Capping and Decapping Series of Boranes

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

Abstract

Whereas many of the capped series of carbonyl clusters of transition metals are known, those of corresponding borane series are unknown. These include the monocapped, bicapped, tricapped, tetracapped and so on. This paper attempts to correlate selected capped series of the carbonyl series with the hypothetical corresponding ones of boranes using 14n and 4n rules. Some selected examples of capped and decapped borane series have been generated and tabulated. The borane clusters are found to follow a precise numerical algorithm. A comparison of selected examples of carbonyl cluster of lower series such as closo, nido and arachno with the corresponding borane clusters has been made. The popularly cited Rudolph system of deducing shapes of clusters is also discussed in terms of decapping series. The use of fragments and their corresponding fragment series enormously simplifies the categorization of molecular formulas into series from which their shapes can be predicted with or without the use of the cluster number (k value). The fragment series vindicates the vital Hoffmann's isolobal concept very well.

Keywords: capping and decapping boranes, capping and decapping carbonyl clusters, categorization of clusters, cluster series, PSEPT, Wade-Mingos rules, Hoffmann and Isolobal concept, chemical fragments, 14n and 4n rules

1. Introduction

Boranes have attracted a lot of attention for a long time(Stock, 1933; Longuet-Higgins et al., 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;).Their fascinating structural design, chemical reactivity to form heteroboranes (Kaszynski,1999),metalloboboranes(Greenwood,1983) and potential versatile applications(Hawthorne et al., 1990, Hawthorne, 1999;Bernard, et al., 2002; Bondarev, et al.,2013; Tachikawa, et al., 2014) have stimulated increased research intensity and expansion of borane chemistry(Li et al, 2006; Alexandrova et al., 2006; Cerdán, et al., 2015). Previous work indicated that boranes can be arranged to form series based on cluster k value (Kiremire, 2014). In this paper, the borane series are generated much easier and more readily using the concept of capping series. Furthermore, borane and carbonyl clusters have been found to be interrelated and form parallel clusters series based upon 4n and 14n rules respectively(Kiremire,2015a; Kiremire, 2015b).

2. Results and Discussion

2.1 Capping Borane Series and Osmium Carbonyl Cluster Cousins

In order for us to reflect upon capping in borane series,it is important to review capping in carbonyl clusters first. Work on capping carbonyl series has recently been published (Kiremire, 2015b). The osmium carbonyl clusters were used as a case study of the capping series (Kiremire, 2015b). It was discovered that the osmium fragment $Os(CO)_2$ of 12 valence electron content and a family member of 14n-2 series is a the capping fragment whereas $Os(CO)_3$ fragment with 14 valence electron content and a member of 14n series is the fragment for extending the same type of series (Kiremire,2015b). Furthermore, the carbonyl cluster series obey the 14n+q rule whereas the main group element clusters follow the 4n+q rule where q is the cluster variable that normally takes even numbers (Kiremire, 2015b) for ordinary series. The cluster series variable q can have negative or positive values including zero. For instance, q can cover the range such as (-10, -8, -6, -4, -2, 0, 2, 4, 6, 8, 10). Of great importance is the cluster number k = 2n ±q/2. The cluster value k for 14n+ q of carbonyl cluster is the same as that of 4n+q of the corresponding main group element. In some cases especially organic compounds k value

corresponds to the number of bonds or linkages of skeletal atoms (Kiremire, 2007). Take the examples of C_2; S = 2[C] = 2[4] = 2[4n] = 4n(mono-capped series), k= 2n = 2x2 =4(quadruple bond) that has been discovered recently(Shaik, et al., 2012) C_2H_2 = $(CH)_2$; S = 2[4n+1] = 4n+2 (closo), k =2n-1= 2x2-1 = 3(triple bond), C_2H_4= $(CH_2)_2$; S= 2[4n+2] = 4n+4(nido), k = 2n-2 = 2x2-2 =2(double bond),C_2H_6 = $(CH_3)_2$; S=2[4n+3] = 4n+6(arachno), k =2n-3 =2x2-3 = 1(single bond).

With the above background information, let us illustrate the capping concept with the octahedral carbonyl cluster $Os_6(CO)_{18}^{2-}$. For the purposes of our illustration, $Os_6(CO)_{18}^{2-}$ may be regarded as $Os_6(CO)_{19}$(equivalent number of valence electrons). Capping the cluster, simply means successive additions of $Os(CO)_2$ fragment. Since the fragment $Os(CO)_2$ belongs to 14n-2 series, its k-value is given by k =2n+1= 2x1+1 = 3. This means when capping or decapping takes place the cluster k value changes by 3. This is shown in Scheme 1. As can be discerned from Scheme 1, the number of osmium atoms increases by one for every step while the number of carbonyl ligands increase by two. When a cluster is decapped, the opposite happens. The $Os_6(CO)_{19}$ carbonyl cluster has a total of 86 valence electrons (V_{CC}) and belongs to 14n+2 closo series. Since the method of using series to classify a cluster is not common, it is important to briefly demonstrate it. The $Os_6(CO)_{19}$ carbonyl cluster may be expressed in fragments as F = $[Os(CO)_3]_6$(CO). The corresponding cluster series can then be calculated from the fragments as S =6[$Os(CO)_3$]+ CO. The fragment $Os(CO)_3$ has a content of 8+3x2 = 14 valence electrons. Applying the 14n rule utilized in our earlier work (Kiremire, 2015b), the fragment belongs to S = 14n (n = 1) series. Hence all the fragments are then converted into valence electron equivalents. Thus, S = 6[8+3x2]+2 = 6[14]+ 2 = 6[14n]+2. The interesting aspect about the algebra of series, it is found that the multiplier does not affect the value of 14n in case of transition carbonyl clusters or 4n in the case of the main group elements. What matters is the value of n of the fragment under consideration. In this regard, 6[14n] = 14n (where n = 6) in this case. Therefore the overall value of the cluster series S =6[14n]+2 = 14n+2. Hence, this cluster is a member of closo series. Its valence content is also obtained from the series S = 14n+2. THUS, when n = 6, S= 14(6) +2 = 86. This value is the same as the valence electrons obtained from the formula F=$Os_6(CO)_{19}$ = 8x6+19x2 = 86. A paper explaining using series to categorize clusters into series and predicting their possible shapes is in press (Kiremire, 2015). Since $Os_6(CO)_{19}$ is a closo cluster of six skeletal elements (6 Os) we can look for its corresponding borane (cousin) closo cluster of 4n+2 series. In order to do that we must convert 14n+2 to 4n+2 by removing 10n electrons. Since we are considering an octahedral cluster of 6 skeletal atoms, n =6. Hence, 10n = 10x6 = 60. Therefore, the borane cluster valence electrons (V_{BC}) = V_{CC} – 60 = 86-60 = 26. The valence electrons of the borane cluster will include those of 6 boron skeletal atoms and the accompanying hydrogen atoms. Let the valence electrons of boron skeletal atoms be V_B = 6x3 =18. Hence the remaining valence electrons will be for the hydrogen atoms. Thus, V_H =26-18= 8. Hence, the number of the hydrogen atoms expected to combine with the 6 boron atoms will be 8. Therefore the corresponding borane cluster formula will be given by F =B_6H_8. We can verify to see if F = B_6H_8 cluster is also closo as follows F=B_6H_8=$(BH)_6H_2$. For this cluster S_F = 6[BH]+2[H] = 6[3+1]+2[1] = 6[4]+2 = 6[4n]+2 = 4n+2. If we put n = 6 into the cluster formula we get S_F =4(6)+2 = 26. Also the k value is given by k = 2n-1 = 2(6)-1 = 11. The number of valence electrons for the cluster B_6H_8, V = 3x6+8 = 26. However, we know that the closo boranes occur as negatively charged species and so B_6H_8 does exist as $B_6H_6^{2-}$(Cotton and Wilkinson, 1980). The addition of $Os(CO)_2$ capping fragment to $Os_6(CO)_{19}$ carbonyl cluster produces $Os_7(CO)_{21}$ –a mono-capped closo cluster (C^1C). Its cluster series is readily determined from F = $Os_7(CO)_{21}$ =$[Os(CO)_3]_7$; S = 7[14n] = 14n, k = 2n = 2x7 = 14. Clearly the capping of $Os_6(CO)_{19}$ to form $Os_7(CO)_{21}$ the k value has changed from 11 to 14 by a value of 3 as expected. The borane cluster corresponding to $Os_7(CO)_{21}$is deduced as explained for $Os_6(CO)_{19}$ cluster. The borane cluster deduced is B_7H_7.The cluster series for F =B_7H_7=$(BH)_7$; S = 7[4n] = 4n, k = 2n = 7x2 =14. The k value for B_7H_7 is the same as that of $Os_7(CO)_{21}$ carbonyl cluster. What is clearly seen is that the octahedral closo cluster B_6H_8 has been transformed into a hypothetical mono-capped borane B_7H_7. The analysis of the transformation shows clearly that one of the hydrogen atoms in B_6H_8 has been converted into a boron atom or removed and replaced with a boron atom during the capping process. The successive conversion of hydrogen atoms into B atoms gives the borane products $B_7H_7(7,7)$ Ξ $Os_7(CO)_{21}$, $B_8H_6(8,6)$ Ξ $Os_8(CO)_{23}$, $B_9H_5(9,5)$ Ξ $Os_9(CO)_{25}$, $B_{10}H_4(10,4)$Ξ $Os_{10}(CO)_{27}$, $B_{11}H_3(11,3)$ Ξ $Os_{11}(CO)_{29}$, $B_{12}H_2(12,2)$ Ξ $Os_{12}(CO)_{31}$, $B_{13}H_1(13,1)$Ξ $Os_{13}(CO)_{33}$ and $B_{14}H_0(14,0)$ = B_{14} Ξ $Os_{14}(CO)_{35}$. The capping sequence can numerically be expressed as (6,8)→(7,7)→(8,6)→(9,5)→(10,4)→(11,3)→(12,2)→(13,1)→(14,0). We can also work out the k values of the corresponding series of the capped boranes in order to be more familiar with the method of using fragments. Starting with B_8H_6 as an example, F = B_8H_6 = $(BH)_6$$(B)_2$. In this form, we can convert it the series fragments as S=6[BH] + 2[B]. The fragment, [BH] = [3+1]=[4] in terms of valence electrons. Since the fragment has only one skeletal atom, the fragment belongs to the series S = 4n. However the fragment [B] = [3] valence electrons is short of one to become 4n. Hence, its series is given by S=[3]=[4-1]=[4n-1]. We can therefore determine the

