

A Hypothetical Model for the Formation of Transition Metal Carbonyl Clusters Based upon 4n Series Skeletal Numbers

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Received: August 23, 2016 Accepted: September 6, 2016 Online Published: September 29, 2016

doi:10.5539/ijc.v8n4p78

URL: <http://dx.doi.org/10.5539/ijc.v8n4p78>

Abstract

Skeletal numbers of elements have been introduced as derivatives of the 4n series method. They are based on the number of valence electrons present in the skeletal element. They are extremely useful in deducing possible shapes of skeletal elements in molecules or clusters especially the small to medium ones. For large skeletal clusters, the skeletal numbers may simply be regarded as identity numbers. In carbonyl clusters, they can be used as a guide to facilitate the distribution of the ligands such as CO, H and charges onto the skeletal atoms. A naked skeletal cluster may be viewed as a reservoir for skeletal linkages which get utilized when ligands or electrons get bound to it. The sum of linkages used up by the ligands bound to a skeletal fragment and the remaining cluster skeletal numbers is equal to the number of the skeletal linkages present in the original 'naked parent' skeletal cluster. The skeletal numbers can be used as a quick way of testing whether or not a skeletal atom obeys the 8-or 18-electron rules.

Keywords: Linkages, skeletal, numbers, clusters, fragments, 18-electron rule, carbonyls, series

1. Introduction

The recently developed 4n series method has been found to analyze and categorize atoms, molecules, fragments and clusters (Kiremire, 2016a, 2016b, 2016c). The method highly complements Wade-Mingos rules which have been in existence for more than forty years (Wade, 1991; Mingos, 1972, 1984, 1991). Other methods for dealing with electron counting in clusters have been devised (Lipscomb, 1976; King, 1986a, 1986b; Jensen, 1978; Teo, et al, 1984; Wales, 2005; Wheeler and Hoffmann, 1986; Jemmis, et al, 2000, 2001a, 2001b). However on closer scrutiny of the 4n series method, it has become apparent that we could go further and assign skeletal linkage numbers to elements and ligands which greatly simplifies the prediction of structures of molecules and clusters. The skeletal numbers are especially very helpful in assigning a specific number of carbonyl ligands to skeletal metal elements and hence generating carbonyl cluster isomers. Furthermore, it makes it easier to deduce whether or not clusters obey the 18-electron rule. The observation of behavior of k values in the hydrocarbons involving the addition of hydrogen atoms to skeletal carbon fragments (Kiremire, 2016e) have triggered the need to observe the behavior of k values by adding the carbonyl (CO) ligands to transition metal skeletal fragments. The impact of this work has been to introduce the concept of assigning skeletal numbers to the atoms of the main group elements and the transition metals.

2. Results and Discussion

2.1 Assignment of Skeletal Linkages (K Values) to Elements

The procedure for categorization and structural prediction of fragments, molecules and clusters using the 4n series method is now well established (Kiremire, 2016a, 2016b, 2016c). What is more interesting and exciting is that on closer scrutiny of the 4n series method is that skeletal elements and ligands can actually be assigned skeletal k values. For instance, the single carbon atom [C], with valence electron content of four [4], $S=1[4+0]=4n+0(n=1)$, and $k=2n(n=1)=2$. Hence, a carbon atom is assigned a k value of 2. For the nitrogen atom, N with valence electron content of 5, $S=4n+1(n=1)$ and $k=2n-0.5=1.5$ while boron, B with valence electrons 3, $S=4n-1(n=1)$ and $k=2n+0.5=2.5$. The assigned k values of the main group elements are given in Table 1. In the case of transition metals, the $S=14+q$ is taken as equivalent (Kiremire, 2015a; Hoffmann, 1982) to $S=4n+q$. The k values of transition metals are given in Table 2. Furthermore, the k values of naked metal clusters from 1 to 10 for first row transition metals are given in Table 3. The addition of a hydrogen atom to a carbon atom produces the fragment [CH] which has 5 valence electrons like a nitrogen atom [N]. Hence its series is given by $S=4n+1$ and the k value will also be given by $k=2n-0.5=2(1)-0.5=1.5$. But the carbon atom [C] belongs to $S=4n+0$ with $k=2n+0=2(1)+0=2$. This means that a simple operation of $C(k=2) + H \rightarrow CH(k=1.5)$ results in the decrease of k value by 0.5. Hence, it makes sense if we could assign a value of $k=-0.5$ to a hydrogen atom (H) ligand.

Table 1. Skeletal Values of the Main Group Elements

Group	Series, $S = 4n+q$	$k = 2n-q/2$						
1	$4n-3$	3.5	Li	Na	K	Rb	Cs	
2	$4n-2$	3	Be	Mg	Ca	Sr	Ba	
3	$4n-1$	2.5	B	Al	Ga	In	Tl	
4	$4n+0$	2	C	Si	Ge	Sn	Pb	
5	$4n+1$	1.5	N	P	As	Sb	Bi	
6	$4n+2$	1	O	S	Se	Te	Po	
7	$4n+3$	0.5	F	Cl	Br	I	At	
8	$4n+4$	0	Ne	Ar	Kr	Xe	Rn	

Table 2. Skeletal Values of Transition Metals

3d-TM*	4d-TM*	5d-TM*	Series, $S = 4n+q$	$k = 2n-q/2$	Comments	Possible cluster
Sc	Y	La	$4n-11$	7.5	Possible Dimerization	M_2L_{14} or ML_7H, ML_7X
Ti	Zr	Hf	$4n-10$	7	Mono-skeletal cluster	ML_7
V	Nb	Ta	$4n-9$	6.5	Possible Dimerization	M_2L_{12} or ML_6H, ML_6X
Cr	Mo	W	$4n-8$	6	Mono-skeletal cluster	ML_6
Mn	Tc	Re	$4n-7$	5.5	Possible Dimerization	M_2L_{10} or ML_5H, ML_5X
Fe	Ru	Os	$4n-6$	5	Mono-skeletal cluster	ML_5
Co	Rh	Ir	$4n-5$	4.5	Possible Dimerization	M_2L_8 or ML_4H, ML_4X
Ni	Pd	Pt	$4n-4$	4	Mono-skeletal cluster	ML_4
Cu	Ag	Au	$4n-3$	3.5	Possible Dimerization	M_2L_6 , or M_3H, ML_3X
Zn	Cd	Hg	$4n-2$	3	Mono-skeletal cluster	ML_3

* Transition Metals, L = 2-Electron donor, e.g. CO, PPh₃, X = Cl, Br, I

Table 3. Skeletal Values of Selected Naked Skeletal Clusters of First Row Transition Metals

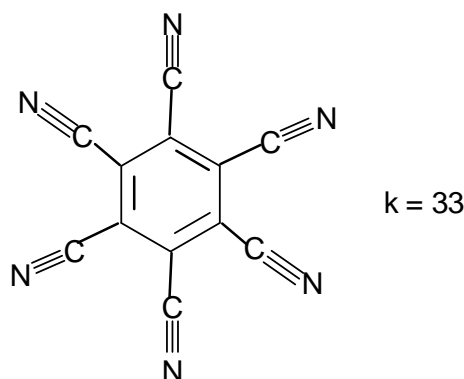
n	1	2	3	4	5	6	7	8	9	10
Sc _n	7.5	15	22.5	30	37.5	45	52.5	60	67.5	75
Ti _n	7	14	21	28	35	42	49	56	63	70
V _n	6.5	13	19.5	26	32.5	39	45.5	52	58.5	65
Cr _n	6	12	18	24	30	36	42	48	54	60
Mn _n	5.5	11	16.5	22	27.5	33	38.5	44	49.5	55
Fe _n	5	10	15	20	25	30	35	40	45	50
Co _n	4.5	9	13.5	18	22.5	27	31.5	36	40.5	45
Ni _n	4	8	12	16	20	24	28	32	36	40
Cu _n	3.5	7	10.5	14	17.5	21	24.5	28	31.5	35
Zn _n	3	6	9	12	15	18	21	24	27	30

2.2 The Power of Skeletal Numbers

2.2.1 The Skeletal Numbers and Main Group Elements

When skeletal atoms are combined alone or with ligands such as hydrogen atoms to form fragments or molecules, the corresponding skeletal numbers are handled in the same manner. Let us take the following simple illustrations.

$C(k=2)+C(k=2)\rightarrow C_2(k=4)\rightarrow C\equiv C$; $B(k=2.5)+N(k=1.5)\rightarrow BN(k=4)\rightarrow B\equiv N$; $CN^+(k=2+1.5+0.5=4)\rightarrow [(C\equiv N)^+]$; $CB^-(k=2+2.5-0.5=4)\rightarrow [(C\equiv B)^-]$; $CH(k=1.5)+CH(k=1.5)\rightarrow C_2H_2(k=3)\rightarrow HC\equiv CH$; $C(k=2)+C(k=2)+2H(k=-1)\rightarrow C_2H_2(k=4-1=3)\rightarrow HC\equiv CH$; $CO(k=2+1=3)\rightarrow C\equiv O$; $NO^+(k=1.5+1+0.5=3)\rightarrow [(N\equiv O)^+]$; $CN^-(k=2+1.5-0.5=3)\rightarrow [(C\equiv N)^-]$; $C_2H_4[k=2(2)-4(0.5)=2]\rightarrow H_2C=CH_2$; $O_2[k=2(1)=2]\rightarrow O=O$; $C_2H_6[2(2)-6(0.5)=1]\rightarrow H_3C-CH_3$; $F_2(k=0.5+0.5=1)\rightarrow F-F$; $C_4H_4(k=8-2=6)$, $C_6H_6[k=12-3=9]$, benzene, benzene hexacarbonitrile $[C_{12}N_6, k=12(2)+6(1.5)=33]$, see BC-1]. The fact that the number of bonds of benzenehexacarbonitrile as counted from the structure BC-1 is the same as that calculated from the skeletal numbers of the atoms in the formula underpins the power of the skeletal numbers. It should also be noted that a negative charge is taken the same as an electron from a donor atom by the 4n series while a positive charge does the opposite.



