International Journal of Chemistry; Vol. 8, No. 3; 2016
ISSN 1916-9698 E-ISSN 1916-9701
Published by Canadian Center of Science and Education

The Application of the 4n Series Method to Categorize Metalloboranes

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: June 27, 2016 Accepted: July 13, 2016 Online Published: July 26, 2016

doi:10.5539/ijc.v8n3p62 URL: http://dx.doi.org/10.5539/ijc.v8n3p62

Abstract

Metalloboranes have been categorized by using 4n series method. More than one hundred metalloboranes have been analyzed and characterized by the method. The clusters have been found to be centered within the series range S = 4n+6 to 4n-8. According to the classification, the clusters of series S= 4n+0 are mono-capped, S = 4n-2, bi-capped, S = 4n-4, tri-capped, S = 4n-6, tetra-capped and S= 4n-8, penta-capped. Whereas the known stable boranes have almost non-existent capped boranes, such clusters are prevalent within metalloborane complexes. This implies that metal fragments have the potency of stabilizing the fragile capped boranes.

Keywords: 4n series, metalloboranes, capped-clusters, isolobal, numerical, valency

1. Introduction

The Wade-Mingos rules (Wade, 1971; Mingos, 1972, 1984, 1991; Cox, et al, 1981) have widely been utilized to categorize clusters. The 4n series method of categorizing clusters that has recently been developed (Kiremire, 2015a; 2015b) complements the PSEPT method. The method is a systematic numerical approach of electron-counting of valence electrons in atoms, fragments, molecules and clusters. The categorization of metalloboranes using the 4n series method is hereby presented in this paper.

2. Results and Discussion

2.1 Background to the Application of the 4n Series Method

The evolution of the 4n series method for analyzing and categorizing clusters has been discussed extensively (Kiremire, 2015a, 2015b). In this paper, the 4n series method is being extended to classification of metallaborane clusters. Adequate examples have been provided to demonstrate the flexibility and the power of the method so as to enable the readers to be more familiar with it. The cluster complexes used have been taken from a wide spectrum of sources but mostly from the work by Fehlner and Grimes (Fehlner, 2002; Callahan, et al, 1974; Grimes, 1974). In addition, the vital isolobal relationship between transition metals and main group elements will be utilized (Hoffmann, 1982; Kiremire, 2015a). The relationship is summarized below.

$$14n+q \underset{+10n}{\overset{-10n}{\rightleftharpoons}} 4n+q$$

This means that the valence electrons from the transition metal fragments have to be lowered to the level of the main group fragments by subtracting 10 unit sets of electrons. If it is one fragment, a numerical value of 10 is subtracted, for two, 2x10, three, 3x10 and so on. It has been found much easier to work with 4n series rather than 14n series. The cluster number k is defined as k = 2n-½ q. In terms of categorization of clusters, S =4n+2 represents the closo cluster, 4n+4(nido), 4n+6 (arachno), 4n+8 (hypho) and 4n+10 (klapo). The capping series start from S =4n+0(mono-capped), 4n-2(bi-capped), 4n-4(tri-capped), 4n-6(tetra-capped) and so on. The proposed capping symbol which was discussed in earlier work is Cp = C^1C (mono-capped), Cp = C^2C (bi-capped), Cp = C^3C (tri-capped) and Cp = C^4C (tetra-capped) (Kiremire, 2015b). The S = 4n+0 represents a mono-capped cluster and the symbol C^1 is used. For any additional +1(-2), that is, the series S = 4n-2, we get another capping and hence an additional symbol C^1 is added. Thus, the series S = 4n+1(-2), the net capping symbol becomes, Cp = $C^1+C^1 = C^2$, and for S = 4n+3(-2) = 4n-6, Cp = $C^1+C^3 = C^4$. Thus, S = 4n-6 series represents, a tetra-capped cluster. Let us consider the following examples (most of which are known from the application of Mingo-Wades rules) as illustrations of the application of the 4n series method of categorizing clusters.

2.2 B_5H_9

The molecular formula is decomposed into mono-fragments with electron valence content of four. Hence, B_5H_9 is split

into five [BH] fragments. These fragments consist of 5 boron atoms and 5 hydrogen atoms. Since, B_5H_9 has 5 boron atoms and 9 hydrogen atoms, the remaining 4 hydrogen atoms will be added separately. This is summarized by the work out below.