cluster series of the molecular formula B_8H_6 as $S_F=6[4n]+2[4n-1] = [4n] + [4n-2]$. As stated earlier, the multiplier does not change 4n except the integer associated with it. Hence, $S_F=4n +4n-2=4n-2$ (4n+4n is simply =4n). If n=8, then the value of $S_F=4(8)-2=30$ which is the same as the valence electrons given by $V=B_8H_6=8x3+6=30$. This tells us that the series formula makes sense. We can try one more borane cluster B_9H_5. The order of formulating fragments to determine molecular formula series does not matter. The borane formula B_9H_5 can be broken into F = 9[B]+5[H] fragments. By inserting in the respective valence electrons we can derive the series S_F =9[3]+5 =9[4-1]+5 = 9[4n-1]+5 =4n-9+5 = 4n-4(again according to the algebra of these series, 9x4n = 4n). To verify that the series formula is correct, insert n=9 into the formula then, S_F =4(9)-4=32. The number of valence electrons of $B_9H_5=9x3+5$ =32. Since the series of the cluster is given by $S_F=4n-4$, the k value of the borane cluster is obtained from k=2n+2=2(9)+2=20. The k values for the remaining capped boranes, $B_{10}H_4$, $B_{11}H_3$, $B_{12}H_2$, $B_{11}H_1$ and B_{14} can be worked out in the same way. Starting with the k value of B_6H_8, they are k = 11,14,17,20, 23,26,29,32 and 35 respectively. The last k value =35 is for the B_{14} cluster, the final capping product of the $B_6H_6^{2-}$ series. The B_{14} cluster belongs to the series $S=(B)_{14}$; $S=14[3]=14[4-1]=14[4n-1]$ = 4n-14. The k value for B_{14} can be calculated from k = 2n+7 = 2(14)+7 =35 .The capping term is given by $Cp = C^1+C^7$ = $C^8C[M-6]$ is shown in Scheme 1. The capping expression is derived from the knowledge of the series. For instance, if we write the series S = 4n-14 as S = 1(4n)+7(-2), then the (4n) represents a mono-capped term while every (-2) after (4n) represents an additional capping. Hence, the total cappings after the inner core octahedral closo cluster will be 1+7 = 8. That is what the symbol $C_p=C^1+C^7=C^8C[M-6]$ stands for. The [M-6] means the inner core comprises of six skeletal atoms which constitute an octahedral closo fragment and the C^8 symbol means that eight atoms surround the six atoms as capping elements. This may be viewed as a cluster within a cluster. That is, a nucleus of six surrounded by other eight atoms and the total number of atoms for the whole cluster is 14. The fascinating immense power of fragments and series can be illustrated by deducing the series of the giant carbonyl cluster $Ni_{38}Pt_6(CO)_{48}(H)^{5-}$complex. We can split the cluster into the following fragments S=38[Ni(CO)]+6[Pt(CO)]+4CO+H+5=38[10+2]+6[10+2]+4x2+1+5= 44[10+2]+14= 44[12]+14=44[14n-2]+14 =14n-88+14 =14n-74. This means the cluster belongs to S=14n-74 series. For S=14n-74=1(14n)+37(-2), $C_P=C^1+C^{37}=C^{38}C[M-6]$. This symbol implies there are six atoms forming an octahedral cluster nucleus surrounded by 38 other capping atoms. Indeed, it is amazing that the x-ray crystal structure showed six platinum atoms constituting an octahedral nucleus in the center surrounded by 38 nickel atoms in the giant cluster (Rossi and Zanello, 2011) of 44 skeletal atoms. The number of skeletal atoms in the complex is 44. Inserting n =44 into S=14n-74 gives S=14(44)-74=542. The sum of valence electrons of the complex V=44x10+2x48+1+5=542. Therefore, the series can be viewed to represent the valence content of the cluster or fragment. The capping formulation was explained in our earlier work (Kiremire, 2015b). The geometries of the possible isomers of carbonyl clusters $Os_6(CO)_{19}$ (f-1), $Os_7(CO)_{21}$ (f-2), $Os_8(CO)_{23}$ (f-3), $Os_9(CO)_{25}$(f-4), $Os_{10}(CO)_{27}$(f-5), $Os_{11}(CO)_{29}$(f-6), and $Os_{12}(CO)_{31}$(f-7) are given in Figure 1. On the basis of the capping principle of the boranes, we can deduce the final capping clusters derived from the selected closo boranes as follows and is indicated in brackets: $BH_3(B_4)$, $B_2H_4(B_6)$, $B_3H_5(B_8)$, $B_4H_6(B_{10})$, $B_5H_7(B_{12})$,$B_6H_8(B_{14})$, $B_7H_9(B_{16})$, $B_8H_{10}(B_{18})$, $B_9H_{11}(B_{20})$, $B_{10}H_{12}(B_{22})$,$B_{11}H_{13}(B_{24})$ and $B_{12}H_{14}(B_{26})$. Theoretical studies of the cluster $B_{12}H_6$ have recently been conducted (Ohishi,et al., 2009; Szwacki, et al., 2009). This cluster is predicted to be stable with aromatic properties. This cluster may be regarded as a tetracapped derivative of $B_8H_{10}(B_8H_8^{2-})$ closo borane. Also the naturally occuring boron cluster B_{12} (Higoshi and Ishii, 2001) may be regarded as the final capping member of the closo series based on $B_5H_7(B_5H_5^{2-})$. Furthermore, a fullerene-type boron cluster B_{40} has been discovered by laser-vaporization experiments (Zhai et al., 2014). This may be considered to belong to a series given by S = 40[B] = 40[3] =40[4-1] =40[4n-1] = 4n-40, and the capping series $C_P = C^1+C^{20} = C^{21}C[M-19]$ where [M-19] =$B_{19}H_{19}^{2-}(B_{19}H_{21})$. In other words, it may be regarded as a derivative of $B_{19}H_{21} (B_{19}H_{19}^{2-})$ closo borane. Among boron clusters which are being studied theoretically (Zhai, et al., 2003) include B_{36} and B_{42}. The two clusters may be considered to belong to the capped series $C^{19}C[M-17]$ and $C^{22}C[M-20]$ where [M-17]= $B_{17}H_{17}^{2-}(B_{17}H_{19})$ and [M-20] =$B_{20}H_{20}^{2-}(B_{20}H_{22})$ respectively. The capped series of selected boranes BH_3 to $B_{12}H_{12}^{2-}(B_{12}H_{14})$ are shown in Table 1. The table could be expanded if necessary.