BC-1 Structure of benzenehexacarbonitrile

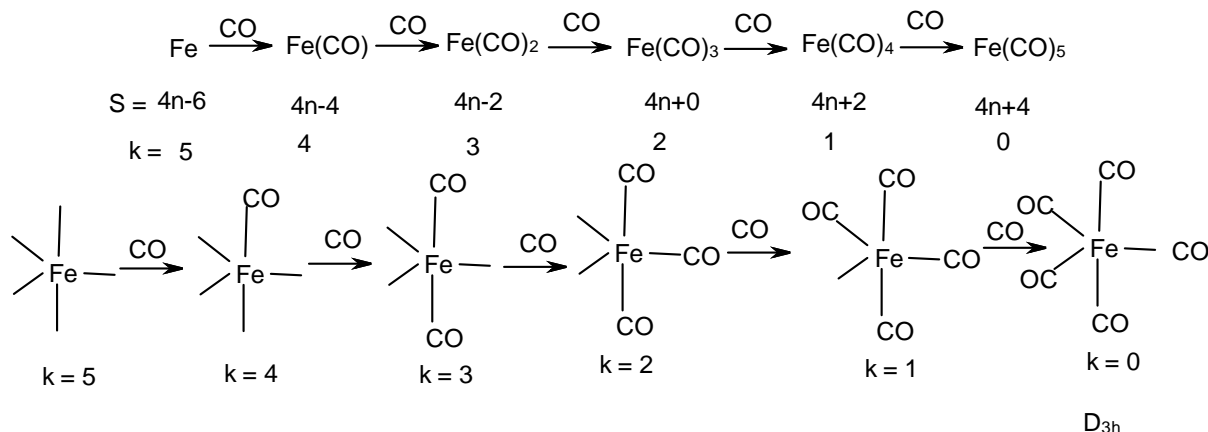
The chemical fragments C_2 , CN^+ , BN , and CB^- have been shown to possess quadruple bonds (Shaik, et al, 2012) by high level computations although the concept is still controversial. However the skeletal numbers derived from the 4n series approach agree with their results. Also most of the bond orders of chemical fragments obtained from molecular orbital energy level diagrams (Housecroft, et al, 2005) agree with the k values obtained from skeletal numbers of atoms. For the diatomic fragments, the k value obtained is simply the same as the bond order.

2.3 The Effect of Adding CO Ligands on Skeletal Linkages of Clusters

2.3.1 Single Metal Skeletal Element (M_1)

2.3.1.1 Fe Skeletal Element

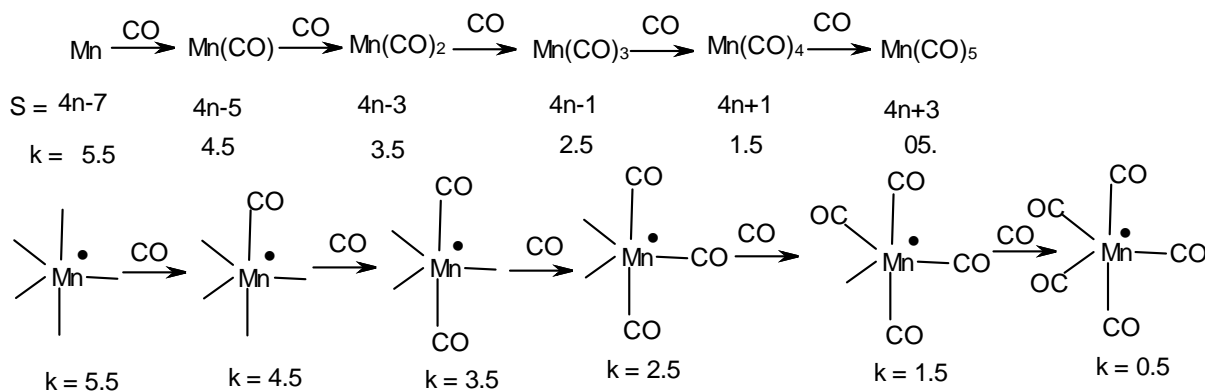
Let us illustrate this by successive addition of CO ligands to Fe skeletal element. This summed up in Scheme 1. What happens to the k value when the CO ligands are step-by-step added to a single metal atom? Let us use Fe ($S=4n-6$) atom again as our illustration. The Fe atom belongs to the series $S=4n-6$, $k=2n+3=2(1)+3=5$. Addition of the first $:CO$ ligand, we get the $Fe(CO)$ fragment. This can be expressed by a simple equation $Fe + CO \rightarrow Fe(CO)$. Since in 4n series, we are dealing with valence electron content, the $:CO$ ligand contributes two more electrons to the series $S=4n-6+2 \rightarrow S=4n-4$. This means that we get the fragment $Fe(CO)$ which belongs to the series $S=4n-4$ and $k=2n+2=2(1)+2=4$. Thus, the k value of Fe ($k=5$) has decreased to $Fe(CO)$ ($k=4$). Further addition of $:CO$ ligand, we get another fragment $Fe(CO)_2$ ($S=4n-2$, $k=2n+1=3$). The next fragment becomes $Fe(CO)_3$ ($S=4n+0$, $k=2n=2$). This will be followed by $Fe(CO)_4$ ($S=4n+2$, $k=2n-1=2(1)-1=1$). The last fragment will be $Fe(CO)_5$ ($S=4n+4$, $k=2n-2=2(1)-2=0$). Clearly the k value of 5 for the Fe skeletal atom implies the number of the skeletal coordinate bonds or electron pairs to be received from the ligands to form coordinate bonds so as to enable the Fe skeletal atom attain the 18-electron rule. Since the Fe atom has 8 valence electrons, it makes sense that it requires additional 5 pairs (10 electrons) electrons so as to obey the 18-electron rule. We know that the addition of one CO ligand decreases the skeletal k value by 1, therefore we could assign a value of $k=-1$ to the CO ligand. In this way, the CO ligand or any other ligands may be regarded as 'neutralizing agents' of the cluster skeletal bonds or linkages of the original naked parent skeletal fragment. Each electron provided by a ligand or a charge, neutralizes the skeletal linkages by k value of 0.5 as deduced from the 4n series. That is, a single electron reduces the skeletal value of a cluster by 0.5. This implies that we could as well assign a hydrogen atom (H) ligand, a value of $k=-0.5$.



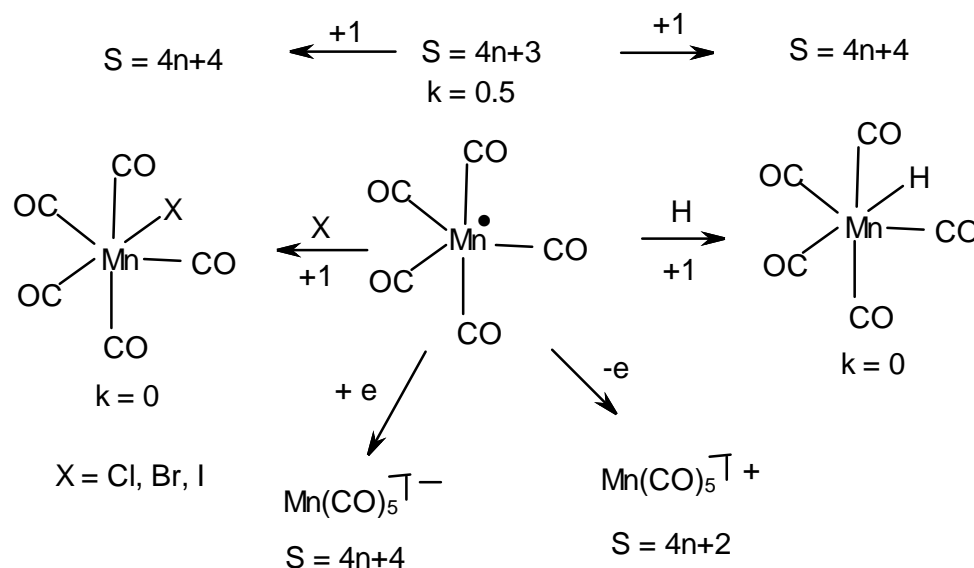
Scheme 1. Successive addition of CO ligands on Fe skeletal element

2.3.1.2 Mn Skeletal Element

Another good example is Mn skeletal element with $S=4n-7$ and a k value of $2n+3.5=2(1)+3.5=5.5$. The successive addition of CO ligands to Mn is summarized in Scheme 2. As in the case of Fe element, the k value decreases by 1 until it reaches the value of 0.5. If another CO ligand were to be added, we would get Mn(CO)_6 with $S=4n+5$, and k value of $2n-2.5=2(1)-2.5=-0.5$. The Mn(CO)_5 fragment produced may be regarded as a form of free radical. It can receive an electron or a hydrogen atom in order for it to obey the 18-electron rule. These possibilities are shown in Scheme 3. What is also observed is that for the cluster number to reach zero, $k=0$ (see Table 4), the number of ligands must have the same numerical value as the metallic skeletal element. The changes in k values for first row mono-skeletal transition metal elements when CO ligands are added are indicated in Table 4. The mono-skeletal elements $\text{Sc}(k=7.5)$, $\text{Ti}(k=7)$, $\text{V}(6.6)$, $\text{Cr}(k=6)$, $\text{Mn}(k=5.5)$ and $\text{Fe}(k=5)$ can take up carbonyl ligands including hydrogen atoms and or negative charges to “neutralize” the appropriate k values. Hence, the chemical fragments and clusters such as HFe(CO)_4^- , Fe(CO)_4^{2-} , Co(CO)_4^- , Ti(CO)_6^{2-} , V(CO)_6^- are known (Cotton, et al, 1980; Housecroft, et al, 2005; Meissler, et al, 2014). The complex CpTi(CO)_4^- (Ti, $k=7$) is also known (Gardner, et al, 1987).



Scheme 2. Successive addition of CO ligands on Mn skeletal element

Scheme 3. Possible reactions of Mn(CO)_5 fragment

2.3.1.3 A Simple Test for the 18-Electron Rule

In principle, the carbonyl complexes to be formed by mono-skeletal atoms of the first row transition elements are expected to have hypothetical formulas as follows: $\text{Sc} \rightarrow k=7.5 \rightarrow \text{Sc(CO)}_7(\text{H})$; $\text{Ti} \rightarrow k=7 \rightarrow \text{Ti(CO)}_7$; $\text{V} \rightarrow k=6.5 \rightarrow \text{V(CO)}_6(\text{H})$; $\text{Cr} \rightarrow k=6 \rightarrow \text{Cr(CO)}_6$; $\text{Mn} \rightarrow k=5.5 \rightarrow \text{Mn(CO)}_5(\text{H})$; $\text{Fe} \rightarrow k=5 \rightarrow \text{Fe(CO)}_5$; $\text{Co} \rightarrow k=4.5 \rightarrow \text{Co(CO)}_4(\text{H})$; $\text{Ni} \rightarrow k=4 \rightarrow \text{Ni(CO)}_4$; $\text{Cu} \rightarrow k=3.5 \rightarrow \text{Cu(CO)}_3(\text{H})$; and $\text{Zn} \rightarrow k=3 \rightarrow \text{Zn(CO)}_3$. The homologous transition metals of the corresponding elements in the second and third rows are expected to form similar carbonyl complexes. For instance, Fe(CO)_5 is expected to have sister clusters Ru(CO)_5 and Os(CO)_5 . All these three carbonyls are known (Cotton and Wilkinson, 1980; Douglas, et al, 1994; Housecroft, et al, 2005; Miessler, et al, 2014). The changes in k values for the first row transition metals as CO ligands are added is shown in Table 4. When all the skeletal linkages of an element are fully filled up (saturated, see Scheme 1), the mono-skeletal element then obeys the 18-electron rule. Other examples include, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ ($k=5-2 \times 2.5=0$), $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$ ($k=6-2 \times 3=0$), $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$ ($k=6-3-3=0$), $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl}$ ($k=5-2.5-2-0.5=0$), Fe(CO)_4^{2-} ($k=5-4-1=0$), $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}^+$ ($k=4.5-2 \times 2.5+0.5=0$), $(\eta^5\text{-C}_5\text{H}_5)\text{Ni(NO)}$ ($k=4-2.5-1.5=0$), $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(CO)}_2$ ($k=7-2 \times 2.5-2=0$), $(\eta^5\text{-C}_5\text{H}_5)\text{V(CO)}_4$ ($k=6.5-2.5-4=0$), $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo(CO)}$ ($k=6-2.5 \times 2-1=0$), $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_3$ ($k=5.5-2.5-3=0$). When a mono-skeletal element cluster attains a value of $k=0$, then that element should be regarded as having obeyed the 18-electron rule.

