Borane Clusters Hiding Inside Carbonyl Clusters

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ABSTRACT

This paper is based upon the 14n Rule for transition metal carbonyl clusters and the for 4n rule for borane clusters. It reveals that the when the shielding 10n electrons are removed from the 14n based cluster what remains is a cluster that obeys the 4n rule. For instance it shows that $Os_5(CO)_{16}$ (14n+2) cluster of 72 valence electrons corresponds to $B_5H_5^{2-}$ (4n+2) of 22 electron cluster, and $Rh_6(CO)_{16}$ (14n+2) corresponds to $B_6H_6^{2-}$ cluster(4n+2) of 26 electrons. It is also shows that some of the giant clusters are equivalent to simple borane clusters when the shielding electrons are removed. The borane clusters so derived can readily be categorized into series which correspond to those of the carbonyl clusters. The isolobal concept has also been found to conform to cluster series.

Key words: Carbonyl and borane series, Hiding boranes, Nuclear clusters, Giant Clusters, Clusters within clusters, Isolobal series, Chemical Fragments.

INTRODUCTION

The existence of series in boranes and carbonyl clusters were discovered by Wade and Mingos[1-2]. Their studies were supported by Molecular Orbital Theory. Recently, it has been found that the carbonyl and borane clusters in fact do encompass a wide spectrum of series[3-4]. These series which are interrelated and are based on 14n and 4n rules[3-4]. If the carbonyl series are given by $ST = 14n+q$ and the corresponding main group elements are given by $SG = 4n+q$ where q can take up multiple integers of 2, positive or negative, then it became clear that $ST = (14n+q)-10n = SG = 4n+q$. This implies that if we remove 10n value electrons from the valence electrons (V) of a carbonyl cluster

we will have the remaining electrons (V_T) available for conversion into a corresponding formula of a compound of the main group element. With this in mind, the correlation was focused mainly on converting carbonyl clusters into borane clusters. These findings are presented in Table 1.

RESULTS AND DISCUSSION

The removal of 10n electrons from carbonyl clusters clearly revealed the close relationship between the 14n series for the transition metal carbonyl clusters and the 4n series of main group elements especially the boranes. The method involves first calculating the valence electrons(V) of the carbonyl cluster. Then subtracting
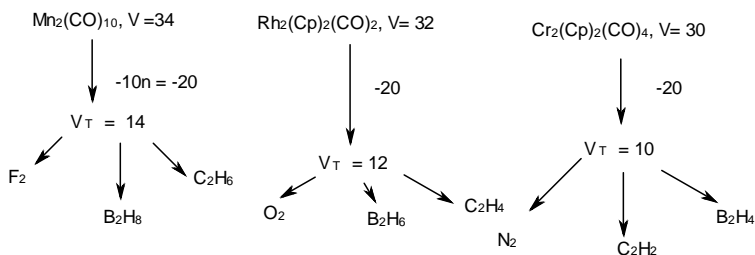
Table 1: Equivalence Relationship of Carbonyl and Borane Clusters