2.2 Decapping Borane Series and the Corresponding Osmium Carbonyl Cluster Series

As mentioned earlier, the fragment $Os(CO)_2$ with a content of 12 valence electrons and a member of the series 14n-2 was used in the capping series of an octahedral osmium cluster complex,$Os_6(CO)_{19}$. If we do the reverse, instead of successively adding the capping fragment to the cluster, we can successively remove the fragment from the initial closo cluster. The new cluster species generated constitute the decapping osmium series. The corresponding cousin boranes may be produced in the same manner to generate decapping borane series. For instance, the removal of $Os(CO)_2$ from $Os_6(CO)_{19}$ produces $Os_5(CO)_{17}$ cluster. Its series can be derived as follows: S=5[Os(CO)_3]+2CO=5[8+3x2]+4=5[14]+4=5[14n]+4=14n+4. Hence, this cluster with a valence

electron content of 74, is member of nido series ($14n+4$). In order to get its corresponding borane cousin cluster we must remove the $10n$ electrons. The corresponding borane cluster will have 5 skeletal atoms and so $n = 5$. Therefore the number of valence electrons to be removed $=10n=10\times5 = 50$. Thus the required borane cluster will have $74-50=24$ valence electrons. These electrons have to be distributed among a borane cluster with 5 boron skeletal toms and the accompanying hydrogen atoms. Thus, applying the same approach used above in the octahedral cluster $V_{BC}=24$, $V_B=3\times5 =15$ and $V_H = 24-15=9$. Therefore the corresponding borane cluster cousin is given by $F = B_5H_9$. The decapping series of $Os_6(CO)_{19}$ are summarized in Scheme 2. The corresponding k value decreases by 3. The negative k values imply that the existence of such species is quite remote. The series are quite precise. Whereas the capping ones terminated at B_{14} [with 42 valence electrons] and $Os_{14}(CO)_{35}$[182], the decapping process ends at 7(CO)[14] and 14H[14] and the figures in brackets indicate the total valence electron content. The former termination shows the production of 14 borons and the later shows the production of 7 carbonyls with 14 valence electrons and no cluster atom and 14 hydrogen atoms with 14 valence electrons. It is important to note that the capping fragments also follow the law of parallel series. For instance $Os(CO)_2$ fragment is a member of $14n-2$ with 12 electrons, while the (B,-H) fragment with its electron content of 2 follows the $4n-2$ rule. There is a difference of 10 ($10n = 10\times1$) valence electrons between 12 and 2.

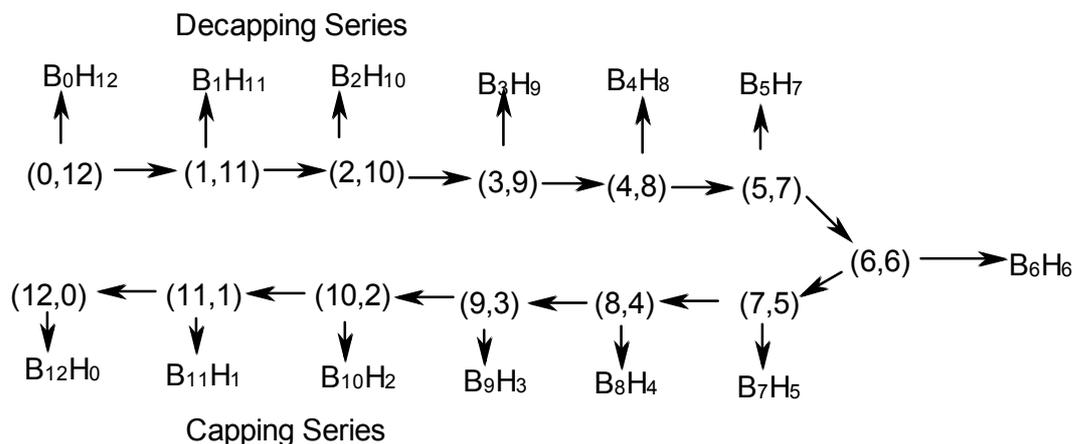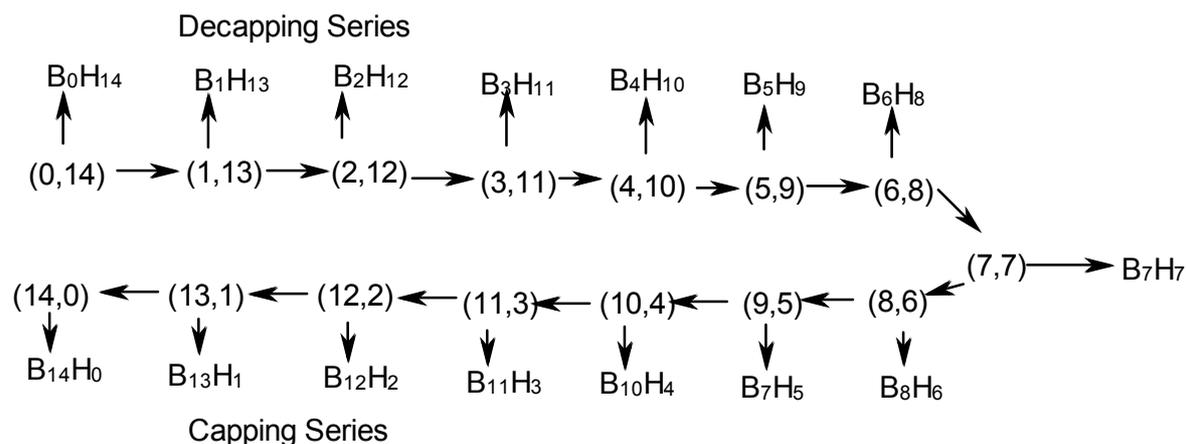## 2.3 Numerical Generation of Capping and Decapping Borane Series

When the structures of boranes are scrutinized, an interesting numerical sequence is discerned. Let B_5H_7 ($B_5H_5^{2-}$) be represented by (5,7) numbers. The closo cluster B_5H_7 {S= 5[BH]+2H ={5[3+1]+2 =5[4]+2 = 5[4n]+2 = 4n+2} belongs to $4n+2$ closo series. In order to find a cousin carbonyl cluster say that of osmium, we must add $10n$ electrons to elevate it to $14n+2$ series. The cluster B_5H_7 with 5 skeletal atoms has a content of 22 total valence electrons. The $10n$ electrons to be added$=10n=10\times5=50$. Therefore the carbonyl cluster cousin of the borane cluster will have $22+50 = 72$ total valence electrons (V_{CC}). These electrons must be distributed among 5 osmium skeletal atoms and the carbonyl ligands. The 5 osmium atoms will need $V_{os}=5\times8=40$. This leaves the electrons for the CO ligands ($V_{CO})=V_{cc}=72-40 = 32$. Hence, the number of carbonyl ligands needed (N_{CO})$=32/2=16$. Therefore osmium carbonyl cluster cousin complex is given by $F = Os_5(CO)_{16}$. Regarding B_5H_7 cluster (5,7), the first number represents the boron atoms and the second one the hydrogen atoms. For this series, the mono-capped cluster will be (6,6)= B_6H_6(mono-capped). This runs parallel to $Os_6(CO)_{18}$ which is obtained by adding $Os(CO)_2$ capping fragment to $Os_5(CO)_{16}$. The set (7,5)=B_7H_5(bicapped)$\Xi Os_7(CO)_{20}$, (8,4)=B_8H_4(tricapped) Ξ $Os_8(CO)_{22}$, (9,3)=B_9H_3(tetracapped) Ξ $Os_9(CO)_{24}$, (10,2)=$B_{10}H_2$(pentacapped) Ξ $Os_{10}(CO)_{26}$, (11,1)=$B_{11}H_1$(hexacapped) Ξ $Os_{11}(CO)_{28}$, (12,0)=B_{12}(heptacapped) Ξ $Os_{12}(CO)_{30}$,. In these series, $B_5H_7(B_5H_5^{2-})$ is an D_{3h} (trigonal bipyramid) closo cluster. The rest are capping borane clusters based on the trigonal bipyramid geometry. The B_5H_7 capping ends in B_{12}. In the $4n$ series, the number of electrons required is 2. This is equivalent to adding a boron atom (+3e) and removing a hydrogen atom (-1e) or converting a H atom into a B atom. As can be seen from a series of numbers, (5,7)→(6,6) →(7,5) →(8,4) →(9,3) →(10,2) →(11,1) and (12,0) follow a precise natural numerical sequence. The sum of each set of numbers is a constant 12. Illustrations of numerical generation of capping and decapping series of borane clusters based on $B_5H_5^{2-}$ (B_5H_7) and $B_6H_6^{2-}$(B_6H_8) closo boranes are shown in Schemes 3 and 4.