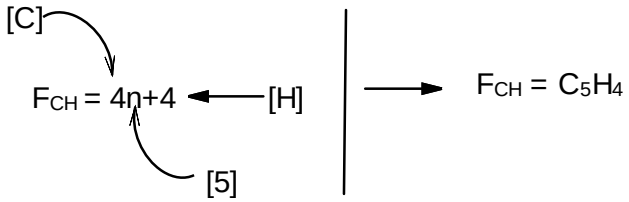
$$5[BH] \rightarrow 5[3+1] = 5[4+0] \rightarrow 4n+0(n=5)$$

Balancing the hydrogen atoms: [9-5](H) = 4(H)→0+4(n=0)

S = 4n+4(n=5); Nido cluster,

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

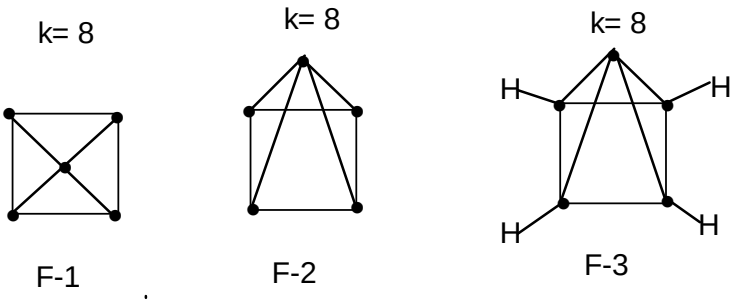
The skeletal shape of B_5H_9 is shown in F-1 as a projection and F-2 as square pyramid. A diagram showing the transformation of series into an equivalent hydrocarbon is given in Scheme 1. The skeletal shape of the hydrocarbon analogue C_5H_4 as an isomer corresponding to B_5H_9 is shown in F-3. Most of the examples have been taken from an outstanding review by Fehlner (Felner, 2002).



Scheme 1. Converting a series Formula into a corresponding Hydrocarbon molecular formula

This means that B_5H_9 is equivalent to C_5H_4.

The B_5H_9 cluster has 5 skeletal atoms M-5 and is a nido type of cluster. Therefore, it is derived from M-6 closo cluster which has an octahedral shape. Hence, the B_5H_9 cluster has a square pyramid pyramid shape with k value = 8.



2.3 $C_2B_3H_7$

$$2[C] = 2[4+0] \rightarrow 4n+0(n=2)$$

$$3[BH] = 3[4+0] \rightarrow 4n+0(n=3)$$

$$[7-3](H) = 4(H) \rightarrow 0+4(n=0)$$

S = 4n+4(n=5); Nido series, k = 8

The shape will be similar to that of B_5H_9 discussed above. Again, in this example the molecular formula has been decomposed into mono-fragments each with valence electron content of four in line with 4n series method.

2.4 $C_5H_3Me_2^+$

$$5[C] \rightarrow 4n+0(n=5)$$

$$3H \rightarrow 0+3(n=0)$$

$$2Me \rightarrow 0+2(n=0)$$

Charge, q→0-1(n=0), q = charge

S = 4n+4(n=5); Nido cluster, k = 8. Therefore, $C_5H_3Me_2^+$ cluster is also expected to have a shape similar to that of B_5H_9.

2.5 $(C_4H_4)Fe(CO)_3$

$$1[Fe(CO)_3] = 1[8+6] = 1[14+0] \rightarrow 1[14+0-10] = 1[4+0] \rightarrow 4n+0(n=1)$$

$$4[C] \rightarrow 4n+0(n=4)$$

$$4H \rightarrow 0+4(n=0)$$

S = 4n+4(n=5); Nido series, k =2n-2 = 2(5)-2 = 8

Hence, the skeletal shape is similar to that of B_5H_9.

2.6 $B_3H_7Fe_2(CO)_6$

$$2[Fe(CO)_3] \rightarrow 4n+0(n=2)$$

$$3[BH] \rightarrow 4n+0(n=3)$$

$$[7-3](H) = 4H \rightarrow 0+4(n=0)$$

S = 4n+4(n=5);

Nido cluster, k =8. Shape is similar to that of B_5H_9.

2.7 $Fe_5(C)(CO)_{15}$

$$5[Fe(CO)_3] \rightarrow 4n+0(n=5)$$

$$C \rightarrow 0+4(n=0)$$

S = 4n+4(n=5). The $Fe_5(C)(CO)_{15}$ cluster is member of Nido clan of clusters and its skeletal is similar to that of B_5H_9 cluster.

2.8 $(Cp^*Ir)_2B_4H_8$

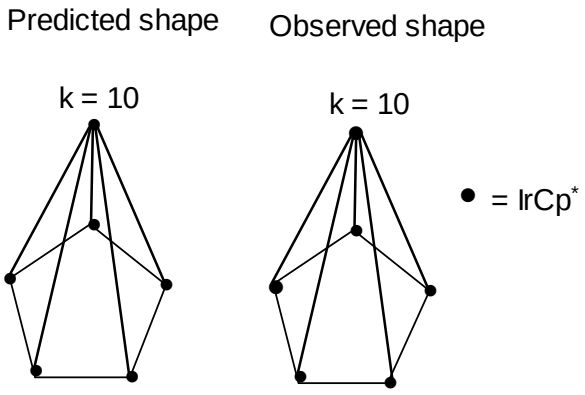
$$2[Cp^*Ir] \rightarrow 2[5+9] = 2[14+0] \rightarrow 4n+0(n=2)$$

