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The Main Group Elements, Fragments, Compounds and Clusters Obey the 4n Rule and Form 4n Series: They are Close relatives to Transition Metal Counterparts via the 14n Linkage

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Abstract

The paper presents numbers which were derived from 4n-based series in a matrix table. The numbers agree precisely with the total number of valence electrons surrounding the respective skeletal elements. The series approach focuses mainly on the number of skeletal elements and their respective number of valence electron content regardless of the origin of the electrons and the type of skeletal elements. For instance, any 6 skeletal elements of transition metal carbonyls surrounded by 86 valence electrons coded as (6,86), series S = 14n+2 normally adopt an octahedral geometry whereas (6,26) series S = 4n+2 for main group elements also tend to adopt an octahedral shape. The transition metal carbonyl cluster series were extensively covered in our previous articles. This paper demonstrates that the main group fragments, clusters and molecules which we normally explain by terms such as valency, valence electrons and octet rule also obey the 4n-based series. The fragments, molecules and clusters of the main group elements correspond well to those of respective transition metal clusters especially the carbonyls if the masking electrons are removed from them. Hence, the series approach is a qualitative method that acts as a unifier of some transition metal clusters with some main group elements clusters.

Keywords: unifying cluster series, fragments, Isolobal fragments and series, valence electron content, valence matrix table, skeletal elements, octet and eighteen electron rules, k-values, multiple bonds, coding system, counting bonds using series

1. Introduction

The discovery of Isolobal principle was a milestone in the history of chemical sciences (Hoffmann, 1982). The principle ably links the concepts of organic, inorganic and organometallic chemistry (Hoffmann, 1982) by using chemical fragments. The fragments are extremely useful in explaining numerous carbonyl and borane shapes of clusters which have attracted the attention of scientists for many years(Lipscomb, 1963, Wade, 1971,1976, Rudolph, 1976**,** Pauling, 1977, Jensen, 1978, Cotton, et al, 1980, Mingos,1972, 1984, Douglas, et al, 1994, King, 2002, Jemmis, 2001a, 2001b,2002, 2003, 2005,2006, 2008, Bowen, et, al, 2007, King, et al, 2009, Welch, 2013**).** It was recently discovered that transition metal carbonyl clusters could readily be categorized using a matrix table (Kiremire, 2016a, 2016b) derived from 14n-based series. What is interesting is that the valence electron content of a given carbonyl cluster, correspond precisely with a number that is found in the matrix table or its extension. For instance, the set of numbers (6, 86) represents six skeletal atoms of a cluster surrounded by a total of 86 valence electrons from the skeletal elements, cluster ligands and the charge if present. As we know, there is a wide range of clusters that that qualify for this code including $M_6(CO)_{16}$, M = Co, Rh and Ir; $Os_6(CO)_{18}^{2-}$, $Ru_6(C)(CO)_{17}$, and $Co_6(CO)_{15}^{2-}$. Using the code notation (6, 86), it becomes easy to categorize the clusters by first removing the 'backbone electrons' of the series, 6x14 = 84 from the total 86. The remaining 2 electrons are added for balancing the electron valence content. This can be formulated as S = 14n+2 = 86 where n = 6. This set of numbers represents CLOSO series. Furthermore, a carbonyl cluster of 6 skeletal atoms surrounded by 86 valence electrons normally adopt an octahedral shape (O_h)(Cotton and Wilkinson, 1980). It has been established that the carbonyl clusters follow the 14n±q series while those of the main group elements follow the parallel series 4n±q where q is an even integer (Kiremire, 2015). In the previous work, emphasis was placed mainly on carbonyl clusters. In this paper, the focus will be placed mainly on clusters of the main group elements covering the range of small to large clusters. An attempt will be made to correlate them with the transition metal carbonyls where necessary.

2. Results and Discussion

Derivation of Numbers in the Matrix Table 1.

Since use of series to categorize clusters and fragments is not well known, it is important to explain briefly their origins and applications. It was recently found that categorization of carbonyl clusters is readily done using 14n-based series. A sample of the series is represented in the matrix form shown in Table 1. Let us consider the series S = 14n+0, when n = 1, S value is 14, when n= 1, S =14+2 = 14; n =1, and S = 14n+4 =18, and n =1, S =14n+6 = 20 and so on. These numbers are given in first row of Table 1. The numbers of second row (n =2) of the Table and other rows are generated similarly. The hypothetical numbers in Table 1 have been derived from cluster series covering the range S = 14n-2 to 14n+12. For transition metal carbonyl series, most non-capped clusters lie within the series S= 14n+2 (CLOSO), 14n+4 (NIDO), 14n+6 (ARACHNO), 14n+8(HYPHO), and 14n+10 (KLAPO). Although the capping range stops at S= 14n-12, a large number of palladium carbonyls such as $Pd_{23}(CO)_{20}L_{10}$(L = PMe_2Ph), S = 14n-32, $C^{17}C$[M-6] and $Pd_{38}(CO)_{28}L_{12}$, S = 14n-52, $C^{27}C$[M-11] fall in the range of cluster series far below S = 14n-12 (Kiremire, 2015, 2016). The corresponding numerical numbers based upon 4n series for main group elements is shown in Table 2 which is the counterpart of Table 1 for transition metal carbonyl clusters. Table 3 gives a few selected examples of metal carbonyl complexes which belong to different family members (family branches) of the 'clan series' S = 14n+2 (CLOSO), 14n+4(NIDO) and 14n+6 (ARACHNO). Table 4 is the counterpart of Table 3 and gives a wide range of selected fragments of different families of the clan series S = 4n+0 (MONO-CAPPED), 4n+2(CLOSO), 4n+4(NIDO), 4n+6 (ARACHNO) up to S = 4n+10. Table 4 covers simple two skeletal element clusters such as C_2 CN^+ to more complex seven skeletal element clusters such as As_7^{3-} (Zintyl ion) and Sb_7^{3-}. A comparison between 14n+4 and 4n+4 for n values 1 to 10 giving selected example of each n-value to underpin the isolobal corresponding relationship between family members for transition metal fragments and main group elements. This is given in Table 5. The table also indicates that fragments which correspond to similar families have the same k values. For instance, $Rh_2(Cp)_2(CO)_2$ (S = 14n+4, k = 2) and C_2H_4 (S = 4n+4, k =2). This means we have a Rh=Rh double bond in the former and another double bond in the later C=C in the latter. This study clearly indicates that the compounds and fragments of the main group elements tend to obey the law of series based upon 4n skeletal backbone while the transition metal clusters especially the carbonyl series obey the law of series based upon 14n skeletal backbone.

The 18-Electron Rule and the Cluster Series Trees.

