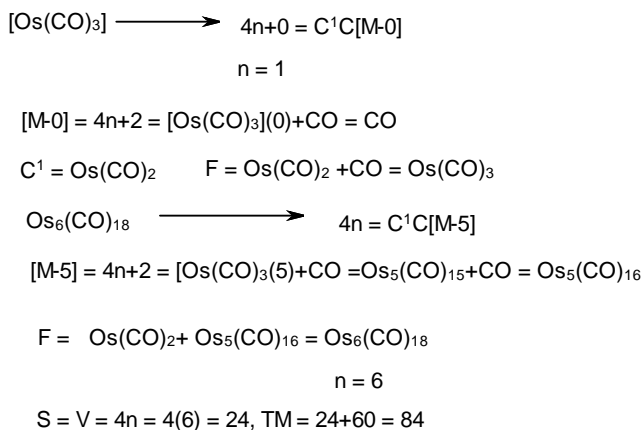
The ideal shape of the cluster is that B_5H_9 which is a derivative of CLOSO $\text{B}_6\text{H}_6^{2-}$.
The cluster will have a square pyramid shape.

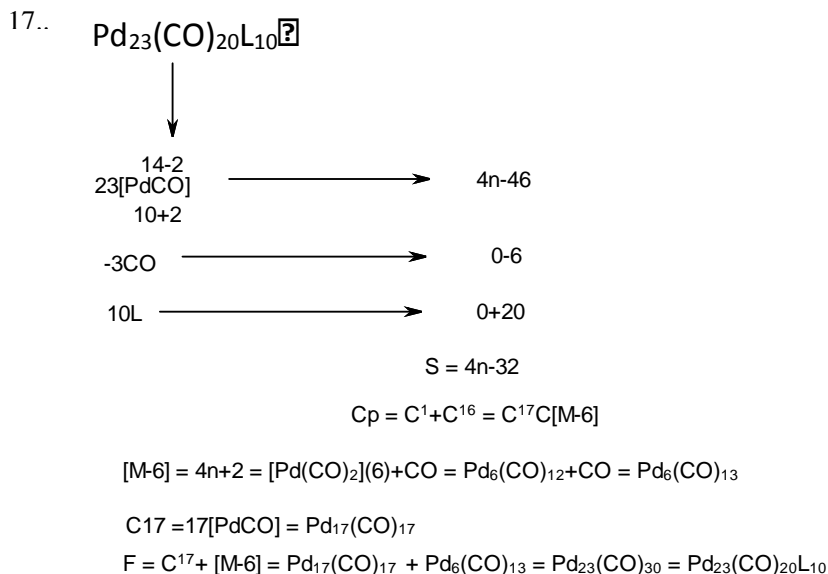


Derived from octahedral $\text{B}_6\text{H}_6^{2-}$

Square pyramid geometry.

12.





The k value of the cluster is given by $k = 2n+16$ since $S = 4n-32$. Since $n = 23$, $k = 2(23)+16 = 62$. The capping fragment PdCO has 12 valence electrons and hence $S = [12] = [14-2] = [4-2] = 4n-2$. For $S = 4n-2$, $k = 2n+1 = 2(1)+1 = 3$. Thus, for every capping, k increases by 3. For $F = \text{C}^{17} + [\text{M}-6]$, $k = 17 \times 3 + 11 = 51 + 11 = 62$.