Table 4. The k Values of Cluster Fragments Generated by adding Carbonyl Ligands to Selected Mono-skeletal Transition Metal Elements

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
	$=4n+q$	$=2n-q/2$		$=4n+q$	$=2n-q/2$		$=4n+q$	$=2n-q/2$
Sc	$4n-11$	7.5	Ti	$4n-10$	7.0	V	$4n-9$	6.5
Sc(CO)	$4n-9$	6.5	Ti(CO)	$4n-8$	6.0	V(CO)	$4n-7$	5.5
Sc(CO) ₂	$4n-7$	5.5	Ti(CO) ₂	$4n-6$	5.0	V(CO) ₂	$4n-5$	4.5
Sc(CO) ₃	$4n-5$	4.5	Ti(CO) ₃	$4n-4$	4.0	V(CO) ₃	$4n-3$	3.5
Sc(CO) ₄	$4n-3$	3.5	Ti(CO) ₄	$4n-2$	3.0	V(CO) ₄	$4n-1$	2.5
Sc(CO) ₅	$4n-1$	2.5	Ti(CO) ₅	$4n+0$	2.0	V(CO) ₅	$4n+1$	1.5
Sc(CO) ₆	$4n+1$	1.5	Ti(CO) ₆	$4n+2$	1.0	V(CO) ₆	$4n+3$	0.5
Sc(CO) ₇	$4n+3$	0.5	Ti(CO) ₇	$4n+4$	0	V(CO) ₇	$4n+5$	-0.5
Sc(CO) ₈	$4n+5$	-0.5						

Table 4 continued

CLUSTER	SERIES =4n+q	k VALUE =2n-q/2	CLUSTER	SERIES =4n+q	k VALUE =2n-q/2	CLUSTER	SERIES =4n+q	k VALUE =2n-q/2
Cr	4n-8	6	Mn	4n-7	5.5	Fe	4n-6	5
Cr(CO)	4n-6	5	Mn(CO)	4n-5	4.5	Fe(CO)	4n-4	4
Cr(CO) ₂	4n-4	4	Mn(CO) ₂	4n-3	3.5	Fe(CO) ₂	4n-2	3
Cr(CO) ₃	4n-2	3	Mn(CO) ₃	4n-1	2.5	Fe(CO) ₃	4n+0	2
Cr(CO) ₄	4n+0	2	Mn(CO) ₄	4n+1	1.5	Fe(CO) ₄	4n+2	1
Cr(CO) ₅	4n+2	1	Mn(CO) ₅	4n+3	0.5	Fe(CO) ₅	4n+4	0
Cr(CO) ₆	4n+4	0	Mn(CO) ₆	4n+5	-0.5			

Table 4 continued

CLUSTER	SERIES =4n+q	k VALUE =2n-q/2	CLUSTER	SERIES =4n+q	k VALUE =2n-q/2	CLUSTER	SERIES =4n+q	k VALUE =2n-q/2
Co	4n-5	4.5	Ni	4n-4	4	Cu	4n-3	3.5
Co(CO)	4n-3	3.5	Ni(CO)	4n-2	3	Cu(CO)	4n-1	2.5
Co(CO) ₂	4n-1	2.5	Ni(CO) ₂	4n+0	2	Cu(CO) ₂	4n+1	1.5
Co(CO) ₃	4n+1	1.5	Ni(CO) ₃	4n+2	1	Cu(CO) ₃	4n+3	0.5
Co(CO) ₄	4n+3	0.5	Ni(CO) ₄	4n+4	0	Cu(CO) ₄	4n+5	-0.5
Co(CO) ₅	4n+5	-0.5						

2.3.2 M₂ Skeletal Systems

Let us consider what happens to the k values when the CO ligands are added to two skeletal transition metal atoms. In the case of chromium, Cr, $S = 4n - 8$ and $k = 2n + 4 = 2(1) + 4 = 6$. Therefore Cr₂ will have k values of 12 arising from $S = 4n - 16$, and $k = 2n + 8 = 2(2) + 8 = 12$. The variation in k values for selected bi-skeletal fragments is indicated in Table 5. This means

Cr₂ (k=12)+12CO(-12)→Cr₂(CO)₁₂, k=0. This clearly means that there is no linkage between the two Cr skeletal elements and hence the Cr₂(CO)₁₂ cluster decomposes into two fragments 2Cr(CO)₆ each of which obeys the 18-electron rule. On the other hand,

Cr₂ (k=12)+ 11CO(k=-11)→Cr₂(CO)₁₁(k=1). This implies, if the complex Cr₂(CO)₁₁ were to be formed, in principle it will be expected to have one metal-metal bond linking up the two chromium skeletal atoms, Cr-Cr. Other M₂ systems can be interpreted in the same way. For instance, Mn₂(k=11)+ 11CO(k=-11)→Mn₂(CO)₁₁(S=4n+8, k=2n-4=2(2)-4=0) while Mn₂(k=11)+10CO(k=-10)→Mn₂(CO)₁₀(k=1). Thus, it is expected that a single Mn-Mn bond will be observed in Mn₂(CO)₁₀ complex. This is what is reported in literature (Cotton and Wilkinson, 1980; Douglas, et al, 1994; Housecroft, et al, 2005; Miessler, et al, 2014). The series showing the stepwise addition of the CO ligands are given in Table 5 for Cr₂, Mn₂ and Fe₂ fragments. Similarly, single bonds are expected for Fe₂(CO)₉(k=5x2-9=1), Co₂(CO)₈(k=4.5x2-8=1), Ni₂(CO)₇(k=4x2-7=1), Cu₂(CO)₆(k=3.5x2-6=1) and Zn₂(CO)₅(k=3x2-5=1), (C_p)₂Zn₂(k=3x2-2x2.5=1), Re₂(η⁵-C₅H₅)₂(CO)₅(k=2x5.5-2x2.5-5=1), Mo₂(η⁵-C₅H₅)₂(CO)₆(k=2x6-2x2.5-6=1), Mo₂(η⁵-C₅H₅)₂(CO)₄(k=2x6-2x2.5-4=3), Cr₂(η⁵-C₅H₅)₂(CO)₆(k=2x6-2x2.5-6=1),

Cr₂(η⁵-C₅H₅)₂(CO)₆(k=2x6-2x2.5-6=1), and Fe₂(η⁵-C₅H₅)₂(CO)₄(k=2x5-2x2.5-4=1). Theoretical studies have been carried out on some bimetallic skeletal carbonyl systems (Ignatyev, et al, 2000; Schaefer III, et al, 2001) as well as the complexes (Freund, et al, 1979) Cr₂(CO)₁₀²⁻ (Cr, k=6) and W₂(CO)₁₀²⁻ (W, k=6). On the basis of k values, these complexes are expected to have single, Cr-Cr and W-W bonds. The existence of complexes such as HCo(CO)₄ (Co, k=4.5) and ReH₉²⁻ (Re, k=5.5) can easily be appreciated in terms of k values of the skeletal elements (Pauling, 1977).

Table 5. The k Values of Cluster Fragments Generated by adding Carbonyl Ligands to Selected Bi-skeletal Transition Metal Elements

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Cr ₂	4n-16	12	Mn ₂	4n-14	11	Fe ₂	4n-12	10
Cr ₂ (CO)	4n-14	11	Mn ₂ (CO)	4n-12	10	Fe ₂ (CO)	4n-10	9
Cr ₂ (CO) ₂	4n-12	10	Mn ₂ (CO) ₂	4n-10	9	Fe ₂ (CO) ₂	4n-8	8
Cr ₂ (CO) ₃	4n-10	9	Mn ₂ (CO) ₃	4n-8	8	Fe ₂ (CO) ₃	4n-6	7
Cr ₂ (CO) ₄	4n-8	8	Mn ₂ (CO) ₄	4n-6	7	Fe ₂ (CO) ₄	4n-4	6
Cr ₂ (CO) ₅	4n-6	7	Mn ₂ (CO) ₅	4n-4	6	Fe ₂ (CO) ₅	4n-2	5
Cr ₂ (CO) ₆	4n-4	6	Mn ₂ (CO) ₆	4n-2	5	Fe ₂ (CO) ₆	4n+0	4
Cr ₂ (CO) ₇	4n-2	5	Mn ₂ (CO) ₇	4n+0	4	Fe ₂ (CO) ₇	4n+2	3
Cr ₂ (CO) ₈	4n+0	4	Mn ₂ (CO) ₈	4n+2	3	Fe ₂ (CO) ₈	4n+4	2
Cr ₂ (CO) ₉	4n+2	3	Mn ₂ (CO) ₉	4n+4	2	Fe ₂ (CO) ₉	4n+6	1
Cr ₂ (CO) ₁₀	4n+4	2	Mn ₂ (CO) ₁₀	4n+6	1	Fe ₂ (CO) ₁₀	4n+8	0
Cr ₂ (CO) ₁₁	4n+6	1	Mn ₂ (CO) ₁₁	4n+8	0			
Cr ₂ (CO) ₁₂	4n+8	0						

2.4 M_x ($x > 2$) Systems

M_3 Systems are treated in the same way as in M_2 systems.