Carbonyl Cluster	Equivalent Borane Cluster	Carbonyl Series	Corresponding Borane Series	Classification
$Mn_2(CO)_{10}$	B_2H_8, C_2H_6, F_2	$14n+6$	$4n+6$	ARACHNO
$Rh_2(Cp)_2(CO)_2$	B_2H_6, C_2H_4	$14n+4$	$4n+4$	NIDO
$Cr_2(Cp)_2(CO)_4$	B_2H_4, C_2H_2	$14n+2$	$4n+2$	CLOSO
$OS_3(CO)_{12}$	B_3H_9 , C_3H_6	$14n+6$	$4n+6$	ARACHNO
$Os_4(CO)_{14}$	B_4H_8	$14n+4$	$4n+4$	NIDO
$OS_4(CO)_{15}$	B_4H_{10}	$14n+6$	$4n+6$	ARACHNO
$Os_4(CO)_{16}$	B_4H_{12}	$14n+8$	$4n+8$	HYPHO
$Os_5(CO)_{16}$	$B_5H_7(B_5H_5]^{2-})$	$14n+2$	$4n+2$	CLOSO
$Fe_5(CO)_{17}$	$B5H_9$	$14n+2$	$4n+2$	CLOSO
$Os_5H_2(CO)_{16}$	B_5H_9	$14n+2$	$4n+2$	CLOSO
$Ni_5(CO)_{12}]^{2-}$	B_5H_{11}	$14n+6$	$4n+6$	ARACHNO
$Rh_5(CO)_{15}]^{2-}$	$B5H_{11}$	$14n+6$	$4n+6$	ARACHNO
$Os_5(CO)_{18}$	B_5H_{11}	$14n+6$	$4n+6$	ARACHNO
$Os_5(CO)_{19}$	B_5H_{13}	$14n+8$	$4n+8$	HYPHO
$Os_6(CO)_{18}$	B_6H_6	$14n$	$4n$	CIC[M-5]
$Os_6L_4(CO)_{17}[L =P(OMe)_3]$	B_6H_{12}	$14n+6$	$14n+6$	ARACHNO
$Rh_6(CO)_{15}(C)]^{2-}$	B_6H_{12}	$14n+6$	$14n+6$	ARACHNO
$Ru_6(C)(CO)_{17}$	$B_6H_6]^{2-}$	$14n+2$	$4n+2$	CLOSO
$Os_6(CO)_{18}]^{2-}$	$B_6H_6]^{2-}$	$14n+2$	$4n+2$	CLOSO
$Os_6H_2(CO)_{19}$	B_6H_{10}	$14n+4$	$4n+4$	NIDO
$Rh_7(CO)_{16}]^{3-}$	B_7H_7	$14n$	$4n$	C¹C[M-6]*
$Os_7(CO)_{21}$	B_7H_7	$14n$	$4n$	C¹C[M-6]
$Rh_7(CO)_{15}(N)]^{2-}$	$B_7H_9 =B_7H_7]^{2-}$	$14n+2$	$4n+2$	CLOSO
$Os_7(CO)_{22}H_2$	B_7H_{11}	$14n+4$	$4n+4$	NIDO
$Os_7H_2(CO)_{21}$	$B_7H_9 =B_7H_7^{2-}$	$14n+2$	$4n+2$	CLOSO
$Os_6Pt(CO)_{18}(H)_8$	B_7H_{11}	$14n+4$	$4n+4$	NIDO
$Os_6Pt_2(CO)_{16}(COD)_2$	B_8H_4	$14n-4$	$4n-4$	C³C[M-5]
$Ni_8(CO)_{14}H_2]^{2-}$	B_8H_8	$14n$	$4n$	C¹C[M-7]
$Rh_8(CO)_{19}(C)$	B_8H_{10}	$14n$	$4n$	C¹C[M-7]
$Ni_8(C)(CO)_{16}]^{2-}$	B_8H_{14}	$14n+6$	$4n+6$	ARACHNO
$Ni_8(CO)_{12}]^{2-}$	B_8H_2	$14n-4$	$4n-4$	C³C[M-5]
$Cu_2Rh_6(C)(CO)_{15}(L)_2$ L =NCMe	$B_8H_{10[}B_8H_8^{2-}]$	$14n+2$	$4n+2$	CLOSO
$Cu_2Ru_6(C)(CO)_{16}(L)2$ L=NCMe	B_8H_6	$14n-2$	$4n-2$	C²C[M-6]
$Os_8(CO)_{22}]^{2-}$	B_8H_6	$14n-2$	$4n-2$	C²C[M-6]
$Os_7(CO)_{19}(Au)_2(diphos)$ diphos = $Ph_2PCH_2CH_2PPh_2$	B_9H_3	$14n-6$	$4n-6$	C⁴C[M-5]
$Rh_9(CO)_{19}]^{3-}$	B_9H_5	$14n-4$	$4n-4$	C³C[M-6]
$Os_9(CO)_{24}]^{2-}$	B_9H_5	$14n-4$	$4n-4$	C³C[M-6]
$Rh_9(CO)_{21}(P)]^{2-}$	B_9H_{13}	$14n+4$	$4n+4$	NIDO
$Ni_9(CO)_{18}]^{2-}$	$B_9H_9]^{2-}$	$14n+2$	$4n+2$	CLOSO
$Ru_6Pt_3(CO)_{21}(H)_4$	B_9H_7	$14n-2$	$4n-2$	C²C[M-7]
$Ru_8Pt_2(CO)_{23}(H)_2$	$B_{10}H_2$	$14n-8$	$4n-8$	C⁵C[M-5]
$Rh_{10}(CO)_{21}]^{2-}$	$B_{10}H_4$	$14n-6$	$4n-6$	C⁴C[M-6]