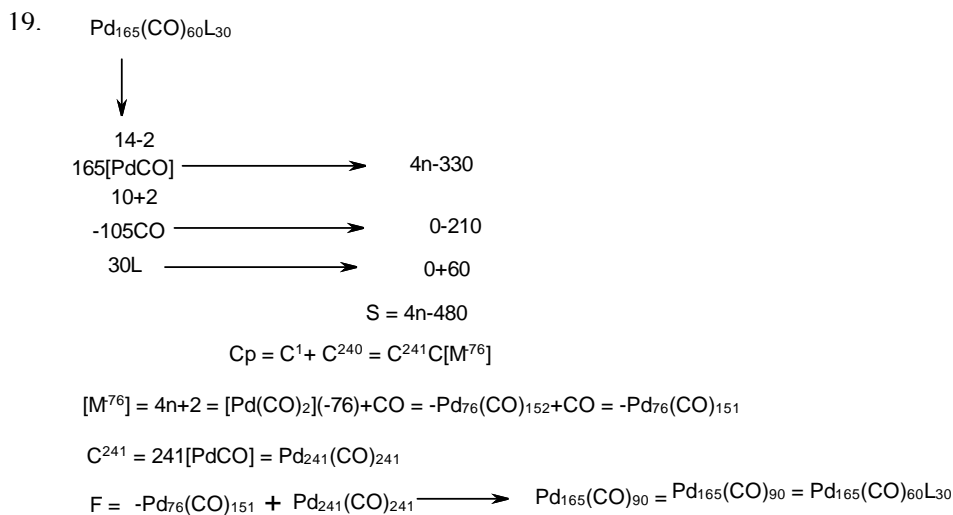
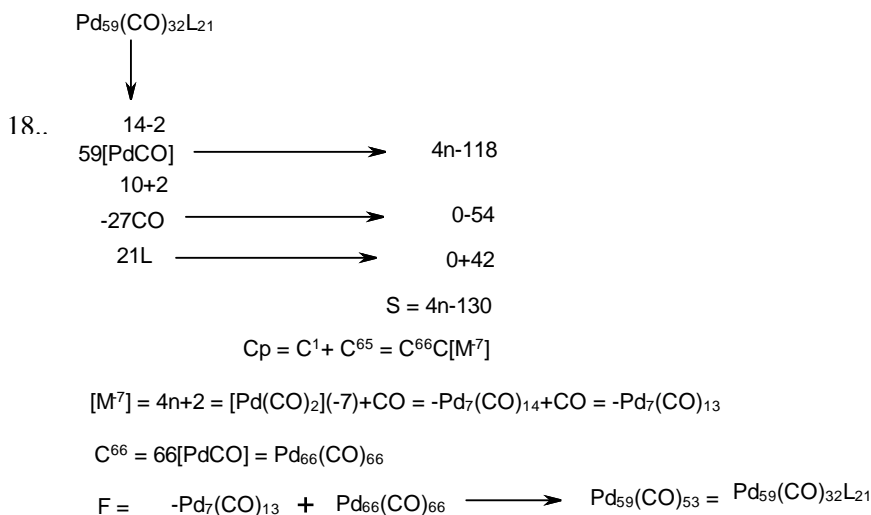