Let us consider the Cr₃ naked skeletal cluster. The chromium atom has 6 valence electrons. Therefore according to the series it belongs to $S = 14n - 8 (n=1)$. When the series formula is converted to the main group series type, it becomes $S = 4n - 8 (n=1)$ and $k = 2n + 4 (n=1) = 2(1) + 4 = 6$. For Cr₃, $S = 4n - 24 (n=3)$ and $k = 2n + 12 (n=3) = 2(3) + 12 = 18$. Table 6 shows the effect on k values of adding the: CO ligands to the small naked skeletal clusters Cr₃ (k = 18), Fe₃ (k = 15), Co₄ (k = 18), Ru₅ (k = 25) and Rh₆ (k = 27). As can be seen from Table 6, the addition of 18CO ligands, all the 18 skeletal linkages will be neutralized to zero, k=0. Thus, Cr₃ (k=18) + 18CO(-18) → Cr₃(CO)₁₈ (k=0). It is clear that the Cr₃ cluster will evenly be fragmented into 3[Cr(CO)₆, k=0]. It has been discovered that for a cluster (M_n), as the CO ligands are added in a step-wise manner, a saturation point is reached when $k=n-1$. Taking the Cr₃ cluster (n=3) as an example, the saturation point occurs when the k₂ value fragment cluster is reached. At that point, the cluster becomes Cr₃(CO)₁₆, with $S=4n+8$ and its hydrocarbon equivalent is C₃H₈. As we very much know, the C₃H₈ hydrocarbon belongs to the alkane series C_nH_{2n+2}. In the case of Fe₃ (k = 15), we need to add on 15CO ligands to neutralize all the skeletal linkages. Thus,

Fe₃(k=15) + 15CO(-15) → Fe₃(CO)₁₅ (k=0) → 3[Fe(CO)₅, k=0]. A saturation point is reached when k=2 and the skeletal cluster becomes Fe₃(CO)₁₃. Some known M_3 clusters include, M_3 (CO)₁₂ (M=Fe, Ru, Os) and these clusters do possess three metal-metal bonds and with the k value of k=3. The variation of k value was also studied for a large naked metallic fragment Pd₂₃. This is shown in Table 7.

2.5 General Observations

2.5.1 The Following Observations Are Noted Regarding the Hypothetical Model

- For every addition of 1 [:CO] ligand to a fixed naked metallic fragment, the skeletal k value decreases by 1.
- The cluster series last digit (determinant) increases by 2 due to the 2 electrons donated by the CO ligand.
- The capping of the series decreases more and more.
- The capping ends at $S = 4n + 0$ which represents mono-capped series. The series also represents the carbon clusters, C_n; n=1 → C₁, n=2 → C₂, n=3 → C₃ and so on.
- At the series formula becomes $S = 4n + 2$ (CLOSO series), the hydrocarbon analogues of the carbonyl clusters commence. For instance, if n=1 → CH₂, n=2 → C₂H₂, n=3, C₃H₂, n=4 → C₄H₂ and so forth.
- The addition of the CO ligands reaches a SATURATION POINT when $k = x - 1$ for a given cluster M_x . This means for x=1, k=0, x=2, k=1, x=3, k=2. For instance, Cr₂ the saturation point is reached at Cr₂(CO)₁₁ ($S = 4n + 6$, k=1, F_{CH}=C₂H₆), and for Mn₂, we get Mn₂(CO)₁₀ ($S = 4n + 6$, k=1, F_{CH}=C₂H₆).
- Complete fragmentation of the naked cluster takes place when k = 0 and all the initial skeletal linkages have been consumed by the CO ligands. For example in the case of the Cr₂(K=12) skeletal fragment, if we add 12CO ligands we get Cr₂(CO)₁₂, then k value of the cluster attains the value of k=0 and Cr₂(CO)₁₂ and hence the cluster decomposes into two fragments as follows, Cr₂(CO)₁₂ → 2[Cr(CO)₆].
- The initial capping process of the naked skeletal fragment increases with the increase in the number of the skeletal metal atoms. For instance, 1[Cr], $S = 14n - 8 (n=1) → 4n - 8 (n=1)$ and $k = 2n + 4 = 2(1) + 4 = 6$, the capping is

given by the formula (Kiremire,2015,2016e) $C_p=C^1+C^4=C^5C[M^{-4}]$. For the Cr_2 fragment, $S=4n-16(n=2)$, $k=2n+8=2(2)+8=12$ and $C_p=C^1+C^8=C^9C[M^{-7}]$; Cr_3 , $S=4n-24$, $k=18$ and $C_p=C^1+C^{12}=C^{13}C[M^{-10}]$. In the case of a particular naked metallic cluster, M_x , $S=4n-r$, the capping stops at $S=4n+0$ when the number of CO ligands $z=r/2$. In the case of Cr_1 , $S=4n-8$, the number of CO ligands needed to produce $S=4n+0$, are $8/2=4$, for Cr_2 , $S=4n-16$, the number of CO ligands needed are $16/2=8$ and for Cr_3 , $S=4n-24$, the number of CO ligands are $24/2=12$. This means that keeping the starting naked metallic cluster constant and adding CO ligands the capping decreases until $S=4n+0$ is attained. Addition of more CO ligands, generates clusters which have hydrocarbon analogues.

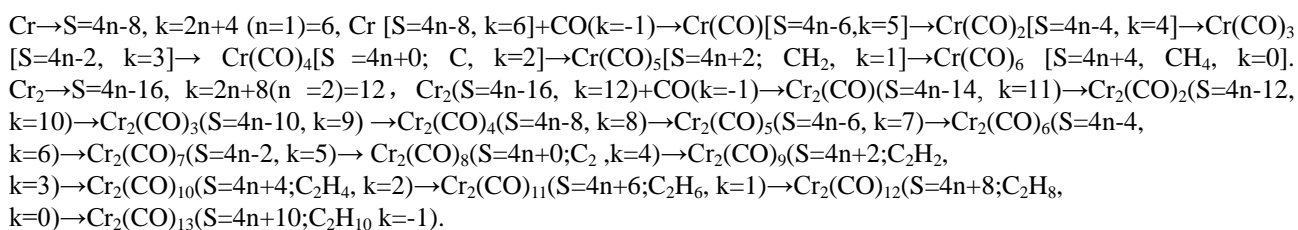
- Also a very important observation is made, that is, the sum of the ligands on the cluster (corresponding to the utilized k values) and the cluster linkages (corresponding to the unutilized k values) present is equal to the original k value of the parent naked metallic cluster. This point is discussed in more details under the heading Fundamental Principle.

2.5.2 Limits of the Carbonyl Cluster Series

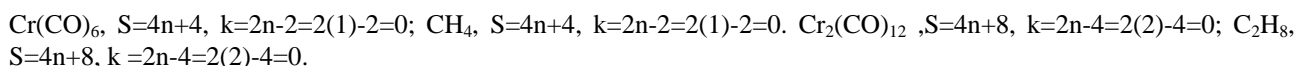
The carbonyl cluster complexes may be regarded as being formed by adding the carbonyl ligands stepwise to a metallic cluster fragment. This may be expressed by a simple equation below.



The naked skeletal fragment, M_x possesses a fixed number of skeletal linkages which can readily be determined by $4n$ series based on its valence electrons. These linkages are neutralized one by one for every addition of the CO ligand. If we represent the series as $S=4n+q$, then when $q \leq 0$ the 'metallic character' increases as the CO ligands are removed, the 'metallic character' of the fragment decreases with the addition of the CO ligands until the series becomes $4n+0$. This series represents the carbon cluster family, $F=C_n$ ($n=1, 2, 3, 4, 5, 6, \dots$). The large carbon clusters such as C_{60} (fullerenes) and C_{70} are members of the carbon clusters which belong to the series $S=4n+0$. The $4n+0$ series is the borderline which may be regarded as the highest level of the 'hydrocarbon' series but also as the beginning of the 'metallic' series. It is interesting to note that carbon has vast industrial applications due its unique properties. The 'hydrocarbon' type series can be expressed by the series $S=4n+q$ ($q \geq 0$). We can also regard the series range such as $S=4n+2, 4n+4, 4n+6$, and so on as indicating the increase in the 'hydrocarbon character' of the carbonyl clusters despite the inclusion of the metallic skeletal elements. Let us consider the following changes in metallic fragments of chromium.



The interpretation of $k=0$ is quite interesting.



This implies that $Cr_2(CO)_{12}$ decomposes into two fragments: $Cr_2(CO)_{12} \rightarrow 2[Cr(CO)_6]$ and $C_2H_8 \rightarrow 2CH_4$. Also, $C_2H_{10} (k=-1) \rightarrow 2CH_4(k=0)+2H[k=2(-0.5)=-1]$; $Cr_2(CO)_{13} (k=-1) \rightarrow 2[Cr(CO)_6, k=0]+CO(k=-1)$. Thus, the cluster series $S=4n-8, 4n-6, 4n-4, 4n-2$ and $4n+0$ associated with Cr fragment may be regarded as having some type of 'metallic character'. On the other hand the series $S=4n+0, 4n+2$, and $4n+4$ which correspond to the fragments C, CH_2 and CH_4 may be regarded as having some type of 'hydrocarbon character'. Hence, the $S=4n+0$ series is the borderline between metallic type and hydrocarbon type of series. In fact, $S=4n+0$ refers to the clusters or fragments which are referred to as being mono-capped (Kiremire, 2015a, 2016e). Other series of fragments may be interpreted in the same way. A good example to illustrate the hydrocarbon character of series is $[H_5Re_6(CO)_{24}]^-$ complex. Using the skeletal numbers, the k value of the cluster is given by $k=6(5.5)+5(-0.5)+24(-1)+1(-0.5)=33-2.5-24-0.5=6$. Since for the series $S=4n+q$, $k=2n-q/2$, then $k=6=2n-q/2$ ($n=6$); $6=2(6)-q/2$, $q=12$. Hence, $S=4n+12(n=6) \rightarrow C_6H_{12}$. This implies that the shape of $[H_5Re_6(CO)_{24}]^-$ complex will be similar to one of the isomers of C_6H_{12} . This is found to be the case (Housecroft and Sharpe, 2005 and the ideal shapes are sketched in Figure 1. The reverse of the hypothetical formation of carbonyl cluster may be represented as: $M_x(CO)_y \rightarrow M_x + yCO$. This involves the removal of CO ligands from the original cluster. In this manner, the cluster may be viewed as going from a hydrocarbon-type to a more metallic type of cluster fragments. Ideally, this should give rise to the recovery of naked parent metallic fragment M_x . The corresponding cluster

k values of the fragment should be on the increase. Very interesting extensive work on the metal carbonyls that involves stripping off the CO ligands has been done by several research groups (Butcher, et al, 2002, 2003; Crawford, et al, 2006; Critchley, et al, 1999; Dyson, et al, 2001; Henderson, et al, 1998, 2009). When the structure of the series is carefully analyzed, the hydrocarbon chain type terminates or reaches a saturation point or limit that corresponds to the corresponding hydrocarbon alkane series $F=C_nH_{2n+2}$. Hence, for $M_1 \rightarrow CH_4 \rightarrow 4n+4$, and if $M=Fe$, then the complex will be $Fe(CO)_5$. For $M_2 \rightarrow C_2H_6 \rightarrow 4n+6$; $M_2=Cr_2 \rightarrow Cr_2(CO)_{11}$; $M_2=Mn_2 \rightarrow Mn_2(CO)_{10}$; $M_2=Fe_2 \rightarrow Fe_2(CO)_9$; and for $M_{23}=Pd_{23} \rightarrow C_{23}H_{48} \rightarrow S=4n+48 \rightarrow Pd_{23}(CO)_{70}$ (see Table 7).