$Ru_{10}(C)_2(CO)_{24}]^{2-}$	$B_{10}H_8$	$14n-2$	$4n-2$	$C^2C[M-8]$
$Os_{10}(CO)_{24}(C)]^{2-}$	$B_{10}H_4$	$14n-6$	$4n-6$	$C^4C[M-6]$
$Ni_{11}(CO)_{20}H_2]^{2-}$	$B_{11}H_{11}$	$14n$	$4n$	$C^1C[M-10]$
$Rh_{11}(CO)_{23}]^{3-}$	$B_{11}H_5$	$14n-6$	$4n-6$	$C^4C[M-7]$
$Fe_6Pd_6(CO)_{24}(H)]^{3-}$	$B_{12}H_4$	$14n-8$	$4n-8$	$C^5C[M-7]$
$Ru_6Pt_3(AuL)_2(CO)_{21}(H)_2$	$B_{11}H_5$	$14n-6$	$4n-6$	$C^4C[M-7]$
$Rh_{12}(CO)_{25}H_2$	$B_{12}H_4$	$14n-8$	$4n-8$	$C^5C[M-7]$
$Rh_{12}(CO)_{23}C_2]^{4-}$	$B_{12}H_{10}$	$14n-2$	$4n-2$	$C^2C[M-10]$
$Rh_{12}(C)_2(CO)_{25}$	$B_{12}H_{10}$	$14n-2$	$4n-2$	$C^2C[M-10]$
$Rh_{12}(CO)_{24}(C)_2]^{2-}$	$B_{12}H_{10}$	$14n-2$	$4n-2$	$C^2C[M-10]$
$Rh_{12}(CO)_{23}(N)_2(H)]^{3-}$	$B_{12}H_2$	$14n$	$4n$	$C^1C[M-11]$
$Rh_{12}(CO)_{27}Sb]^{3-}$	$B_{12}H_{14} = B_{12}H_{12}]^{2-}$	$14n+2$	$4n+2$	CLOSO
$Rh_{13}(CO)_{24}H_2]^{3-}$	$B_{13}H$	$14n-12$	$4n-12$	$C^7C[M-6]$
$Rh_{14}(CO)_{26}]^{2-}$	$B_{13}H$	$14n-16$	$4n-16$	$C^9C[M-5]$
$Rh_{15}(CO)_{27}]^{3-}$	B_{14}	$14n-18$	$4n-18$	$C^{10}C[M-5]$
$Rh_{17}(CO)_{30}]^{3-}$	$B_{15}H$	$14n-22$	$4n-22$	$C^{12}C[M-5]$
$Rh_{17}(CO)_{32}(S)_2]^{3-}$	$B_{17}H_{11}$	$14n-6$	$4n-6$	$C^4C[M-13]$
$Os_{17}(CO)_{36}]^{2-}$	$B_{13}H$	$14n-28$	$4n-38$	$C^{15}C[M-2]$
$Os_{20}(CO)_{40}]^{2-}$	B_{14}	$14n-38$	$4n-38$	$C^{20}C[M-0]$
$Rh_{23}(CO)_{38}(N)_4]^-$	$B_{23}H_5$	$14n-18$	$4n-18$	$C^{10}C[M-13]$
$Pd_{23}(CO)_{22}(L)_{10}$	$B_{21}H$	$14n-28$	$4n-28$	$C^{15}C[M-8]$
$Ni_{14}Pt_{10}(CO)_{30}]^{4-}$	$B_{21}H$	$14n-32$	$4n-32$	$C^{17}C[M-7]$
$Rh_{28}(CO)_{41}(N)_4(H)_2]^{4-}$	$B_{26}H_2$	$14n-32$	$4n-32$	$C^{17}C[M-11]$
$Pd_{28}Pt_{13}(L)_{12}(L_1)(CO)_{27}$	$B_{30}H_2$	$14n-72$	$4n-72$	$C^{37}C[M-4]$
$L=PPh_3, L1 =PMe_3$				