The 18 electron rule which is extremely useful and has been widely used (Tolman, 1972; Jensen 2005) as can be seen from Table 1 belongs to the series S = 14n +4(NIDO). The 18 valence electron content occurs when n =1 is inserted into the formula S = 14n+4. This means that in this case, each cluster fragment has one skeletal element surrounded by a total of 18 valence electrons. This figure of 18 is just one slot or box in the first row (n = 1) in Table 1. A large number of transition metal complexes especially carbonyls fall into this box numbered 18. These include among others, $M(CO)_5$, M = Fe, Ru, Os; $Ni(CO)_4$,$Cr(C_6H_6)_2$, $M(C_5H_5)_2$, Fe,Ru, Os; $M(CO)_6$,M =Cr, Mo, W, $(C_4H_4)Fe(CO)_3$, $V(CO)_6^{-}$, $Mn(CO)_6^+$,$Fe(CO)_4^{2-}$,$(Cp)_2Ti(CO)_2$,$Mn(CO)_6^+$,$Fe(CO)_4^{2-}$,$(Cp)_2Ti(CO)_2$,$(C_4H_6)Fe(CO)_3$,$(C_6H_6)Cr(CO)_3$,$(Cp)Co(CO)_2$,(Cp)$V(CO)_4$,and $M(NH3)_6^{3+}$, M=Co, Rh, Ir. If we regard n = 1 for S = 14n+4 as a branch of a large tree whose base is S = 14n+4, and n =2 as a second branch and n =3 as a third branch, and so on, then we can have a good understanding what the series represent. We can regard the tree as representing a CLAN TREE of cluster series with branches representing families with individual clusters as family members of that branch. Hence, the above complexes may be regarded as members of the cluster family of the first branch (n =1) for the 'clan series' S = 14n+ 4 (NIDO). Sketches of the cluster trees are shown below T-1 for S= 14n+4, T-2 for S = 14n+2 and T-3 for S = 14n+6. More clan trees of other series can be designed in the similar manner to include series for main group elements in T-4 and T-5 as well as the selected families for bi-capped series T-6, mono-capped series T-7, closo series T-8, nido series T-9 and arachno series T-10. As an illustration of the origin of the clan tree of series, let us consider the NIDO series S = 14n+4 (T-1). The numbers 18(n=1), 32(n=2), 46(n=3), 60(n=4) and 74(n=5) are simply extracted from the Matrix Table 1 under the column labeled S = 14n+4.The numerical values are simply obtained by substituting the value of n into the series formula = 14n+4.The sequence of the numbers is such that from one number to the next, there is a difference of 14. This is clearly a result of the change in n value by on since the series formula S = 14n+4 remains constant. The significance of these numbers can be illustrated by S = 14n+4 = 18 when n =1. The value S = 18 for n =1 represents a large number of transition metal complexes which have one central metal atom (skeletal element) surrounded by a total of 18 valence electrons. THIS IS THE BASIS OF THE 18 ELECTRON RULE which was put forward by Langmuir (Langmuir, 1921). Examples of complexes which obey the 18 electron rule are many including $Fe(CO)_5$, $Ni(CO)_4$, $Fe(\eta^5\text{-}C_5H_5)_2$, and $Co(NH_3)_6^{3+}$. The selected numbers shown in other clan trees (T-2 to T-10) of series were also extracted from Table 1 in a similar manner.

The Applications of Series to Predict Possible Shapes and Linkages of Molecules and Clusters

The carbonyl clusters of low nuclearity, there is a correlation between the k-value and the linkages or bonds. For example, $Rh_2(Cp)_2(CO)_2$, S = 14n+4 ≡4n+4, k = 2n-2 = 2(2)-2 = 2. A sketch of the complex is shown in S-1 indicating the presence of a double bond. Similarly $Mo_2(Cp)_2(CO)_4$, S = 14n+2 ≡4n+2, k = 2n-1 = 2(2)-1 = 3. This means, the complex is expected to have an Mo≡Mo triple bond (Meissler, et al, 2014). A sketch of the triple bond is shown in S-2 as well as other multiple bonds shown in S-3 and S-4 for $Mo(Cp)(CO)_2GeR$ and $Ga_2R_2^{2-}$(Robinson, et al,1997, 1998). We can also predict the skeletal shape of a cluster based on the value of n and k value as presented in the cluster trees. For instance, k = 2 for n = 2 in T-1. This means two skeletal atoms are linked with a double bond as shown in S-1. For n = 2 and k = 3, this gives us a triple bond as in S-2 while in T-3, k = 1 for n = 2 giving us a single bond as in $Mn_2(CO)_{10}$ complex. For the same series T-1 (14n+4), when n = 4, k = 6. The characteristic shape for this is a tetrahedral (T_d) as sketched in S-5. For n = 5 and k = 8 for S = 4n+4, the characteristic shape is a square pyramid sketched in S-6 and k =9 for M-5 gives a trigonal bipyramid as a characteristic shape (S-7) for S = 14n+2 closo series and finally for k = 11 and n = 6 for S = 14n+2, the characteristic shape is O_h(S-8).

Derivation of Cluster Formulas from Cluster Series Formula

The cluster series formula carries some important information. The formula gives us the valence electron content of a cluster formula in question. It also gives the cluster number k which is related to cluster linkages and for ordinary molecules the k value is the same as the number of bonds linking up the skeletal atoms. For instance k = 3 for N_2 means that the two nitrogen atoms are linked with a triple bond. Furthermore, a knowledge of the series can assist us derive the appropriate cluster formula of the fragment for a given number of skeletal atoms. Let us consider a specific example as an illustration. Let the series be S = 14n+6 (ARACHNO) and n = 2. The figure [14] in the series formula represents the backbone fragment electrons of the series, n = the number of skeletal atoms in the formula and 6 = the excess 'determinant' electrons of the series after 14n. In this particular case, 6 tells us we are dealing with ARACHNO series. If the determinant number was 2, we will be dealing with CLOSO series and so on. The following scheme (Scheme 1) summarizes how the appropriate carbonyl clusters of different transition metal atoms can be generated from the series formula S = 14n+6 for n = 2 for the generation of the $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$ carbonyls. In Scheme 2, it is demonstrated how the carbonyl clusters, $Fe_2(Cp)_2(CO)_4$, $Rh_4(CO)_{12}$,$Rh_6(CO)_{16}$ and the main group element clusters $B_6H_6^{2-}$, and the hypothetical Zintyl ion type of clusters M_6^{2-}, M = C, Si, Ge,Sn, and Pb can derived from a series formula.

Keeping the Number of Skeletal Elements Constant and Varying the Number of Valence Electron Content

