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Categorization of Metalloboranes using Skeletal Numbers

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Article Info

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Abstract

Metalloboranes have been analyzed and categorized using skeletal numbers. Skeletal numbers are extremely helpful in categorizing chemical clusters literally ranging from a single to an infinite number of skeletal elements of the main group and transition metals. The method involves decomposing a cluster formula comprising of a number of skeletal elements using skeletal numbers into a single whole number (K). Knowing the number of skeletal elements in a cluster (n), the K(n) parameter is obtained. The type of series S=4n+q is readily derived from the K(n) parameter. This is followed by the derivation of the capping parameter, $Kp=C^yC[Mx]$ and the categorization parameter $K^*=C^y+D^z$ where y+z=n, the number of skeletal elements in the cluster. The cluster valence electrons can be calculated from the relationship VE=12y+14z+2 for transition metal clusters or VE=2y+4z+2 for main group elements or VE=2y+4z+2+10m where m=the number of transition metal elements present when a cluster has a mixture of elements from the main group and transition metals. The categorization parameter can also act as a guide to predict a possible symmetry of a cluster and to construct an isomeric skeletal shape of a cluster. This approach was used to categorize more than 20 metalloborane clusters as well as a few non-metalloborane clusters for comparison purposes. The isomeric skeletal structures so constructed obey the 8 or 18 electron rule as defined by coordination theory.

Keywords: Capping theory; Capping parameter; Categorization parameter; Coordination theory; Skeletal number; 4N series.

Introduction

In chemistry, some clusters have been categorized as closo, nido, arachno, hypho and klado, among others [1-7]. In this regard, the polyhedral skeletal electron pair theory (PSEPT) has been extremely useful in this process [8-11]. On closer analysis, it was observed that the transition metal clusters follow the series S=14n+q while the main group element clusters follow a parallel series S=4n+q where n represents the number of skeletal elements in a cluster and q is a numerical determinant that determines the category of the cluster. For categorization of clusters, it was found to be more convenient to utilize the S=4n+q for both main group and transition metal clusters except when the cluster valence electrons are being calculated whereby S=14n+q is applied for transition metal clusters [3,4]. The skeletal numbers which were derived from the series have been found to be extremely useful in the derivation of chemical graph theory and equations for calculating cluster valence equations [6]. In addition, they can be used as a guide to predict the possible geometrical and graphical structures of clusters [6]. Furthermore, skeletal numbers can be regarded as individual contributions to the skeletal cluster number parameter K(n) by the elements working together as a 'team' in the cluster. The 4N series approach was earlier applied to categorize metalloboranes. In this paper, the application of skeletal numbers to categorize metalloboranes will be demonstrated.

Results and Discussions

The application of the skeletal number to categorizing clusters is a new concept [5] and the K(n) parameter is usually a whole number. Since this approach is new, the skeletal numbers have been reproduced in table 1.

SN=K	V=2K	G	V+G	3d	4d	5d			
7.5	15	3	18	Sc	Y	Lu			
7.0	14	4	18	Ti	Zr	Hf			
6.5	13	5	18	V	Nb	Ta			
6.0	12	6	18	Cr	Mo	W			
5.5	11	7	18	Mn	Tc	Re			
5.0	10	8	18	Fe	Ru	Os			
4.5	9	9	19	Co	Rh	Ir			
4.0	8	10	18	Ni	Pd	Pt			
3.5	7	11	18	Cu	Ag	Au			
3.0	6	12	18	Zn	Cd	Hg			
				2s	3s	4s	5s	6s	7s
3.5	7	1	8	Li	Na	K	Rb	Cs	Fr
3.0	6	2	8	Be	Mg	Ca	Sr	Ba	Ra
2.5	5	3	8	B	Al	Ga	In	Tl	
2.0	4	4	8	C	Si	Ge	Sn	Ba	
1.5	3	5	8	N	P	As	Sb	Bi	
1.0	2	6	8	O	S	Se	Te	Po	
0.5	1	7	8	F	Cl	Br	I	At	
0.0	0	8	8	Ne	Ar	Kr	Xe	Rn	

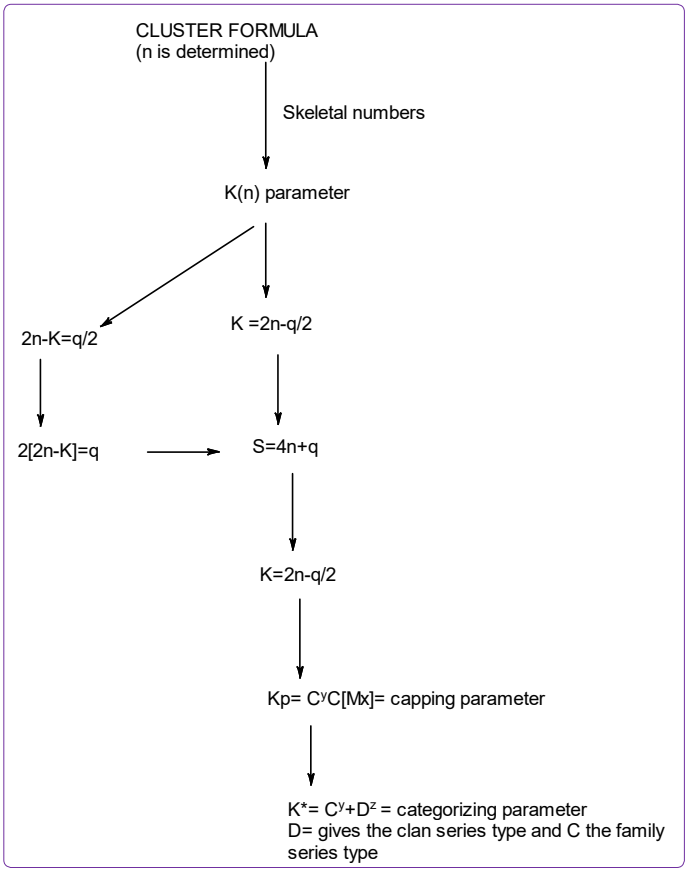
Table 1. The skeletal numbers of the main group and transition element

SN: Skeletal Number; V: Valence; G: Group valence electrons.

The Condensed outline of the Method for categorization of Clusters

The first step in cluster categorization is to convert the cluster formula into a number. This approach focuses on the compounds or clusters from the main group or transition metals. This is now possible since each of the periodic group of elements was assigned a skeletal number as well as the ligands. The determination of the K value for a ligand is simple; LIGANDS: FOR EVERY 1 ELECTRON DONATED, K=-0.5 AND FOR EVERY 1 ELECTRON REMOVED, K=+0.5. So the cluster number K is readily calculated for any cluster with or without ligands. This is summarized in Scheme 1 and illustrated by in the following examples and worked out exercises most of them with detailed explanations.

In the examples 1-7, the use of skeletal numbers to categorize clusters has been highlighted. A cluster is categorized into a CLAN series D^z and the family series C^y via the categorization parameter $K^*= =C^y+D^z$. The same parameter can be used to calculate the cluster valence electrons VE=12y+14z+2 for transition metals and VE=2y+4z+2 for main group elements. The same parameter can be used as a guide to predict the shape of the cluster. For instance, $K^*=C^0+D^6$, is an octahedral symmetry, $K^*=C^1+D^6$ is a mono-capped octahedron, $K^*=C^2+D^6$; bi-capped octahedron, $K^*=C^3+D^6$; is a tri-capped octahedron and so on. Also a list of worked out examples mainly metabollanes from 1 to 22 were analyzed and categorized into clans and families and are given in table 2. Their graphical skeletal structures constructed according to skeletal valence principle: while they may involve inflated cluster valence electrons, they generate the correct cluster formulas, they act as a guide for predicting possible structure of the cluster, and above all, the capping cluster formula which is so accurate in determining cluster valence electrons, is based on the same principles.



Scheme 1. Derivation of the series formula and categorizing parameter.

Coordination Theory

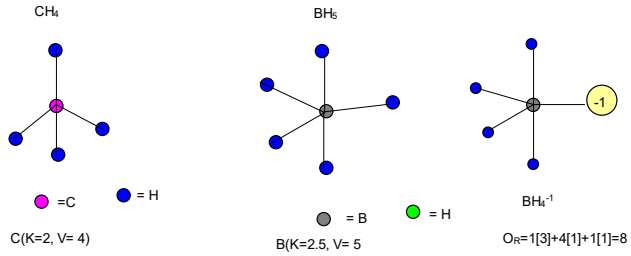
According to the 4N series approach to clusters it makes understanding much easier if we regard each linkage line to a skeletal element(node) as donating 1 electron to the nodal point. In that way, methane, CH_4 can be explained as the central carbon atom which has its own 4 electrons receiving donations from the 4H atoms in order to attain the 8-electron configuration. Each of the 4 hydrogen ligands has donated 1 electron to the node and the octet rule has been obeyed. This is the way coordination theory is viewed according to the 4N series approach. This is illustrated in EX-1A. However if we consider BH5, according to the 4N series approach, the node(B) has 3 valence electrons and the addition of 5 electrons to the node will give the node a total of 8 electrons enabling the node to achieve the eighteen electron rule. In fact, the cluster BH_5 appears in a disguised form as BH_4^-. According to the4N series method, there is no difference between a charge of –ve one and 1H ligand donor.