14n+2	14n+0	14n-2	14n-4	14n-6
$Os_6(CO)_{19}$[86] $\longrightarrow$	$Os_7(CO)_{21}$[98] $\longrightarrow$	$Os_8(CO)_{23}$[110] $\longrightarrow$	$Os_9(CO)_{25}$[122] $\longrightarrow$	$Os_{10}(CO)_{27}$[134]
B_6H_8[26]	B_7H_7[28]	B_8H_6[30]	B_9H_5[32]	$B_{10}H_4$[34]
[M-6]	C^1C[M-6]	C^2C	C^3C	C^4C
4n+2	4n+0	4n-2	4n-4	4n-6
				$\Downarrow$
	14n-14	14n-12	14n-10	14n-8
	$Os_{14}(CO)_{35}$[182] $\longleftarrow$	$Os_{13}(CO)_{33}$[170] $\longleftarrow$	$Os_{12}(CO)_{31}$[158] $\longleftarrow$	$Os_{11}(CO)_{29}$[146]
	B_{14}[42]	$B_{13}H_1$[40]	$B_{12}H_2$[38]	$B_{11}H_3$[36]
	C^8C	C^7C	C^6C	C^5C
	4n-14	4n-12	4n-10	4n-8

Scheme 1. Capping Series based on Closo Octahedral Geometry.

14n+2: Closo	14n+4 :Nido	14n+6 : Arachno	14n+8 : Hypho	14n+10 : Klapo	14n+12 : Klapo
$Os_6(CO)_{19}[86] \rightarrow$	$Os_5(CO)_{17}[74] \rightarrow$	$Os_4(CO)_{15}[62] \rightarrow$	$Os_3(CO)_{13}[50] \rightarrow$	$Os_2(CO)_{11}[38] \rightarrow$	$Os(CO)_9[26]$
$B_6H_8[26]$	$B_5H_9[24]$	$B_4H_{10}[22]$	$B_3H_{11}[20]$	$B_2H_{12}[18]$	$BH_{13}[16]$
4n+2	4n+4	4n+6	4n+8	4n+10	4n+12, k =-4
k =11	k =8	k =5	k =2	k =-1	↓
					$(CO)_7[14]$ 14n+14
					$H_{14}[14]$ 4n+14

Scheme 2. Decapping Series based on Closo Octahedral Geometry

Scheme 3. Numerical   Generation of Capping and Decapping Boranes based on $B_5H_5^{2-}$

Scheme 4. Numerical Generation of Capping and Decapping Borane Series based on $B_6H_6^{2-}$

2.4 Capping and Decapping Borane Series

We have demonstrated the concept of numerical generation of capping and decapping borane series for closo $B_5H_5^{2-}$ and $B_6H_6^{2-}$ clusters. The results of these are given in Schemes 3 and 4. Starting with any member of the closo series $B_nH_n^{2-}$, borane molecules and fragments can be derived by the applying the numerical method illustrated in Schemes 3 and 4. This has been done for the series, n = 1 to n = 12. The results are given in Tables 1 and 2.

2.5 Finding a Borane Fragment or Cluster in Tables 1 and 2

It is quite easy to find a given borane molecule or fragment if the sum of the atoms in the given formula including any charge if present add up to the value on the top of Table 1 or 2. Take the following examples for illustrations. First, BH_3 (1+3 = 4), the sum of the atoms is 4. When we look at Table 1 and identify the column headed by 4, it seen that BH_3 is a member of the closo series. Next, $B_2H_6(2+6 = 8)$, this is found in the column headed by 8 in Table 2 and belongs to Nido series. Consider B_4H_{10} (4+10 =14). Again, we follow the procedure and check at the column headed by 14. The molecule belongs to arachno series in Table 2. Let us consider B_8H_{12} (8+12 = 20). This is found in Table 2 and is a member of Nido series. It is observed the when B_mH_n (m=n), the cluster belongs to Mono-capped series 4n. When m <n, the cluster is in Table 2 of Decapping Series and when m>n the cluster is in Table 1 of Capping Series. Consider B_9H_1(9+1 =10, m>n), the cluster will be found in

Table 1 in the column headed by 10. The cluster is a member of penta-capped series. For clusters such as $B_4H_7(4+7 =11)$ in which the sum of m and n is an odd number are not considered in this paper as they are not linked to 4n+2 series. Also for m+n (even number)> 26 will lie outside the range of Tables 1 and 2. Just to test the importance of Tables 1 and 2, we looked at some of the boranes mentioned in Lipscomb's Nobel Prize Lecture of 1976. They are listed according to the increasing sum of m+n value as follows $B_2H_6[8]$, $B_4H_8[12]$, $B_4H_{10}[14]$, $B_5H_9[14]$, $B_6H_8[14]$, $B_4H_{16}[20]$, $B_8H_{14}[22]$, $B_{10}H_{14}[24]$, and $B_{12}H_{14}[26]$. All these boranes are found in Tables 1 and 2 under the column headed by the number indicated in the bracket after the formula. Tables 1 and 2 may be expanded as required.

2.6 Shapes of Borane and Corresponding Carbonyl Clusters

The shapes of the borane closo (4n+2) clusters $B_nH_n^{2-}$ for n =5-12 are well known (Cotton and Wilkinson ,1980). They are used as a basis on which the shapes of other borane clusters below them such as Nido (4n+4), Arachno (4n+6), and Hypho (4n+8) series are determined using Wade's rules (Welch, 2013). Take the example of $B_6H_6^{2-}(B_6H_8)$ of 4n+2 closo series with 26 valence electrons as a basis to deduce the shapes of related clusters. The cluster has an ideal O_h geometry (Greenwood and Earnshaw, 1998) (see Fig. 1, f-1). The corresponding carbonyl closo cluster of 14n+2 series will have 26+6x10 = 86 valence electrons. Many carbonyl clusters with 6 skeletal atoms and 86 valence electrons also possess an ideal O_h geometry. Among many carbonyl cousins, these include $Rh_6(CO)_{16}$, $Ru_6(C)(CO)_{17}$, $Co_6(CO)_{14}^{4-}$, $Ru_6(CO)_{18}^{2-}$, $Os_6(CO)_{18}^{2-}$, $Os_6(H)(CO)_{18}^{-}$, $Co_6(CO)_{15}^{2-}$, $Rh_6(CO)_{15}I^{-}$, and $Re_6(H)_2(C)(CO)_{18}^{2-}$. The closo(4n+2) borane cluster $B_5H_5^{2-}$ has an ideal trigonal bipyramid shape (D_{3h}, see Fig. 2 : f-1). It has 22 valence electrons. Therefore, its cousin carbonyl clusters (14n+2) will have 22+50 = 72 valence electrons. These carbonyl clusters include, $Os_5(CO)_{16}$, $Os_5(CO)_{15}^{2-}$, $PtRh_4(CO)_{12}^{2-}$, and $Os_5(H)(CO)_{15}^{-}$. Let us consider another borane cluster $B_5H_9(4n+4)$ nido series. It has an ideal square pyramid geometry (C_4v, see Fig.2: f-2) with 24 valence electrons. Its carbonyl cluster cousins will have 24+50 = 74 valence electrons and will belong to 14n+4 nido series. Some examples of carbonyl clusters of this series are $Fe_5(C)(CO)_{15}$, $Ru_5(C)(CO)_{15}$, $Os_5(C)(CO)_{15}$, $Os_5(C)(CO)_{14}^{2-}$, $Ru_5(N)(CO)_{14}^{-}$, $Fe_5(C)(CO)_{14}^{2-}$, and $Fe_5(N)(CO)_{14}^{-}$. These selected examples bring out some similarities between 14n+q series of the carbonyl clusters and the corresponding 4n+q borane clusters.

