

Correlation between the K values and molecular geometries- further link between K and Wade's N value for simple Closco systems

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ABSTRACT

The K value has a strong correlation to molecular geometries of boranes, carboranes, metalloboranes and a large number of transition metal organometallic cluster systems. Its basis is the eight (octet) and eighteen electron rules. This paper provides simple examples which illustrate the link between the three dimensional geometry of a cluster and its K value. It also found that for the simple systems the K value is related to Wade's skeletal electron pairs (SEP) by the equation $K = 3(N-2)$.

Keywords: K values, Molecular Geometries, Wade's N value, Closco Systems.

INTRODUCTION

The derivation of a molecular geometry from a molecular formula is extremely important in chemistry. Unlike the hydrocarbons, the boranes, carboranes and metalloboranes pose some great difficulty in deriving their geometries from their formulas. Due to the fact that boranes and their relatives are electron deficient, they aggregate by forming less familiar and unique three centered-two electron bonds in addition to the more familiar and conventional two centered-two electron bonds producing clusters¹⁻⁵. By calculating the K-value of a cluster⁶⁻⁸, its possible geometry can be predicted for simple systems. The relationship between the K value and the Lipscomb numbers was derived in the previous work⁶⁻⁷. This paper has gone a step further to show that K is also related to Wade's N values for simple closco systems.

This paper focuses on molecules or molecular clusters with skeletal elements which obey either the octet rule or eighteen electron rule or a mixture of these. Our discussion starts with simple molecules to illustrate the concept of utilizing

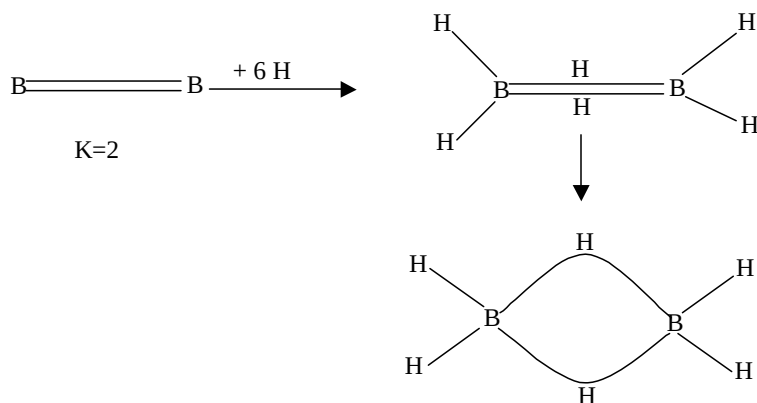
the K value in determining a molecular geometry and then progresses to more complex examples.



Diborane, B_2H_6 like all other boranes is an electron deficient molecule. The boron atoms in the diborane molecule attempt to attain the octet rule in order to acquire stability. In this regard, we can apply the Kiremire's equation⁶⁻⁸ to determine the skeletal linkages around which the octet rule will be fulfilled.

$$K = 1/2(E-V)/2, E = 8 \times 2 = 16, \\ V = 3 \times 2 + 6 = 12, K = 2.$$

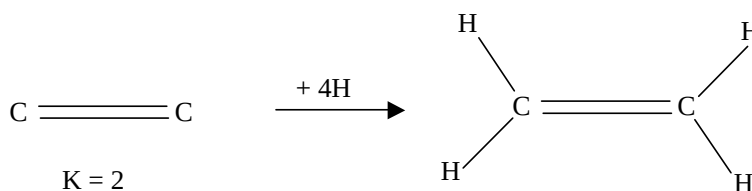
The K value of 2 means that the two boron atoms are joined by 2 bonds. The H atoms are distributed in such away that each B atom obeys the octet rule. This gives a structure in which 2 H atoms will be forced to be imbedded in the 2 skeletal bonds so that each of the skeletal bond acquires to 2 electrons. This produces the bridged hydrogens of the three centered two electron bonds. This is summarized in Fig. 1.