$$4[BH] \rightarrow 4[4+0] \rightarrow 4n+0(n=4)$$

$$4H \rightarrow 0+4(n=0)$$

S = 4n+4(n=6); NIDO

F_B = 4n+4(n=6)→[BH](6)+4(H) =B_6H_6+4H = B_6H_{10}. Since this is a nido cluster, its shape is related that of the nearest closo system $B_7H_7^{2-}$.This is in agreement to the Rudolph series (Rudolph, 1976). The cluster B_6H_{10} has a pentagonal pyramid shape (k = 10). The hydrocarbon equivalent is given by F_{CH} =[C](6)+4(H) = C_6H_4. The k value = 2n-2=2(6)-2 = 10. A sketch of the ideal skeletal shape of B_6H_{10} is given in F-4. This is the expected ideal shape for $(Cp^*Ir)_2B_4H_8$. This is in agreement with the observed shape (Fehlner, 2002).



F-4 Ideal skeletal shape of $(Cp^*Ir)_2B_4H_8$

Two of the skeletal points (enlarged size) refer to the two IrCp* fragments.

2.9 $(Cp^*Ru)_2B_4H_8$

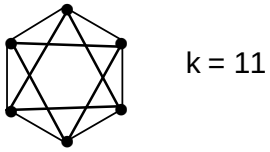
2[Cp*RuH]→4n+0(n=2). This step involves the lowering of [14] valence electron equivalent to [4] valence electron equivalent so as to use 4n series method of categorization.

$$4[BH]\rightarrow 4n+0(n=4)$$

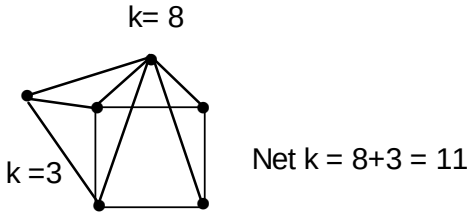
$$(H)=2H\rightarrow 0+2$$

S = 4n+2(n=6); Closo series; k = 2n-1 = 2(6)-1 = 11.

$F_B = 4n+2 = [BH](6)+2 = B_6H_6^{2-}$. The closo boranes are known to be negatively charged (McGlinchey, et al, 2011).The ideal skeletal shape of $B_6H_6^{2-}$ is expected to be octahedral for $(Cp^*Ru)_2B_4H_8$. The expected skeletal shape is shown in F-5A. However, the observed shape is a capped square pyramid (Fehlner, 2002) shown below F-5B. This is due to k isomerism, that is, net k = k(square pyramid)+ k (capping) = 8+3 =11. This is the same as k=11 for octahedral shape. This is in agreement with the series, thus, M-5 square pyramid has corresponding series S = 4n+4(n=5), k =2n-2 =2(5)-2 =8; and the capping fragment $[BH]^{2+}$ has series S =4n-2(n=1), and k =2n+1 = 2(1)+1 = 3. The net cluster, $F_B = B_5H_9+[BH]^{2+} = B_6H_8 = B_6H_6^{2-}$, has a net k =8+3 = 11.



F-5 A. The expected ideal skeletal shape of $(Cp^*Ru)_2B_4H_8$



F-5B. Sketch of Ideal observed shape of $(Cp^*Ru)_2B_4H_8$

2.10 $Cp^*Co)B_4H_8$

$$1[Cp^*Co]\rightarrow 1[5+9] = 1[14+0]\rightarrow 1[14+0-10] = 1[4+0]\rightarrow 4n+0(n=1)$$

$$4[BH]\rightarrow 4n+0(n=4)$$

$$4H\rightarrow 0+4(n=0)$$

S = 4n+4(n=5); this is a nido cluster.

F_B = 4n+4 = [BH](5)+4(H) = B_5H_5+4H = B_5H_9

F_{CH} =4n+4(n=5)= [C](5)+4(H) = C_5H_4

This cluster is expected to have a shape similar to that of B_5H_9.

2.11 (Cp)$WH_3B_4H_8$*

1[Cp*WH_3] =1[5+6+3]=1[14+0]→1[14+0-10] = 1[4+0]→4n+0(n=1)

4[BH]→4n+0(n=4)

4H →0+4(n=0)

S = 4n+4(n=5); this is a nido cluster. F_B = B_5H_9, F_{CH} = C_5H_4, k = 8. Shape is a square pyramid

2.12 $(Cp^*Re)_2B_4H_8$

2[Cp*ReH_2]→2[5+7+2]=2[14+0]→4n+0(n=2)

4[BH]→4n+0(n=4)