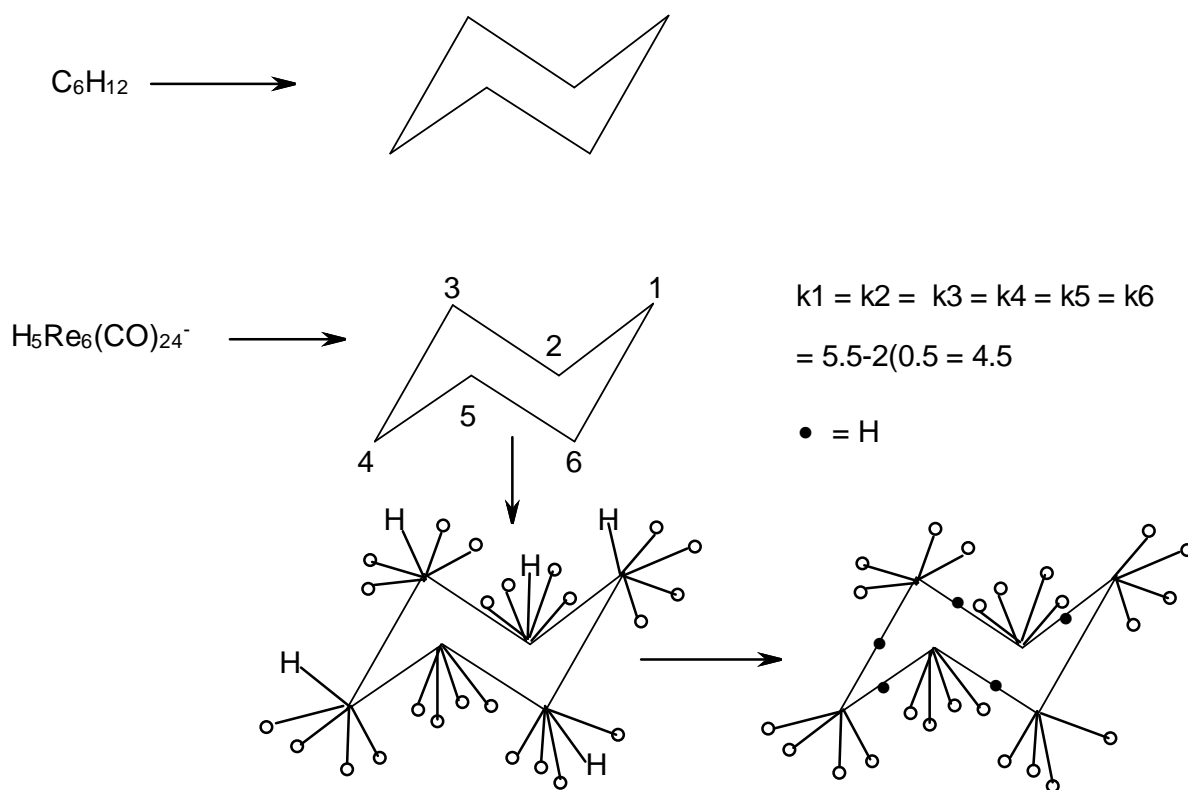


Figure 1. Structural similarity between $H_5Re_6(CO)_{24}^-$ and C_6H_6

Table 6. The k Values of Selected Transition Metal Carbonyl Fragments (M_x , $x = 3-6$)

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Cr_3	$4n-24$	18	Fe_3	$4n-18$	15	Co_4	$4n-20$	18
$Cr_3(CO)$	$4n-22$	17	$Fe_3(CO)$	$4n-16$	14	$Co_4(CO)$	$4n-18$	17
$Cr_3(CO)_2$	$4n-20$	16	$Fe_3(CO)_2$	$4n-14$	13	$Co_4(CO)_2$	$4n-16$	16
$Cr_3(CO)_3$	$4n-18$	15	$Fe_3(CO)_3$	$4n-12$	12	$Co_4(CO)_3$	$4n-14$	15
$Cr_3(CO)_4$	$4n-16$	14	$Fe_3(CO)_4$	$4n-10$	11	$Co_4(CO)_4$	$4n-12$	14
$Cr_3(CO)_5$	$4n-14$	13	$Fe_3(CO)_5$	$4n-8$	10	$Co_4(CO)_5$	$4n-10$	13
$Cr_3(CO)_6$	$4n-12$	12	$Fe_3(CO)_6$	$4n-6$	9	$Co_4(CO)_6$	$4n-8$	12
$Cr_3(CO)_7$	$4n-10$	11	$Fe_3(CO)_7$	$4n-4$	8	$Co_4(CO)_7$	$4n-6$	11
$Cr_3(CO)_8$	$4n-8$	10	$Fe_3(CO)_8$	$4n-2$	7	$Co_4(CO)_8$	$4n-4$	10
$Cr_3(CO)_9$	$4n-6$	9	$Fe_3(CO)_9$	$4n+0$	6	$Co_4(CO)_9$	$4n-2$	9
$Cr_3(CO)_{10}$	$4n-4$	8	$Fe_3(CO)_{10}$	$4n+2$	5	$Co_4(CO)_{10}$	$4n+0$	8
$Cr_3(CO)_{11}$	$4n-2$	7	$Fe_3(CO)_{11}$	$4n+4$	4	$Co_4(CO)_{11}$	$4n+2$	7
$Cr_3(CO)_{12}$	$4n+0$	6	$Fe_3(CO)_{12}$	$4n+6$	3	$Co_4(CO)_{12}$	$4n+4$	6
$Cr_3(CO)_{13}$	$4n+2$	5	$Fe_3(CO)_{13}$	$4n+8$	2	$Co_4(CO)_{13}$	$4n+6$	5
$Cr_3(CO)_{14}$	$4n+4$	4	$Fe_3(CO)_{14}$	$4n+10$	1	$Co_4(CO)_{14}$	$4n+8$	4
$Cr_3(CO)_{15}$	$4n+6$	3	$Fe_3(CO)_{15}$	$4n+12$	0	$Co_4(CO)_{15}$	$4n+10$	3
$Cr_3(CO)_{16}$	$4n+8$	2				$Co_4(CO)_{16}$	$4n+12$	2
$Cr_3(CO)_{17}$	$4n+10$	1				$Co_4(CO)_{17}$	$4n+14$	1
$Cr_3(CO)_{18}$	$4n+12$	0				$Co_4(CO)_{18}$	$4n+16$	0

Table 6 continued

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Ru ₅	4n-30	25	Rh ₆	4n-30	27
Ru ₅ (CO)	4n-28	24	Rh ₆ (CO)	4n-28	26
Ru ₅ (CO) ₂	4n-26	23	Rh ₆ (CO) ₂	4n-26	25
Ru ₅ (CO) ₃	4n-24	22	Rh ₆ (CO) ₃	4n-24	24
Ru ₅ (CO) ₄	4n-22	21	Rh ₆ (CO) ₄	4n-22	23
Ru ₅ (CO) ₅	4n-20	20	Rh ₆ (CO) ₅	4n-20	22
Ru ₅ (CO) ₆	4n-18	19	Rh ₆ (CO) ₆	4n-18	21
Ru ₅ (CO) ₇	4n-16	18	Rh ₆ (CO) ₇	4n-16	20
Ru ₅ (CO) ₈	4n-14	17	Rh ₆ (CO) ₈	4n-14	19
Ru ₅ (CO) ₉	4n-12	16	Rh ₆ (CO) ₉	4n-12	18
Ru ₅ (CO) ₁₀	4n-10	15	Rh ₆ (CO) ₁₀	4n-10	17
Ru ₅ (CO) ₁₁	4n-8	14	Rh ₆ (CO) ₁₁	4n-8	16
Ru ₅ (CO) ₁₂	4n-6	13	Rh ₆ (CO) ₁₂	4n-6	15
Ru ₅ (CO) ₁₃	4n-4	12	Rh ₆ (CO) ₁₃	4n-4	14
Ru ₅ (CO) ₁₄	4n-2	11	Rh ₆ (CO) ₁₄	4n-2	13
Ru ₅ (CO) ₁₅	4n+0	10	Rh ₆ (CO) ₁₅	4n+0	12
Ru ₅ (CO) ₁₆	4n+2	9	Rh ₆ (CO) ₁₆	4n+2	11
Ru ₅ (CO) ₁₇	4n+4	8	Rh ₆ (CO) ₁₇	4n+4	10
Ru ₅ (CO) ₁₈	4n+6	7	Rh ₆ (CO) ₁₈	4n+6	9

Table 6 continued

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Ru ₅ (CO) ₁₉	4n+8	6	Rh ₆ (CO) ₁₉	4n+8	8
Ru ₅ (CO) ₂₀	4n+10	5	Rh ₆ (CO) ₂₀	4n+10	7
Ru ₅ (CO) ₂₁	4n+12	4	Rh ₆ (CO) ₂₁	4n+12	6
Ru ₅ (CO) ₂₂	4n+14	3	Rh ₆ (CO) ₂₂	4n+14	5
Ru ₅ (CO) ₂₃	4n+16	2	Rh ₆ (CO) ₂₃	4n+16	4
Ru ₅ (CO) ₂₄	4n+18	1	Rh ₆ (CO) ₂₄	4n+18	3
Ru ₅ (CO) ₂₅	4n+20	0	Rh ₆ (CO) ₂₅	4n+20	2
			Rh ₆ (CO) ₂₆	4n+22	1
			Rh ₆ (CO) ₂₇	4n+24	0

Although the series and the skeletal numbers predict that each of the Re skeletal atoms except one should have a hydrogen atom, the structural determination indicates all the hydrogen atoms are bridging (Miessler, et al, 2014) as observed in borane clusters.