Fig. - 1: The derived structure of B_2H_6

Lipscomb's equations¹ for B_2H_6 , $p=2$, $q=4$, $q/2=2$
 $s+x = q = 4$, $s+t = p = 2$, $t+y = p-q/2 = 2 - 4/2 = 0$
 Acceptable solution is (styx = 2002). This corresponds to the structure given in figure 1. In our earlier work, it was shown that in boranes and its relatives⁶⁻⁸ that K is related to s , t and y by $K = s + 2t + y$.

C_2H_4

The C_2H_4 molecule is isoelectronic to B_2H_6 .
 $K = 1/2(E-V)/2$, $E = 8 \times 2 = 16$, $V = 4 \times 2 + 4 = 12$, $K = 2$. Since the K value of C_2H_4 is the same as that of B_2H_6 , its geometry is expected to be similar the skeletal linkages will have no bridging H atoms since the C atoms have adequate electrons to satisfy the octet rule. The structure of C_2H_4 based on the K value of 2 is given in figure 2. Each of the C atom obeys the octet rule.

Fig. -2: The derived geometry of C_2H_4

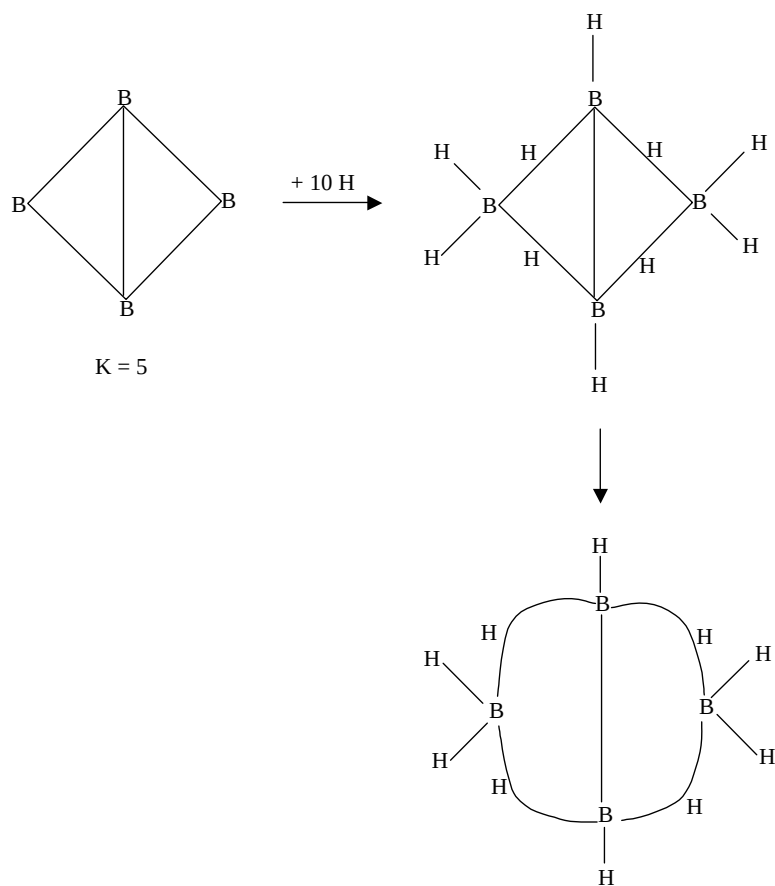
B_4H_{10}

B_4H_{10} is a more complex molecule than B_2H_6 . Its K value is given by

$$K = \frac{1}{2}(E - V) = \frac{1}{2}(32 - 22) = 5.$$

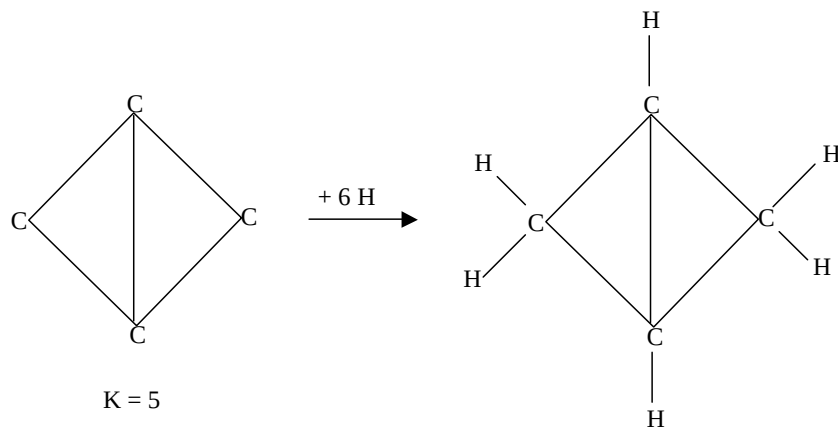
This means it has to have 5 skeletal bonds

in order for the B atoms to satisfy the octet rule. A possible geometry is a square with one diagonal. By adding 4 bridging hydrogens and distributing the remaining 6 Hs in such a way that each B atom satisfies the octet rule we get molecular geometry shown in Fig. 3.

Fig. -3: The derived geometry of B_4H_{10} 