Examples 1-7: The use of skeletal numbers to categorize clusters.

Example 1

CH_4: K=1[2]-4[0.5]=0, n=1,
K(n)=0(1),
2[1]-0=2
S=4n+4
K=2n-2
$Kp=C^{-1}C[M2]$
$K^*=C^{-1}+D^2$
VE=2y+4z+2=2[-1]+4[2]+2=8
VF=1[4]+4[1]=8

BH_5:1[2.5]-5[0.5]=0,n=1
K(n)=0(1)
S=4n+4
K=2n-2
$K^*=C^{-1}+D^2$
VE=2y+4z+2=2[-1]+4[2]+2=8
VF=8



C(K=2, V= 4)

COORDINATION THEORY
Octet rule (O_R= = 1[4]+4[1]=8; Obeys octet rule

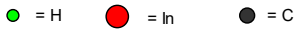
B(K=2.5, V= 5

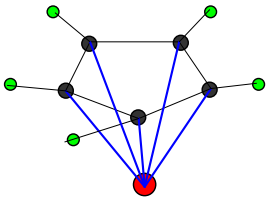
COORDINATION THEORY
O_R=1[3]+5[1]= 8; Obeys octet rule

O_R=1[3]+4[1]+1[1]=8

COORDINATION THEORY

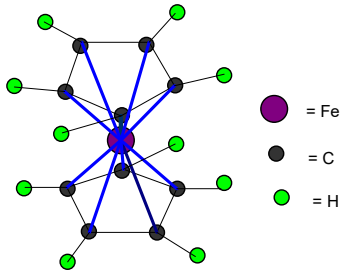
EX-1





COORDINATION THEORY
Indium: Octet rule, O_R= 1[3]+5[1]=8
There are 3 electrons from indium 5 donated from 5 carbon atoms each donating 1electron.
Octet rule is obeyed.

EX-1 B. Induim cluster, CpIn

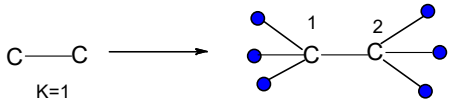


EX-1 C. Ferrocene, $Fe(C_5H_5)_2$

Eighteen electron rule (EER)=1[8]+5[1]+5[1]= 18. Eighteen electron rule obeyed.

Example 2
C_2H_6:K=2[2]-6[0.5]=1,
K(n)=1(2)
2[2]-1=3
S=4n+6
K=2n-3
$K=C^{-2}C[M4]$
$K^*=C^{-2}+D^4$
$K^*=C^y+D^z$
y= -2, z= 4
VE=2y+4z+2 =2[-2]+4[4]+2=14
VF=2[4]+6=14

O_R1=1[4]+1[1]+3[1]=8
O_R2=1[4]+1[1]+3]1]=8



C(K=2, V=4)

EX-2: C_2H_6

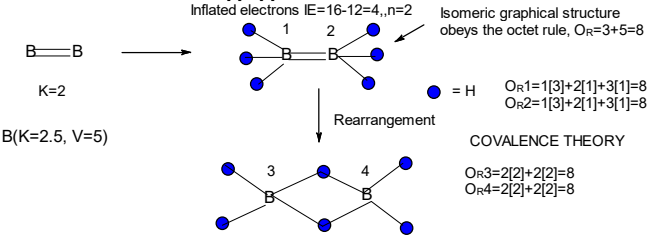
Example 3

B_2H_6: K=2[2.5]-6[0.5]=2,n=2
K(n)=2(2)
2[2]-2=2
S=4n+4
K=2n-2
$Kp=C^{-1}C[M3]$
$K^*=C^{-1}+D^3$;$K^*=C^y+D^z$
VE=2y+4z+2=2[-1]+4[3]+2=12
VF=2[3]+6[1]=12

Pseudo valence electrons=8[2]=16
VE=2[3]+6[1]=12
Inflated electrons IE=16-12=4,,n=2

CO-ORDINATION THEORY

Isomeric graphical structure obeys the octet rule, O_R=3+5=8



O_R1=1[3]+2[1]+3[1]=8
O_R2=1[3]+2[1]+3[1]=8

B(K=2.5, V=5)

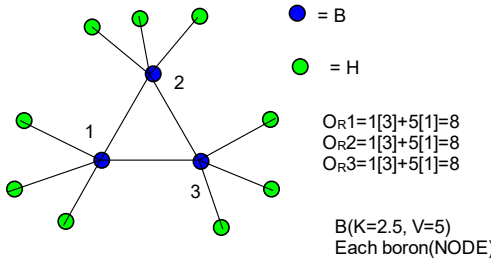
COVALENCE THEORY

O_R3=2[2]+2[2]=8
O_R4=2[2]+2[2]=8

EX-3: B_2H_6

Example 4

B_3H_9: K=3[2.5]-9[0.5]=3, n=3
K(n)=3(3)
2[3]-3=3
S=4n+6
K=2n-3
$Kp=C^{-2}C[M5]$
$K^*=C^{-2}+D^5$
VE=2y+4z+2=2[-2]+4[5]+2=18
VF=3[3]+9[1]=18



O_R1=1[3]+5[1]=8
O_R2=1[3]+5[1]=8
O_R3=1[3]+5[1]=8

B(K=2.5, V=5)
Each boron(NODE) has 5 linkages.

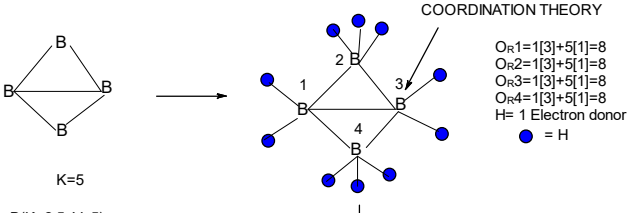
Isomeric structure of B_3H_9

Example 5

Pseudovalence electrons(PSVE)=[5+10]x2=30
VE=4[3]+10=22
Inflated valence electrons=30-22=8, n=4

B_4H_{10}: K=4[2.5]-10[0.5]=5

COORDINATION THEORY

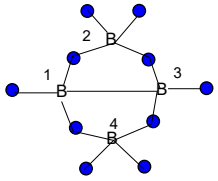


O_R1=1[3]+5[1]=8
O_R2=1[3]+5[1]=8
O_R3=1[3]+5[1]=8
O_R4=1[3]+5[1]=8
H= 1 Electron donor

B(K=2.5, V=5)

Rearrangement

COVALENCE THEORY



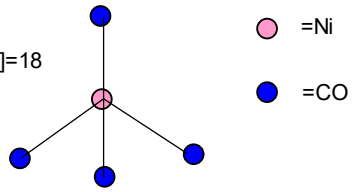
O_R1=4[2]=8
O_R2=4[2]=8
O_R3=4[2]=8
O_R4=4[2]=8

Example 6

$Ni(CO)_4$: K=1[4]-4[1]=0,n=1
K(n)=0(1)
2[1]-0=2
S=4n+4
K=2n-2
$Kp=C^{-1}C[M2]$
$K^*=C^{-1}+D^2$
VE=12y+14z+2=12[-1]+14[2]+2=18
VF=1[10]+4[2]=18

Eighteen electron rule (EER)

EER=1[10]+4[2]=18

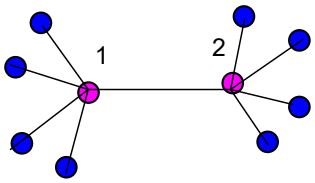


EX-6:$Ni(CO)_4$

Ni(K=4, V=8); nickel has 8 skeletal valences.
It can accommodate 4 two-electron donors.

Example 7

$Co_2(CO)_8$:K=2[4.5]-8[1]=1,n=2
K(n)=1(2)
2[2]-1=3
S=4n+6
K=2n-3
$Kp=C^{-2}C[M4]$
$K^*=C^{-2}+D^4$
VE=12y+14z+2=12[-2]+14[4]+2=34
VF=2[9]+8[2]=18+16=34



EER1=1[9]+1[1]+4[2]=18
EER2=1[9]+1[1]+4[2]=18

EX-7

Co(K=4.5, V=9)
Alternatively, we can regard 1 Co providing 4.5 skeletal numbers and 2 Co skeletal elements providing 9 skeletal numbers each of which can accomodate 2 valence electrons. This is illustrated in the figure of example 6. Each skeletal number represents 2 electrons. Hence, we have a Co-Co metal-metal bond containing 2 electrons and 8 CO ligands each donating a pair of electrons, giving a total of 9 electron pairs. On the other hand, 1 cobalt element has 9 skeletal valences of single electron donors and hence we get a complex such as CoH_5^{4-}. According to the 4N series formalism, there is no distinction between a H atom donating a single electron, and an electron charge donation.

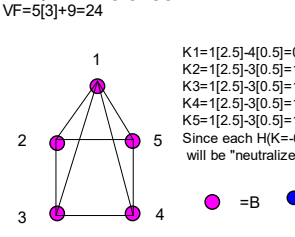
All the isomeric graphical structures are constructed in line with coordination theory and they obey the octet rule for main group elements or eighteen electron rules for transition metals.