*C^1C = MONOCAPPED CLOSO, C^2C = BICAPPED CLOSO, AND SO ON.

$Mn_2(CO)_{10}, V =34$ $Rh_2(Cp)_2(CO)_2, V= 32$ $Cr_2(Cp)_2(CO)_4, V= 30$

$-10n = -20$ -20 -20

$V_T = 14$ $V_T = 12$ $V_T = 10$

F_2 C_2H_6 O_2 C_2H_4 B_2H_4

B_2H_8 B_2H_6 N_2 C_2H_2

Scheme 1: Removal of 10 n Electrons

$Rh_6(CO)_{16}$ $Rh_7(CO)_{21}$

$V = 86$ $V = 98$

$-10n = -10(6) = -60$ $-10n = -10(7) = -70$

$VT = 26$ $VT = 28$

$VB = 6 \times 3 = 18$ $VH = VT-VB = 26-18 = 8$ $VB = 7 \times 3 = 21$ $VH = VT-VB = 28-21 = 7$

$FB = B_6H_8 = B_6H_6^{2-}$ $FB = B_7H_7$
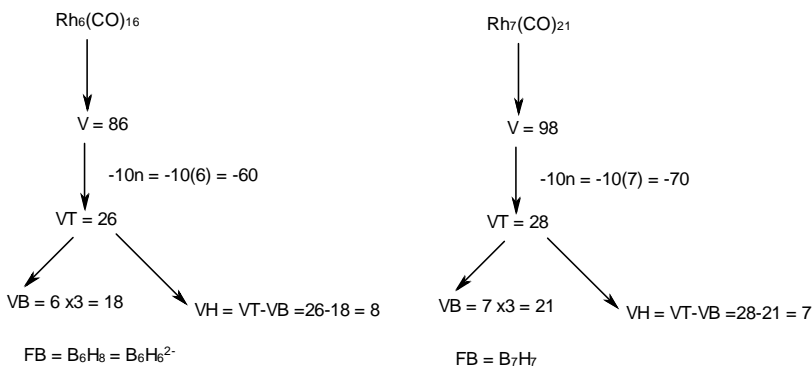
Scheme 2: Further illustration of sripping off the 10n electrons

the equivalent 10n electrons. The remaining electrons (V_T) are distributed between equivalent valence electrons of boron skeletal atoms (V_B) and the valence electrons of the hydrogen atoms (V_B) assumed to be associated with boron skeletal atoms. For example, $Os_5(CO)_{16}$, V = 8X5+16X2 = 72, V_T = 72-50 = 22, V_B = 5X3 = 15, $V_H = V_T-V_B$ = 22-15 = 7. Hence, the borane cluster formula (F_B) corresponding to $Os_5(CO)_{16}$ cluster = $B_5H_7 = B_5H_5^{2-}$. Other borane clusters have been derived in the same way. More examples are illustrated in Schemes 1 and 2.