Let us consider keeping the number of skeletal elements constant and changing the number of valence electron around them. This is simply illustrated in Table 6. As indicated in Table 6, two skeletal elements have been selected. If the skeletal atoms are transition metals in carbonyl clusters are surrounded by 28 electrons (S = 14n+0, n = 2), then k = 2n-0 = 2(2)-0 = 4. The increase in valence electrons by 2 from 28 to 30 changes the series to S = 14n+2 with k = 2n-1 = 2(2)-1 = 3. A good example for this is $Mo_2(Cp)_2(CO)_4$ which has an Mo≡ Mo triple bond(Meissler, et al, 2014).When the valence electrons are increased again by 2 to S = 32 the series formula becomes S = 14n+4 with k= 2n-2 = 2(2)-2 = 2. This means that the two skeletal atoms get linked up by a double bond. This is what is indeed observed in $Rh_2(Cp)_2(CO)_2$ carbonyl cluster complex where a Rh=Rh bond is present(Meissler, et al, 2014). Further increase of the valence electrons by 2 the series formula becomes S = 14n+6 and k = 2n-3 = 2(2)-3 = 1. Thus, the bond order has decreased further to 1. The linkage between the two skeletal atoms is one. This is what is observed in $Mn_2(CO)_{10}$ where Mn—Mn single bond is present(Meissler, et al, 2014). A similar variation in bond order is experienced in moving from C_2H_6(S= 4n+6 = 14, k =2n-3= 2(2)-3 = 1) where C—C single bond is known to C_2H_4(S= 4n+4 = 12, k =2n-2= 2(2)-2= 2) where we get a C=C double bond. Further decrease in valence electrons by 2 to C_2H_2(S= 4n+2 = 10, k =2n-1= 2(2)-1= 3) where we get a C≡C triple bond. Finally, when 2 more valence electrons are removed to produce C_2(S= 4n+0 = 12, k =2n-0= 2(2)-0= 0) where we get a controversial C≣C quadruple bond (Shaik, et al, 2012). Therefore, according to the series approach, if the number of skeletal atoms are kept constant and the number of valence electrons is increased, the k-values or skeletal linkages are decreased and vice versa. In principle, according to the series analysis, if we were to add 2 more electrons to $Mn_2(CO)_{10}$ (S = 14n+6, k = 1), we would get $[Mn_2(CO)_{10}]^{2-}$, S = 14n+8, k = 2n-4 = 2(2)-4 = 0. This implies that $[Mn_2(CO)_{10}]^{2-}$ is unstable and decomposes into $2[Mn(CO)_5]^-$ ions which belong to the series S = 14n+4 that obeys the 18 electron rule. In the same way, adding 2 electrons to C_2H_6(S = 4n+6, k =2n-3 = 2(2)-3 = 1) we would get $[C_2H_6]^{2-}$(S = 4n+8, k = 2n-4 = 2(2)-4 = 0).What this implies by having k = 0, is that the system$[C_2H_6]^{2-}$(k = 0) is unstable and it decomposes to form $2[CH_3]^-$ ions. These are equivalent to having 2 CH_4 molecules which obey the series S = 4n+4 and this is consistent with the octet rule.

Table 1. Matrix Numbers for Valence Electron Content for Transition Metals

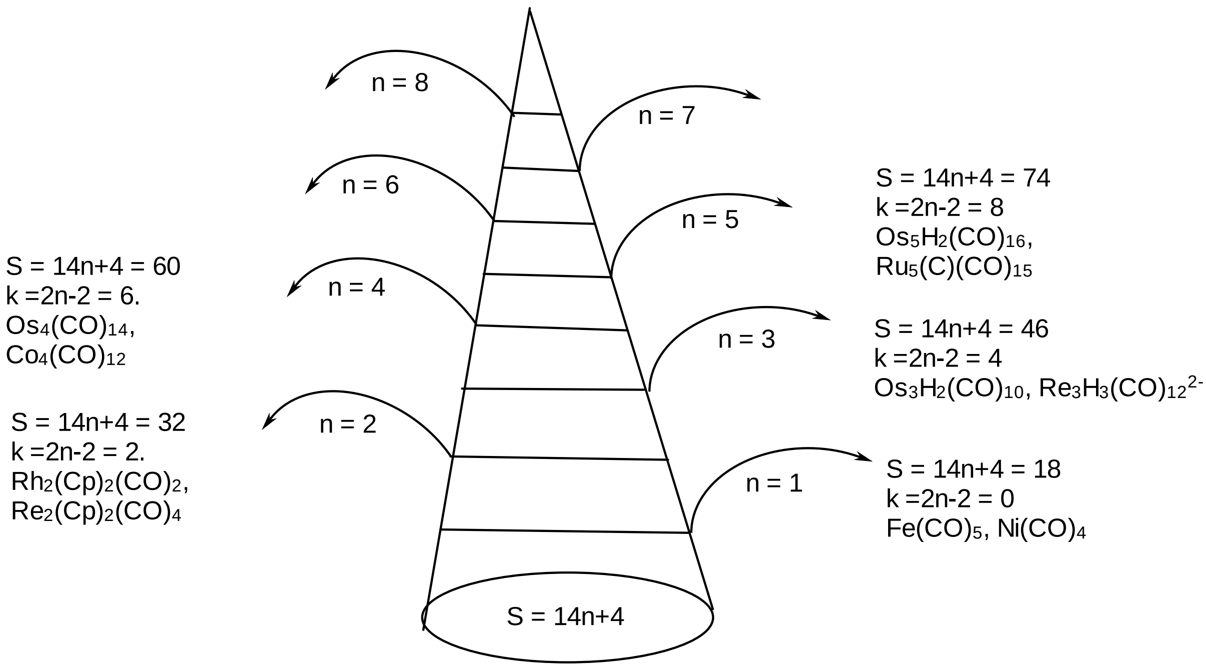
14n-12	14n-10	14n-8	14n-6	14n-4	14n-2	14n+0	14n+2	14n+4	14n+6	14n+8	14n+10	14n+12	n
2	4	6	8	10	12	14	16	18	20	22	24	26	1
16	18	20	22	24	26	28	30	32	34	36	38	40	2
30	32	34	36	38	40	42	44	46	48	50	52	54	3
44	46	48	50	52	54	56	58	60	62	64	66	68	4
58	60	62	64	66	68	70	72	74	76	78	80	82	5
72	74	76	78	80	82	84	86	88	90	92	94	96	6
86	88	90	92	94	96	98	100	102	104	106	108	110	7
100	102	104	106	108	110	112	114	116	118	120	122	124	8
114	116	118	120	122	124	126	128	130	132	134	136	138	9
128	130	132	134	136	138	140	142	144	146	148	150	152	10
142	144	146	148	150	152	154	156	158	160	162	164	166	11
156	158	160	162	164	166	168	170	172	174	176	178	180	12
170	172	174	176	178	180	182	184	186	188	190	192	194	13
184	186	188	190	192	194	196	198	200	202	204	206	208	14
198	200	202	204	206	208	210	212	214	216	218	220	222	15
212	214	216	218	220	222	224	226	228	230	232	234	236	16
226	228	230	232	234	236	238	240	242	244	246	248	250	17
240	242	244	246	248	250	252	254	256	258	260	262	264	18
254	256	258	260	262	264	266	268	270	272	274	276	278	19
268	270	272	274	276	278	280	282	284	286	288	290	292	20
282	284	286	288	290	292	294	296	298	300	302	304	306	21
296	298	300	302	304	306	308	310	312	314	316	318	320	22
310	312	314	316	318	320	322	324	326	328	330	332	334	23
324	326	328	330	332	334	336	338	340	342	344	346	348	24
338	340	342	344	346	348	350	352	354	356	358	360	362	25
352	354	356	358	360	362	364	366	368	370	372	374	376	26
366	368	370	372	374	376	378	380	382	384	386	388	390	27
380	382	384	386	388	390	392	394	396	398	400	402	404	28
394	396	398	400	402	404	406	408	410	412	414	416	418	29
408	410	412	414	416	418	420	422	424	426	428	430	432	30