Categorization of Clusters into Clans and Families

The sample of clusters mainly metaboranes were categorized into clans (D^z) and families (C^y). As can be seen from table 2, they range from D^4 to D^{15} and with families from C^{-2} to C^5. The following clan series of the metalloboranes were identified, $D^4(1)$, $D^5(3)$, $D^6(8)$, $D^7(4)$, $D^9(1)$, $D^{10}(1)$, $D^{11}(1)$, $D^{12}(1)$ and $D^{15}(1)$. Also some D^6 samples were added for comparative purposes. They belong to the family series C^1, C^2, C^3, C^4, C^7 and C^8 of the D^6 clan. The isomeric skeletal shape is also provided with explanation for each of the clusters analyzed and categorized. The corresponding isomeric skeletal structures are from figures 1-24. The categorization symbol $K^*=C^y+D^z$ can be viewed as representing a nucleus, D^z and the outer shell C^y. The valence electrons of the cluster comes from the nuclear component which follow the VE1=S=14z+2 while the capping electrons are given by VE2=12y giving the total valence electrons VE=VE2+VE1=12y+14z+2.

The added D^6 clan series have families ranging from C^1 to C^8.The isomeric graphical skeletal structures of clusters adopted in this paper are constructed based on the simple coordination theory as defined in this work. Once such a structure has been constructed, the original cluster formula usually emerges from it. Furthermore, each node obeys the 8-electron or 18-electron rule if it is from the main group or transition metals respectively. Each of the linkage in the cluster represents a 1-electron donor to the node (vertex). Each node is linked to the number of lines in accordance with the skeletal valence of the fragment at the vertex. The decomposition of a cluster formula into a number followed by the categorization of the cluster into clan and family type ($K^*=C^y+D^z$) is well explained in each of the 22 cluster examples selected.

1. B_5H_9:K=5[2.5]-9[0.5]=8,n=5
K(n)=8(5)
2[5]-8=2
S=4n+4(nido family)
K=2n-2
$Kp=C^{-1}C[M6]$
$K^*=C^{-1}+D^6$
One skeletal element is missing in order for it to attain an octahedral symmetry.
The ideal expected shape is a square pyramid C_{4v}..
VE=2y+4z+2=2[-1]+4[6]+2=24
VF=5[3]+9=24



K1=1[2.5]-4[0.5]=0.5
K2=1[2.5]-3[0.5]=1
K3=1[2.5]-3[0.5]=1
K4=1[2.5]-3[0.5]=1
K5=1[2.5]-3[0.5]=1
Since each H(K=-0.5), K=1 will be "neutralized" by 2H atoms.

=B

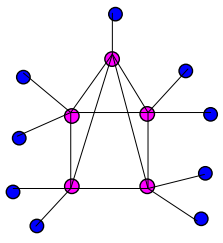


Figure 1. Isomeric graphical shape of B_5H_9. The skeletal numbers apart from being used to predict the shape of the skeletal elements, can also be used as a guide to sketch the tentative ligand distributions onto the skeletal elements. Since the ligands carry negative skeletal numbers, their addition to a skeletal node should result in the node having the net K value of zero. That is, the node has attained either the 8 or 18 electron rule. The K values of the nodes reflect the number of ligands needed to neutralize the K value of the node to zero.

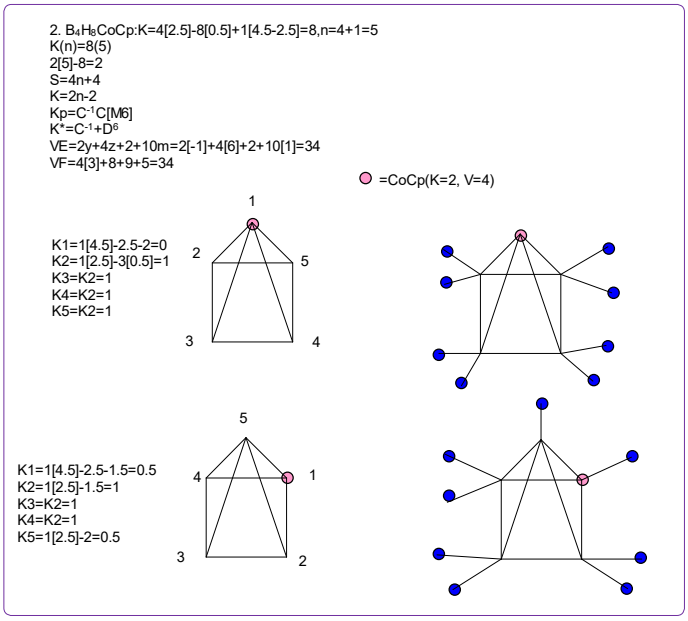


Figure 2. Isomeric structures of B_4H_4CoCp. In this example, skeletal numbers have been applied as a guide to determine the possible distributions of the ligands at every node. Alternatively, if the skeletal valence of each node is known, then the ligands are readily added to the node. In this case, CoCp*(K=4.5-2.5=2. V=4). This means the fragment has 4 linkages while boron node B K=2.5, V=5 will have 5 linkages. There are 3 linkages already at the base. For the boron node the base needs 2 linkages to satisfy the valence rule and for the CoCp* fragment of valence 4, only one linkage to be added on is needed.

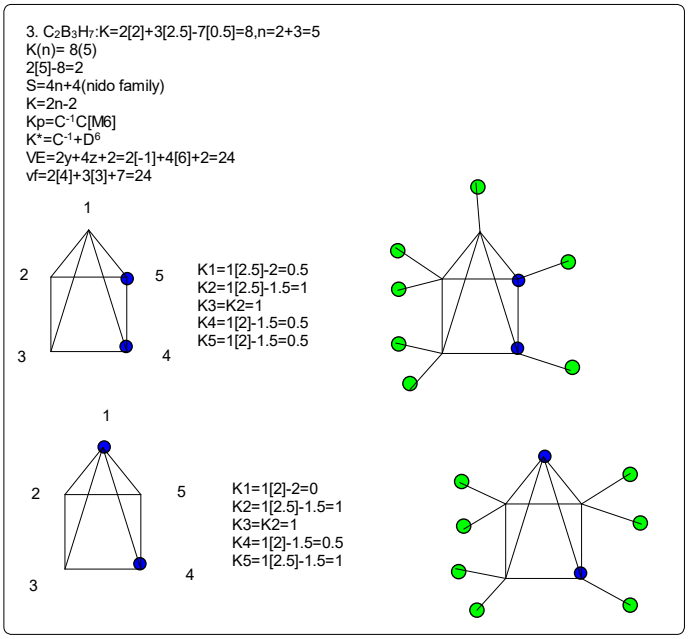


Figure 3. Isomeric structures of $C_2B_3H_7$. Skeletal numbers have been applied to the skeletal elements. Also the skeletal valences at each node could be used. For the skeletal elements boron, K=2.5, V=5. That means each boron node has 5 linkages while carbon with K=2, V=4 has 4 linkages. With this information, the hydrogen atoms can easily be assigned to the skeletal atoms.

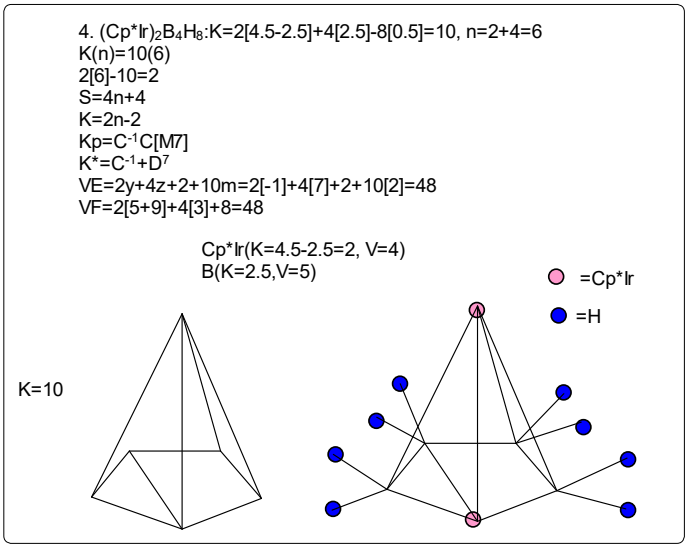


Figure 4. Isomeric skeletal structure of $(Cp^*Ir)_2B_4H_8$. The skeletal valence rule can assist us distribute the ligands onto the node points. This is easier than using skeletal numbers as in the examples discussed earlier. At the Cp*Ir nodal point, the valence is 4 and hence there will be 4 linkages. On the other hand at the boron(B) node, the skeletal valence is 5, and so there will be 5 linkages.