C_4H_6 is isoelectronic with B_4H_{10} . Hence its K value is also 5.

The structure of one of C_4H_6 isomers will be similar to that of B_4H_{10} and is shown in figure 4. In this case each of the C atoms obeys the octet rule.

Fig. -4: The derived geometry of C_4H_6



Let us calculate the K value of B_5H_9 .
 $K = \frac{1}{2} (E - V) = \frac{1}{2} (40 - 24) = 8.$

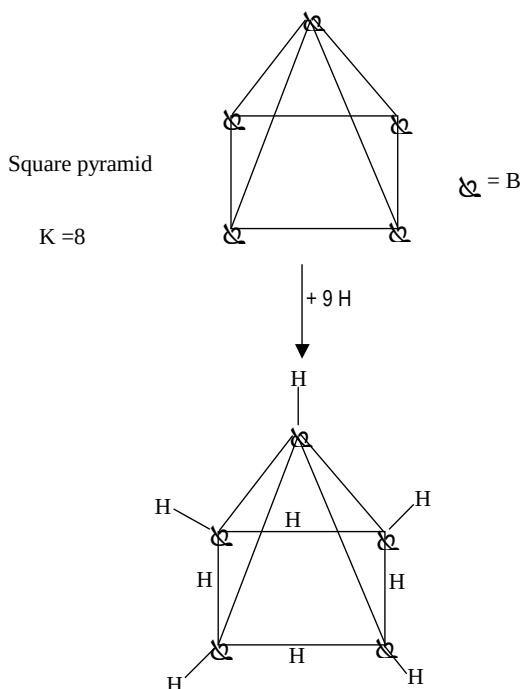


Fig. - 5a: The derived geometry of B_5H_9

The B_5H_9 borane will have 8 skeletal bonds in order to obey the octet rule. A possible geometry consistent with this is a square pyramid shown in figure 5a.

Lipscomb's equations for B_5H_9

$s + x = 4$, $s + t = 5$, $t + y = 3$; possible styx solutions (2302), (3211) and (4120).

A sketch of Lipscomb numbers 4120 isomer is given in figure 5b.

As can be seen from figure 5b, the central B atom is linked to the 4 other B atoms via a t (closed BBB) skeletal bond and 2 y (BB) bonds. These will constitute 4 linkages to the central atom each with an average of 1 electron. Hence, the B atom will attain an octet rule (8) by the sum of 4(from linkages)+ 3(from B atom) + 1(from the terminal H atom).



The borane B_5H_{11} has a K value of 7. A possible geometry is shown in Figure 6a.

Lipscomb's equations:

$s + x = 6$, $s + t = 5$, $t + y = 2$;
 possible styx solutions (3203), (4112), and (5021).
 One of the isomers corresponding to the (3203) set is given in Figure 6b.