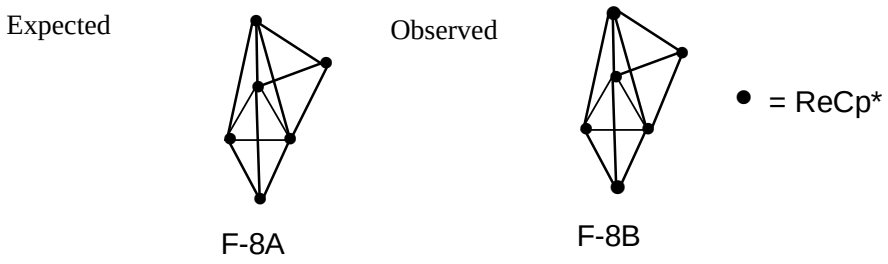
[8- 4-4](H)→0+0

S = 4n+0(n=6)

The cluster belongs to mono-capped series.

F_B = 4n+0 = [BH](6)+0(H) = B_6H_6; F_{CH} = [C](6)+0(H) = C_6.

This is a mono-capped cluster with symbol Cp = C^lC[M-5]. It is a mono-capped trigonal bipyramid (F-8A). This is in agreement with the observed cluster 2.10 in F-8B.



F-8A F-8B

F-8A. Expected ideal skeletal shape of $(Cp^*Re)_2B_4H_8$

F-8B. Observed ideal skeletal shape of $(Cp^*Re)_2B_4H_8$

2.13 $(Cp^*Cr)_2B_4H_8$

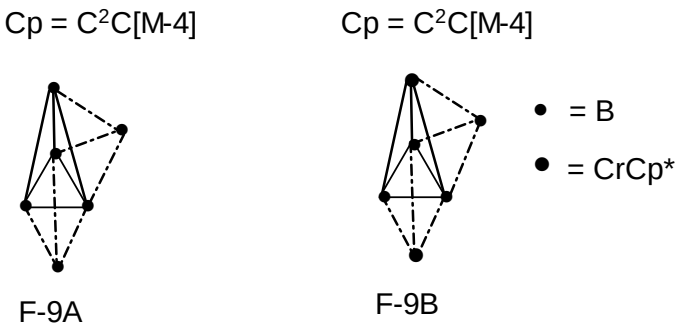
2[Cp*CrH_3]→2[5+6+3]=2[14+0]→2[14+0-10]=2[4+0]→4n+0(n=2)

4[BH]→4[4+0]→4n+0(n=4)

[8-6-4](H)=-2(H) →0-2(n=0)

S = 4n-2(n=6)

This is a bi-capped tetrahedral, Cp = C^2C[M-4]. The skeletal sketch of $(Cp^*Cr)_2B_4H_8$ is shown in F-9A. The observed similar shape (Fehlner, 2002) is shown in F-9B.



F-9A F-9B

Dotted lines denote capping

F-9A. Expected ideal skeletal shape of $(Cp^*Cr)_2B_4H_8$

F-9B. Observed ideal skeletal shape of $(Cp^*Cr)_2B_4H_8$

2.14 $(Cp^*W)_3(H)B_8H_8$

$$3[Cp^*WH_3]\rightarrow 3[5+6+3]=3[14+0] \rightarrow 3[14+0-10]=3[4+0]\rightarrow 4n+0(n=3)$$

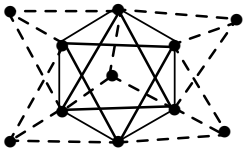
$$8[BH]\rightarrow 8[3+1] =8[4+0]\rightarrow 4n+0(n=8)$$

$$[9-9-8](H) = -8(H)\rightarrow 0-8(n=0)$$

$$S =4n-8(n=11)$$

$$Cp = C^1+C^4 = C^5C[M-6]$$

This means the cluster is a penta-capped octahedral. The predicted skeletal sketch is shown in F-10. This is almost similar to the observed shape (Fehlner, 2002).



Dotted lines denote capping

F-10. Sketch of ideal skeletal shape of penta-capped $(Cp^*W)_3(H)B_8H_8$

2.15 $Cp^*_2Re_2H_2B_4H_8$

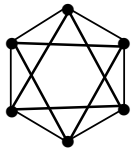
$$2(Cp^*ReH_2] = 2[5+7+2] = 2[14+0]\rightarrow 2[14+0-10]=2[4+0]\rightarrow 4n+0(n=2)$$

$$4[BH] = 4[3+1] = 4[4+0]\rightarrow 4n+0(n=4)$$

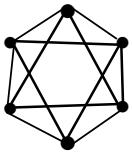
$$[10-4-4](H) = 2(H)\rightarrow 0+2(n=0)$$

$$S= 4n+2(n=6), \text{Closo system.}$$

This corresponds to $B_6H_6^{2-}$ cluster which has an octahedral shape. The expected shape is sketched in F-11A and the observed one is given in F-11B.