2.7 Rudolph Decapping Series of Clusters

In order to understand the Rudolph system of correlating shapes of clusters, we need to briefly interpret the numbers in Table 3. Let us take a few examples. Consider the row beginning with the set (6,8). This set represents a borane of formula B_6H_8. This borane is a member of the closo series which exist in ionic form in this case $B_6H_6^{2-}$. The next set (5, 9) which is derived by rearranging (6,8) by removing one from 6 leaving 5 and adding it to 8 giving us 9 represents B_5H_9 which is a nido cluster. Doing the same rearrangement on (5,9) produces the set (4, 10). This set represents the borane B_4H_{10} which is an arachno cluster. The remaining sets of numbers (3,11), (2,12), (1, 13) and (0, 14) represent B_3H_{11}, B_2H_{12}, BH_{13}, and H_{14} respectively. Some of the fragments represented by numbers are just of academic interest as they may not exist. The first column of numbers represent some members of closo series. These are (1,3) →BH_3, (2,4)→B_2H_4, (3,5)→B_3H_5, (4,6)→B_4H_6, (5,7)→B_5H_7, (6, 8)→B_6H_8, and so on. The next column represents members of the nido series and so on. Rudolph analyzed the structures of boranes and identified the geometrical relationship linking the closo(4n+2) geometry with the corresponding nido(4n+4) and hypho(4n+6) geometries. This relationship is now well known (Rudolph, 1976). However, with our knowledge of series, this geometrical relationship of boranes and other clusters is part of the Decapping Series. The Rudolph decapping series has been represented numerically in Table 3. The numbers shown in Table 3 can be translated into borane clusters and fragments. Let us consider some of the numbers in the first column. Take (5,7) →B_5H_7→$B_5H_5^{2-}$. Thus, (5,7) represents the closo ion $B_5H_5^{2-}$ which belongs to (4n+2) series. Similarly, (6,8) → B_6H_8 → $B_6H_6^{2-}$; (7,9) → B_7H_9 → $B_7H_7^{2-}$;(8,10) → B_8H_{10} → $B_8H_8^{2-}$;(9,11) → B_9H_{11} → $B_9H_9^{2-}$;(10,12) → $B_{10}H_{12}$ → $B_{10}H_{10}^{2-}$;(11,13) → $B_{11}H_{13}$ → $B_{11}H_{11}^{2-}$; and(12,14) → $B_{12}H_{14}$ → $B_{12}H_{12}^{2-}$. The horizontal movement in Table 3 gives the decapped members derived from the corresponding closo series. The set of numbers (5,7)→(4,8)→(3,9) represent B_5B_7, B_4H_8 and B_3B_9 respectively; (6,8)→(5,9)→(4,10) represent B_6H_8 (shape Fig. 1: f-1), B_5H_9 (shape Figure 2: f-2), and B_4H_{10} (shape Figure 2:f-3)respectively. Let us consider the series (7,9)→(6, 10)→(5,11). These numbers correspond to $B_7H_9(B_7H_7^{2-})$, B_6H_{10} and B_5H_{11} borane clusters which form part of Rudolph decapping series(Cotton and Wilkinson, 1980). Applying the concept of fragments and their series the k-values corresponding to the formulas of the clusters can be calculated as follows.

$$F = B_7H_9 = (BH)_7H_2 \; ; \; S = 7[4n]+ 2 = 4n+2 \; (Closo \; Series), \; k = 2n-1 = 2\times7-1 = 13$$

$$F = B_6H_{10} = (BH)_6H_4 \; ; \; S = 6[4n]+ 4 = 4n+4 \; (Nido \; Series), \; k = 2n-2 = 2\times6-2 = 10$$

$$F = B_5H_{11} = (BH)_5H_6 \; ; \; S = 5[4n] + 6 = 4n+6 (Arachno \; Series), \; k = 2n-3 = 2x5-3 = 7$$

The skeletal shapes of the $B_7H_7{}^{2-}$, B_6H_{10} and B_5H_{11} are shown in Figure 3. The other sets of numbers can be translated into formulas in the same manner.

2.8 Applying Isolobal Fragments to Deduce Cluster Series and Predict Possible Cluster Shapes

Take $B_5H_5{}^{2-}$ as an example. The method has been developed for categorization (Kiremire, 2015) of clusters using 4n or 14n rule and will be applied here. We can write the formula as $(BH)_5{}^{2-}$. The series can be derived from $S = 5[BH]+2 = 5[3+1]+2 = 5[4]+2 = 5[4n]+2 = 4n+2$. Since $B_5H_5{}^{2-}$ belongs to 4n+2 series, it is a closo cluster. The cluster k-value $= 2n-1 = 2x5-1 = 9$ based on the cluster series (4n+2). This k-value is characteristic of a trigonal bipyramid geometry (Figure 2:f-1). Consider a carborane $C_2B_3H_5$. We can write the formula as $(CH)_2(BH)_3$. The series of the molecula formula can be derived from $S_T = 2[CH] + 3[BH] = 2[4+1] + 3[3+1] = 2[5]+ 3[4]= 2[4n+1]+3[4n] = 4n+2 +4n = 4n+2$. This means that the cluster belongs to the closo series with k-value $= 2n-1 = 2x5-1 = 9$. This implies the cluster will have an ideal skeletal shape of a trigonal bipyramid (Figure 2:f-1). Another example $(C_4H_4)Fe(CO)_3$. The cluster formula can be decomposed into the fragments $F =[Fe(CO)_3]+ 4[CH]$ and the corresponding cluster series can be derived from the valence electrons of the fragments as follows $S =1[8+3x2]+4[4+1] = 1[14]+ 4[5] = 1[14]+4[5] = 1[14n]+4[4n+1] = 1[4n]+4[4n+1] = 4n+4n+4 = 4n+4$. Hence, the cluster $(C_4H_4)Fe(CO)_3$ is a member of $S = 4n+4$ (nido) series. To simplify the analysis of the series for structural identification, 14n has been taken to be similar to 4n and the additions or multiples of 4n do not affect it and it remains as 4n. In other words, in series, y(4n) or y(14n) = 4n or 14n where y = is an integer, 1,2, 3 , and son. Therefore the cluster belongs to nido series (4n+4) with k-value of $2n-2 = 2x5-2 = 8$. This k value of 8 is a characteristic of a square pyramid geometry(see Figure 2: f-2). Thus, all the 4 carbon atoms are bonded to Fe and agrees with $(\eta^4$-$C_4H_4)Fe(CO)_3$ formulation. Let us consider the metalloborane $B_4H_8Fe(CO)_3$. Using the same approach, $S_T =[Fe(CO)_3]+ 4[BH_2] = [14n]+4[4n+1] = 4n+4n+4 = 4n+4$. This is also a nido cluster with $k = 8$. It will have a similar geometry as $C_4H_4)Fe(CO)_3$. The cobalt complex $(B_4H_8)Co(\eta^5$-C_5H_5 can be analyzed using the same approach. $F = B_5H_9 = (BH)_5H_4; S = 5[4n]+4 = 4n+4$ (Nido) series; $k = 2n-2 = 2x5-2 = 8$.

$$F= (B_4H_8)Fe(CO)_3 = (BH_2)_4Fe(CO)_3; S= 4[4n+1]+[14n] = 4n+4+ 4n = 4n+4 \; (Nido) \; series, \; k =8.$$

$$F = (B_4H_8)Co(\eta^5\text{-}C_5H_5) = BH_2)_4Co(\eta^5\text{-}C_5H_5)= (BH_2)_4 (CoC_P); S = 4[4n+1]+ [14n] = 4n+4+ 4n = 4n+4$$
$$(Nido) \; series, \; k =8.$$

$$F= (C_4H_4)Fe(CO)_3 = (CH)_4 [Fe(CO)_3]; S = 4[4n+1]+[14n] = 4n+4+4n = 4n+4(Nido) \; series, \; k = 8$$

The equivalence of the cluster k value implies that there is a similarity of the symmetries of the skeletal shapes of the clusters and these are shown in Figure 4. It is found that the cobalt cluster has two isomers(Greenwood and Earnshaw, 1998). What is also interesting is that if we regard the borane cluster B_5H_9 as $(B_4H_8)(BH)$ and compare this with $(B_4H_8)[Fe(CO)_3]$, $(B_4H_8)[Co(\eta^5$-$C_5H_5)]$ and $(C_4H_4)[Fe(CO)_3]$, it is observed that the fragment [BH] belongs to 4n series while $[Co(\eta^5$-$C_5H_5)] \rightarrow 14n$, and $[Fe(CO)_3]$ also belong to the 14n series. We also now know that 14n is similar to 4n, meaning that these fragments are isolobal.