Equivalence relationship in series

Then the carbonyl series of transition metals and that of the main group elements are scrutinized, then the equivalence relationship between them is clearly discerned. That is if the carbonyl series of the transition metal are given by ST = 14n+p and that of the main group elements by SG = 4n+q such that p = q including the sign before it, then the equivalence relationship between the series does exist. In actual fact, such series are isolobal. For instance, 14n+2 = 4n+2 (closo seris), 14n+4 = 4n+4 (nido), 14n+6 =4n+6(arachno), 14n+0 = 4n+0 (monocapped), 14n-2 = 4n-2(bicapped), 14n-4 =4n-4(tricapped), 14n-6 =4n-6(tetracapped), 14n-8 =4n-8(pentacapped)and 14n-10 = 4n-10(hexacapped) and so on. Therefore, the removal of 10n electrons from a transition metal carbonyl series converts it into an equivalent series of the main group element. This is the principle underlying the clusters presented in Table 1. Many examples other than those presented in the table can be derived.

Structural Relationship of the Cluster Series Closo, Nido and Arachno

It is important to briefly explain the terms closo, nido and arachno before touching on equivalence relationship between boranes and carbonyl clusters. These are terms that evolved with the discovery of boranes. They are actually series of compounds which were found to possess structural relationship that was observed within them and reported by Rudolph[2a]. The closo ones have the ideal geometries with all the atoms linked with triangular sides. An example is the octahedral $B_6H_6^{2-}$with six skeletal atoms[M-6]. When one atom is removed an ideal square pyramid shape is

produced such as B_5H_9 (M-5). The resulting shape is that of a nido cluster regarded as derived from the octahedral closo system [M-6]. The removal of another atom from B_5H_9 (M-5) gives a 4-skeletal atom cluster B_4H_{10}(M-4). This is regarded as arachno with two atoms missing from the shape of the original closo octahedral geometry. As we have observed, the spectrum of series especially the carbonyls is wide.

Consider $Os_5(CO)_{16}$ and $B_5H_5^{2-}$ clusters. For the carbonyl cluster, n = 5, 14n = 14x5 = 70 and number of valence electrons(V) =5x8+16x2 = 72 and hence its series (ST = 14n +2 = 72). Also its corresponding cluster number k = 2n-1 = 2x5-1 = 9. This means the carbonyl cluster belongs to 14n+2 series. In the case of the borane cluster, n =5 as well, 4n =4x5 =20 and V =5x3+5+2 = 22 and so SG = 4n+2 = V and likewise it belongs to 4n +2 series. Its k value = 2n-1 = 2x5-1 =9. This implies that $Os_5(CO)_{16}$ and $B_5H_5^{2-}$ clusters are equivalent and their cluster number k values are equal. Hence, it is likely that their skeletal atom geometries will be similar. Indeed, the skeletal atoms of the two clusters portray a trigonal bipyramid[5] shape as sketched in Figure 1.
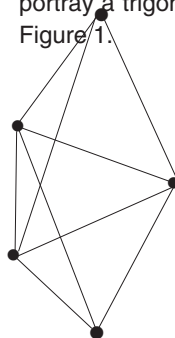

etal Trigonal bipyramid (D₃h).geometry

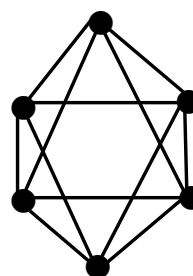**Fig. 1: Skel *et al* Trigonal bipyramid (D$_{3h}$) geometry**


Fig. 2: Skel *et al* Octahedral geometry (O$_h$)

The clusters $Rh_6(CO)_{16}$ (V = 86) and $B_6H_6^{2-}$ (26) are equivalent[5] since the former belongs to 14n+2 while the later 4n+2. Furthermore, their cluster number values k = 11 are equal and they also have an octahedral skeletal geometry as sketched in Figure 2. Just to familiarize ourselves with the method of establishing the equivalence relationship, let us work on this example.
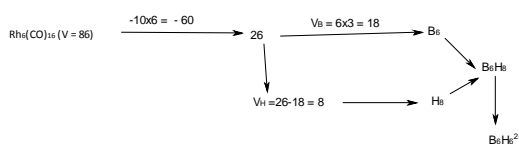
Scheme 3: Illustration of an Equivalence Relationship

In exploring the equivalence relationship further, let us focus on diatomic skeletal systems further. The cluster system $Rh_2(Cp)_2(CO)_2$[6] is equivalent to B_2H_6, C_2H_4, and O_2. The rhodium cluster belongs to the nido series 14n+4 and with k- value of k = 2n-2 = 2. This means that the two atoms are linked with a double bond, Rh=Rh. Similarly, in the diatomic atoms O_2, and C_2 in C_2H_4 will be doubly linked, O=O, and C=C.