Table 2. Derived Series of some Palladium carbonyl Clusters

CLUSTER	SERIES	CAPPING SYMBOL
$\text{Pd}_{38}(\text{CO})_{28}\text{L}_{12}$	4n-52	$\text{C}^{27}\text{C}[\text{M}-11]$
$\text{Pd}_{20}\text{Ni}_{26}(\text{CO})_{54}^{6-}$	4n-70	$\text{C}^{36}\text{C}[\text{M}-10]$
$\text{Pd}_{16}\text{Ni}(\text{CO})_{22}\text{L}_4^{2-}$	4n-14	$\text{C}^8\text{C}[\text{M}-9]$
$\text{Pd}_{12}(\text{CO})_{15}\text{L}_7$	4n-4	$\text{C}^3\text{C}[\text{M}-9]$
$\text{Pd}_{23}(\text{CO})_{22}\text{L}_{10}$	4n-28	$\text{C}^{15}\text{C}[\text{M}-8]$
$\text{Pd}_{36}(\text{CO})_{28}\text{L}_{14}$	4n-56	$\text{C}^{29}\text{C}[\text{M}-7]$
$\text{Au}_4\text{Pd}_{32}(\text{CO})_{28}\text{L}_{14}$	4n-56	$\text{C}^{29}\text{C}[\text{M}-7]$
$\text{Au}_4\text{Pd}_{28}(\text{CO})_{22}\text{L}_{16}$	4n-48	$\text{C}^{25}\text{C}[\text{M}-7]$
$\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$	4n-4	$\text{C}^3\text{C}[\text{M}-7]$
$\text{Pd}_{10}(\text{CO})_{14}\text{L}_4$	4n-4	$\text{C}^3\text{C}[\text{M}-7]$
$\text{Pd}_{33}\text{Ni}_9(\text{CO})_{41}\text{L}_6^{4-}$	4n-70	$\text{C}^{36}\text{C}[\text{M}-6]$
$\text{Au}_2\text{Pd}_{28}(\text{CO})_{26}\text{L}_{10}$	4n-36	$\text{C}^{24}\text{C}[\text{M}-6]$
$\text{HPd}_{30}(\text{CO})_{26}\text{L}_{10}^-$	4n-46	$\text{C}^{24}\text{C}[\text{M}-6]$
$\text{Pd}_{29}(\text{CO})_{28}\text{L}_7^{2-}$	4n-44	$\text{C}^{23}\text{C}[\text{M}-6]$
$\text{Pd}_{23}(\text{CO})_{20}\text{L}_{10}$	4n-32	$\text{C}^{17}\text{C}[\text{M}-6]$
$\text{Pd}_{30}(\text{CO})_{26}\text{L}_{10}$	4n-48	$\text{C}^{25}\text{C}[\text{M}-5]$
$\text{Pd}_{16}(\text{CO})_{13}\text{L}_9$	4n-20	$\text{C}^{11}\text{C}[\text{M}-5]$
$\text{Ti}_2\text{Pd}_{12}(\text{CO})_9\text{L}_9^{2+}$	4n-16	$\text{C}^9\text{C}[\text{M}-5]$
$\text{Pd}_8(\text{CO})_{10}\text{L}_4$	4n-4	$\text{C}^3\text{C}[\text{M}-5]$
$\text{Pd}_{23}(\text{CO})_{20}\text{L}_8$	4n-36	$\text{C}^{19}\text{C}[\text{M}-4]$
$\text{AuPd}_{22}(\text{CO})_{20}\text{L}_8$	4n-36	$\text{C}^{19}\text{C}[\text{M}-4]$
$\text{Pd}_{37}(\text{CO})_{28}\text{L}_{12}$	4n-68	$\text{C}^{35}\text{C}[\text{M}-2]$
$\text{Pd}_{35}(\text{CO})_{23}\text{L}_{15}$	4n-64	$\text{C}^{33}\text{C}[\text{M}-2]$
$\text{Pd}_{29}\text{Ni}_3(\text{CO})_{22}\text{L}_{13}$	4n-58	$\text{C}^{30}\text{C}[\text{M}-2]$
$\text{Pd}_3(\text{CO})_3\text{L}_3$	4n+0	$\text{C}^1\text{C}[\text{M}-2]$
$\text{Os}_{17}(\text{CO})_{36}^{2-}$	4n-28	$\text{C}^{15}\text{C}[\text{M}-2]$
$\text{Pd}_{34}(\text{CO})_{24}\text{L}_{12}$	4n-64	$\text{C}^{33}\text{C}[\text{M}-1]$
$\text{Os}_{20}(\text{CO})_{40}^{2-}$	4n-38	$\text{C}^{20}\text{C}[\text{M}-0]$
$\text{Pd}_{54}(\text{CO})_{40}\text{L}_{14}$	4n-108	$\text{C}^{55}\text{C}[\text{M}^{-1}]$
$\text{Pd}_{39}(\text{CO})_{23}\text{L}_{16}$	4n-78	$\text{C}^{40}\text{C}[\text{M}^{-1}]$
$\text{Pd}_{52}(\text{CO})_{36}\text{L}_{14}$	4n-108	$\text{C}^{55}\text{C}[\text{M}^{-3}]$
$\text{Pd}_{16}(\text{CO})_7\text{L}_6$	4n-38	$\text{C}^{20}\text{C}[\text{M}^{-4}]$
$\text{Pd}_{59}(\text{CO})_{32}\text{L}_{21}$	4n-130	$\text{C}^{66}\text{C}[\text{M}^{-7}]$
$\text{Pd}_{59}(\text{CO})_{36}\text{L}_{14}$	4n-136	$\text{C}^{69}\text{C}[\text{M}^{-10}]$
$\text{Pd}_{69}(\text{CO})_{36}\text{L}_{18}$	4n-168	$\text{C}^{85}\text{C}[\text{M}^{-16}]$
$\text{Pd}_{165}(\text{CO})_{60}\text{L}_{30}$	4n-480	$\text{C}^{241}\text{C}[\text{M}^{-76}]$