[M-6] $C_p = C^1C[M-6]$

f-1   f-2

$C_p = C^2C[M-6]$ $C_p = C^3C[M-6]$ $C_p = C^4C[M-6]$

f-3   f-4   f-5

$C_p = C^5C[M-6]$ $C_p = C^6C[M-6]$

f-6   f-7
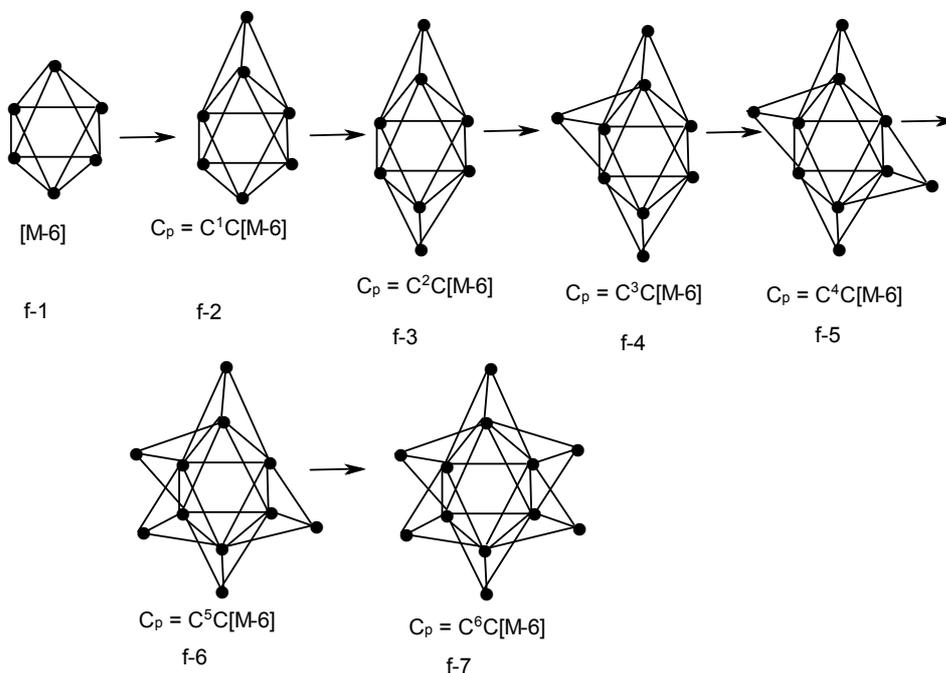
Fiigure 1. Sketches of Selected Possible Capping Series of O_h Geometry

#

k = 9   k = 8

k = 5

f-1   f-2   f-3
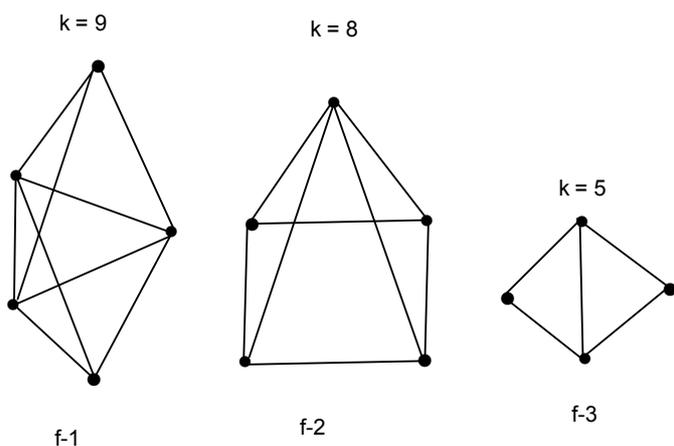
Figure 2. Possible Skeletal Shapes of M-5 and M-4 Clusters

#
#
#
#
#
#
#
#

k = 13   k = 10   k = 7
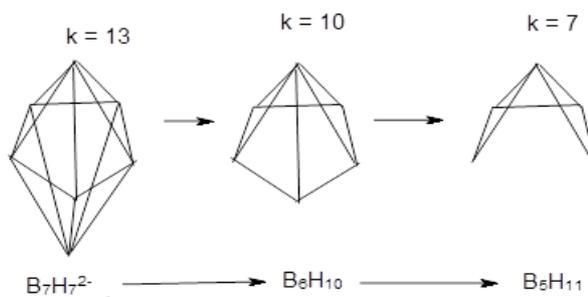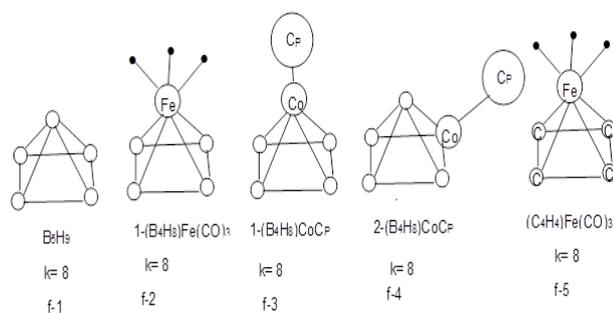
$B_7H_7^{2-}$ ⟶ B_6H_{10} ⟶ B_5H_{11}

Figure 3. The Skeltal Shapes of $B_7H_7^{2-}$, B_6H_{10} and B_5H_{11}

Figure . Skeletal shapes of some 4n+4 Clusters

Table 1. The Capping Series of Closo (4n+2) Fragments from H_2 to $B_{12}H_{14}$

	2		4		6		8		10		12		14	
Closo(4n+2)	0,2	H_2	1,3	BH_3	2,4	B_2H_4	3,5	B_3H_5	4,6	B_4H_6	5,7	B_5H_7	6,8	B_6H_8
MonoCP(4n)	1,1	BH	2,2	B_2H_2	3,3	B_3H_3	4,4	B_4H_4	5,5	B_5H_5	6,6	B_6H_6	7,7	B_7H_7
BiCP(4n-2)	2,0	B_2	3,1	B_3H_1	4,2	B_4H_2	5,3	B_5H_3	6,4	B_6H_4	7,5	B_7H_5	8,6	B_8H_6
TriCP(4n-4)			4,0	B_4	5,1	B_5H_1	6,2	B_6H_2	7,3	B_7H_3	8,4	B_8H_4	9,5	B_9H_5
TetraCP(4n-6)					6,0	B_6	7,1	B_7H_1	8,2	B_8H_2	9,3	B_9H_3	10,4	$B_{10}H_4$
PentaCP(4n-8)							8,0	B_8	9,1	B_9H_1	10,2	$B_{10}H_2$	11,3	$B_{11}H_3$
HexaCP(4n-10)									10,0	B_{10}	11,1	$B_{11}H_1$	12,2	$B_{12}H_2$
Hepta CP(4n-12)											12,0	B_{12}	13,1	$B_{13}H_1$
OctaCP(4n-14)													14,0	B_{14}