Table 2. Matrix Numbers for Valence Electron Content for Main Group Elements

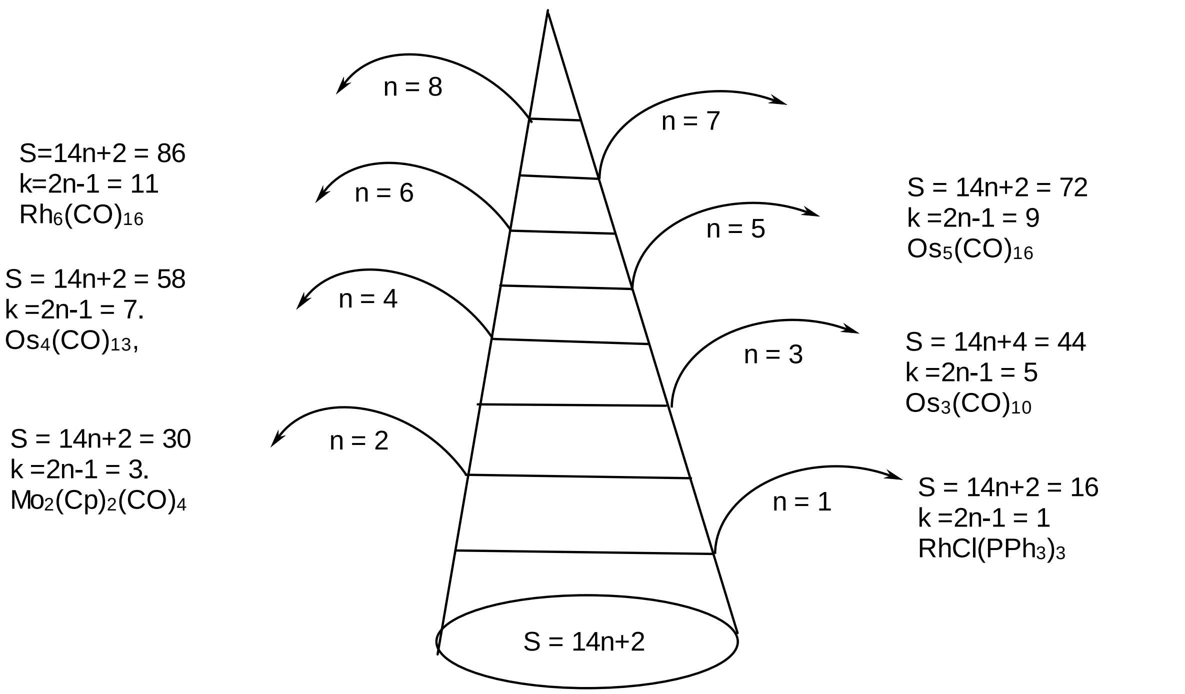
4n-12	4n-10	4n-8	4n-6	4n-4	4n-2	4n+0	4n+2	4n+4	4n+6	4n+8	4n+10	4n+12	n
-8	-6	-4	-2	0	2	4	6	8	10	12	14	16	1
-4	-2	0	2	4	6	8	10	12	14	16	18	20	2
0	2	4	6	8	10	12	14	16	18	20	22	24	3
4	6	8	10	12	14	16	18	20	22	24	26	28	4
8	10	12	14	16	18	20	22	24	26	28	30	32	5
12	14	16	18	20	22	24	26	28	30	32	34	36	6
16	18	20	22	24	26	28	30	32	34	36	38	40	7
20	22	24	26	28	30	32	34	36	38	40	42	44	8
24	26	28	30	32	34	36	38	40	42	44	46	48	9
28	30	32	34	36	38	40	42	44	46	48	50	52	10
32	34	36	38	40	42	44	46	48	50	52	54	56	11
36	38	40	42	44	46	48	50	52	54	56	58	60	12
40	42	44	46	48	50	52	54	56	58	60	62	64	13
44	46	48	50	52	54	56	58	60	62	64	66	68	14
48	50	52	54	56	58	60	62	64	66	68	70	72	15
52	54	56	58	60	62	64	66	68	70	72	74	76	16
56	58	60	62	64	66	68	70	72	74	76	78	80	17
60	62	64	66	68	70	72	74	76	78	80	82	84	18
64	66	68	70	72	74	76	78	80	82	84	86	88	19
68	70	72	74	76	78	80	82	84	86	88	90	92	20
72	74	76	78	80	82	84	86	88	90	92	94	96	21
76	78	80	82	84	86	88	90	92	94	96	98	100	22
80	82	84	86	88	90	92	94	96	98	100	102	104	23
84	86	88	90	92	94	96	98	100	102	104	106	108	24
88	90	92	94	96	98	100	102	104	106	108	110	112	25
92	94	96	98	100	102	104	106	108	110	112	114	116	26
96	98	100	102	104	106	108	110	112	114	116	118	120	27
100	102	104	106	108	110	112	114	116	118	120	122	124	28
104	106	108	110	112	114	116	118	120	122	124	126	128	29
108	110	112	114	116	118	120	122	124	126	128	130	132	30