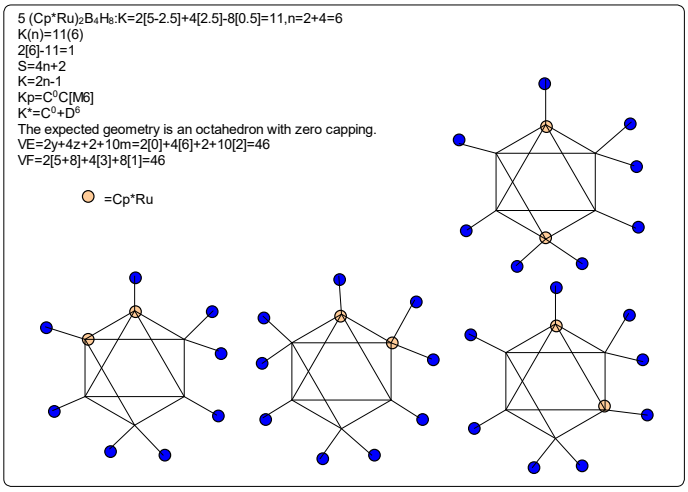


Figure 5. Isomeric skeletal structures of $(Cp^*Ru)_2B_4H_8$. Ligand distribution follows the skeletal valence rule. For instance, RuCp*(K=5-2.5=2.5, V=2K=5), and B(K=2.5, V=5). This means that both RuCp* and B will each have 5 linkages. Thus RuCp* is equivalent to B in terms of connectivities. When the valence rule is followed, the skeletal elements and the ligands fit so well as to generate the parent cluster formula.

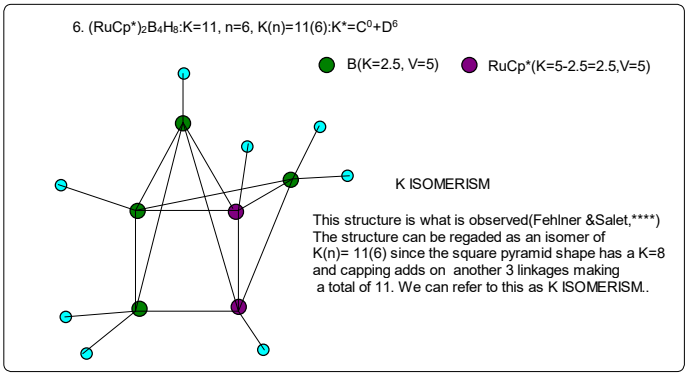


Figure 6. The graphical isomeric skeletal structure of $(RuCp^*)_2B_4H_8$. The skeletal valence= 5 and each fragment will have 5 linkages at each node. This allows us to distribute the ligands accordingly. This is shown in figure 6.

7. $(Cp^*Cr)_2B_4H_8$:K=2[6-2.5]+4[2.5]-8[0.5]=13,n=2+4=6
K(n)=13(6)
2[6]-13=-1
S=4n-2
K=2n+1
Kp=C^2C[M4]
K*=C^2+D^4
Bi-capped tetrahedral symmetry(unsaturated,K=7 not 6).
VE=2y+4z+2+10m=2[2]+4[4]+2+10[2]=42
VF=2[5+6]+4[3]+8[1]=42
Cp*Cr(K=6-2.5=3.5, V=7), B(K=2.5, V=5)

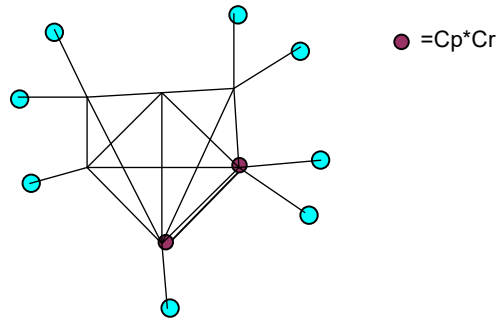


Figure 7. Isomeric skeletal structure of $(Cp^*Cr)_2B_4H_8$. Accordingly to the capping series, D^4 follows the S=4n+2 family of clusters. Hence, its linkages are given by K=2n-2=2[4]-1=7. That is, it is a tetrahedron linked by 7 linkages instead of the normal 6 linkages. The double capping will then be superimposed onto the 7 linked tetrahedral shape. The fragment Cp*Cr(K=6-2.5=3,5, V=7). The fragment will possess 7 skeletal valences. This is reflected in the figure 7. The fragment Cp*Cr(K=3.5, V=7) has a valence of 7. Hence, it will have seven connectivities around it. Likewise, boron will also have 5 connectivities.

8. $(Cp^*W)_3B_8H_9$: K=3[6-2.5]+8[2.5]-9[0.5]=26,n=3+8=11
K(n)=26(11)
2[11]-26=-4
S=4n-8
K=2n+4
Kp=C^5C[M6]
K*=C^5+D^6
This is a penta-capped octahedron.
VE=2y+4z+2+10m=2[5]+4[6]+2+10[3]=66
VF=3[5+6]+8[3]+9[1]=66

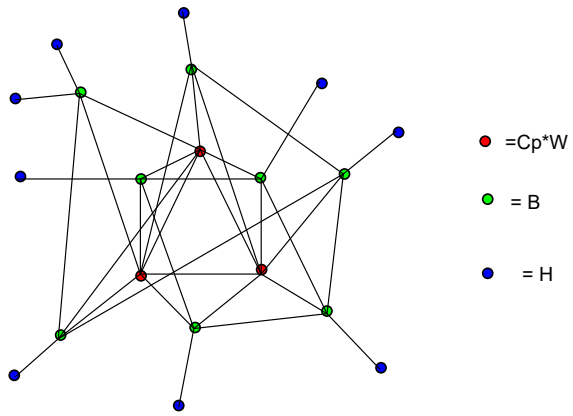


Figure 8. Isomeric skeletal structure of $(WCp^*)_3B_8H_9$. The fragment WCp*(K=6-2.5=3.5, V=7) has a skeletal valence of 7. Hence, it will have 7 connectivities around it whereas boron will have 5 connectivities since its skeletal number is 2.5.

9. $Mn(CO)_4B_3H_8$:K=1[5.5-4]+3[2.5]-8[0.5]=5,n=1+3=4
K(n)=5(4)
2[4]-5=3
S=4n+6
K=2n-3
Kp=$C^{-2}C$[M6]
K*=C^{-2}+D^6
VE=2y+4z+2+10m=2[-2]+4[6]+2+10[1]=32
VF=1[7+8]+3[3]+8[1]=32

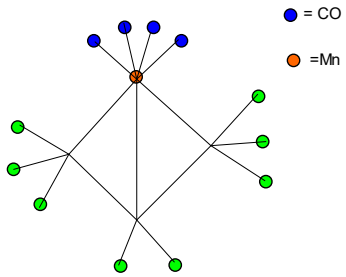


Figure 9. Isomeric skeletal structure of $Mn(CO)_4B_3H_8$. The fragment $Mn(CO)_4$(K=5.5-4=1.5, V=3). This means it will have 3 linkages to it. The boron will portray its usual connectivity of 5.

10 $(Cp^*Re)_2B_4H_8$:K=2[5.5-2.5]+4[2.5]-8[0.5]=12,n=2+4=6
K(n)=12(6)
2[6]-12=0
S=4n+0
K=2n+0
Kp=C^1C[M5]
K*=C^1+D^5
This symbol predicts a mono-capped trigonal bipyramid.
VE=2y+4z+2+10m=2[1]+4[5]+2+10[2]=44
VF=2[5+7]+4[3]+8[1]=44

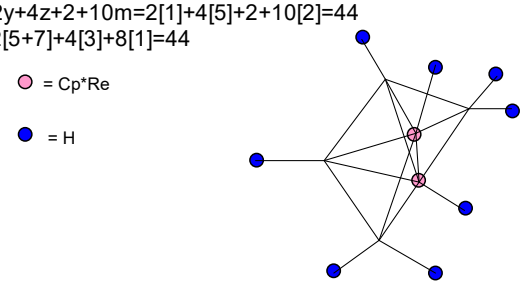


Figure 10. Isomeric structure of $(Cp^*Re)_2B_4H_8$. The fragment ReCp*(K=5.5-2.5=3, V=6) has a valence of 6. Hence, it will have 6 linkages around it. The boron element will have the usual 5 skeletal linkages.

11. $(Cp^*Re)B_3H11$:K=1[5.5-2.5]+3[2.5]-11[0.5=5, n=1+3=4
K(n)=5(4)
2[4]-5=3
S=4n+6
K=2n-3
Kp=$C^{-2}C$[M6]
K*=C^{-2}+D^6
The cluster is 2 skeletal elements short to attain an octahedral symmetry.
VE=2y+4z+2+10m=2[-2]+4[6]+2+10[1]=32

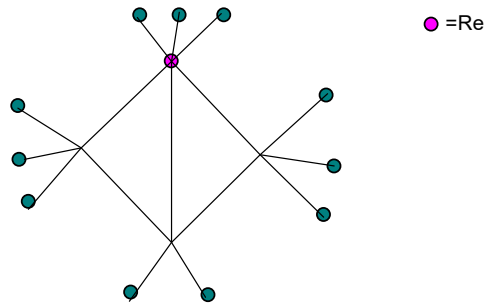


Figure 11. Isomeric skeletal structure of $Gp^*ReB_3H_{11}$. The fragment ReCp*(K=5.5-2.5=3, V=6) has a skeletal valence of 6. These are taken up by the 3 linkages and 3 hydrogen atoms. Boron has 5 linkages.