	16		18		20		22		24		26	
Closo(4n+2)	7,9	B_7H_9	8,10	B_8H_{10}	9,11	B_9H_{11}	10,12	$B_{10}H_{12}$	11,13	$B_{11}H_{13}$	12,14	$B_{12}H_{14}$
MonoCP(4n)	8,8	B_8H_8	9,9	B_9H_9	10,10	$B_{10}H_{10}$	11,11	$B_{11}H_{11}$	12,12	$B_{12}H_{12}$	13,13	$B_{13}H_{13}$
BiCP(4n-2)	9,7	B_9H_7	10,8	$B_{10}H_8$	11,9	$B_{11}H_9$	12,10	$B_{12}H_{10}$	13,11	$B_{13}H_{11}$	14,12	$B_{14}H_{12}$
TriCP(4n-4)	10,6	$B_{10}H_6$	11,7	$B_{11}H_7$	12,8	$B_{12}H_8$	13,9	$B_{13}H_9$	14,10	$B_{14}H_{10}$	15,11	$B_{15}H_{11}$
TetraCP(4n-6)	11,5	$B_{11}H_5$	12,6	$B_{12}H_6$	13,7	$B_{13}H_7$	14,8	$B_{14}H_8$	15,9	$B_{15}H_9$	16,10	$B_{16}H_{10}$
PentaCP(4n-8)	12,4	$B_{12}H_4$	13,5	$B_{13}H_5$	14,6	$B_{14}H_6$	15,7	$B_{15}H_7$	16,8	$B_{16}H_8$	17,9	$B_{17}H_9$
HexaCP(4n-10)	13,3	$B_{13}H_3$	14,4	$B_{14}H_4$	15,5	$B_{15}H_5$	16,6	$B_{16}H_6$	17,7	$B_{17}H_7$	18,8	$B_{18}H_8$
Hepta CP(4n-12)	14,2	$B_{14}H_2$	15,3	$B_{15}H_3$	16,4	$B_{16}H_4$	17,5	$B_{17}H_5$	18,6	$B_{18}H_6$	19,7	$B_{19}H_7$
OctaCP(4n-14)	15,1	$B_{15}H_1$	16,2	$B_{16}H_2$	17,3	$B_{17}H_3$	18,4	$B_{18}H_4$	19,5	$B_{19}H_5$	20,6	$B_{20}H_6$
	16,0	B_{16}	17,1	$B_{17}H_1$	18,2	$B_{18}H_2$	19,3	$B_{19}H_3$	20,4	$B_{20}H_4$	21,5	$B_{21}H_5$
			18,0	B_{18}	19,1	$B_{19}H_1$	20,2	$B_{20}H_2$	21,3	$B_{21}H_3$	22,4	$B_{22}H_4$
					20,0	B_{20}	21,1	$B_{21}H_1$	22,2	$B_{22}H_2$	23,3	$B_{23}H_3$
							22,0	B_{22}	23,1	$B_{23}H_1$	24,2	$B_{24}H_2$
									24,0	B_{24}	25,1	$B_{25}H_1$
											26,0	B_{26}

Table 2. Decapping Series of Closo (4n+2) Fragments from H_2 to $B_{12}H_{14}$.

	4		6		8		10		12		14	
Closo(4n+2)	1,3	BH_3	2,4	B_2H_4	3,5	B_3H_5	4,6	B_4H_6	5,7	B_5H_7	6,8	B_6H_8
Nido(4n+4)	0,4	H_4	1,5	B_1H_5	2,6	B_2H_6	3,7	B_3H_7	4,8	B_4H_8	5,9	B_5H_9
Arachno(4n+6)			0,6	H_6	1,7	B_1H_7	2,8	B_2H_8	3,9	B_3H_9	4,10	B_4H_{10}
Hypho(4n+8)					0,8	H_8	1,9,		2,10	B_2H_{10}	3,11	B_3H_{11}
							0,10		1,11	B_1H_{11}	2,12	B_2H_{12}
							H_{10}		0,12	H_{12}	1,13	B_1H_{13}
											0,14	H_{14}

	16		18		20		22		24		26	
Closo(4n+2)	7,9	B_7H_9	8,10	B_8H_{10}	9,11	B_9H_{11}	10,12	$B_{10}H_{12}$	11,13	$B_{11}H_{13}$	12,14	$B_{12}H_{14}$
Nido(4n+4)	6,10	B_6H_{10}	7,11	B_7H_{11}	8,12	B_8H_{12}	9,13	B_9H_{13}	10,14	$B_{10}H_{14}$	11,15	$B_{11}H_{15}$
Arachno(4n+6)	5,11	B_5H_{11}	6,12	B_6H_{12}	7,13	B_7H_{13}	8,14	B_8H_{14}	9,15	B_9H_{15}	10,16	$B_{10}H_{16}$
Hypho(4n+8)	4,12	B_4H_{12}	5,13	B_5H_{13}	6,14	B_6H_{14}	7,15	B_7H_{15}	8,16	B_8H_{16}	9,17	B_9H_{17}
	3,13	B_3H_{13}	4,14	B_4H_{14}	5,15	B_5H_{15}	6,16	B_6H_{16}	7,17	B_7H_{17}	8,18	B_8H_{18}
	2,14	B_2H_{14}	3,15	B_3H_{15}	4,16	B_4H_{16}	5,17	B_5H_{17}	6,18	B_6H_{18}	7,19	B_7H_{19}
	1,15	B_1H_{15}	2,16	B_2H_{16}	3,17	B_3H_{17}	4,18	B_4H_{18}	5,19	B_5H_{19}	6,20	B_6H_{20}
	0, 16		1,17	B_1H_{17}	2,18	B_2H_{18}	3,19	B_3H_{19}	4,20	B_4H_{20}	5,21	B_5H_{21}
			0,18	H_{18}	1,19	B_1H_{19}	2,20	B_2H_{20}	3,21	B_3H_{21}	4,22	B_4H_{22}
					0,20	H_{20}	1,21	B_1H_{21}	2,22	B_2H_{22}	3,23	B_3H_{23}
							0,22	H_{22}	1,23	B_1H_{23}	2,24	B_2H_{24}
									0,24	H_{24}	1,25	B_1H_{25}
											0,26	H_{26}

Table 3. Rudolph Decapping Series in Numbers

0,2												
1,3	0,4											
2,4	1,5	0,6										
3,5	2,6	1,7	0,8									
4,6	3,7	2,8	1,9	0,10								
5,7	4,8	3,9	2,10	1,11	0,12							
6,8	5,9	4,10	3,11	2,12	1,13	0,14						
7,9	6,10	5,11	4,12	3,13	2,14	1,15	0,16					
8,10	7,11	6,12	5,13	4,14	3,15	2,16	1,17	0,18				
9,11	8,12	7,13	6,14	5,15	4,16	3,17	2,18	1,19	0,20			
10,12	9,13	8,14	7,15	6,16	5,17	4,18	3,19	2,20	1,21	0,22		
11,13	10,14	9,15	8,16	7,17	6,18	5,19	4,20	3,21	2,22	1,23	0,24	
12,14	11,15	10,16	9,17	8,18	7,19	6,20	5,21	4,22	3,23	2,24	1,25	0,26

Closo	Nido	Arachno	Hypho	Klapo
4n+2	4n+4	4n+6	4n+84	n+10

3. Conclusion

A close analysis of carbonyl clusters series based on 14n rule and boranes based on 4n rule, shows that the carbonyl clusters and fragments have corresponding boranes and fragments. For instance, $Fe(CO)_5(S=14n+4)$ has a corresponding borane cluster fragment $BH_5(S=4n+4)$ while $Fe_2(CO)_9$ (S =14n+6) has a corresponding B_2H_8 (S= 4n+6) cluster, $Mo_2(\eta^5\text{-}C_5H_5)(CO)_4(S=14n+2)$ has a cousin borane $B_2H_4(S=4n+2)$. The B_2H_4 closo cluster may be regarded to exist as ionic species $B_2H_2^{2-}$. Furthermore, the carbonyl clusters $Fe_3(CO)_{12}$ (S=14n+6) and $Ir_4(CO)_{12}$ (S =14n+4)have the corresponding borane relatives with the formula $B_3H_9(S = 4n+6)$ and $B_4H_8(S = 4n+4)$ respectively. The inter-conversion from a borane to carbonyl cluster and vice versa was explained earlier.