Table 3. Selected Examples conforming to Series of Transition Metals

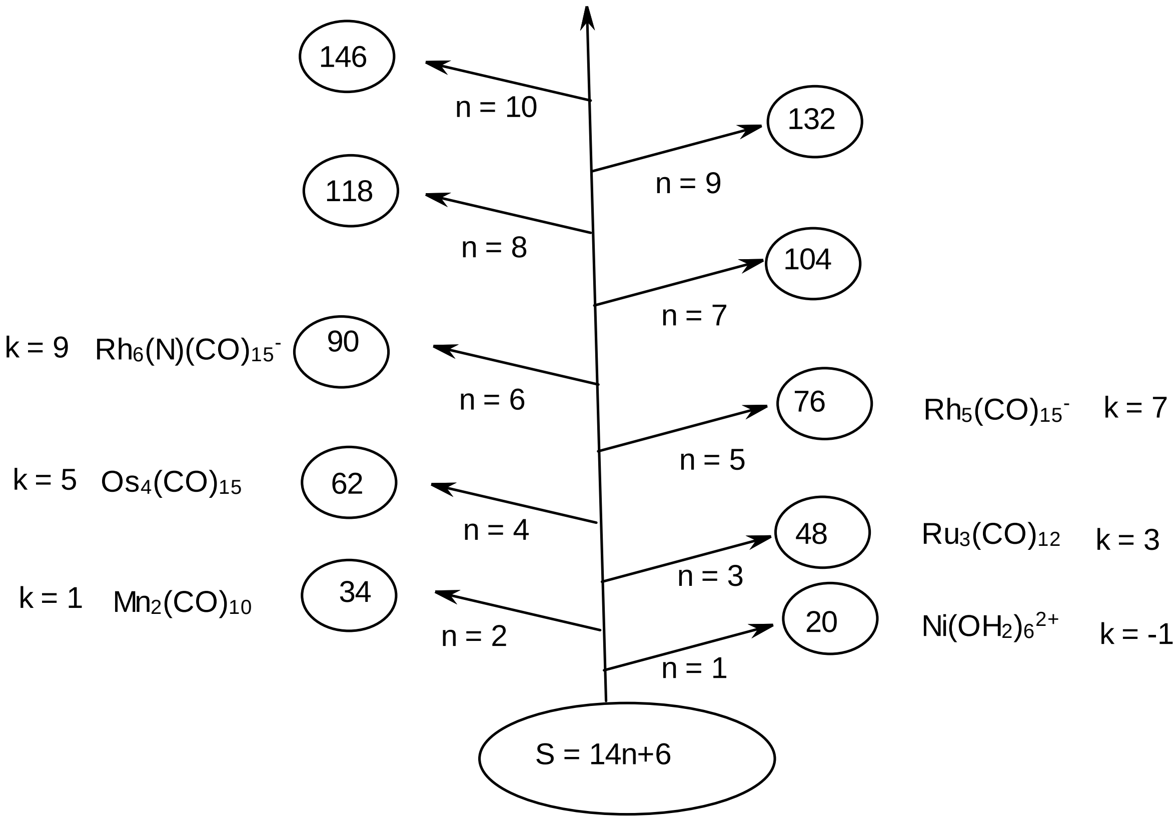
SERIES(S) S = 14n+q	n VALUE	S-VALUE = V	CODE	EXAMPLES	k VALUE k = 2n-q/2
14n+2	1	16	(1,16)	$Os(CO)_4$, $RhCl(L)_3$, L= PPh_3, $Pt(H)L_2$, $PtCl(C_2H_4)^-$, $(Cp)_2TiCl_2$, $Ir(Cl)L_2(CO)$	1
14n+2	2	30		$Mo_2(Cp)_2(CO)_4$	3
14n+2	3	44	(3,44)	$Os_3(CO)_{10}$	5
14n+2	4	58	(4,58)	$Os_4(CO)_{13}$	7
14n+2	5	72	(5,72)	$Os_5(CO)_{16}$	9
14n+2	6	86	(6,86)	$Os_6(CO)_{18}^{2-}$, $Co_6(CO)_{16}$, $Rh_6(CO)_{16}$, $Ir_6(CO)_{16}$, $Rh_6(C)(CO)_{15}^{2-}$, $Re_6(C)(CO)_{19}^{2-}$	11
14n+2	7	100	(7,100)	$Os_7(H)_2(CO)_{21}$, $Rh_7(N)(CO)_{15}^{2-}$ $Co_7(N)(CO)_{15}^{2-}$	13
14n+4	1	18	(1,18)	$M(CO)_5$, M = Fe, Ru, Os; $Ni(CO)_4$,$Cr(C_6H_6)_2$, $M(C_5H_5)_2$, Fe,Ru, Os; $M(CO)_6$,M =Cr, Mo, W, $(C_4H_4)Fe(CO)_3$, $V(CO)_6^-$, $Mn(CO)_6^+$,$Fe(CO)_4^{2-}$,$(Cp)_2Ti(CO)_2$, $(C_4H_6)Fe(CO)_3$,$(C_6H_6)Cr(CO)_3$, $(Cp)Co(CO)_2$,$(Cp)V(CO)_4$,$M(NH3)_6^{3+}$, M=Co, Rh,Ir	0
14n+4	2	32	(2,32)	$Rh_2(Cp)_2(CO)_2$,$Re_2(Cp)_2(CO)_4$, $Re_2H_2(CO)_8$	2
14n+4	3	46	(3,46)	$Os_3H_2(CO)_{10}$,$Re_3H_3(CO)_{10}^{2-}$	4
14n+4	4	60	(4,60)	$Os_4(CO)_{14}$, $Os_4 H_4(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Re_4 H_6(CO)_{12}^{2-}$	6
14n+4	5	74	(5,74)	$Os_5 H_2(CO)_{16}$, $Os_5(C)CO)_{15}$, $Os_5(C)CO)_{14}^{2-}$, $Os_5(C)CO)_{15}$, $Ru_5(C)CO)_{15}$, $Ru_5(N)CO)_{14}^-$,	8
14n+6	1	20	(1,20)	$Os(CO)_6$	-1
14n+6	2	34	(2,34)	$M_2(CO)_{10}$,M = Mn, Tc, Re $Fe_2(CO)_9$,$M_2(CO)_8$, M =Co, Rh, Ir; $Os_2(CO)_8^{2-}$,$Mo_2(Cp)_2(CO)_6$, $M_2(Cp)_2(CO)_4$,M =Fe,Os $Cr_2(Cp)_2(CO)_6$, $Cr_2(Cp)_2(NO)_4$, $FeCo(Cp)(CO)_6$	1
14n+6	3	48	(3,48)	$M_3(CO)_{12}$,M = Fe, Ru, Os $Re_3H_3(CO)_{12}$, $Os_3H_2(CO)_{11}$	3
14n+6	4	62	(4,62)	$Os_4(CO)_{15}$, $Re_4(CO)_{16}^{2-}$,	5
14n+6	5	76	(5,76)	$Os_5(CO)_{18}$, $Rh_5(CO)_{15}^-$, $Ni_5(CO)_{12}^-$, $Ni_3 Cr_2(CO)_{16}^{2-}$, $Ni_3 Mo_2(CO)_{16}^{2-}$, $Ni_3 W_2(CO)_{16}^{2-}$, $Ru Ir_4(CO)_{15}^{2-}$, $PtRh_4(CO)_{14}^{2-}$	7
14n+6	6	90	(6,90)	$Co_6(C)(CO)_{15}^{2-}$, $Os_6(P)(CO)_{18}^-$, $Rh_6(C)(CO)_{15}^{2-}$, $Rh_6(N)(CO)_{15}^-$,	9



T-1. Sketch of Clan Tree of S = 14n+4 Cluster Series with some of its Family Cluster Branches



T-2. Sketch of Clan Tree of S = 14n+2 Cluster Series with some of its Family Cluster Branches



T-3 ARACHNO SERIES

1. $Rh_2(Cp)_2(CO)_2$

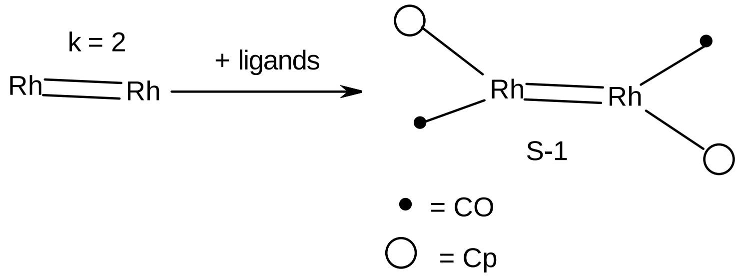
$$\overset{14+0}{2[Rh(Cp)]} \longrightarrow 4n+0$$

$$\overset{9+5}{2CO} \longrightarrow 0+4$$

n = 2 S = 4n+4

k = 2n-2 = 2(2)-2 = 2

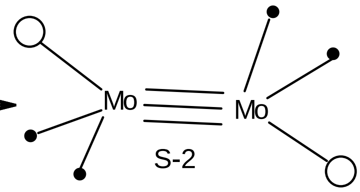
SKELETAL SHAPE



2. $Mo_2(Cp)_2(CO)_4$

SKELETAL SHAPE

$$\overset{14+1}{\underset{6+5+4}{2[Mo(Cp)(CO)_2]}} \longrightarrow 4n+2 \qquad \overset{k=3}{Mo \equiv Mo} \xrightarrow{+\text{ ligands}}$$



S-2

n = 2 S = 4n+2

k = 2n-1 = 2(2)-1 = 3

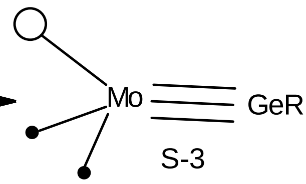
• = CO

○ = Cp

3. $Mo(Cp)(CO)_2GeR$

SKELETAL SHAPE

$$\overset{14+1}{\underset{6+5+4}{1[Mo(Cp)(CO)_2]}} \longrightarrow 4n+1 \qquad \overset{k=3}{Mo \equiv GeR} \xrightarrow{+\text{ ligands}}$$