Table 7. The k Values Generated by Adding CO ligands to a Large Naked Metallic Fragment

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Pd ₂₃	4n-92	92						
Pd ₂₃ (CO)	4n-90	91	Pd ₂₃ (CO) ₁₆	4n-60	76	Pd ₂₃ (CO) ₃₁	4n-30	61
Pd ₂₃ (CO) ₂	4n-88	90	Pd ₂₃ (CO) ₁₇	4n-58	75	Pd ₂₃ (CO) ₃₂	4n-28	60
Pd ₂₃ (CO) ₃	4n-86	89	Pd ₂₃ (CO) ₁₈	4n-56	74	Pd ₂₃ (CO) ₃₃	4n-26	59
Pd ₂₃ (CO) ₄	4n-84	88	Pd ₂₃ (CO) ₁₉	4n-54	73	Pd ₂₃ (CO) ₃₄	4n-24	58
Pd ₂₃ (CO) ₅	4n-82	87	Pd ₂₃ (CO) ₂₀	4n-52	72	Pd ₂₃ (CO) ₃₅	4n-22	57
Pd ₂₃ (CO) ₆	4n-80	86	Pd ₂₃ (CO) ₂₁	4n-50	71	Pd ₂₃ (CO) ₃₆	4n-20	56
Pd ₂₃ (CO) ₇	4n-78	85	Pd ₂₃ (CO) ₂₂	4n-48	70	Pd ₂₃ (CO) ₃₇	4n-18	55
Pd ₂₃ (CO) ₈	4n-76	84	Pd ₂₃ (CO) ₂₃	4n-46	69	Pd ₂₃ (CO) ₃₈	4n-16	54
Pd ₂₃ (CO) ₉	4n-74	83	Pd ₂₃ (CO) ₂₄	4n-44	68	Pd ₂₃ (CO) ₃₉	4n-14	53
Pd ₂₃ (CO) ₁₀	4n-72	82	Pd ₂₃ (CO) ₂₅	4n-42	67	Pd ₂₃ (CO) ₄₀	4n-12	52
Pd ₂₃ (CO) ₁₁	4n-70	81	Pd ₂₃ (CO) ₂₆	4n-40	66	Pd ₂₃ (CO) ₄₁	4n-10	51
Pd ₂₃ (CO) ₁₂	4n-68	80	Pd ₂₃ (CO) ₂₇	4n-38	65	Pd ₂₃ (CO) ₄₂	4n-8	50
Pd ₂₃ (CO) ₁₃	4n-66	79	Pd ₂₃ (CO) ₂₈	4n-36	64	Pd ₂₃ (CO) ₄₃	4n-6	49
Pd ₂₃ (CO) ₁₄	4n-64	78	Pd ₂₃ (CO) ₂₉	4n-34	63	Pd ₂₃ (CO) ₄₄	4n-4	48
Pd ₂₃ (CO) ₁₅	4n-62	77	Pd ₂₃ (CO) ₃₀	4n-32	62	Pd ₂₃ (CO) ₄₅	4n-2	47

Table 7 continued

CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE	CLUSTER	SERIES	k VALUE
Pd ₂₃ (CO) ₄₆	4n+0	46	Pd ₂₃ (CO) ₆₂	4n+32	30	Pd ₂₃ (CO) ₇₈	4n+64	14
Pd ₂₃ (CO) ₄₇	4n+2	45	Pd ₂₃ (CO) ₆₃	4n+34	29	Pd ₂₃ (CO) ₇₉	4n+66	13
Pd ₂₃ (CO) ₄₈	4n+4	44	Pd ₂₃ (CO) ₆₄	4n+36	28	Pd ₂₃ (CO) ₈₀	4n+68	12
Pd ₂₃ (CO) ₄₉	4n+6	43	Pd ₂₃ (CO) ₆₅	4n+38	27	Pd ₂₃ (CO) ₈₁	4n+70	11
Pd ₂₃ (CO) ₅₀	4n+8	42	Pd ₂₃ (CO) ₆₆	4n+40	26	Pd ₂₃ (CO) ₈₂	4n+72	10
Pd ₂₃ (CO) ₅₁	4n+10	41	Pd ₂₃ (CO) ₆₇	4n+42	25	Pd ₂₃ (CO) ₈₃	4n+74	9
Pd ₂₃ (CO) ₅₂	4n+12	40	Pd ₂₃ (CO) ₆₈	4n+44	24	Pd ₂₃ (CO) ₈₄	4n+76	8
Pd ₂₃ (CO) ₅₃	4n+14	39	Pd ₂₃ (CO) ₆₉	4n+46	23	Pd ₂₃ (CO) ₈₅	4n+78	7
Pd ₂₃ (CO) ₅₄	4n+16	38	Pd ₂₃ (CO) ₇₀	4n+48	22	Pd ₂₃ (CO) ₈₆	4n+80	6
Pd ₂₃ (CO) ₅₅	4n+18	37	Pd ₂₃ (CO) ₇₁	4n+50	21	Pd ₂₃ (CO) ₈₇	4n+82	5
Pd ₂₃ (CO) ₅₆	4n+20	36	Pd ₂₃ (CO) ₇₂	4n+52	20	Pd ₂₃ (CO) ₈₈	4n+84	4
Pd ₂₃ (CO) ₅₇	4n+22	35	Pd ₂₃ (CO) ₇₃	4n+54	19	Pd ₂₃ (CO) ₈₉	4n+86	3
Pd ₂₃ (CO) ₅₈	4n+24	34	Pd ₂₃ (CO) ₇₄	4n+56	18	Pd ₂₃ (CO) ₉₀	4n+88	2
Pd ₂₃ (CO) ₅₉	4n+26	33	Pd ₂₃ (CO) ₇₅	4n+58	17	Pd ₂₃ (CO) ₉₁	4n+90	1
Pd ₂₃ (CO) ₆₀	4n+28	32	Pd ₂₃ (CO) ₇₆	4n+60	16	Pd ₂₃ (CO) ₉₂	4n+92	0
Pd ₂₃ (CO) ₆₁	4n+30	31	Pd ₂₃ (CO) ₇₇	4n+62	15			

Table 8. The Capping Series obtained from Stripping Pd₂₃(CO)₄₆ Cluster

Cluster	Series	Capping Symbol	Cluster	Series	Capping Symbol
Pd ₂₃ (CO) ₄₆	4n+0	C ¹ C[M-22]	Pd ₂₃ (CO) ₂₈	4n-36	C ¹⁹ C[M-4]
Pd ₂₃ (CO) ₄₅	4n-2	C ² C[M-21]	Pd ₂₃ (CO) ₂₇	4n-38	C ²⁰ C[M-3]
Pd ₂₃ (CO) ₄₄	4n-4	C ³ C[M-20]	Pd ₂₃ (CO) ₂₆	4n-40	C ²¹ C[M-2]
Pd ₂₃ (CO) ₄₃	4n-6	C ⁴ C[M-19]	Pd ₂₃ (CO) ₂₅	4n-42	C ²² C[M-1]
Pd ₂₃ (CO) ₄₂	4n-8	C ⁵ C[M-18]	Pd ₂₃ (CO) ₂₄	4n-44	C ₂₃ C[M-0]
Pd ₂₃ (CO) ₄₁	4n-10	C ⁶ C[M-17]	Pd ₂₃ (CO) ₂₃	4n-46	C ²⁴ C[M ⁻¹]
Pd ₂₃ (CO) ₄₀	4n-12	C ⁷ C[M-16]	Pd ₂₃ (CO) ₂₂	4n-48	C ²⁵ C[M ⁻²]
Pd ₂₃ (CO) ₃₉	4n-14	C ⁸ C[M-15]	Pd ₂₃ (CO) ₂₁	4n-50	C ²⁶ C[M ⁻³]
Pd ₂₃ (CO) ₃₈	4n-16	C ⁹ C[M-14]	Pd ₂₃ (CO) ₂₀	4n-52	C ²⁷ C[M ⁻⁴]
Pd ₂₃ (CO) ₃₇	4n-18	C ¹⁰ C[M-13]	Pd ₂₃ (CO) ₁₉	4n-54	C ²⁸ C[M ⁻⁵]
Pd ₂₃ (CO) ₃₆	4n-20	C ¹¹ C[M-12]	Pd ₂₃ (CO) ₁₈	4n-56	C ²⁹ C[M ⁻⁶]
Pd ₂₃ (CO) ₃₅	4n-22	C ¹² C[M-11]	Pd ₂₃ (CO) ₁₇	4n-58	C ³⁰ C[M ⁻⁷]
Pd ₂₃ (CO) ₃₄	4n-24	C ¹³ C[M-10]	Pd ₂₃ (CO) ₁₆	4n-60	C ³¹ C[M ⁻⁸]
Pd ₂₃ (CO) ₃₃	4n-26	C ¹⁴ C[M-9]	Pd ₂₃ (CO) ₁₅	4n-62	C ³² C[M ⁻⁹]
Pd ₂₃ (CO) ₃₂	4n-28	C ¹⁵ C[M-8]	Pd ₂₃ (CO) ₁₄	4n-64	C ³³ C[M ⁻¹⁰]
Pd ₂₃ (CO) ₃₁	4n-30	C ¹⁶ C[M-7]	Pd ₂₃ (CO) ₁₃	4n-66	C ³⁴ C[M ⁻¹¹]
Pd ₂₃ (CO) ₃₀	4n-32	C ¹⁷ C[M-6]	Pd ₂₃ (CO) ₁₂	4n-68	C ³⁵ C[M ⁻¹²]
Pd ₂₃ (CO) ₂₉	4n-34	C ¹⁸ C[M-5]	Pd ₂₃ (CO) ₁₁	4n-70	C ³⁶ C[M ⁻¹³]

Table 8 continued

Cluster	Series	Capping Symbol
Pd ₂₃ (CO) ₁₀	4n-72	C ³⁷ C[M ⁻¹⁴]
Pd ₂₃ (CO) ₉	4n-74	C ³⁸ C[M ⁻¹⁵]
Pd ₂₃ (CO) ₈	4n-76	C ³⁹ C[M ⁻¹⁶]
Pd ₂₃ (CO) ₇	4n-78	C ⁴⁰ C[M ⁻¹⁷]
Pd ₂₃ (CO) ₆	4n-80	C ⁴¹ C[M ⁻¹⁸]
Pd ₂₃ (CO) ₅	4n-82	C ⁴² C[M ⁻¹⁹]
Pd ₂₃ (CO) ₄	4n-84	C ⁴³ C[M ⁻²⁰]
Pd ₂₃ (CO) ₃	4n-86	C ⁴⁴ C[M ⁻²¹]
Pd ₂₃ (CO) ₂	4n-88	C ⁴⁵ C[M ⁻²²]
Pd ₂₃ (CO) ₁	4n-90	C ⁴⁶ C[M ⁻²³]
Pd ₂₃	4n-92	C ⁴⁷ C[M ⁻²⁴]