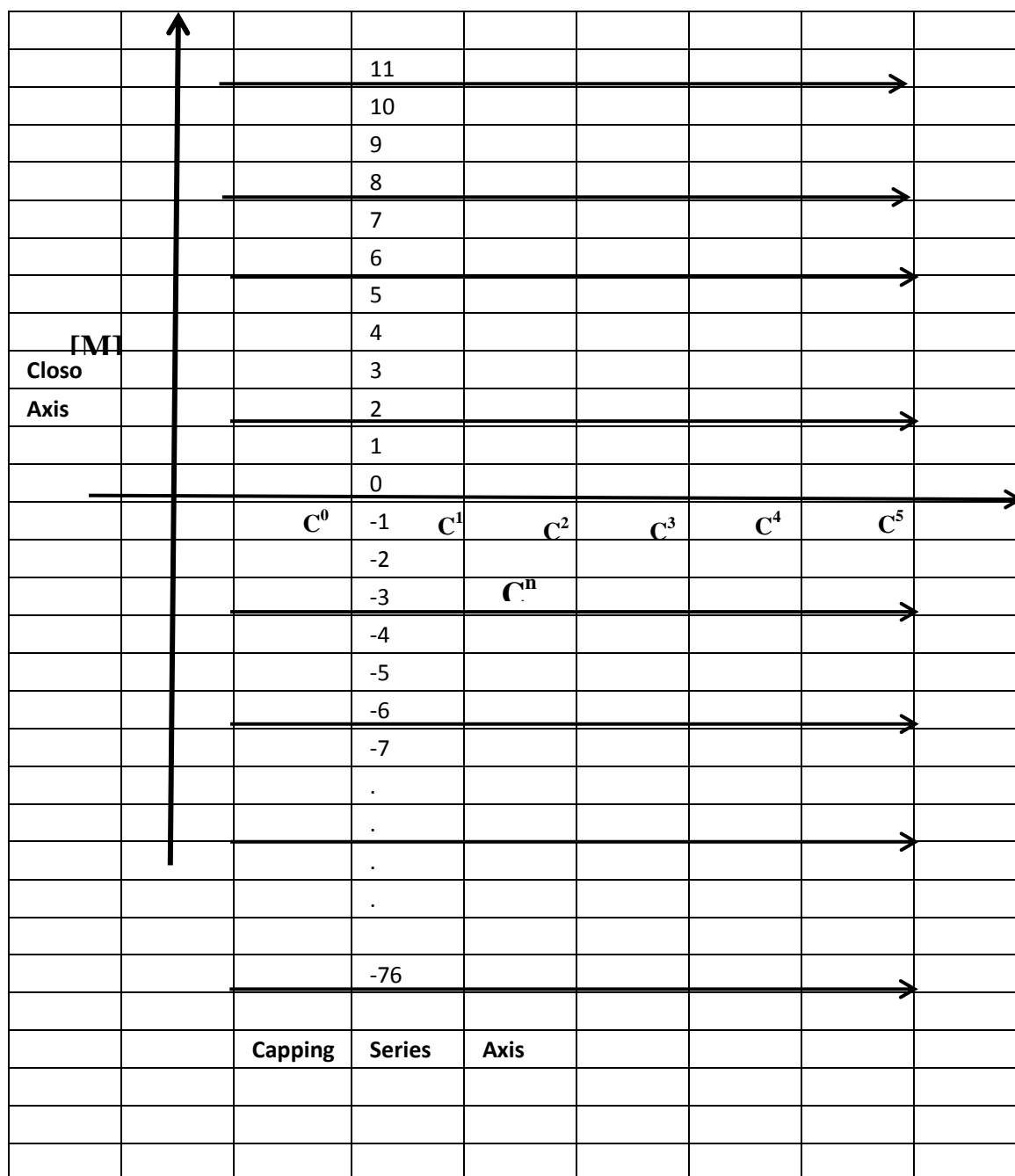


Figure 1. Underground High ways of Capping Carbonyl Clusters

Table 3. Palladium Capping Generating Function of Carbonyl Clusters

C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	C ¹⁰
4n	4n-2	4n-4	4n-6	4n-8	4n-10	4n-12	4n-14	4n-16	4n-18
Pd(CO) ₂	Pd(CO)	Pd							
Pd ₂ (CO) ₄	Pd ₂ (CO) ₃	Pd ₂ (CO) ₂	Pd ₂ (CO)	Pd ₂					
Pd ₃ (CO) ₆	Pd ₃ (CO) ₅	Pd ₃ (CO) ₄	Pd ₃ (CO) ₃	Pd ₃ (CO) ₂	Pd ₃ (CO)	Pd ₃			
Pd ₄ (CO) ₈	Pd ₄ (CO) ₇	Pd ₄ (CO) ₆	Pd ₄ (CO) ₅	Pd ₄ (CO) ₄	Pd ₄ (CO) ₃	Pd ₄ (CO) ₂	Pd ₄ (CO)	Pd ₄	
Pd ₅ (CO) ₁₀	Pd ₅ (CO) ₉	Pd ₅ (CO) ₈	Pd ₅ (CO) ₇	Pd ₅ (CO) ₆	Pd ₅ (CO) ₅	Pd ₅ (CO) ₄	Pd ₅ (CO) ₃	Pd ₅ (CO) ₂	Pd ₅ (CO)
Pd ₆ (CO) ₁₂	Pd ₆ (CO) ₁₁	Pd ₆ (CO) ₁₀	Pd ₆ (CO) ₉	Pd ₆ (CO) ₈	Pd ₆ (CO) ₇	Pd ₆ (CO) ₆	Pd ₆ (CO) ₅	Pd ₆ (CO) ₄	Pd ₆ (CO) ₃
Pd ₇ (CO) ₁₄	Pd ₇ (CO) ₁₃	Pd ₇ (CO) ₁₂	Pd ₇ (CO) ₁₁	Pd ₇ (CO) ₁₀	Pd ₇ (CO) ₉	Pd ₇ (CO) ₈	Pd ₇ (CO) ₇	Pd ₇ (CO) ₆	Pd ₇ (CO) ₅