12. $Cp^*FeB_4H_{11}$:K=1[5-2.5]+4[2.5]-11[0.5]=7,n=1+4=5
K(n)=7(5)
2[5]-7=3
S=4n+6
K=2n-3
$Kp=C^{-2}C[M7]$
$K^*=C^{-2}+D^7$
VE=2y+4z=2+10m=2[-2]+4[7]+2+10[1]=36
VF=36
The cluster is left with 2 skeletal capping elements to become a pentagonal bipyramid.

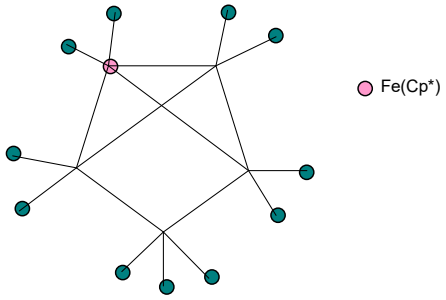


Figure 12. Isomeric skeletal structure of $(Cp^*Fe)B_4H_{11}$.

13.$(Cp^*Re)_2B_6H_6$:K=2[5.5-2.5]+6[2.5-0.5]=18, n=2+6=8
K(n)=18(8)
2[8]-18=-2
S=4n-4
K=2n+2
$Kp=C^3C[M5]$; $K^*= C^3+D^5$
Tri-capped trigonal bi-pyramid.
VE=2y+4z+2+10m=2[3]+4[5]+2+10[2]=48
VF=2[5+7]+6[3+1]=48

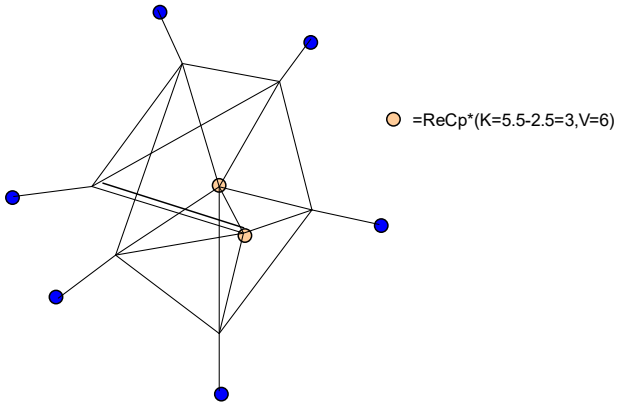


Figure 13. Isomeric skeletal structure of $(ReCp^*)_2B_6H_6$.

14. $(Cp^*Re)_2B_7H_7$: K=2[5.5-2.5]+7[2.5-0.5]=20,n=2+7=9
K(n)=20(9)
2[9]-20=-2
S=4n-4
K=2n+2
$Kp=C^3C[M6]$
$K^*=C^3+D^6$
Tri-capped octahedral geometry.
VE=2y+4z+2+10m=2[3]+4[6]+2+10[2]=6++24+2+20=52
vf=2[5+7]+7[3+1]=52

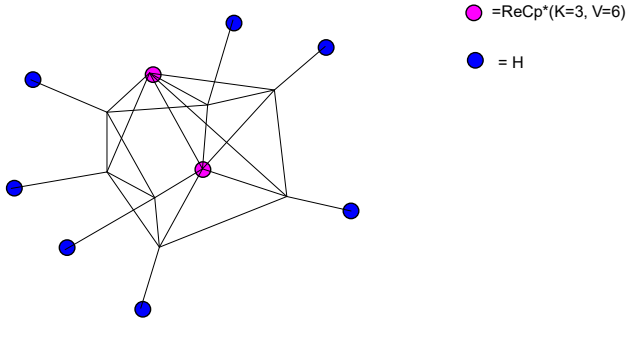


Figure 14. Isomeric skeletal structure of $(Cp^*Re)_2B_7H_7$.

15. $Fe(CO)_4B_6H_{10}$: K=1[5-4]+6[2.5]-10[0.5]=11,n=1+6=7
K(n)=11(7)
2[7]-11=3
S=4n+6
K=2n-3
$Kp=C^{-2}C[M9]$
$K^*=C^{-2}+D^9$
VE=2y+14z+2+10m=2[-2]+4[9]+2+10[1]=44
VF=1[8+8]+6[3]+10[1]=44

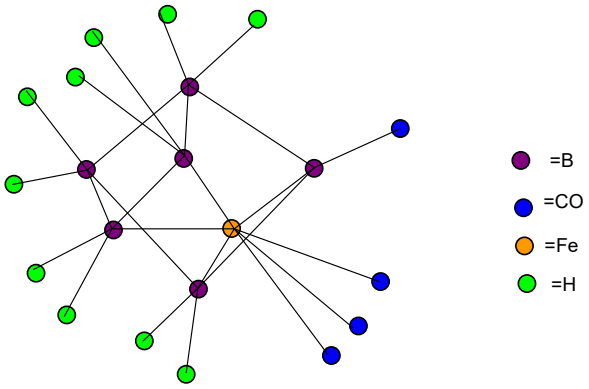


Figure 15. Isomeric skeletal structure of $Fe(CO)_4B_6H_{10}$.

16.$(CpCo)_3B_5H_5$:K=3[4.5-2.5]+5[2.5]-5[0.5]=16,n=3+5=8
K(n)=16(8)
2[8]]-16= 0
S=4n+0
K=2n+0
$Kp=C^1C[M7]$
$K^*=C^1+D^7$
Mono-capped pentagonal bipyramid.
VE=2y+4z+2+10m=2[1]+4[7]+2+10[3]=62
VF=3[5+9]+5[3]+5[1]=62

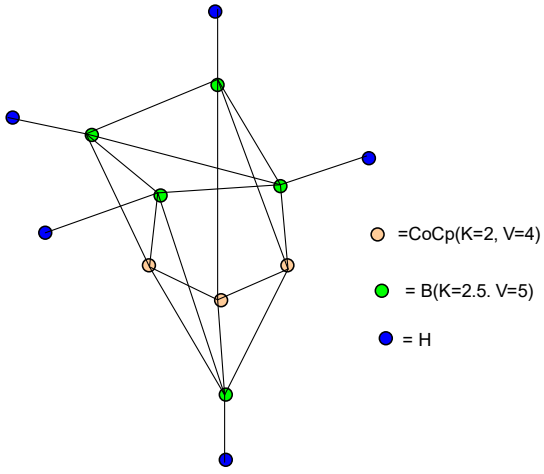


Figure 16. Isomeric skeletal structure of $(CpCo)_3B_5H_5$.

17. $FeB_7H_{12}(CO)_4^{-1}$:K=1[5]+7[2.5]-12[0.5]-4[1]-1[0,5]=12,n=1+7=8
K(n)=12(8)
2[8]-12=4
S=4n+8
K=2n-4
$Kp=C^{-3}C[M11]$
$K^*=C^{-3}+D^{11}$
VE=2y+4z+2+10m=2[-3]+4[11]+2+10[1]=50
VF=1[8]+7[3]+12[1]+4[2]+1[1]=50

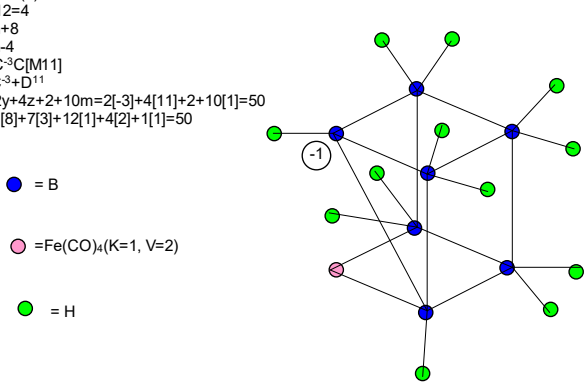


Figure 17. isomeric skeletal structure of $FeB_7H_{12}(CO)_4^{-1}$.

18. $(CpCo)B_5H_9$:K=1[4.5-2.5]+5[2.5]-9[0.5]=10,n=1+5=6

K(n)=10(6)

2[6]-10=2

S=4n+4(nido)

K=2n-2

Kp=C^{-1}C[M7]

K*=C^{-1}+D^7

VE=2y+4n+2+10m=2[-1]+4[7]+2+10[1]=38

VF=1[5+9]+5[3]+9[1]=38

The isomeric structure has not been provided as it can be generated in the same procedures as above ones.