F-11A



F-11B

● = ReCp*

● = B

F-11A. Sketch of expected ideal skeletal shape of $(Cp^*Re)_2(H)_2B_4H_8$

F-11B. Sketch of the observed skeletal shape of $(Cp^*Re)_2(H)_2B_4H_8$

2.16 $Cp^*_2Re_2B_6H_6$

$$2[Cp^*ReH_2]=2[5+7+2]=2[14+0]=2[14+0-10] =2[4+0] \rightarrow 4n+0(n=2)$$

$$6[BH]= 6[3+1] =6[4+0] \rightarrow 4n+0(n=6)$$

$$[6-4-6](H) = -4H \rightarrow 0-4(n=0)$$

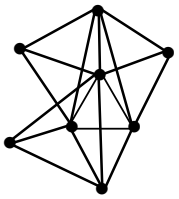
$$S = 4n-4(n=8)$$

$$Cp = C^3C[M-5]$$

This means that the cluster is expected to have an inner shape of trigonal bipyramid with three atoms in capping positions.

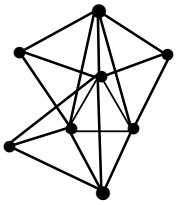
The expected ideal shape tri-capped trigonal bipyramid skeletal shape is shown in F-12A. This in agreement with the observed shape (Fehlner, 2002) of $Cp^*_2Re_2B_6H_6$ sketched in F-12B.

$Cp = C^3C[M-5]$



F-12A

$Cp = C^3C[M-5]$



F-12B

● = ReCp*

● = B

F-12A. Sketch of expected ideal skeletal shape of $(Cp^*Re)_2B_6H_6$

F-12B. Sketch of observed skeletal shape of $(Cp^*Re)_2B_6H_6$

2.17 $Cp^*_2Re_2B_7H_7$

$$2[Cp^*ReH_2]=2[5+7+2]=2[14+0]=2[14+0-10] =2[4+0] \rightarrow 4n+0(n=2)$$

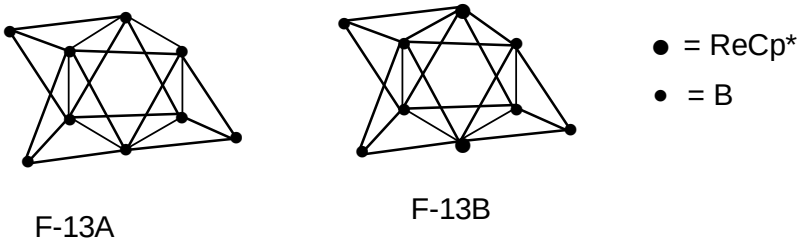
$$7[BH]= 7[3+1] =7[4+0] \rightarrow 4n+0(n=7)$$

$$[7-4-7](H) = -4H \rightarrow 0-4(n=0)$$

$$S = 4n-4(n=9)$$

$$Cp = C^3C[M-6]$$

Thus, $Cp^*_2Re_2B_7H_7$ expected to be a tri-capped octahedral complex. The proposed skeletal sketch is given in F-13A. The shape is similar to the one reported in literature (Fehlner, 2002) and its sketch is shown in F-13B.



F-13A F-13B

F-13A. Sketch of expected ideal skeletal shape of $(Cp^*Re)_2B_7H_7$

F-13B. Sketch of the observed skeletal shape of $(Cp^*Re)_2B_7H_7$

2.18 Categorization of Metalloboranes

More than than one hundred metalloborane clusters were categorized using the 4n series method. The results are shown in Tables 1 and 2. Table 2 lists mainly the capped clusters for ease of reference. The clusters form a wide range of series starting with S =4n+6 (arachno) and ending with 4n-8 (penta-capped). The range covers eight families of clusters. This is in contrast to the known stable boranes which comprise only of three main family groups namely, 4n+6 (arachno), 4n+4 (nido) and 4n+2 (closo) with almost no known stable capped boranes (Kiremire, 2015b). According to the 4n series method, the capping series start at 4n+0 and progress to higher capped series. Since capping is prevalent in metalloborane and rare in known borane clusters, it implies that metalloborane clusters indirectly stabilize and promote the existence of fragile capped boranes which are unable to exist on their own.