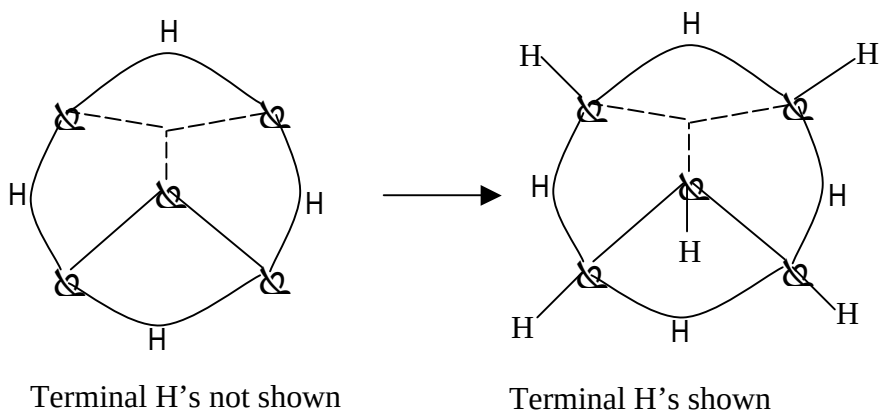
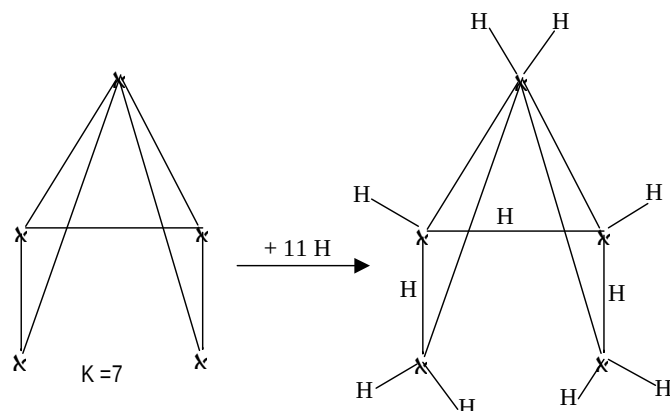
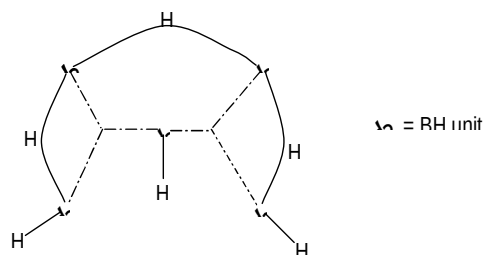


Fig. - 5b: The valence bond sketch of B_5H_9

Fig. -6a: Derived geometry of B_5H_{11} Fig. -6b: The Lipscomb structure of B_5H_{11}

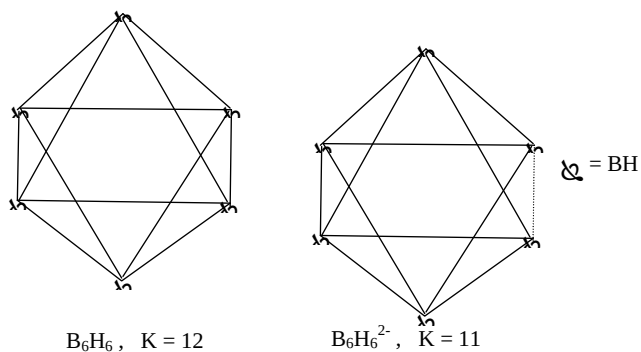
The central boron atom will have 4 linkages from the 2 t bonds. The bridging H atoms will correspond to the base linkages of figure 6a.

Hypothetical B_6H_6 versus $B_6H_6^{2-}$

The K value for the hypothetical B_6H_6 cluster is given by

$$K = \frac{1}{2} (E - V) = \frac{1}{2} (48 - 24) = 12.$$

Such a borohydride molecule is expected to have an octahedral geometry with 12 linkages as shown in figure 7a. Each of the linkages can be considered to be a 1 electron donor to the boron atom and hence each of the B atoms will obey the octet rule. On the other hand $B_6H_6^{2-}$, $K=11$, its geometry will be one link less (represented by the dotted line) than the octahedral as shown in Fig. 7b.