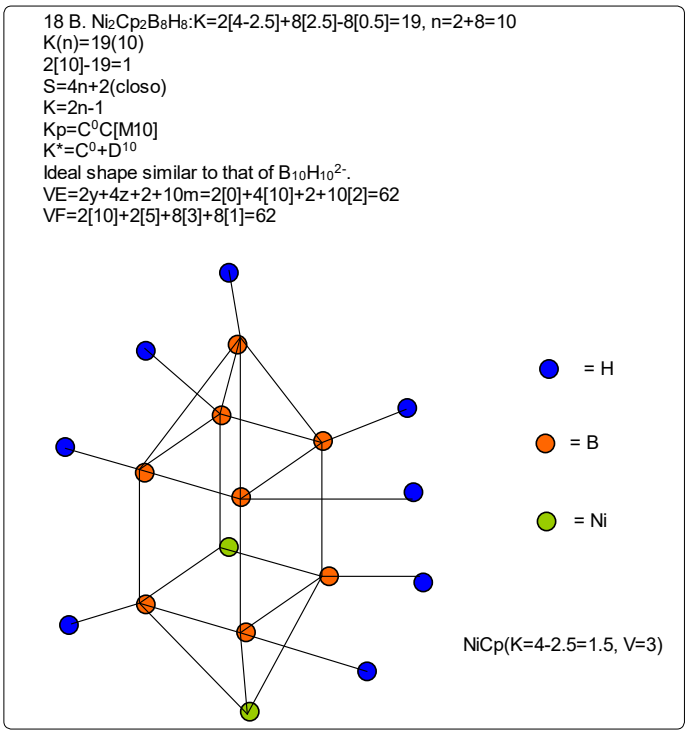


Figure 18. Isomeric skeletal structure of $(NiCp)_2B_8H_8$.

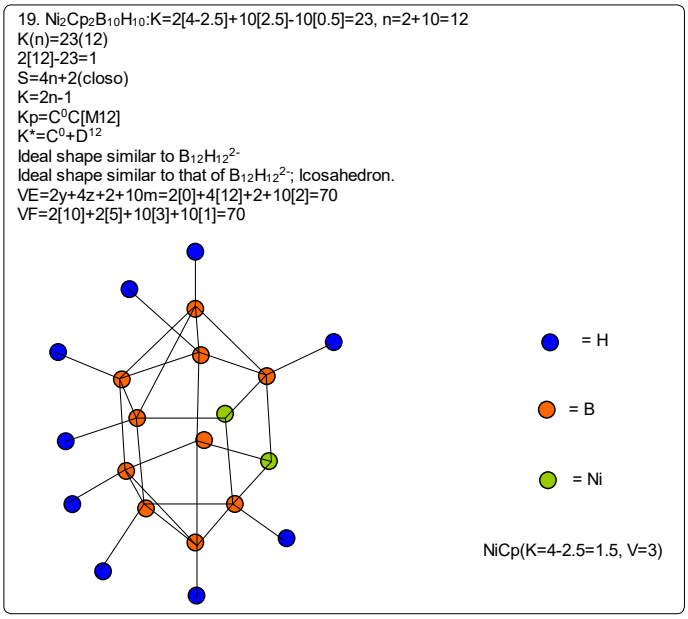


Figure 19. Isomeric graphic structure for $(NiCp)_2B_{10}H_{10}$.

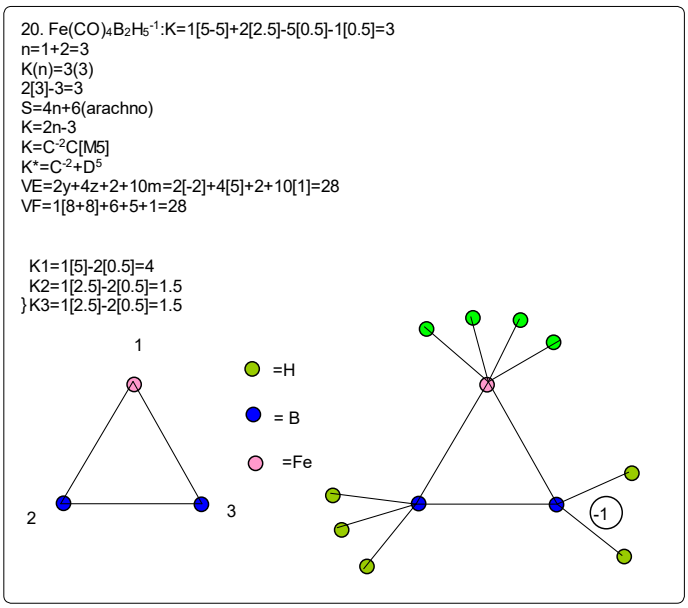


Figure 20. Isomeric skeletal structure of $Fe(CO)_4B_2H_5^{-1}$.

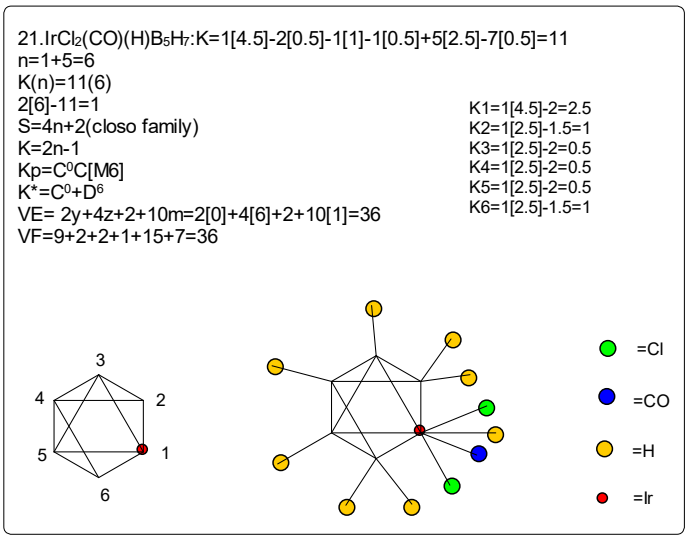


Figure 21. Isomeric skeletal structure of $IrCl_2(CO)(H)B_5H_7$.

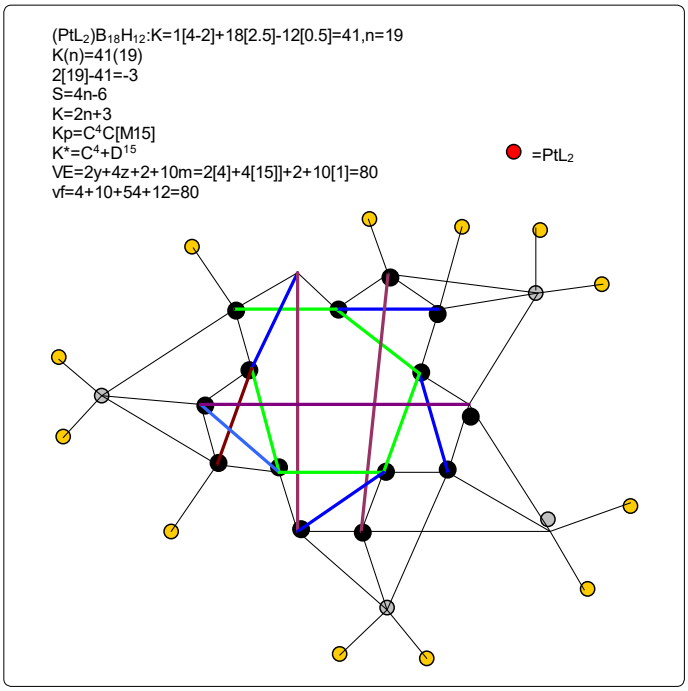


Figure 22. Isomeric graphical structure of $(PtL_2)B_{18}H_{12}$.

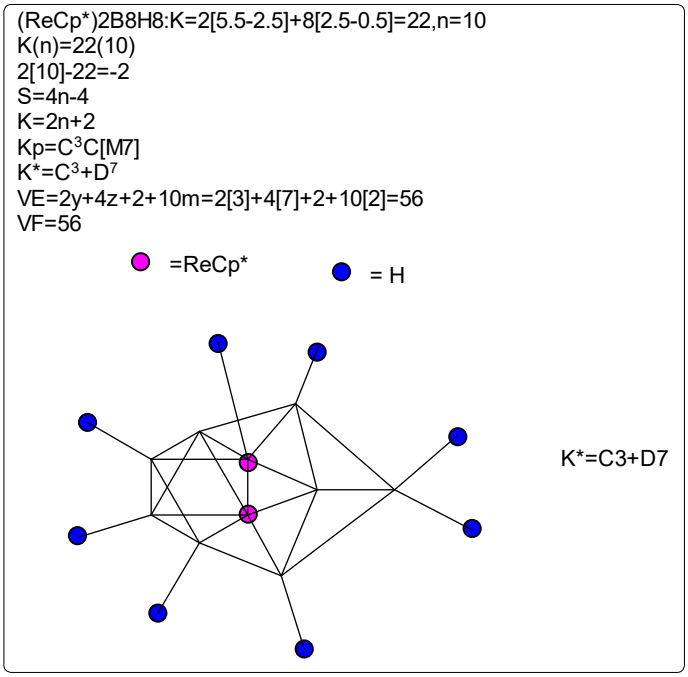


Figure 23. Isomeric skeletal structure of $(ReCp^*)_2B_8H_8$.