Pd ₈ (CO) ₁₆	Pd ₈ (CO) ₁₅	Pd ₈ (CO) ₁₄	Pd ₈ (CO) ₁₃	Pd ₈ (CO) ₁₂	Pd ₈ (CO) ₁₁	Pd ₈ (CO) ₁₀	Pd ₈ (CO) ₉	Pd ₈ (CO) ₈	Pd ₈ (CO) ₇
Pd ₉ (CO) ₁₈	Pd ₉ (CO) ₁₇	Pd ₉ (CO) ₁₆	Pd ₉ (CO) ₁₅	Pd ₉ (CO) ₁₄	Pd ₉ (CO) ₁₃	Pd ₉ (CO) ₁₂	Pd ₉ (CO) ₁₁	Pd ₉ (CO) ₁₀	Pd ₉ (CO) ₉
Pd ₁₀ (CO) ₂₀	Pd ₁₀ (CO) ₁₉	Pd ₁₀ (CO) ₁₈	Pd ₁₀ (CO) ₁₇	Pd ₁₀ (CO) ₁₆	Pd ₁₀ (CO) ₁₅	Pd ₁₀ (CO) ₁₄	Pd ₁₀ (CO) ₁₃	Pd ₁₀ (CO) ₁₂	Pd ₁₀ (CO) ₁₁
⁰ Pd ₁₁ (CO) ₂	⁹ Pd ₁₁ (CO) ₂	⁸ Pd ₁₁ (CO) ₂	⁷ Pd ₁₁ (CO) ₁	⁶ Pd ₁₁ (CO) ₁	⁵ Pd ₁₁ (CO) ₁	⁴ Pd ₁₁ (CO) ₁	³ Pd ₁₁ (CO) ₁	² Pd ₁₁ (CO) ₁	¹ Pd ₁₁ (CO) ₁
² Pd ₁₂ (CO) ₂	¹ Pd ₁₂ (CO) ₂	⁰ Pd ₁₂ (CO) ₂	⁹ Pd ₁₂ (CO) ₂	⁸ Pd ₁₂ (CO) ₂	⁷ Pd ₁₂ (CO) ₁	⁶ Pd ₁₂ (CO) ₁	⁵ Pd ₁₂ (CO) ₁	⁴ Pd ₁₂ (CO) ₁	³ Pd ₁₂ (CO) ₁
⁴ Pd ₁₃ (CO) ₂	³ Pd ₁₃ (CO) ₂	² Pd ₁₃ (CO) ₂	¹ Pd ₁₃ (CO) ₂	⁰ Pd ₁₃ (CO) ₂	⁹ Pd ₁₃ (CO) ₂	⁸ Pd ₁₃ (CO) ₂	⁷ Pd ₁₃ (CO) ₁	⁶ Pd ₁₃ (CO) ₁	⁵ Pd ₁₃ (CO) ₁
⁶ Pd ₁₄ (CO) ₂	⁵ Pd ₁₄ (CO) ₂	⁴ Pd ₁₄ (CO) ₂	³ Pd ₁₄ (CO) ₂	² Pd ₁₄ (CO) ₂	¹ Pd ₁₄ (CO) ₂	⁰ Pd ₁₄ (CO) ₂	⁹ Pd ₁₄ (CO) ₂	⁸ Pd ₁₄ (CO) ₂	⁷ Pd ₁₄ (CO) ₁