Table 1. Categorization of Metalloboranes

Complex	Series	k value	n	Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
	S = 4n+q	k = 2n-(q/2)				cluster	cluster
$Mn(CO)_4(B_3H_8)$	4n+6	5		4	Arachno	B_4H_{10}	C_4H_6
$(Cp^*Ir)H_2B_3H_7$	4n+6	5		4	Arachno	B_4H_{10}	C_4H_6
$Cp^*ReH_3B_3H_8$	4n+6	5		4	Arachno	B_4H_{10}	C_4H_6
$Mn(CO)_3(B_3H_8)$	4n+4	6		4	Nido	B_4H_8	C_4H_4
$B_5H_9L_2$	4n+8	6		5	Hypho	B_5H_{13}	C_5H_8
$Cp^*FeB_4H_{11}$	4n+6	7		5	Arachno	B_5H_{11}	C_5H_6
$Ir(CO)L_2(B_4H_9)$	4n+6	7		5	Arachno	B_5H_{11}	C_5H_6
$R_2C_2B_3H_5^{2-}$	4n+6	7		5	Arachno	B_5H_{11}	C_5H_6
$C_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(Cp^*RuH)_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$Fe(CO)_3B_4H_8$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(CpCo)\ B_4H_8$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$Fe(CO)_3C_4H_4$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(Cp^*RuH)_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(Cp^*Co)B_4H_8$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(Cp^*Co)_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$[Fe(CO)_3]_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$(Cp^*Rh)_2B_3H_7$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$C_5H_5^+$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$B_4H_8Fe(CO)_3$	4n+4	8		5	Nido	B_5H_9	C_5H_4
$Bi_3Mo_2(CO)_6^{3-}$	4n-4	12		5	$C^3C[M-2]$	B_5H_1	C_5-4H

Table 1. Continued

Complex	Series	k value	n	Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$(CpFe)B_5H_{10}$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
(Cp^*Ir)		10		6		B_6H_{10}	C_6H_4
$B_3H_7Co_2(CO)_5$	4n+4				Nido		
$(Cp^*RuH)_2Me_2C_2B_2H_4$		10		6		B_6H_{10}	C_6H_4
	4n+4				Nido		
$(Cp^*Ru)_2\ HB_4H_9$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$(Cp^*Ir)_2B_4H_8$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$(Cp^*RuH)_2$		10		6		B_6H_{10}	C_6H_4
$C_2B_2H_4Me_2$	4n+4				Nido		
$(Cp^*Ir)_2B_4H_8$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$R_2C_2B_4H_4^{2-}$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$IrL_2(CO)(B_5H_8)$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$CuL_2B_5H_8$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$(Cp^*Ru)_2B_3H_6Co(CO)_4$		10		6		B_6H_{10}	C_6H_4
	4n+4				Nido		
$(Cp^*Co)_2B_2H_2S_2$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$C_2B_4H_8$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
$(Cp^*Ru)_2B_4H_{10}$	4n+4	10		6	Nido	B_6H_{10}	C_6H_4
CB_5H_9	4n+4	10		6	Nido	B_6H_{10}	C_6H_4

Table 1. Continued

Complex	Series	k value	n Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$(Cp^*Re)_2H_2B_4H_8$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$H_2Os_6(CO)_{18}$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(CpCo)_3B_3H_5$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Co)_2B_4H_2Br_4$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Ru)_2B_4H_8$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Ru)_3B_3H_8$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Ir)\ B_3H_5Co_2(CO)_5$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Ru)_2B_4H_8$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(CpCo)_3B_3H_3(CO)$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*Co)_2B_4H_6$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*ReH_2)\ (CO)B_4H_6$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(CpCo)_2B_2H_5Mo_2(CO)_6(I)$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*ReH_2)_2B_4H_4$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Ru)_2B_3H_4Co(CO)_3$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Re)_2B_4H_8$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Cr)_2B_4H_8$	4n-2	13	6	C^2C[M-4]	B_6H_4	C_6-2H
$(Cp^*Cr)_2B_4H_8$	4n-2	13	6	C^2C[M-4]	B_6H_4	C_6-2H
$(Cp^*Cr)_2(CO)_2B_4H_2$	4n-4	14	6	C^3C[M-3]	B_6H_2	C_6-4H
$(Cp^*Re)_2B_4H_4$	4n-4	14	6	C^3C[M-3]	B_6H_2	C_6-4H

Complex	Series	k value	n Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$Co_5(CO)_{14}B_2H$	4n+2	13	7	Closo	$B_7H_7^{2-}$	C_7H_2
$Bi_3Ni_4(CO)_6^{2-}$	4n+2	13	7	Closo	$B_7H_7^{2-}$	C_7H_2
$(Cp^*Co)_3B_4H_4$	4n+0	14	7	C^1C[M-6]	B_7H_7	C_7
$(Cp^*Mo)_2B_5H_9$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Cr)_2B_4H_7Co(CO)_3$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Re)_2B_6H_2Cl_5$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Ru)_3Co(CO)_3(BH)_3$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$Me_4C_4B_4H_4$	4n+4	14	8	Nido	B_8H_{12}	C_8H_4
$(Cp^*Ni)_4B_4H_4$	4n+4	14	8	Nido	B_8H_{12}	C_8H_4
$Bi_4Ni_4(CO)_6^{2-}$	4n+2	15	8	Closo	$B_8H_8^{2-}$	C_8H_2
$(CpCo)_4B_4H_4$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8
$(CpCo)_4B_4H_4$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8
$(Cp^*Re)_2B_4H_4\ Co_2(CO)_5$	4n-4	18	8	C^3C[M-5]	B_8H_4	C_8-4H
$(Cp^*Re)_2B_6H_6$	4n-4	18	8	C^3C[M-5]	B_8H_4	C_8-4H
$(Cp^*Re)_2B_6H_4Cl_2$	4n-4	18	8	C^3C[M-5]	B_4H_4	C_8-4H
$(Cp^*Rh)_2\ (Co)_3(CO)_8B_3H(Cl)$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8
$Cp^*Ni)_4B_5H_5$	4n+4	16	9	Nido	B_9H_{13}	C_9H_4
$(CpNi)_3CB_5H_6$	4n+4	16	9	Nido	B_9H_{13}	C_9H_4
$Bi_3Ni_6(CO)_9^{2-}$	4n+0	18	9	C^1C[M-8]	B_9H_9	C_9
$(Cp^*Re)_2B_7H_{11}$	4n+0	18	9	C^1C[M-8]	B_9H_9	C_9
$(Cp^*Re)_2B_7H_7$	4n-4	20	9	C^3C[M-6]	B_9H_5	C_9-4H