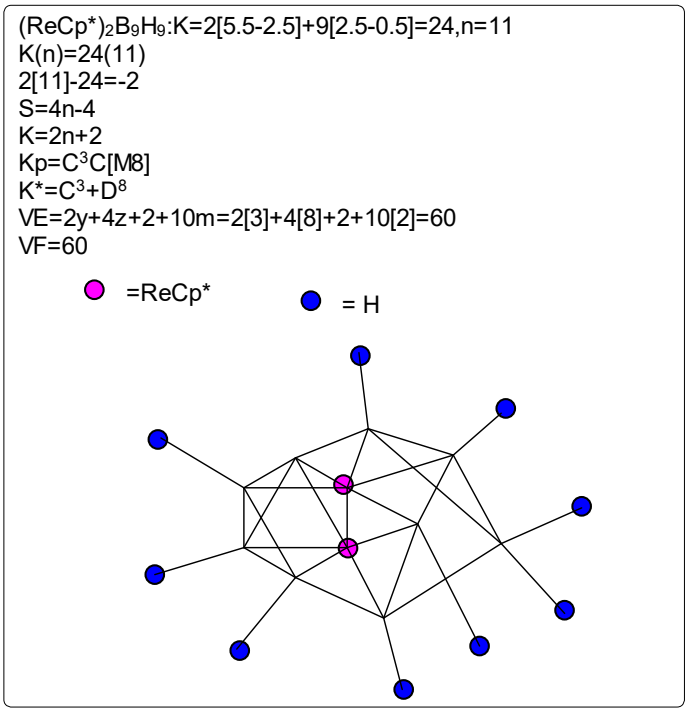


Figure 24. Isomeric skeletal structure of $(ReCp^*)_2B_9H_9$.

	Cluster	K(n)	SERIES	Kp	K*(clans)	VE	VF
1	$(Cp^*Cr)_2B_4H_8$	13(6)	4n-2	$C^2C[M4]$	C^2+D^4	42	42
2	$Fe(CO)_4B_2H_5^{-1}$	3(3)	4n+6	$C^{-2}C[M5]$	$C^{-2}+D^5$	28	28
3	$(Cp^*Re)_2B_4H_8$	12(6)	4n+0	$C^1C[M5]$	C^1+D^5	44	44
4	$(Cp^*Re)_2B_6H_6$	18(8)	4n-4	$C^3C[M5]$	C^3+D^5	48	48
5	$(Cp^*Re)\ B_3H_{11}$	5(4)	4n+6	$C^{-2}C[M6]$	$C^{-2}+D^6$	32	32
6	$Mn(CO)_4B_3H_8$	5(4)	4n+6	$C^{-2}C[M6]$	$C^{-2}+D^6$	32	32
7	B_5H_9	8(5)	4n+4	$C^{-1}C[M6]$	$C^{-1}+D^6$	24	24
8	$C_2B_3H_7$	8(5)	4n+4	$C^{-1}C[M6]$	$C^{-1}+D^6$	24	24
9	$IrCl_2(CO)(H)B_3H_7$	11(6)	4n+2	$C^0C[M6]$	C^0+D^6	36	36
10	$(Cp^*Ru)_2B_4H_8$	11(6)	4n+2	$C^0C[M6]$	C^0+D^6	46	46
11	$(Cp^*Re)_2B_7H_7$	20(9)	4n-4	$C^3C[M6]$	C^3+D^6	52	52
12	$(Cp^*W)_3B_8H_9$	26(11)	4n-8	$C^5C[M6]$	C^5+D^6	66	66
13	$Cp^*FeB_4H_{11}$	7(5)	4n+6	$C^2C[M7]$	$C^{-2}+D^7$	36	36
14	$(Cp^*Ir)_2B_4H_8$	10(6)	4n+4	$C^{-1}C[M7]$	$C^{-1}+D^7$	48	48
15	$(CpCo)\ B_5H_9$	10(6)	4n+4	$C^{-1}C[M7]$	$C^{-1}+D^7$	38	38
16	$(CpCo)_3B_5H_5$	16(8)	4n+0	$C^1C[M7]$	C^1+D^7	62	62
	$(Cp^*Re)_2B_8H_8$	22(10)	4n-4	$C^3C[M7]$	C^3+D^7	56	56
	$(Cp^*Re)_2B_9H_9$	24(11)	4n-4	$C^3C[M8]$	C^3+D^8	60	60
17	$Fe(CO)_4B_6H_{10}$	11(7)	4n+6	$C^{-2}C[M9]$	$C^{-2}+D^9$	44	44
	$(Cp^*Re)_2B_9H_9$	26(12)	4n-4	$C^3C[M9]$	C^3+D^9	64	64
18	$(NiCp)_2B_8H_8$	19(10)	4n+2	$C^0C[M10]$	C^0+D^{10}	62	62
19	$Fe(CO)_4B_7H_{12}^{—}$	12(8)	4n+8	$C^{-3}C[M11]$	$C^{-3}+D^{11}$	50	50
20	$(NiCp)_2B_{10}H_{10}$	23(12)	4n+2	$C^0C[M12]$	C^0+D^{12}	70	70
21	$PtL_2B_{18}H_{12}$	41(19)	4n-6	$C^4C[M15]$	C^4+D^{15}	80	80
22	$Os_7(CO)_{21}$	14(7)	4n+0	$C^1C[M6]$	C^1+D^6	98	98
23	$Os_8(CO)_{22}^{2-}$	17(8)	4n-2	$C^2C[M6]$	C^2+D^6	110	110
24	$Os_9(CO)_{24}^{2-}$	20(9)	4n-4	$C^3C[M6]$	C^3+D^6	122	122
25	$Os_{10}(CO)_{26}^{2-}$	23(10)	4n-6	$C^4C[M6]$	C^4+D^6	134	134
26	$Rh_{13}(CO)_{24}H_2^{3-}$	32(13)	4n-12	$C^7C[M6]$	C^7+D^6	170	170
27	$Ir_{14}(CO)_{27}^{2-}$	35(14)	4n-14	$C^8C[M6]$	C^8+D^6	182	182

Table 2. A collection of selected metaborane clusters.

Derivation of Information from the Categorization Parameter $K^*=C^Y+D^Z$

Once a cluster formula has been converted into a categorization parameter $K^*=C^y+D^z$ all the important information is concealed into that symbol. All that is needed to know is whether it refers to the main group or transition metals. For instance, $K^*=C^3+D^6$; refers to a cluster with 9 skeletal elements (n=3+6=9), VE=12y+14z+2=12[3]+14[6]+2=122 (transition metals) and VE=2y+4z+2=2[3]+4[6]+2=32 (main group elements). The ideal shape will be a tri-capped octahedron as shown in figure 25. The clan series do generate an infinite range of K(n) and VE series. The numerical series from n=0 to n=37 for D^4 and D^6 for both main group and transition metals are given in table 3. In order to highlight the significance of categorization of clusters into clans, a small sample of D^5 series was categorized and is given in the examples G1 to G6. The final categorization results of the D^5 series are: $K^*=C^5+D^5$; C^9+D^5; $C^{10}+D^5$; $C^{11}+D^5$;$C^{12}+D^5$;and $C^{17}+D^5$. Also selected clan series of D^5 are given in table 4. The positions of the K(n) and VE values of G1 to G6 clusters are highlighted in table 4.The D^5 and D^6 represent clan clusters whose structures are centered around an ideal trigonal bipyramid and octahedral nuclei respectively. The ideal structures are shown in figure 26.

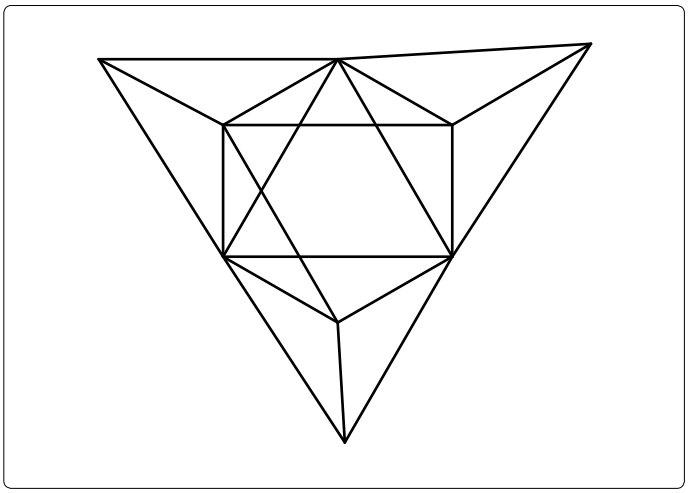


Figure 25. An ideal isomeric structure of a tri-capped octahedral symmetry.

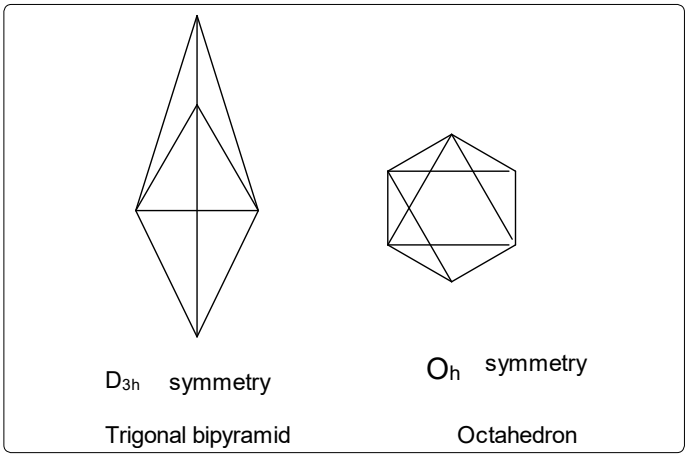


Figure 26. Ideal symmetries of trigonal bipyramid and octahedral nuclei.