However in the case of B_2H_6 the double bond is represented by two banana bonds[5] as sketched in Figure 3.
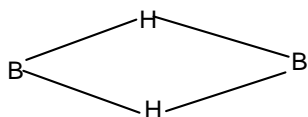
Fig. 3: Sketch of Banana bods of B_2H_6

The carbonyl complex[6], $Cr_2(Cp)_2(CO)_4$ belongs to closo series (14n+2) with k = 2n-1 = 2x2-1 =3. This means that the two chromium atoms are triply linked, that is, Cr≡Cr. As can be seen from Table 1, this complex is equivalent to C_2H_2(4n+2), with k=2n-1 =3. The C_2H_2 diatomic skeletal molecule indeed has a triple bond, C≡C. The $Mn_2(CO)_{10}$ belongs to the Arachno series(14n+6) with k =2n-3 =2x2-3=1.

Therefore the manganese carbonyl has a single bond Mn-Mn. It is equivalent to C_2H_6 (C-C)

and F_2(F-F) which belong to 4n+6 series and do have single bonds. What is fascinating is what the shape of B_2H_8(4n+6) will be. What is also interesting is that theoretical studies[7] which have been done on BH_5(4n+4) and B_2H_8(4n+6) molecules which unlike their hydrocarbon counterparts CH_4 (4n+4) and C_2H_6 (4n+6) are unstable. On the basis of the work done by Olah, etal[7], the possible structures of the hypothetical molecules BH_5 and B_2H_8 are sketched in Figure 4. Also according to the series, the B_2H_8(4n+6) molecule is expected to have a single bond k = 2n-3 = 2x2-3 = 1. As can be deduced from the series, the counterparts for BH_5 are CH_4 and its analogues such as SiH_4, GeH_4, SnH4 and PbH_4 belong to 4n+4 series as well as carbonyls such as $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$ which belong to 14n+4 series. The bond between the H_2 and B atom is a simplified form of a three-centered bond.
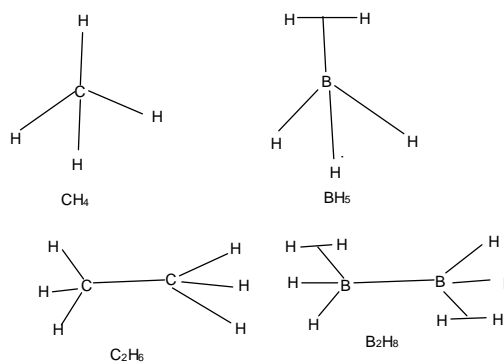
Fig. 4: Possible shapes of the hypothetical molecules BH_5 and B_2H_8 and their known hydrocarbon counterparts

Capping series

The capping carbonyl series give rise to corresponding capped boranes. Many of the hypothetical capped borane series equivalents are useful in categorization of carbonyl clusters. For instance $Os_{10}(C)(CO)_{24}^{2-}$ is equivalent to $B_{10}H_4$. The series for $B_{10}H_4$ can be determined as n = 10, 4n = 40 and V = 10x3+4 = 34 and hence SG = 4n-6 =34 = V. This series can be written as 4n +3(-2). We know from the knowledge of series that 4n represents the first capping C^1 and that every (-2) multiple after the 4n represents an additional capping, this means that the series 4n-6, has Cp = $C^1 + C^3 = C^4$C. By extrapolating $B_{10}H_4$ to Os_{10}(C

)$(CO)_{24}^{2-}$ complex, then it can be deduced that the carbonyl cluster is tetra-capped octahedral $C^4C[M-6]$ as it known to be the case[8]. This code is also important as it indicates that the cluster is in the row number six[M-6] beginning from M-1 of the column in which the closo [M-6] is found and then the cluster capped based on [M-6] is in column number six from the closo system [M-6] in the capping series[3-4].