⁸ Pd ₁₅ (CO) ₃	⁷ Pd ₁₅ (CO) ₂	⁶ Pd ₁₅ (CO) ₂	⁵ Pd ₁₅ (CO) ₂	⁴ Pd ₁₅ (CO) ₂	³ Pd ₁₅ (CO) ₂	² Pd ₁₅ (CO) ₂	¹ Pd ₁₅ (CO) ₂	⁰ Pd ₁₅ (CO) ₂	⁹ Pd ₁₅ (CO) ₂
⁰ Pd ₁₆ (CO) ₃	⁹ Pd ₁₆ (CO) ₃	⁸ Pd ₁₆ (CO) ₃	⁷ Pd ₁₆ (CO) ₂	⁶ Pd ₁₆ (CO) ₂	⁵ Pd ₁₆ (CO) ₂	⁴ Pd ₁₆ (CO) ₂	³ Pd ₁₆ (CO) ₂	² Pd ₁₆ (CO) ₂	¹ Pd ₁₆ (CO) ₂
² Pd ₁₇ (CO) ₃	¹ Pd ₁₇ (CO) ₃	⁰ Pd ₁₇ (CO) ₃	⁹ Pd ₁₇ (CO) ₃	⁸ Pd ₁₇ (CO) ₃	⁷ Pd ₁₇ (CO) ₂	⁶ Pd ₁₇ (CO) ₂	⁵ Pd ₁₇ (CO) ₂	⁴ Pd ₁₇ (CO) ₂	³ Pd ₁₇ (CO) ₂
⁴ Pd ₁₈ (CO) ₃	³ Pd ₁₈ (CO) ₃	² Pd ₁₈ (CO) ₃	¹ Pd ₁₈ (CO) ₃	⁰ Pd ₁₈ (CO) ₃	⁹ Pd ₁₈ (CO) ₃	⁸ Pd ₁₈ (CO) ₃	⁷ Pd ₁₈ (CO) ₂	⁶ Pd ₁₈ (CO) ₂	⁵ Pd ₁₈ (CO) ₂
⁶ Pd ₁₉ (CO) ₃	⁵ Pd ₁₉ (CO) ₃	⁴ Pd ₁₉ (CO) ₃	³ Pd ₁₉ (CO) ₃	² Pd ₁₉ (CO) ₃	¹ Pd ₁₉ (CO) ₃	⁰ Pd ₁₉ (CO) ₃	⁹ Pd ₁₉ (CO) ₃	⁸ Pd ₁₉ (CO) ₃	⁷ Pd ₁₉ (CO) ₂
⁸ Pd ₂₀ (CO) ₄	⁷ Pd ₂₀ (CO) ₃	⁶ Pd ₂₀ (CO) ₃	⁵ Pd ₂₀ (CO) ₃	⁴ Pd ₂₀ (CO) ₃	³ Pd ₂₀ (CO) ₃	² Pd ₂₀ (CO) ₃	¹ Pd ₂₀ (CO) ₃	⁰ Pd ₂₀ (CO) ₃	⁹ Pd ₂₀ (CO) ₃
⁰	⁹	⁸	⁷	⁶	⁵	⁴	³	²	¹