2.5.3 Capping and De-capping Series

The addition of carbonyl ligands(CO) to M_x , that is, $M_x + yCO \rightarrow M_x(CO)_y$ corresponds to the decrease in de-capping process whereas the opposite $M_x(CO)_y \rightarrow M_x + yCO$ corresponds to the increase in the capping process. These opposing processes are reflected in Tables 7 and 8. The removal of CO ligands from transition metal carbonyl clusters has been an intense field of research (Critchley, et al, 1999, Douglas, et al, 2001, Butcher, et al, 2002, 2003, Crawford, et al, 2006, Henderson, et al, 2009). The silicon clusters $Si_n(n=4-10)$ were theoretically studied(Slee, et al, 1989) using extended Hückel calculations. According to series, Si and C skeletal atoms belong to the same series, $S=4n+0$, $Cp=C^1C$ (mono-capped series). Thus, $Si_4, Cp=C^1C[M-3]$, $Si_5, Cp=C^1C[M-4]$, $Si_6, Cp=C^1C[M-5]$, $Si_7, Cp=C^1C[M-6]$, $Si_8, Cp=C^1C[M-7]$, $Si_9, Cp=C^1C[M-8]$ and $Si_{10}, Cp=C^1C[M-9]$. The cluster, $Si_7, Cp=Cp=C^1C[M-6]$, is expected to have a mono-capped octahedral skeletal shape similar to that of $Os_7(CO)_{21}$ or $Rh_7(CO)_{16}^{3-}$ (Hughes, et al, 2000). The complex, $Ru_6Pd_6(CO)_{24}^{2-}$ (Ru, $k=5, Pd, k=4$); $k(\text{cluster})=6(5)+6(4)-24-1=29$; $q/2=2n-k$, $n=12$, $q/2=2(12)-29=-5$, $q=-10$, $S=4n-10$, $Cp=C^1+C^5=C^6C[M-6]$. This means 6 of the skeletal metal atoms are capped around an inner octahedral nucleus as was reported (Butcher, et al, 2003). Another good example regarding capping is $Ni_{38}Pt_6(CO)_{48}(H)^{5-}$. The k value of the cluster is given by $k=38(4)+6(4)-48-0.5-2.5=125$. From the knowledge of series we know that $k=2n-q/2$ and hence $q/2=2n-k$, $n=38+6=44$, $q/2=2(44)-125=-37$, $q=-74$. Hence $S=4n+q=4n-74$, $Cp=C^1+C^{37}=C^{38}C[M-6]$. This means the giant cluster of 44 skeletal metal atoms, 6 will constitute an octahedral nucleus and the remaining 38 will form a capping shell which is also found to form a tetrahedral structure (Rossi and Zanella, 2011). What is also interesting is that all the 6 nuclear atoms are platinum and the shell comprises of the nickel atoms. The skeletal numbers can also be applied to a cluster with a mixture of main group and transition metal skeletal elements. A good example is $Te_2Ru_4(CO)_{10}Cu_2Cl_2^{2-}$. The skeletal numbers of the atoms the charge in the cluster, $Te(k=1)$, $Ru(k=5)$, $Cu(k=3.5)$, $CO(k=-1)$, and $Cl(k=-0.5)$, and $2-(k=-1)$. Hence $k=2(1)+4(5)+2(3.5)-10-1-1=17$, $q/2=2n-k$, $n=2+4+2=8$, $q/2=2(8)-17=-1$, $q=-2$. The cluster series will be $S=4n-2(n=8)$, $Cp=C^1+C^1=C^2C[M-6]$. The ideal skeletal shape is a bi-capped octahedron and geometry has been observed (Shieh, et al, 2012). The valence electron content, $Ve=4n-2=4(8)-2=30$. $V_M=30+10(6)=90$. Thus, $V_M=Ve+10n$ where n =number of metal atoms present in a cluster.

2.5.4 Application of Skeletal Numbers to Isolobal Relationship

The isolobal principle (Hoffmann, 1982) simply refers to chemical fragments or molecules which are chemically similar in terms of structures. The isolobal relationship can readily be verified using skeletal numbers. Consider the following fragments, $Mn(CO)_5$, $k=5.5-5=0.5$, CH_3 , $k=2-1.5=0.5$. Hence, $Mn(CO)_5 \leftrightarrow CH_3$; $Fe(CO)_4$, $k=5-4=1$, CH_2 , $k=2-1=1 \rightarrow Fe(CO)_4 \leftrightarrow CH_2$; $Ir(CO)_3$, $k=4.5-3=1.5$, CH , $k=2-0.5=1.5 \rightarrow Ir(CO)_3 \leftrightarrow CH$, $Fe(CO)_3$, $k=5-3=2$, $Co(Cp)$, $k=4.5-2.5=2$, C , $k=2 \rightarrow Fe(CO)_3 \leftrightarrow Co(Cp) \leftrightarrow C$. Some of the fragments can be handled in the same manner.

Table 9. Examples to Illustrate the Principle of Conservation of Skeletal Value Content of the Naked Parent Cluster Fragment

$M_1(K=5)$			$M_2(K=10)$			$M_3(15)$		
K_S	$K_L(CO)$	K_T	K_S	$K_L(CO)$	K_T	K_S	$K_L(CO)$	K_T
5	0	5	10	0	10	15	0	15
4	1	5	9	1	10	14	1	15
3	2	5	8	2	10	13	2	15
2	3	5	7	3	10	12	3	15
1	4	5	6	4	10	11	4	15
0	5	5	5	5	10	10	5	15
			4	6	10	9	6	15
			3	7	10	8	7	15
			2	8	10	7	8	15
			1	9	10	6	9	15
			0	10	10	5	10	15
						4	11	15
						3	12	15
						2	13	15
						1	14	15
						0	15	15

2.6 The Conservation of Cluster Skeletal Linkage Content Principle

A naked transition metal element possesses an inherent number of skeletal linkages by virtue of its valence electrons. When the skeletal element reacts with suitable ligands such as CO and H some or all the linkages are used up, the fragment develops a tendency towards the attainment of the ultimate 18-electron rule. The 18-electron rule implies the maximization of all the atomic orbitals of the orbital set [s(1),p(3) and d(5)](Pauling,1977). Since 1[:CO] neutralizes 1 skeletal k unit, it is proposed that we assign it a value of $k=-1$. We also know that it donates 2 electrons, and so every ligand donor of 2 electrons may similarly be assigned a k value of -1 and for 1 electron donor such as H and Cl or a unit negative charge ligands are correspondingly assigned a numerical value of $k=-0.5$. As can be seen from Table 9, $|k_L|+k_S=k_T$ where k_L represents the used up k-values of the initial skeletal fragment, k_S = the skeletal linkages still available and k_T = the original skeletal linkages of the parent naked fragment. This result is very important because if we know the value of k_T and $|k_L|$, then we can deduce the value of k_S and hence use it as a guiding tool in designing and predicting the shape of the carbonyl cluster. This important principle is hereby expressed in an equation form. This relationship is well illustrated in Table 9.

$$k_T = |k_L| + k_S \quad \dots\dots \quad \dots\dots(i)$$

Taking the example of $Os_3(CO)_{12}$, $k_{Os}=3 \times 5=15=k_T$, $k_{CO}=12(-1)=-12=k_L$. Therefore $k_S=15-12=3$. This means that $Os_3(CO)_{12}$ will have a skeletal triangular shape comprising of the three osmium skeletal elements. We also note that $|k_L|+k_S=12+3=15=k_T$. The negative sign of k_L indicates the skeletal linkages used up by the ligands and k_S refers to the remaining linkages of the skeletal elements. Let us look at some selected examples of osmium carbonyls to test the above principle. Examples are $Os_3H_2(CO)_{10}$; $k_T=3 \times 5=15$, $k_L=-2(0.5)-10(1)=-11$. Hence $k_S=15-11=4$. The sum of $|k_L|$ and $k_S=15=k_T$. Other examples include, $Os_3(CO)_{12}$ ($k_T=3 \times 5=15$, $k_L=-12 \rightarrow k_S=3$, triangle), $Os_4(CO)_{14}$ ($k_T=4 \times 5=20$, $k_L=-14 \rightarrow k_S=6$, tetrahedral); $Os_4(CO)_{16}$, ($k_T=20$, $k_L=-16$, $k_S=4$, square); $Os_5(CO)_{16}$, ($k_T=25$, $k_L=-16$, $k_S=9$, trigonal bipyramid) and $Os_5(CO)_{19}$, ($k_T=25$, $k_L=-19$, $k_S=6$, two triangles joined at one of the edges. The shapes of these carbonyls are well known (Hughes and Wade, 2000; Greenwood and Earnshaw (1998).

2.7 Applications of Skeletal Numbers to Predict Shapes of Carbonyl Cluster Structures Including the Tentative Distribution of the Ligands on Skeletal Elements

2.7.1 Possible Shapes of the Skeletal Linkages

The main concept is that a skeletal atom possesses naturally inherent linkages as deduced by 4n series. When a ligand is attached to the skeletal atom, it utilizes or neutralizes some of those linkages depending upon the number of electrons that ligand donates to the skeletal element. For every electron donated by the ligand or a negative charge, 0.5 of the linkage is utilized or removed from the skeletal element. Since a :CO ligand donates 2 electrons, it utilizes or removes 1 skeletal value from the element. On this basis, a CO ligand is assigned a value of $k=-1$. Similarly we can assign H• atom a value of $k=-0.5$ and one negative charge, $k=-0.5$. The implications of this is that for 1 Fe($k=5$) when combined with 5CO[$k=5 \times (-1)=-5$] ligands, the net k value of the cluster becomes zero ($k = 0$). Hence $Fe(CO)_5$, $k = 0$. The k values for transition elements may be regarded as the number of electron pairs needed for the element to obey the 18 electron rule. Hence Sc, $k=7.5$ pairs= $7.5 \times 2=15$ electrons required for it to obey the 18 electron rule. Accordingly, the other transition metal elements in the same period will require the following electrons, Ti($k=7$), 14 electrons; V($k=6.5$), 13; Cr($k=6$), 12; Mn($k=5.5$), 11; Fe($k=5$), 10; Co($k=4.5$), 9; Ni($k=4$), 8; Cu($k=3.5$), 7 and Zn($k=3$), 6. We can also tentatively assign possible shapes of the skeletal linkages to individual skeletal atoms. This is shown in Figure 2.