Fig. -7a and 7b: Derived geometries of B_6H_6 and $B_6H_6^{2-}$

The Lipscombs equations for the two borane systems:

$$B_6H_6; s + x = 0, s + t = 6, \text{ and } t + y = 6.$$

This gives styx = (0600).

For the $B_6H_6^{2-}$; $s + x = 0$, $s + t = 4$ and $t + y = 7$. The solution becomes (0430).

Caboranes

The K-value also correlates to the geometrical structures of carboranes.

For instance the $C_2B_4H_6$ has a K-value of 11. Its geometry will be similar to that of $B_6H_6^{2-}$. A possible isomer is shown in figure 8. In each of the geometries each of the skeletal atoms obeys the octet rule.

Fig. -8: The derived geometry of $C_2B_4H_6$ cluster



The $C_2B_3H_7$ cluster has a K-value of 8. This means that $C_2B_3H_7$ cluster will be bound by eight linkages. Therefore the ideal geometry will be a square pyramid as in the case of B_5H_9 . There are two possible isomers of $C_2B_3H_7$ which are shown in Fig. 9.

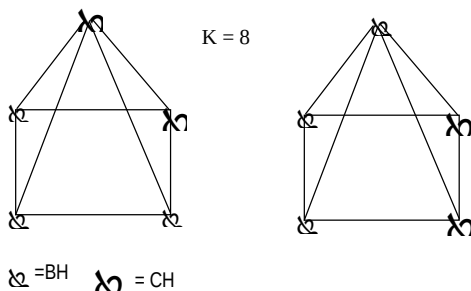


Fig. -9: Possible isomers of $C_2B_3H_7$



The K-value of $C_3B_3H_7$ cluster is given by $K = \frac{1}{2} (E - V) = \frac{1}{2} (48 - 28) = 10$. This ideally means that $C_3B_3H_7$ cluster is bound by 10 sides. This corresponds to a pentagonal pyramid. The possible isomers are shown in Fig. 10.

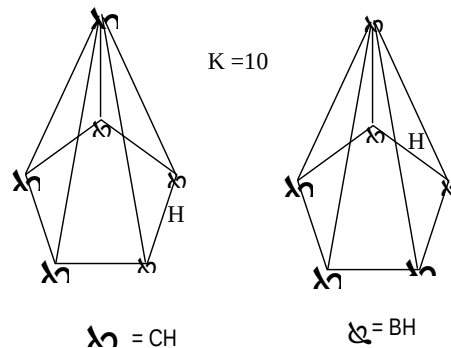
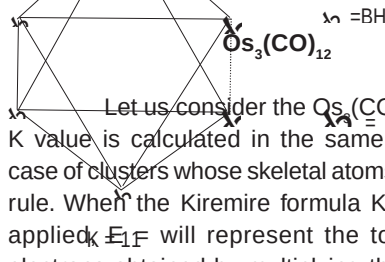


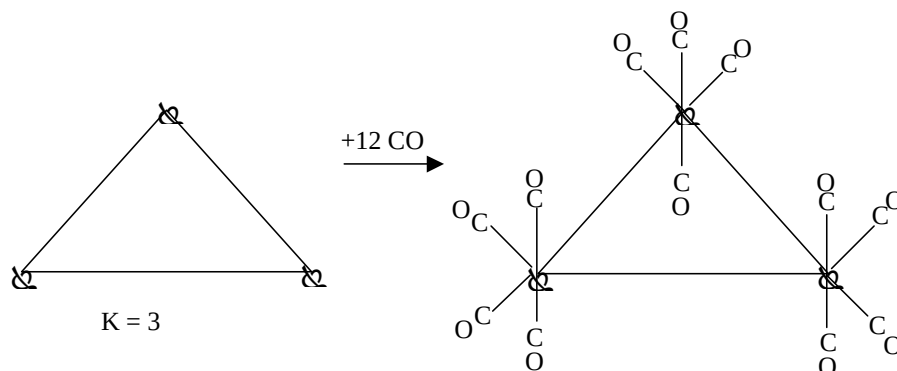
Fig. -10: The possible isomers of $C_3B_3H_7$ cluster