Complex	Series	k value	n Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$(C_6H_6)RuB_9H_9^{2-}$	4n+2	19	10	Closo	$B_{10}H_{10}^{2-}$	$C_{10}H_2$
$(C_6H_6)RuB_9H_9$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(CpCo)_3B_6H_7Co(CO)_2$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(Cp^*Co)_4B_6H_6$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(Cp^*Ru)_2(C_6H_6)RuB_7H_7$	4n-2	21	10	C^2C[M-8]	$B_{10}H_8$	C_{10}-2H
$(Cp^*Ru)_2(C_6H_6)RuB_7H_7$	4n-2	21	10	C^2C[M-8]	$B_{10}H_8$	C_{10}-2H
$(Cp^*Re)_2B_8H_8$	4n-4	22	10	C^3C[M-7]	$B_{10}H_6$	C_{10}-4H
$B_{11}H_{14}^-$	4n+4	20	11	Nido	$B_{11}H_{15}$	$C_{11}H_4$
$Ir(CO)(L_2)(S)B_9H_{10}$	4n+4	20	11	Nido	$B_{11}H_{15}$	$C_{11}H_4$
$B_{10}H_{12}TlMe^{2-}$	4n+4	20	11	Nido	$B_{11}H_{15}$	$C_{11}H_4$
$(Cp^*Re)_2B_9H_9$	4n-4	24	11	C^3C[M-8]	$B_{11}H_7$	C_{11}-4H
$(Cp^*W)_3HB_8H_8$	4n-8	26	11	C^5C[M-6]	$B_{11}H_5$	C_{11}-8H
$(CpNi)_2B_{10}H_{10}$	4n+2	23	12	Closo	$B_{12}H_{12}^{2-}$	$C_{12}H_2$
$(Cp^*Re)_2B_{10}H_{10}$	4n-4	26	12	C^3C[M-9]	$B_{12}H_8$	C_{12}-4H
$(Cp^*Re)_2B_{10}H_{10}$	4n-4	26	12	C^3C[M-9]	$B_{12}H_8$	C_{12}-4H

Table 1. Continued

Complex	Series	k value	n Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$(Cp^*Co)_2B_4H_6$	4n+2	11	6	Closo	$B_6H_6^{2-}$	C_6H_2
$(Cp^*ReH_2)(CO)B_4H_6$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(CpCo)_2B_2H_5Mo_2(CO)_6(I)$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*ReH_2)_2B_4H_4$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Ru)_2B_3H_4Co(CO)_3$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Re)_2B_4H_8$	4n+0	12	6	C^1C[M-5]	B_6H_6	C_6
$(Cp^*Cr)_2B_4H_8$	4n-2	13	6	C^2C[M-4]	B_6H_4	C_6-2H
$(Cp^*Cr)_2B_4H_8$	4n-2	13	6	C^2C[M-4]	B_6H_4	C_6-2H
$(Cp^*Cr)_2(CO)_2B_4H_2$	4n-4	14	6	C^3C[M-3]	B_6H_2	C_6-4H
$(Cp^*Re)_2B_4H_4$	4n-4	14	6	C^3C[M-3]	B_6H_2	C_6-4H
$(Cp^*Co)_3B_4H_4$	4n+0	14	7	C^1C[M-6]	B_7H_7	C_7
$(Cp^*Mo)_2B_5H_9$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Cr)_2B_4H_7Co(CO)_3$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Re)_2B_6H_2Cl_5$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(Cp^*Ru)_3Co(CO)_3(BH)_3$	4n-2	15	7	C^2C[M-5]	B_7H_5	C_7-2H
$(CpCo)_4B_4H_4$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8
$(CpCo)_4B_4H_4$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8
$(Cp^*Re)_2B_4H_4\ Co_2(CO)_5$	4n-4	18	8	C^3C[M-5]	B_8H_4	C_8-4H
$(Cp^*Re)_2B_6H_6$	4n-4	18	8	C^3C[M-5]	B_8H_4	C_8-4H
$(Cp^*Re)_2B_6H_4Cl_2$	4n-4	18	8	C^3C[M-5]	B_4H_4	C_8-4H
$(Cp^*Rh)_2(Co)_3(CO)_8B_3H(Cl)$	4n+0	16	8	C^1C[M-7]	B_8H_8	C_8