S-3

$$\underset{4+1}{1[GeR]} \longrightarrow 4n+1$$

• = CO

○ = Cp

n = 2 S = 4n+2

k = 2n-1 = 2(2)-1 = 3

4. $[Ga_2R_2]^{2-}$

$$\overset{4+0}{\underset{3+1}{2[GaR]}} \longrightarrow 4n+0$$

$$q \longrightarrow 0+2$$

q = CHARGE

S = 4n+2 k = 2n-1 = 2(2)-1 = 3

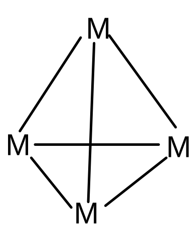
SKELETAL SHAPE

$$[RGa \equiv GaR]^{2-}$$

S-4

Tetrahedral, T_d

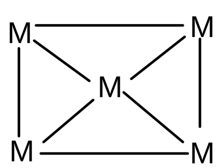
k =6, M-4



S-5

Square pyramid, C_{4v}

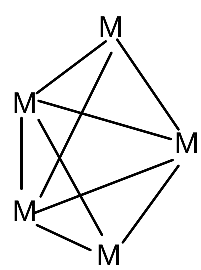
k = 8, M - 5



S-6

Trigonal bipyramid, D_{3h}

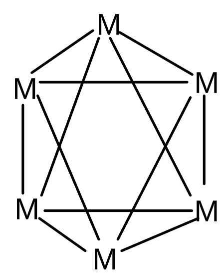
k = 9, M-5



S-7

Octahedral, O_h

k = 11, M - 6

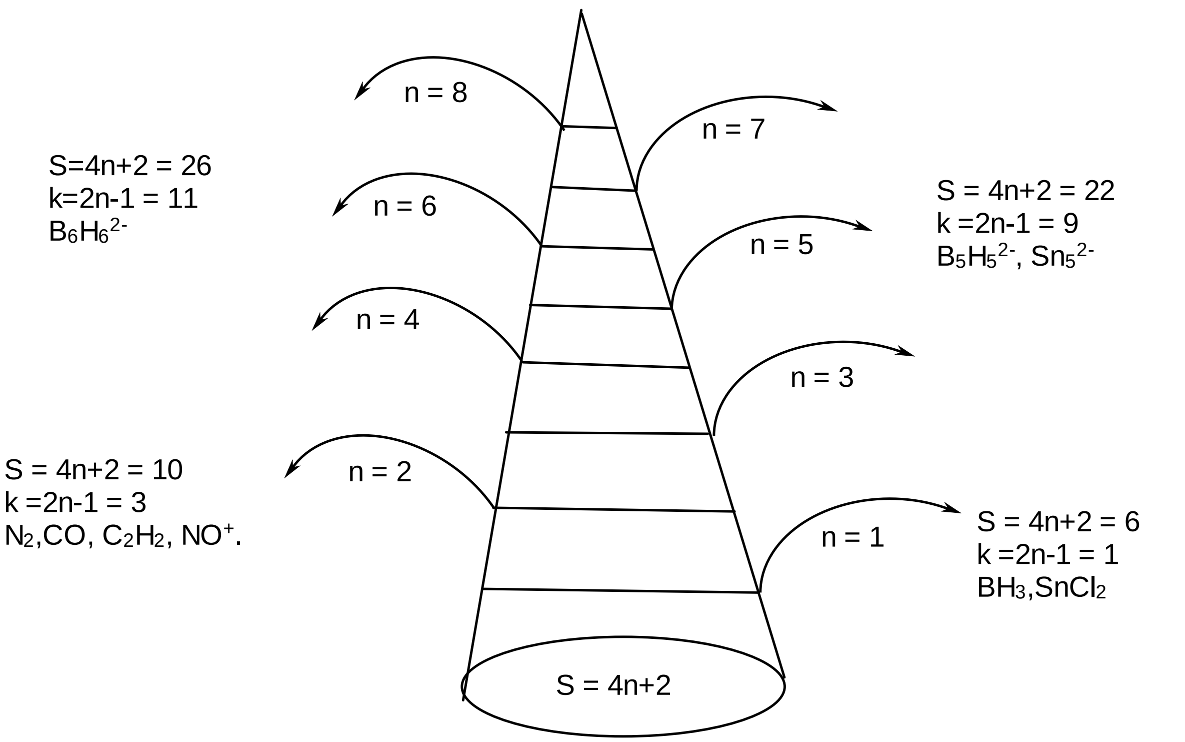


S-8

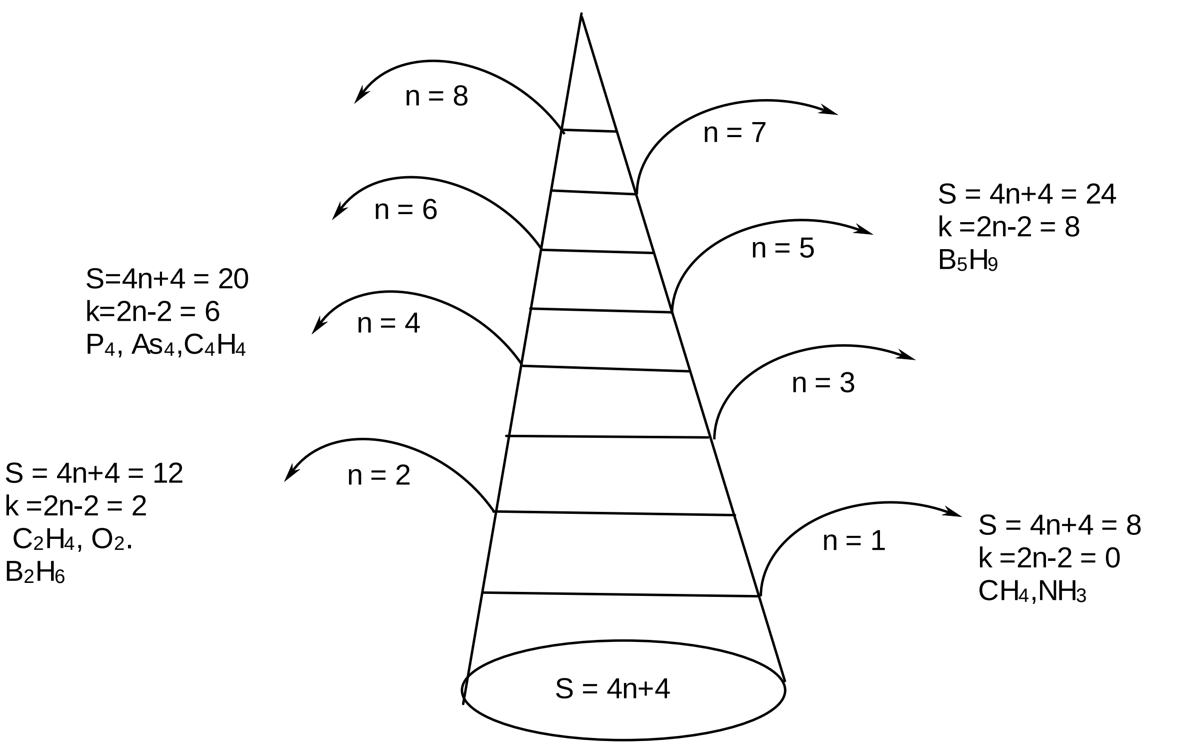
Table 4. Selected Examples of fragments conforming to Series of Main Group Elements