The variation of the skeletal number in similar cluster formulas

Let us focus on the case of the following clusters $(Cp^*M)_2B_4H_8$, M=Ir, Ru, Re and Cr as an illustration of the concept. The corresponding K(n) parameter and categorization parameter K* are as follows;10(6),$C^{-1}+D^7$; 11(6),C^0+D^6; 12(6),C^1+D^5;13(6),C^2+D^4. The K values for Ir, Ru, Re, and Cr are 4.5, 5.0, 5.5 and 6 respectively the K(n) parameter starting with K=10 to 11, 12 and then 13 for the same number of skeletal elements n=6. As can be seen, the number of skeletal elements remains the same while the value of the cluster number K increases. This results into the increase in the capping index while the nuclear index is decreasing. In the parameter $K^*=C^y+D^z$ and n=y+z. Since n is constant, the increase in y will naturally result in the corresponding decrease in z. Hence, the increase in the K value results in the increase of the capping index (the outer shell expands) and a decrease in the nuclear index (nucleus shrinks).

Table 3. The variation of K(n) parameter with cluster valence electrons startrom n=0 for D4 and D6 series

	D^4									D^6							
	K	n	VEMG	VETM	K	n	VEMG	VETM		K	n	VEMG	VETM	K	n	VEMG	VETM
	-5	0	10	10	52	19	48	238		-7	0	14	14	50	19	52	242
	-2	1	12	22	55	20	50	250		-4	1	16	26	53	20	54	254
	1	2	14	34	58	21	52	262		-1	2	18	38	56	21	56	266
	4	3	16	46	61	22	54	274		2	3	20	50	59	22	58	278
	7	4	18	58	64	23	56	286	**5,6**	**5**	**4**	**22**	**62**	62	23	60	290
	10	5	20	70	67	24	58	298	**7,8**	**8**	**5**	**24**	**74**	65	24	62	302
1	**13**	**6**	**22**	**82**	70	25	60	310	**9,10**	**11**	**6**	**26**	**86**	68	25	64	314
	16	7	24	94	73	26	62	322	**22**	**14**	**7**	**28**	**98**	71	26	66	326
	19	8	26	106	76	27	64	334	**23**	**17**	**8**	**30**	**110**	74	27	68	338
	22	9	28	118	79	28	66	346	**11,24**	**20**	**9**	**32**	**122**	77	28	70	350
	25	10	30	130	82	29	68	358	**25**	**23**	**10**	**34**	**134**	80	29	72	362
	28	11	32	142	85	30	70	370		26	11	36	146	83	30	74	374
	31	12	34	154	88	31	72	382		29	12	38	158	86	31	76	386
	34	13	36	166	91	32	74	394	**26**	**32**	**13**	**40**	**170**	89	32	78	398
	37	14	38	178	94	33	76	406	**27**	**35**	**14**	**42**	**182**	92	33	80	410
	40	15	40	190	97	34	78	418		38	15	44	194	95	34	82	422
	43	16	42	202	100	35	80	430		41	16	46	206	98	35	84	434
	46	17	44	214	103	36	82	442		44	17	48	218	101	36	86	446
	49	18	46	226	106	37	84	454		47	18	50	230	104	37	88	458

VEMG: Cluster Valence Electrons for Main Group Elements; VETM: Cluster Valence Electrons of Transition.

Table 4. The variation of the K(n) values starting with n=0 for D^4 cluster series.

D5	T4		
K	n	VEMG	VETM
-6	0	12	12
-3	1	14	24
0	2	16	36
3	3	18	48
6	4	20	60
9	5	22	72
12	6	24	84
15	7	26	96
18	8	28	108
21	9	30	120
24	10	32	132
27	11	34	144
30	12	36	156
33	13	38	168
36	14	40	180
39	15	42	192
42	16	44	204
45	17	46	216
48	18	48	228
51	19	50	240
54	20	52	252
57	21	54	264
60	22	56	276

G1. $F=Os_{10}(C)(CO)_{24}$:K=10[5]-1[2]-24[1]=10,n=10

K(n)=24(10)

S=4n-8

K=2n+4

$Kp=C^5C[M5]$

$K^*=C^5+D^5$

$K^*=C^y+D^z$

VE=12y+14z+2=12[5]+14[5]+2=132

VF=10[8]+1[4]+24[2]=132

G2. $Rh_{14}(CO)_{25}^{4-}$:K=14[4.5]-25[1]-4[0.5=36,n=14

K(n)=36(14)

S=4n-16

K=2n+8

$Kp=C^9C[M5]$

$K^*=C^9+D^5$

$K^*=C^y+D^z$

VE=12y+14z+2=12[9]+14[5]+2=180

VF=14[9]+25[2]+4[1]=180

G3. $Rh_{15}(CO)_{27}^{3-}$:K=15[4.5]-27[1]-3[0.5]=39,n=15

K(n)=39(15)

2[15]-39=-9

S=4n-18

K=2n+9

$Kp=C^{10}C[M5]$

$K^*=C^{10}+D^5$

$K^*=C^y+D^z$

VE=12y+14z+2=12[10]+14[5]+2=192

VF=15[9]+27[2]+3[1]=192

G4. $Pd_{16}(CO)_{13}L_9$:K=16[4]-13[1]-9[1]=42,n=16

K(n)=42(16)

2[16]-42=-10

S=4n-20

K=2n+10

Kp=C^{11}C[M5]

K*=C^{11}+D^5

VE=12y+14z+2=12[11]+14[5]+2=204

VF=16[10]+13[2]+9[2]=204

G5. $Rh_{17}(CO)_{30}^{3-}$: K=17[4.5]-30[-1]-3[0.5]=45,n=17

K(n)=45(17)

2[17]-45=-11

S=4n-22

K=2n+11

Kp=C^{12}C[M5]

K*=C^{12}+D^5

VE=12y+14z+2=12[12]+14[5]+2=216

VF=17[9]+30[2]+3[1]=216

G6. $Rh_{22}(CO)_{37}^{4-}$:K=22[4.5]-37[1]-4[0.5]=60,n=22

K(n)=60(22)

2[22]-60=-16

S=4n-32

K=2n+16

Kp=C^{17}C[M5]

K*=C^{17}+D^5

VE=12y+14z+2=12[17]+14[5]+2=276

VF=22[9]+37[2]+4[1]=276

Conclusion

A good range of metalloboranes have been analyzed and categorized into clans and families of clusters using skeletal numbers. The cluster valence electrons and isomeric skeletal structures can readily be derived. The metalloborane $(Cp^*W)_3B_8H_9$ with a categorizing parameter K*=C^5+D^6 was found surprisingly highly capped unlike other metalloboranes. A formula for calculating cluster valence electrons for a cluster with a mixture of non-metals was derived namely: VE=2y+4z+2+10m where y is a capping index for C^y elements and z is a capping index for D^z elements and m is the number of metal skeletal elements in the cluster. Thus in the case of the $(Cp^*W)_3B_8H_9$, y=5,z=6 and m=3 which gives us a cluster valence value of 66. The 10m component of the formula is for metal adjustment to take into account the additional cluster valence electrons introduced by metal atoms present.

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References

1. Greenwood NN. Metalloboranes. *Pure Appl Chem*. 1983; 55(9): 1415-1430. doi: 10.1351/pac198355091415
2. Housecroft CE, Sharpe AG. Inorganic Chemistry. 2nd Edition. Pearson, Prentice Hall, Harlow, England. 2005.
3. Kiremire EM. The Application of the 4n Series Method to Categorize Metalloboranes. *Int J Chem*. 2016; 8(3): 62-73. doi: 10.5539/ijc.v8n3p62
4. Kiremire EM. Classification of Zintl Ion Clusters Using 4n Series Approach. *Orient J Chem*. 2016; 32(4): 1731-1738. doi: 10.13005/ojc/320401
5. Kiremire EM. The Outstanding Applications of Skeletal Numbers to Chemical Clusters. *Int J Chem*. 2017; 9(3): 28-48. doi: 10.5539/ijc.v9n3p28
6. Kiremire EM. The Capping Theory of Chemical Clusters Based on 12N/14N Series. *Int J Chem*. 2018; 10(4): 130-154. doi: 10.5539/ijc.v10n4p130
7. Miessler GL, Fischer PJ, Tarr DA. Inorganic Chemistry. 5th Edition, Pearson Education, Inc., Upper Saddle River. 2013.
8. Mingos DMP. A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nature Physical Science*. 1972; 236: 99-102. doi: 10.1038/physci236099a0
9. Wade K. The structural significance of the number of skeletal bonding electron-pairs in carboranes, the higher boranes, and borane anions and various transition metal carbonyl cluster compounds. *Chem Commun*. 1971; 792-793. doi: 10.1039/C29710000792
10. Wade A. Structural and Bonding Patterns in Cluster Chemistry. *Adv Inorg Chem Radiochem*. 1976; 18: 1-66. doi: 10.1016/S0065-2792(08)60027-8
11. Welch AJ. The significance of Wade's rules. *Chem Commun*. 2013; 49: 3615-3616. doi: 10.1039/C3CC00069A