A number of carbonyl clusters have well documented known capped closo clusters with known shapes. For instance, $O_6(CO)_{18}$ is a mono-capped(mono-capped trigonal bipyramid) cluster of $Os_5(CO)_{16}$(trigonal bipyramid). These have corresponding borane clusters with formulas B_6H_6 and B_5H_7 or $B_5H_5^{2-}$. Similarly $Os_7(CO)_{21}$ is a mono-capped closo cluster of $Os_6(CO)_{18}^{2-}$ and both have well documented structures. Their counterpart borane cousins are B_7H_7 and B_6H_8 or $B_6H_6^{2-}$. However, the shapes of B_6H_6 and B_7H_7 are not known. The osmium carbonyl capping fragment $Os(CO)_2$ belong to the series S = 14n-2 with k value of k = 2n+1 =3 since n = 1 while the borane capping fragment F =[+B, -H] ; and S =[3, -1] = [2] = [4n-2] and k = 2n+1=3. The difference in k value between one cluster to the next in the capping series is 3 whereas in the normal series the value is 2. The series S =14n-2 and S =4n-2 differ by 10n =10x1= 10. This also applies to the capping fragments $Os(CO)_2$[12] and [+B, -H] = [2] which differ by 10 units. The change within the same type of series involves the fragment $Os(CO)_3$[14] with 14 electron content and it belongs to the series S=14n, and k=2n=2x1=2. Addition of $Os(CO)_3$ is similar to adding 14n or 4n in similar series. The series remain unaffected by addition of $Os(CO)_3$ fragment. Selected hypothetical capped closo boranes have been generated and these are shown in Table 1. For completeness, the corresponding decapped series have been produced as well. Close analysis of the series indicates that Rudolph's system of correlating clusters is part of the decapping series. What is also intereting is the fact that the boranes are formed according to the mathematical precision of the generating numerical series. The capping series in Table I end with B_n clusters where n is an even number while the decapping series in Table 2 end with H_n where n is an even number. This implies that the well known boron clusters such as B_{12} may be regarded as the last member of capping series of B_5H_7 or $B_5H_5^{2-}$. The isolobal fragments and their corresponding series are extremely useful in categorizing clusters and fragments very rapidly. In addition, geometries of clusters may readily be deduced using the series of fragments of given molecular formulas. Can the series imply or reveal the mystery or mechanism in which the clusters are formed? For example, does the formation of $B_6H_8(B_6H_6^{2-})$ go through $BH_{13} \rightarrow B_2H_{12} \rightarrow B_3H_{11} \rightarrow B_4H_{10} \rightarrow B_5H_9 \rightarrow B_6H_8$ capping process or does it go via the alternative closo series route of $BH_3 \rightarrow B_2H_4 \rightarrow B_3H_5 \rightarrow B_4H_6 \rightarrow B_5H_7 \rightarrow B_6H_8$? What is clear and certain as deduced from the series in the Tables 1 and 2 is that the borane clusters are formed according to mathematical numerical precision many of which are still unknown.

References

Alexandrova, A. N., Boldyrev, A. I., Zhai, H., & Wang, L. (2006). All-Boron Clusters as potential new inorganic ligands and building blocks in chemistry. *Coord. Chem. Rev., 250*, 2811-2866. http://dx.doi.org/10.1016/j.ccr.2006.03.032

Bernard, R., Cornu, D., Gruner, B., Dozol, J., & Miele, B. (2002). Synthesis of [B12H12]2-Based extractants and their applications for the treatment of nuclear wastes. *J. Organomet. Chem., 657*(1/2), 83-90. http://dx.doi.org/10.1016/S0022-328X(02)01540-1

Bondarev, O., Khan, A., Tu, X., Sevryugina, Y., Jalisatgi, S., & Hawthorne, M. F. (2013). Synthesis of

closo-[B12(OH)11NH]3-:A new Heterobifunctional Dodecaborane Scaffold for Drug Delivery Applications. *J. Am. Chem. Soc., 135*(35), 13204-13211. http://dx.doi.org/10.1021/ja4069613

Cerdán, L., Braborec, J., Garcia-Moreno, I., Costela, A., & Londesborough, M. G. S. (2015). A Borane Laser. Nature Communications, 6, Number 5958. http://dx.doi.org/10.1038/ncomms6958

Cotton, F. A., & Wilkinson, G. (1980). Advanced Inorganic Chemistry, 4th Ed., John Wiley and Sons, New York.

Greenwood, N. N., & Earnshaw, A. (1998). Chemistry of the Elements, 2nd Ed. Butterworth, Oxford.

Greenwood, N. N. (1983). Metalloboranes. *Pure and Appl. Chem., 55*(9), 1415-1430.

Hawthorne, M. F., & Maderna, A. (1999). Applications of Radiolabbed Boron Clusters to the Diagnosis and Treatment of Cancer. *Chem. Rev. 99*, 3421-3434. http://dx.doi.org/10.1021/cr980442h

Hawthorne, M. F., Varadarajan, A., Knobler, C. B., Chakrabarti, S., Paxton, R. J., Beatty, B. G., & Curtis, F. L. (1990). Radiometallacarboranes as Tumor Imaging Reagents. *J. Am. Chem. Soc., 112*(13), 5365-5366. http://dx.doi.org/10.1021/ja00169a062

Higashi, I., & Ishii, T. (2001). Two-Diamensional Icosahedral B12 Networks in Boron Rich Crystals. Forma 16, 187-207.

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

Housecroft, C. E., & Sharpe, A. G. (2005). Inorganic Chemistry, 2nd Ed., Pearson, Prentice Hall, Harlow, England.

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., & 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

Kaszynski, P. (1999). Four Decades of Organic Chemistry of closo-Boranes: A Synthetic Toolbox for Constructing Liquid Crystal Materials. Collect. *Czech. Commun., 64*, 895-926. http://dx.doi.org/10.1135/cccc19990895

King, R. B. (1986). Metal Cluster Topology. *Inorg. Chimica Acta, 116*, 99-107. http://dx.doi.org/10.1016/S0020-1693(00)82162-3

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. (2015). Isolobal Series of Chemical Fragments. Orient. *J. Chem., 31*(3), 2015, in press.

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

Li, Y., & Sneddon, L. G. (2006). Improved Synthetic Route to n-B18H22. *Inorg. Chem., 45*(2), 470-471. http://dx.doi.org/10.1021/ic051712z

Lipscomb, W. N. (1963). Boron Hydrides. W. A. Bejamin, Inc., New York.

Longuet-Higgins, H. C., & Bell, R. P. (1943). The Structure of the Boron Hydrides. *J. Chem. Soc.,* 250-255. http://dx.doi.org/10.1039/jr9430000250

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

Ohishi, Y., Kimura, K., Yamaguchi, M., Uchida, N., & Kanayama, T. (2009). Energy barrier of Structure B12H6+ to B12H5+ and B12H4+ Clusters. *J. Chem. Phys. Conference Series, 176*, 012030. http://dx.doi.org/10.1088/1742-6596/176/1/012030

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

Rudolph, R. W. (1976). Boranes and heteroboranes: a paradigm for the electron requirements of clusters? *Acc. Chem. Res., 9*(12), 446-452. http://dx.doi.org/10.1021/ar50108a004

Shaik, S., Danovich, D., Wu, W., Su, P., Rzepa, H. S., & Hiberty, P. C. (2012). Quadruple bonding in C2 and analogous eight valence electron species. *Nature Chemistry, 4*, 195-200. http://dx.doi.org/10.1038/nchem.1263

Shriver, D. F., & Atkins, P. W. (1999). Inorganic Chemistry, 3rd Ed. Oxford University Press.

Stock, A. (1933). The Hydrides of Boron and Silicon. New York; Cornell University Press. http://dx.doi.org/10.1021/j150356a019

Szwacki, N. G., Weber, V., & Tymczak, C. J. (2009). Borozene, B12H6. *Nanoscale Research Letters*, 1085-1089. http://dx.doi.org/10.1007/s11671-009-9362-2

Takikawa, S., Miyoshi, T., Koganel, H., El-Zaria, M. E.,Vinas, C., Suzuki, M., Ono, K., & Nakimura, H. (2014). Spermidinium closo-dodecaborate-encapsulating liposomes as efficient boron delivery vehicles for neutron capture therapy. *Chem. Commun., 50*, 12325-12328. http://dx.doi.org/10.1039/C4CC04344H

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

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

Copyrights