SERIES(S)	n VALUE	S-VALUE = V	CODE	EXAMPLES	k VALUE
S = 4n+q					k = 2n-q/2
4n+0	1	4	(1,4)	C, BH, BeX_2, X=H,F, Cl, Br, I	2
4n+0	2	8	(2,8)	C_2, B_2H_2, CN^+, CB^-	4
4n+2	1	6	(1,6)	BX_3, X = H,F, Cl, Br, I; O, NH, $SnCl_2$	1
4n+2	2	10	(2,10)	C_2H_2, CO, CN^-,N_2, NO^+, BNR_2	3
4n+2	5	22	(5,22)	$B_5H_5^{2-}$, M_5^{2-}, M = Sn, Pb Bi_5^{3+}, $C_2B_3H_5$	9
4n+2	6	26	(6,26)	$B_6H_6^{2-}$	11
4n+4	1	8	(1,8)	MX_4, M= C, Si, Ge, Sn, Pb; X =H,F, Cl, Br, I;H_2CO, HX, X = F, Cl, Br, I;H_2M, M = O,S, Se MX_4, M = C, Si, Ge, Sn, Pb; X = H, F, Cl, Br, I	0
4n+4	2	12	(2, 12)	C_2H_4, NO^-, O_2, S_2, B_2H_6, C_3	2
4n+4	3	16	(3, 16)	C_3H_4, BN_2^{3-}	4
4n+4	4	20	(4, 20)	M_4, M =N, P,As, Sb, Bi, $InBi_3^{2-}$, $GaBi_3^{2-}$	6
4n+4	5	24	(5,24)	B_5H_9, N_5^+	8
4n+6	1	10	(1,10)	PF_5, ClF_3, SO_2, POF_3, SF_4,SOF_2, SF_4, ICl_4^+, XeF_2	-1
4n+6	2	14	(2,14)	X_2, X = F,Cl, Br, I; C2H6, M_2X_4, M = N, P, As, Sb; X = H, F, Cl, Br, I; O_2^{2-}, S_2X_2, X =F,Cl,Br	1
4n+6	3	18	(3,18)	S_3, C_3H_6	3
4n+6	4	22	(4,22)	B_4H_{10}, C_4H_6, Te_4^{2+}	5
4n+6	6	30	(6,30)	C_6H_6, $B_3N_3H_6$, C_5H_5N	9

SERIES(S)	n VALUE	S-VALUE = V	CODE	EXAMPLES	k VALUE
S = 4n+q					k = 2n-q/2
4n+8	1	12	(1,12)	SF_6, ClF_5, XeF_4, BrF_6^+, ICl_4^-, ClO_3^-, XeF_3^+, XeO_2, XeF_5^+	-2
4n+8	3	20	(3,20)	C_3H_8, BrF_2^+	2
4n+8	4	24	(3,24)	C_4H_8	4
4n+10	1	14	(1,14)	IF_7, AsF_6^-, $XeOF_4$, XeF_5^-, XeF_6, XeO_2F_2	-3
4n+10	4	26	(2,26)	Se_4^{2-}, C_4H_{10}	3
4n+10	5	30	(5,30)	C_5H_{10}	5
4n+10	6	34	(6,34)	S_6^{2+}, $B_2N_4^{8-}$,C_6H_{10}	7
4n+10	7	38	(7,38)	M_7^{3-}, M = As, Sb; P_4S_3	9



T-4. Sketch of Clan Tree of S = 4n+2 Cluster Series with some of its Family Cluster Branches



T-5. Sketch of Clan Tree of S = 4n+4 Cluster Series with some of its Family Cluster Branches

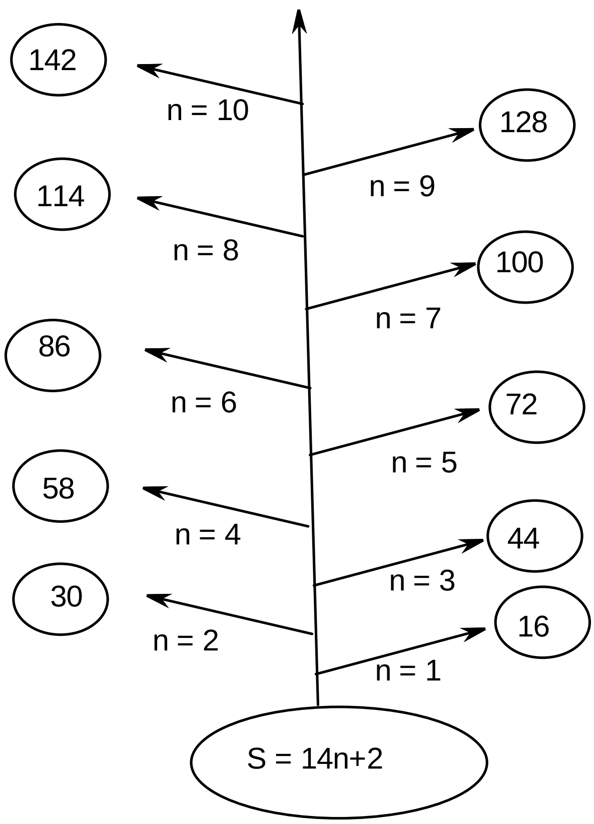
Table 5. The Variation of k value with for selected values of n for S = 14n+4 and S = 4n+4 series

n	14n+4	k value	4n+4	TM*	MG*
		k =2n-2		14n+4	4n+4
1	18	0	8	$Fe(CO)_5$	CH_4
2	32	2	12	$Rh_2(Cp)_2(CO)_2$	C_2H_4
3	46	4	16	$Re_3H_3(CO)_{12}^{2-}$	C_3H_4
4	60	6	20	$Ir_4(CO)_{12}$	C_4H_4, P_4
5	74	8	24	$Ru_5(C)(CO)_{15}$	B_5H_9
6	88	10	28	$Os_6H_2(CO)_{19}$	B_6H_{10}
7	102	12	32	$Os_6Pt(CO)_{18}H_8$	B_7H_{11}
8	116	14	36	$Os_8(CO)_{26}$	B_8H_{12}
9	130	16	40	$Co_9(P)(CO)_{21}^{2-}$ $Ni_9(C)(CO)_{17}^{2-}$	Ge_9^{4-}
10	144	18	44	$Os_{10}(CO)_{32}$	$B_{10}H_{14}$

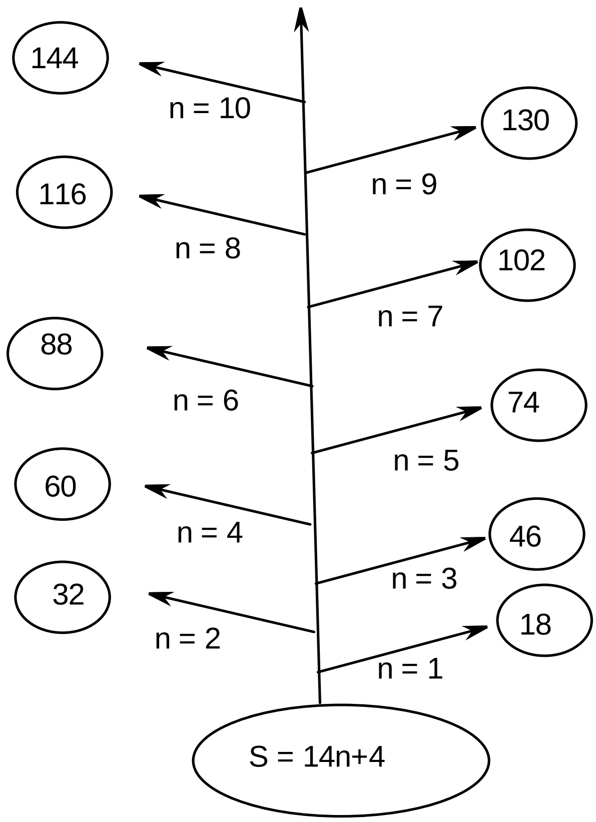
Table 6. Sample to show the variation of k value with Valence Electrons(S-value) when n is constant