3. Conclusion

Palladium forms a wide range of capping carbonyl clusters. The revelation by series method indicate that palladium forms two types of capping clusters –those which undergo capping “above the ground” and those which do so “underground”. The difference between the above the ground and underground capping clusters is that the closo nucleus of the above the ground capping cluster is a positive function or has a positive value and when added to the capping function produces the molecular formula of the cluster with an enhanced molar mass. On the other hand the closo nucleus of the underground capping cluster is negative function and when subtracted from the capping cluster function gives rise to a molecular formula of the cluster with a reduced molar mass. The examples with [M^q] closo nuclear decapping clusters are given above. By using the capping generating series, some known palladium clusters can be generated as indicated in Table 3. A given molecular formula of a cluster of any size can be decomposed into mono-skeletal fragments from which the cluster series can be derived. The simple series such as bicapped, monocapped, closo, nido, arachno, hypho and klapo can readily be utilized to predict the borane-type of geometrical structures or related ones. The discovery of underground capping clusters has introduced a new dimension in the chemistry of carbonyl clusters. Each cap represents a class of series. For instance, C¹ indicates mono-capped series and C¹⁰ shows series with 10 caps. Clearly palladium portraying a series of C²⁴¹ capping in Pd₁₆₅(CO)₆₀L₃₀ is perhaps one of the largest carbonyl cluster containing a large number of skeletal metal atoms. The series method used in the above examples indicate that it gives the same result of categorizing clusters as PSEPT method. A large variety of examples categorized by the series method used in this paper have been provided to indicate the viability and flexibility of the method as well as to make it more familiar to the reader. Since 14n series are isolobal to 4n series, it is much easier and faster to work with 4n series for categorization and structure prediction of clusters. This series method can easily be taught at both undergraduate and postgraduate levels.

References

- Cotton, F. A., & Wilkinson, G. (1980). *Advanced Inorganic Chemistry, 4th Ed.*, John Wiley and Sons, New York.
- Cox, D. N., & Mingos, D. M. P. (1981). Extended Hückel Molecular-orbital Calculations on Dodecahedral Metalloboranes which do not conform to the Polyhedral Skeletal Electron-pair Theory. *J. C. S., Dalton*, 1788-1797. <http://dx.doi.org/10.1039/dt9810001788>
- Hoffmann, R. (1982). Building Bridges between Inorganic and Organic Chemistry. *Angew. Chem. Int. Ed. Engl.*, 21,