Organometallic Compounds

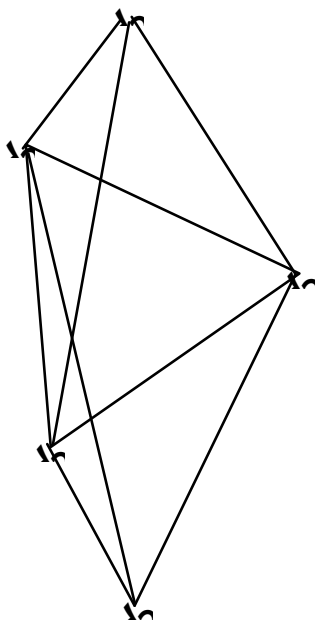
The 18 electron rule plays a key role in the stability of many organometallic compounds of transition metals.

Let us consider the $Os_3(CO)_{12}$ cluster. The K value is calculated in the same way as in the case of clusters whose skeletal atoms obey the octet rule. When the Kiremire formula $K = \frac{1}{2} (E - V)$ is applied, E will represent the total number of electrons obtained by multiplying the total number of transition metal atoms each of which is surrounded by 18 electrons while V is the total number of valence electrons contributed by the metal atoms and the ligands. In the case of $Os_3(CO)_{12}$ cluster, Os contributes 8 electrons and each of the CO ligands contributes 2. Hence, $E = 18 \times 3 = 54$, and $V = 8 \times 3 + 2 \times 12 = 48$ which gives us $K = \frac{1}{2} (E - V) = \frac{1}{2} [54 - 48] = 3$. The skeletal structure of the cluster will be trigonal planar or simply triangular. The CO ligands will then be clustered around the Os atoms arranged in a triangular geometry in such away that the 18 electron rule is obeyed. This is summarized in Fig. - 11.

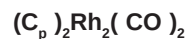


Fig. -11: The derived geometry of $\text{Os}_3(\text{CO})_{12}$ 

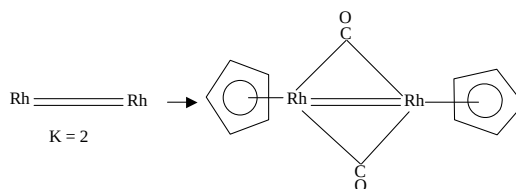
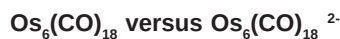
Let us consider another interesting and slightly more complex cluster than $\text{Os}_3(\text{CO})_{12}$. The K-value of $\text{Os}_5(\text{CO})_{16}$ calculated in the same way as in $\text{Os}_3(\text{CO})_{12}$ is 9. This means that the 5 Os skeletal atoms will be arranged in such a way that they are bound by 9 lines. A possible geometry in congruent with this is a trigonal bipyramid as shown in Fig. - 12.

Fig. -12: The skeletal framework of $\text{Os}_5(\text{CO})_{16}$ cluster

$K = 9$



The organometallic complex $(\text{C}_p)_2\text{Rh}_2(\text{CO})_2$ gives a good example of a complex with cyclopentadienyl ligand. In this case, C_p is 5 electron donor, Rh donates 9 while the CO donates 2 as in the above examples. Hence $K = \frac{1}{2}(E - V) = \frac{1}{2}(18 \times 2 - 5 \times 2 - 9 \times 2 - 2 \times 2) = \frac{1}{2}(36 - 34) = 2$. This indicates that the two Rh atoms are doubly bonded as in the C_2H_4 or B_2H_6 cases discussed earlier. A plausible geometry is given in Fig. 13.

Fig. -13: The possible geometry of $(\text{C}_p)_2\text{Rh}_2(\text{CO})_2$ cluster

The clusters $\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_6(\text{CO})_{18}^{2-}$ have the K values of 12 and 11 respectively. The ideal geometries will be similar to those of B_6H_6 and $\text{B}_6\text{H}_6^{2-}$ or $\text{C}_2\text{B}_4\text{H}_6$ discussed earlier and shown in figures 7 and 8.