	S-value							S-value	
	V_T	Example	SERIES		k	k value		V_{MG}	Example
n =2	34	$Mn_2(CO)_{10}$	14+6	ARACHNO	2n-3	1	4n+6	14	C_2H_6
	32	$Rh_2(Cp)_2(CO)_2$	14n+4	NIDO	2n-2	2	4n+4	12	C_2H_4
	30	$Mo_2(Cp)_2(CO)_4$	14n+2	CLOSO	2n-1	3	4n+2	10	C_2H_2
	28	$Os_2(CO)_6$	14n+0	MONOCAP	2n-0	4	4n+0	8	C_2

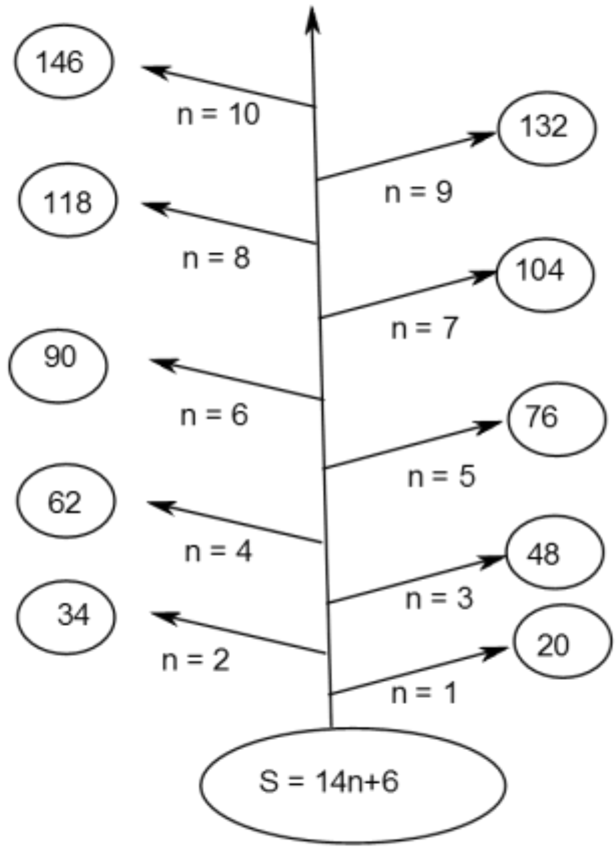
TM = Transition metal cluster, MG = Main group element cluster.



T-8 CLOSO SERIES



T-9 NIDO SERIES



T-10 ARACHNO SERIES

Mn $\longrightarrow$ [14] = $[Mn(H)(CO)_3]$, n = 2, S = 14n+6

F_{MN} = $[Mn(H)(CO)_3](2)+3CO = Mn_2(H)_2(CO)_6+3CO = Mn_2(CO)_7+3CO = Mn_2(CO)_{10}$

Fe $\longrightarrow$ [14] =$[Fe(CO)_3]$, n=2, S=14n+6

$F_{Fe} = [Fe(CO)_3](2)+3CO = Fe_2(CO)_6+3CO = Fe_2(CO)_9$

Co $\longrightarrow$ [14] = $[Co(H)(CO)_2](2)+3CO = Co_2(H)_2(CO)_4+3CO = Co_2(CO)_5+3CO = Co_2(CO)_8$

ISOLOBAL HYDROCARBON

F_C= 4n+6, n =2

C $\longrightarrow$ [4]; $F_c = [C](2)+6H = C_2H_6$

HENCE, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$ ARE ISOLOBAL TO C_2H_6.

SCHEME 1. CONVERSION OF SERIES FORMULA INTO CLUSTER FORMULAS

1. S =14n+6, n = 2, Fe CARBONYL CONTAING, Cp LIGAND

Fe $\longrightarrow$ [14] $\longrightarrow$ [Fe(Cp)(H)]

F_{Fe} = [Fe(H)(Cp)](2)+3CO = $Fe_2(Cp)_2(H)_2$+ 3CO = $Fe_2(Cp)_2(H)_2$+3CO
$Fe_2(Cp_2(CO)$ +3CO = $Fe_2(Cp)_2(CO)_4$

2. S =14n+4, n = 4, Rh CARBONYL WITH Rh AND CO LIGANDS ONLY

Rh $\longrightarrow$ [14] = $[Rh(H)(CO)_2]$

F_{Rh} = [Rh(H)(CO)2](4)+2CO = $Rh_4(H)_4(CO)_8$+2CO = Rh4$(CO)_2(CO)_8$+2CO = $Rh_4(CO)_{10}$+2CO = $Rh_4(CO)_{12}$

3. S =14n+2, n = 6, Rh CO CLUSTER WITH Rh AND CO LIGANDS ONLY

Rh $\longrightarrow$ [14] = $[Rh(H)(CO)_2]$

F_{Rh} = [Rh(H)(CO)2](6)+2CO = $Rh_6(H)_6(CO)_{12}$+CO = $Rh_6(CO)_3(CO)_{12}$+2CO = $Rh_6(CO)_{15}$+CO = $Rh_6(CO)_{16}$

4. F_B= 4n+2 = [BH](6) +2 = $B_6H_6^{2-}$

5. F_C = [C](6)+2 = C_6^{2-} = C_6H_2 F_C = C_6^{2-} = Si_6^{2-} = Ge_6^{2-} = Sn_6^{2-} = Pb_6^{2-}

SCHEME 2. MORE CONVERSION EXAMPLES

3. Conclusion

Just as in transition metal carbonyl clusters which form according to 14n-based series,the elements of the main group periodic table form compounds, ions, fragments and clusters which follow the 4n-based series. Then (n) in the series formula represents the number of skeletal elements in a fragment. For the main group elements a carbon atom(C) or (BH) fragment are good building blocks and each fragment comprises of 4 valence electrons. In the case of transition metal carbonyl clusters the building block or skeletal backbone fragment comprises of 14 valence electrons. A series formula S = 14n+q or S = 4n+q may be regarded as representing many clusters, molecules and fragments. The numerical values corresponding to n =1, 2, 3, 4, and so forth may be considered to be family cluster branches for S= 14n+q or 4n+q. Thus, we may regard, S = 14n+q or 4n+q as a ‘cluster clan tree’ out of which various cluster families emanate. We may regard a carbonyl cluster complex of specific number of skeletal elements and valence electrons to join its family members on any suitable branch corresponding to a particular family clan tree. Thus, the chemical fragments precisely belong to specific cluster families of specific clan tree series. The 18 electron rule(S = 14n+4, n =1, NIDO CLAN TREE) or 16 electron rule(S = 14n+2, n = 1, CLOSO CLAN TREE) or octet rule(S= 4n+4, n = 1, NIDO CLAN TREE, MAIN GROUP ELEMENTS) are special cases of cluster families of specific clan trees. They may be considered to be the first families we encounter at the beginning of the clan trees of series. In summary, the transition metal complexes especially carbonyls have a tendency of forming clusters and fragments in accordance with 14n series whereas the main group element clusters or compounds and fragments are formed according to 4n series.

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