- 711-724. <http://dx.doi.org/10.1002/anie.198207113>
- Hughes, A. K., & Wade, K. (2000). Metal-metal and metal-ligand bond strengths in metal carbonyl clusters. *Coord. Chem. Rev.*, *197*, 191-229. [http://dx.doi.org/10.1016/S0010-8545\(99\)00208-8](http://dx.doi.org/10.1016/S0010-8545(99)00208-8)
- Jemmis, E. D. (2005). Building relationships between polyhedral boranes and elemental boron. *Inorg. Chem.* *18*, 620-628.
- Jemmis, E. D., & Balakrishnarajan, M. M. (2001). Polyhedral boranes and elemental boron. Direct structural relations and diverse electronic requirements. *J. Am. Chem. Soc.*, *123*, 4324-4330. <http://dx.doi.org/10.1021/ja0026962>
- Jemmis, E. D., & Jayasree, E. G. (2003). Analogies between boron and carbon. *Acc. Chem. Res.*, *36*, 816-824. <http://dx.doi.org/10.1021/ar0300266>
- Jemmis, E. D., & Pavankumar, P. N. V. (1984). Stability of Polyhedral Borane anions and Carboranes. *Proc. Indian Acad. Sci.*, *93*(3), 479-489.
- Jemmis, E. D., & Prasad, D. L. V. K. (2008). Unknowns in the chemistry of Boron. *Current Science*, *95*(10), 1277-1283.
- Jemmis, E. D., Balakrishnarajan, M. M., & Pancharatna, P. D. (2001). Unifying electron counting rule for Macropolyhedral Boranes, Metallaboranes, and Metallocenes. *J. Am. Chem. Soc.*, *123*(18), 4313-4323. <http://dx.doi.org/10.1021/ja003233z>
- Jemmis, E. D., Balakrishnarajan, M. M., & Pancharatna, P. D. (2002). Electronic Requirements for Macropolyhedral Boranes. *Chem. Rev.* *102*(1), 93-144. <http://dx.doi.org/10.1021/cr990356x>
- Jemmis, E. D., Jayasree, E. G., & Parameswaran, P. (2006). Hypercarbons in polyhedral structures. *Chem. Soc. Rev.*, *35*, 157-168. <http://dx.doi.org/10.1039/B310618G>
- King, R. B. (2002). Spherical Chemical Bonding Models for three-dimensional aromaticity in deltahedral boranes. *PINSA*, *68*, A, 473-486.
- Kiremire, E. M. (2014). Numerical Sequence of Borane Series. *Orient. J. Chem.*, *30*(3), 1055. <http://dx.doi.org/10.13005/ojc/300317>
- Kiremire, E. M. (2015a). Categorization and Structural Determination of Simple and More Complex Carbonyl Clusters of Rhenium and Osmium Using k values and the Cluster Table. *Orient. J. Chem.* *31*(1), 293-302. <http://dx.doi.org/10.13005/ojc/310133>
- Kiremire, E. M. (2015b). Classification of Transition Metal Carbonyl Clusters Using the 14n Rule Derived from Number Theory. *Orient. J. Chem.* *31*(2), 605-618. <http://dx.doi.org/10.13005/ojc/310201>
- Kiremire, E. M. (2015d). Isolobal Series of Chemical Fragments. *Orient. J. Chem.*, *31*(Spl. Edn), 59-70.
- Kiremire, E. M. R. (2015c). Capping and Decapping Series. *Int. J. Chem.*, *7*(2), 186-197. <http://dx.doi.org/10.5539/ijc.v7n2p186>
- Lee, T., Zhenyang, L., & Mingos, D. M. P. (1989). Polyhedral Skeletal Electron Pair Theory of Bare Clusters. *Inorg. Chem.*, *28*, 2256-2261. <http://dx.doi.org/10.1021/ic00311a004>
- Mednikov, E. G., & Dahl, L.F. (2010). Syntheses, structures and properties of primarily nanosized homo/heterometallic palladium CO/PR₃-ligated clusters. *Phil. Trans. R. Soc.*, *A*(2010), 368, 1301-1332. <http://dx.doi.org/10.1098/rsta.2009.0272>
- Mingos, D. M. P. (1972). A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nature(London), Phys. Sci.*, *236*, 99-102. <http://dx.doi.org/10.1038/physci236099a0>
- Mingos, D. M. P. (1984), Polyhedral skeletal electron-pair approach. *Acc. Chem. Res.*, *17*, 311-319. <http://dx.doi.org/10.1021/ar00105a003>
- Rossi, F., & Zanello, P. (2011). Electron Reservoir Activity of High-Nuclearity Transition Metal Carbonyl Clusters. *Portugaliae Electrochimica Acta*, *29*(5), 309-327. <http://dx.doi.org/10.4152/pea.201105309>
- Wade, K. (1971). The structural significance of the number of skeletal bonding electron-pairs in carboranes, the higher boranes and borane ions and various transition metal carbonyl cluster compounds. *Chem. Commun.*, 792-793. <http://dx.doi.org/10.1039/c29710000792>
- Wade, K. (1976). Structural and Bonding Patterns in Cluster Chemistry. *Adv. Inorg. Chem. Radiochem.*, *18*, 1-16. [http://dx.doi.org/10.1016/s0065-2792\(08\)60027-8](http://dx.doi.org/10.1016/s0065-2792(08)60027-8)
- Wales, D. J., (2005). Electronic Structure of Clusters. *Encyclopedia of Inorganic Chemistry*, 2nd Ed., King R. B., Editor-in-Chief, John-Wiley and Sons, Ltd, Chichester, 3, 1506-1525.

Welch, A. J. (2013). The Significance of Wade's Rules. *Chem. Commun.*, 49, 3615-3616.
<http://dx.doi.org/10.1039/c3cc00069a>

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).