Organometallaboranes and aorganocarboranes

The combination of a transition metal with a borane or carborane fragment, means that the K value must take into account both the 18 electron and the 8 (octet) electron rules in the calculation

of the skeletal linkages. Let us illustrate this by the following examples.



The skeletal elements are Os and B which

will obey the 18 and 8 electron rules respectively. Hence the K value is given by $K = \frac{1}{2} (E - V)$.

$E = 18 \times 3 + 8 = 62$ and $V = 3 + 9 \times 2 + 3 \times 8 + 3 + 2 = 50$. Hence $K = \frac{1}{2} (62 - 50) = 6$. The skeletal and complete cluster geometries are shown in Fig. 14.

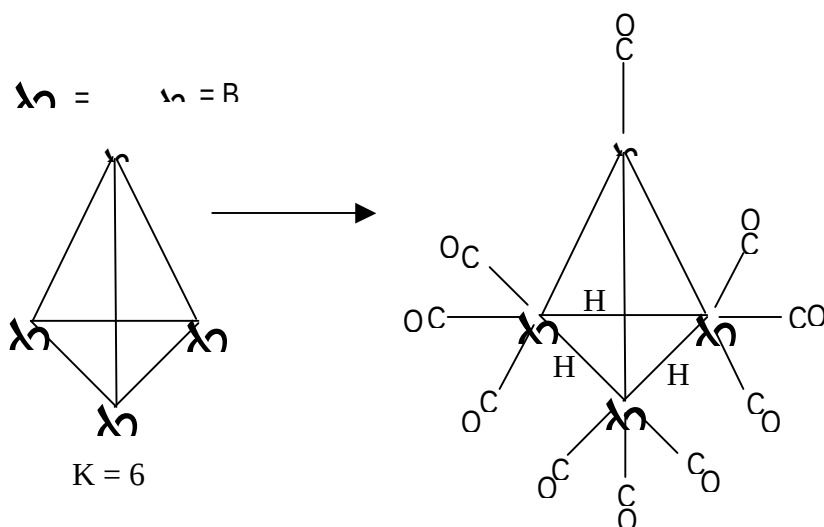
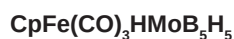


Fig. -14: The derived geometry of $\text{H}_3(\text{CO})_9\text{Os}_3\text{B}(\text{CO})$



The cluster $\text{CpFe}(\text{CO})_3\text{HMoB}_5\text{H}_5$ has Fe, Mo and B as the key skeletal elements. Fe and Mo are assumed to obey the 18 electron rule while B obeys the 8 (octet) rule. The electron contributions will be as follows, Cp 5, Fe 8, Mo 6 and H 1. Hence, the K value will be given by

$$K = \frac{1}{2} (18 \times 2 + 8 \times 5 - 3 \times 2 - 1 - 5 \times 3 - 5) = \frac{1}{2} (76 - 46) = 15.$$

The K value of 15 implies the geometry will be a pentagonal bipyramid. This is shown in Fig. 15.

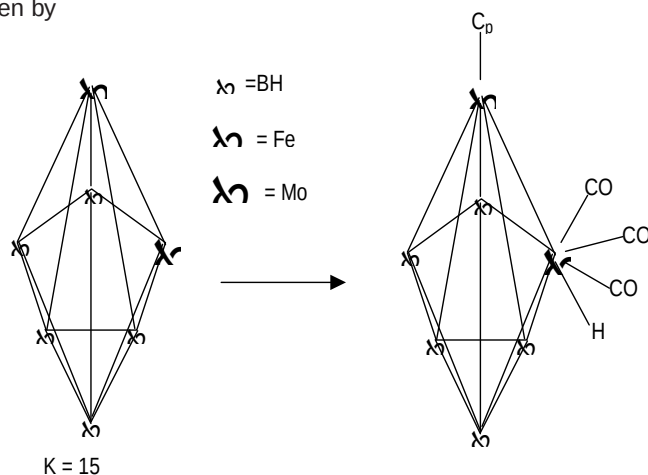


Fig. -15: The derived geometry of $\text{CpFe}(\text{CO})_3\text{HMoB}_5\text{H}_5$ cluster