Table 2: Valence Correlation Between Carbonyl cluster and Main Group Cluster

Generating Function Closo Series		Carbonyl Formula	Main Group V= S= 14n+2	4n+2
F(n)	→	3n+1		
1	4	$Os(CO)_4$	16	6
2	7	$Os_2(CO)_7$	30	10
3	10	$Os_3(CO)_{10}$	44	14
4	13	$Os_4(CO)_{13}$	58	18
5	16	$Os_5(CO)_{16}$	72	22
6	19	$Os_6(CO)_{19}$	86	26
7	22	$Os_7(CO)_{22}$	100	30
8	25	$Os_8(CO)_{25}$	114	34
9	28	$Os_9(CO)_{28}$	128	38
10	31	$Os10(CO)_{31}$	142	42

The derivation of main group compound equivalent to a carbonyl cluster could easily be reflected in Table 2 of closo series. For instance in case of $Os(CO)_4$ (V =16) if 10 (n =1)valence electrons are removed then 6 valence electrons will remain. This corresponds to the elements of group 6(or 16) such O, S, Se, and Te, or a combination of fragments such as CH_2 or CR_2. This clearly is in full agreement with Hoffman's isolobal concept[9]. "In the case of $Os2(CO)_7$[V = 30, S = 14n+2], if we remove 20 electrons (= 10n, n =2), we remain with 10 electrons. The diatomic skeletal chemical species consistent with 10 valence electrons are N_2, C_2H_2, and B_2H_4.

CONCLUSION

The results obtained and displayed in Tables 1and 2 strongly support of power of the 14n and 4n series and their applications to categorize carbonyl and main group element   clusters. They are also in agreement with the Hoffmann's isolobal concept. The assumption is that the skeletal elements in transition metal carbonyl clusters must obey the 18 electron rule while those in the main group elements must obey the octet rule. This work greatly complements what has been published elsewhere in literature on carbonyl and borane clusters[1-2,10-13].

ACKNOWLEDGEMENTS

REFERENCES

1**.**   Wade, K. , *J. Chem. Soc., Dalton*, **1971,** 792-793**.**
2.   (a) Mingos, D. M. P., *Nature Physical Science,* **1972,** 236, 99-102.
       (b) Welch, A. *J. Chem. Soc., Chem. Comm.*, **2013,***49,* 3615-3616.
3.   Kiremire, E.M., *Orient. J. Chem.,* **2014,** 30(4), 1475-1485.
4.   Kiremire, E.M., *Orient. J. Chem.,* **2015,** 31(1), 387-392.

5.   Cotton, F. A., Wilkinson, G., 'Advanced Inorganic Chemistry', 4th Edition, John Wiley & Sons, New York, 1980.

6.   Crabtree, R. H., 'The Organometallic Chemistry of The Transition metals', 4th Edition, John Wiley and Sons, Inc., New Jersey, 2005.

7.   Olah, G. A., Prakash, G. K., S., Rasul, L., PNAS, **2012;** *109(18):* 6825-6828.

8.   Teo, B. K., Longoni,G., Chung, F. R. K., *Inorg. Chem.,* **1984,** *23*, 1257-1266.

9.   Hoffmann, R., *Angew. Chem. Int. Edition,* **1981**, *21(10)*, 711-724.

10.   Hughes, A. K., Wade, K., *Coord. Chem. Rev.,* **2000,** *197*, 191-229.

11.   Rudolph, R. W.,*Accounts Chem. Res.*, **1976**, *9(12)*, 446-452.

12.   Belyakova, O. A., Slovokhotov, Y. L., Russian Chemical Bulletin, *International Edition,* **2003,** *52(11)*, 1-29.

13.   King, R. B., *Inorg. Chimica Acta,* **1986**, *116*, 99-107.