Table 2. Display of mainly capped series

Complex	Series	k value	n Value	Classification	Equivalent Borane	Equivalent Hydrocarbon
$(Cp^*Re)_2B_7H_{11}$	4n+0	18	9	C^1C[M-8]	B_9H_9	C_9
$(Cp^*Re)_2B_7H_7$	4n-4	20	9	C^3C[M-6]	B_9H_5	C_9-4H
$(C_6H_6)RuB_9H_9$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(CpCo)_3B_6H_7Co(CO)_2$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(Cp^*Co)_4B_6H_6$	4n+0	20	10	C^1C[M-9]	$B_{10}H_{10}$	C_{10}
$(Cp^*Ru)_2(C_6H_6)RuB_7H_7$	4n-2	21	10	C^2C[M-8]	$B_{10}H_8$	C_{10}-2H
$(Cp^*Ru)_2(C_6H_6)RuB_7H_7$	4n-2	21	10	C^2C[M-8]	$B_{10}H_8$	C_{10}-2H
$(Cp^*Re)_2B_8H_8$	4n-4	22	10	C^3C[M-7]	$B_{10}H_6$	C_{10}-4H
$(Cp^*Re)_2B_9H_9$	4n-4	24	11	C^3C[M-8]	$B_{11}H_7$	C_{11}-4H
$(Cp^*W)_3HB_8H_8$	4n-8	26	11	C^5C[M-6]	$B_{11}H_5$	C_{11}-8H
$(CpNi)_2B_{10}H_{10}$	4n+2	23	12	Closo	$B_{12}H_{12}^{2-}$	$C_{12}H_2$
$(Cp^*Re)_2B_{10}H_{10}$	4n-4	26	12	C^3C[M-9]	$B_{12}H_8$	C_{12}-4H
$(Cp^*Re)_2B_{10}H_{10}$	4n-4	26	12	C^3C[M-9]	$B_{12}H_8$	C_{12}-4H

3. Conclusion

Capped clusters are relatively common among transition metal carbonyl complexes. On the other hand, such capped clusters are rare in stable borane clusters. In this work, by using the 4n series method, it has been found that capped clusters are prevalent in metalloborane complexes. The capped clusters ranged from 4n+0 to 4n-8 series. This clearly illustrates the fact that metal fragments have a tendency of stabilizing the fragile capped boranes. The 4n series method is extremely useful in categorizing skeletal atoms, molecules, fragments and clusters.

Acknowledgement

The financial support by the University of Nambia and NAMSOV, Namibia is greatly appreciated. Gratitude is also extended to Mrs Merab Kambamu Kiremire for assisting in proof reading the paper.

References

Callahan, K. P., & Hawthorne, M. F. (1974). New Chemistry of Metallocarboranes and Metalloboranes. *Pure and Appl. Chem., 39*(4), 475-495. http://dx.doi.org/10.1351/pac197439040475

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. Chem. Soc., Dalton*, 1788-1797.

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. Chem. Soc., Dalton*, 1788-1797. http://dx.doi.org/10.1039/DT9810001788

Fehlner, T. P. (2002). A Systematic Approach to Varied Roles of Transition Metals in Metallaborane Chemistry. *PINSA,*

68, *A*(6), 579-596.

Grimes, R. N. (1974). Recent Studies of Metalloborane Cage Compounds Derived from Small Carboranes. *Pure and Appl. Chem.*, *39*(4), 455-474. http://dx.doi.org/10.1351/pac197439040455

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

Kiremire, E. M. (2015a). Isolobal Series of Chemical Fragments. *Orient. J. Chem.*, *31*(spl. Edn), 59-70.

Kiremire, E. M. R. (2015b). Capping and Decapping Series of Boranes. *Int. J. Chem. 7*(2), 186-197. http://dx.doi.org/10.5539/ijc.v7n2p186

McGlinnchey, M. J., & Hopf, H. (2011). Reciprocal polyhedral and the Euler relationship: Cage hydrocarbons, C_nH_n and Closo-boranes $B_xH_x^{2-}$. *Beilstein J. Org. Chem.*, *7*, 222-233. http://dx.doi.org/10.3762/bjoc.7.30

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*(9), 311-319. http://dx.doi.org/10.1021/ar00105a003

Mingos, D. M. P. (1991). Theoretical aspects of metal cluster chemistry. *Pure and Appl. Chem.*, *83*(6), 807-812. http://dx.doi.org/10.1351/pac199163060807

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

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