Correlation between the K values and Wade's rules

Wade's formulation predicts the possible geometry of a cluster from the skeletal electron pairs (SEP) of the cluster⁹. A correlation can be made

between Wade's skeletal electron pairs (N + 1) and the K values. The K values represent skeletal linkages between two atoms in a cluster. This is shown in table 1 for simple systems.

Table -1: Table shows a Correlation between K and N variable.

K value	Possible Geometry	N*	(N+1) SEP
1	Linear		
3	Trigonal planar		
4	Square planar		
5	Square planar with a diagonal		
6	Tetrahedral	4	5
8	Square pyramid		
9	Trigonal bipyramid	5	6
10	Pentagonal pyramid		
12	Octahedral	6	7
15	Pentagonal bipyramid	7	8

- Represents the number of vertices or the skeletal atoms.

Many simple clusters possess the skeletal electron pairs (N + 1) of 5, 6, 7 and 8 with the corresponding N values⁹ of 4, 5, 6, and 7. These in turn correspond to the respective K values of 6, 9, 12, and 15. Since K represents the number of linkages (bonds) in a cluster, the K values of 6, 9, 12, and 15 will correspond to the geometries tetrahedral, trigonal bipyramid, octahedral and pentagonal bipyramid respectively. Such geometries belong to the so called CLOSO systems from which the NIDO and ARACHINO systems are derived⁹. A closer look at the K values of the simple closo systems and their corresponding N values, the following relationship expressed by a simple equation is readily discerned.

$$K = 3 (N - 2) \text{ or } N = 1/3 K + 2$$

When K is a multiple of 3, then the value of N is a whole number. This relationship seems to apply for simple systems with N ranging from 4 to 7. Therefore K formula links the valence electrons, the octet or 18 electron principle with the Lipscomb

symbols stys and Wade's N symbol via the following relationship

$$K = \frac{1}{2} (E - V) = s + 2t + y = 3 (N - 2).$$

CONCLUSION

The K value acts as a simple guide in predicting and designing a molecular geometry of a given molecular formula. It is particularly useful for systems where the key skeletal atoms obey the octet or the eighteen electron rules. This paper has utilized simple molecular systems as illustrations. The application of the K value to predicting and designing molecular geometries of complex molecular systems is not clear. Nevertheless, the application of K value is extremely useful in the understanding and teaching of the molecular structures and geometries of simple molecules and clusters. It is our conviction that its popularization will greatly increase the interest in the teaching of structures of simple boranes, carboranes, metallaboranes and metallocarboranes.

REFERENCES

1. Douglas B, McDaniel D., Alexander J., " Concepts and Models of Inorganic Chemistry", 3rd Edition, John Wiley & Sons, Inc., New York (1994).
2. Lipscomb W N, Proceedings of the National Academy of Sciences, **47**, 1791 (1961).
3. Greenwood N N and Earnshaw A., " Chemistry of the Elements", 2nd Edition, Butterworth Heinemann, Oxford, (1998).
4. Lagowski J J, " Modern Inorganic Chemistry", Marcel Dekker, Inc., New York, (1973).
5. Cotton F A, Wilkinson G, Murillo C A and Bochmann M, " Advanced Inorganic Chemistry", 6th Edition, John Wiley & Sons, New York (1999).
6. Kiremire EMR, *Orient. J. Chem.* **22**(1), 29 (2006)
7. Kiremire EMR, *Mat. Sci. Res. Ind.*, **3**(2a), (2006).
8. Kiremire EMR, *Mat. Sci. Res. Ind.*, **4**(1), (2007).
9. Mackay K M, Mackay R A and Henderson W, " Introduction to Modern Inorganic Chemistry", 5th Edition, Stanley Thornes Publishers Ltd., (1998).