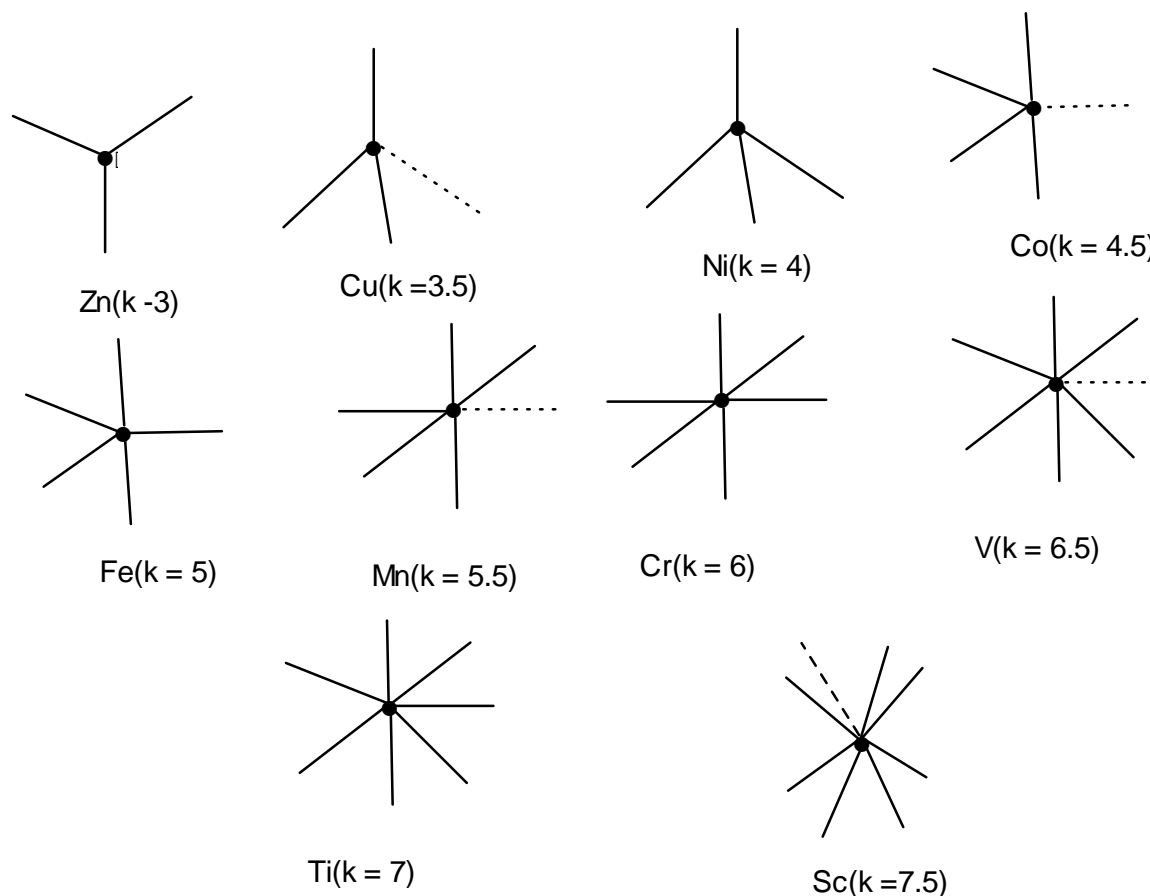


Figure 2. Proposed tentative shapes of the skeletal linkages of first row transition metals

2.7.2 Shapes of Clusters

For complexes with two or more skeletal elements, the skeletal numbers can be used to determine the k value of the cluster and hence the possible skeletal shape. Take the example of $\text{Re}_4(\text{CO})_{16}^{2-}$; $\text{Re}(k=5.5)$, $\text{CO}(k=-1)$, $1\text{charge}(k=-0.2)$. Therefore, the total skeletal linkages of the Re atoms = $4(5.5) = 22$. These have to be 'neutralized' by the ligands and the charge present. The remaining ones will constitute the skeletal bonds or linkages which are remaining to bind the skeletal elements. Hence k value of the complex will be given by $k = 22 + 16(-1) + 2(-0.5) = 22 - 17 = 5$. The possible skeletal ideal shape of one of its isomers is shown in the labeled example 1(Ex-1) below. A possible ideal isomer shape is a square or rectangle with a diagonal. Using the labeled diagram as a basis, we can also use the skeletal numbers to deduce the possible number of CO ligands needed to complete the remaining skeletal linkages on the skeletal atom so as to enable it fulfill the 18-electron rule. The skeletal linkages available are given the labels k_1 to k_4 . From the sketch, the atom labeled 1, has two bonds connected to it. This means it is receiving one electron donation from each of the bonds linked to it. These two electrons will neutralize a k value by $2(-0.5) = -1$. Hence $k_1 = 5.5 - 1 = 4.5$. This means that atom 1 will have 4.5 CO ligands. In essence, there will be 4 CO ligands and the fractional component will represent one of the negative charges. Other k values, $k_2 = 4$, $k_3 = k_1 = 4.5$ and $k_4 = 4$ were similarly calculated. In this way a possible isomer of the cluster can be sketched. This is also shown in Ex-1 below. More examples (Ex-2 to Ex-4) are well explained and provided. As the use skeletal numbers as a concept to predict possible shapes of clusters is being introduced for the first time, more well explained examples have been worked out. These are given in Schemes 4-16.

2.7.3 K-Isomerism of Clusters

Let us take the cluster $\text{Rh}_6(\text{CO})_{16}$ as an illustration. The k value for the octahedral cluster is 11. Using skeletal numbers tentative distribution of carbonyl ligands on skeletal rhodium atoms can be sketched. Some of the selected isomers are given in Figure 3. The calculated k values on each rhodium atoms indicate the number of carbonyl ligands that can be accommodated according to $4n$ series approach using the skeletal numbers. Isomer-1 has already been given in F-9b. It is given here for comparison purposes.

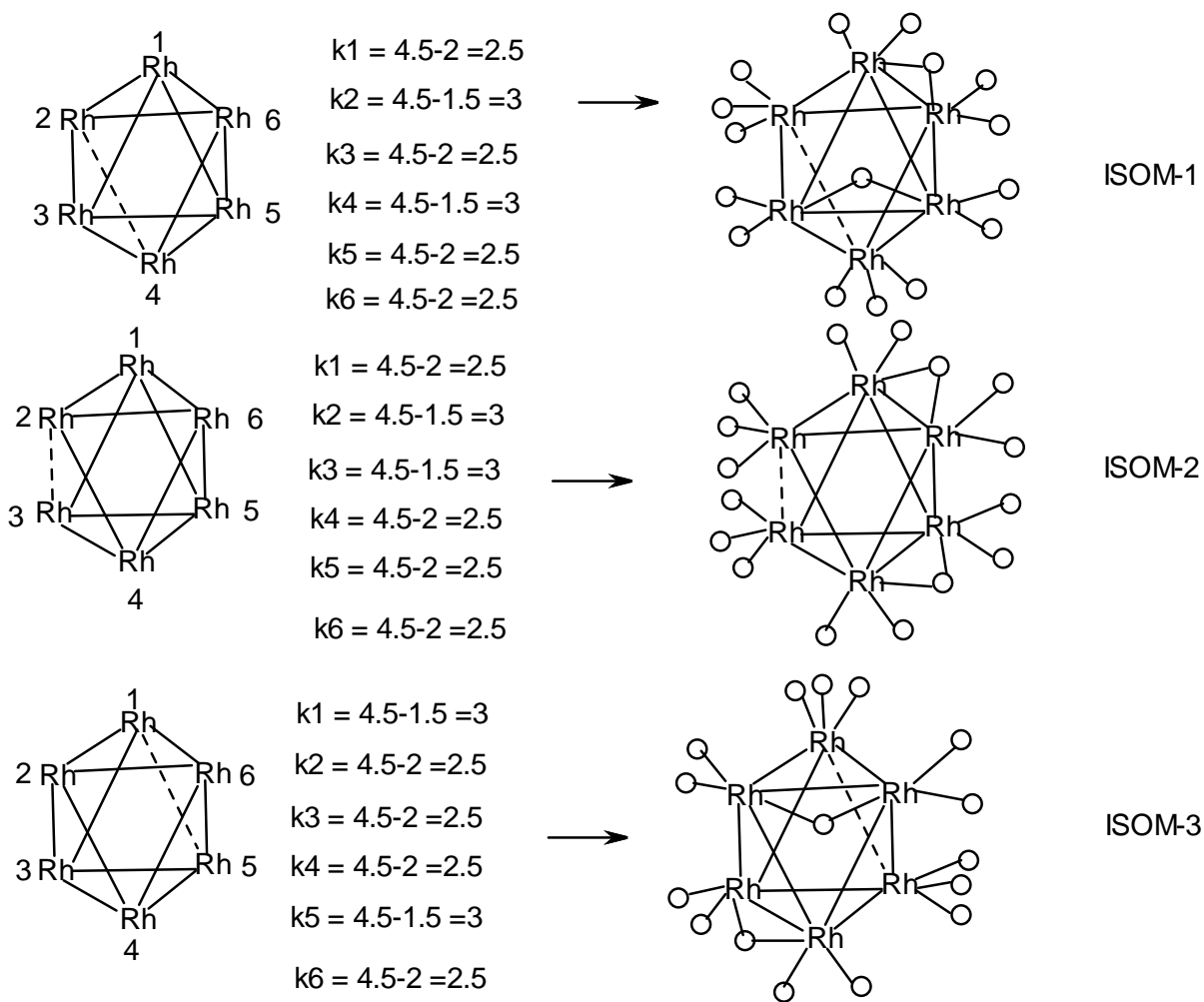
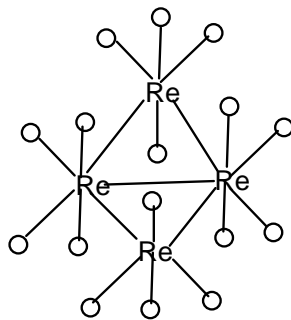
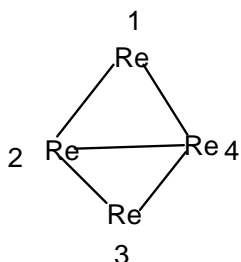


Figure 3. Sketches of selected possible isomers of $Rh_6(CO)_{16}$.

Ex-1. $\text{Re}_4(\text{CO})_{16}^{2-}$ $\text{Re}(v=7), S = 14n-7(n=1) \longrightarrow 4n-7(n=1), k = 2n+3.5 = 2(1)+3.5 = 5.5$

$k = 4(5.5) - 16 - 1 = -17 \longrightarrow 22 - 17 = 5$

$k_1 = 5.5 - 2(0.5) = 5.5 - 1 = 4.5 = k_3$ $k_2 = 5.5 - 3(0.5) = 5.5 - 1.5 = 4 = k_4$



Ex-1

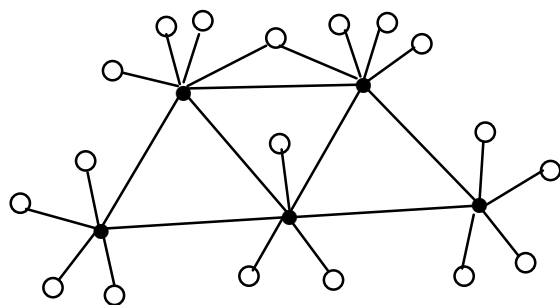
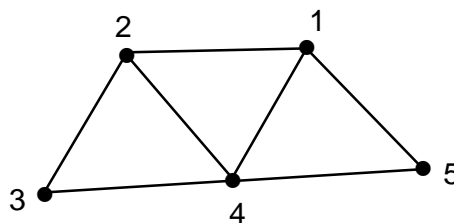
Ex-2. $\text{Os}_5(\text{CO})_{18}$ $\text{Os}(k=5), k(\text{CO}) = -1$

$k = 5(5) - 18 = 25 - 18 = 7$

$k_1 = 5 - 3(0.5) = 5 - 1.5 = 3.5 = k_2$

$k_3 = 5 - 2(0.5) = 5 - 1 = 4 = k_5$

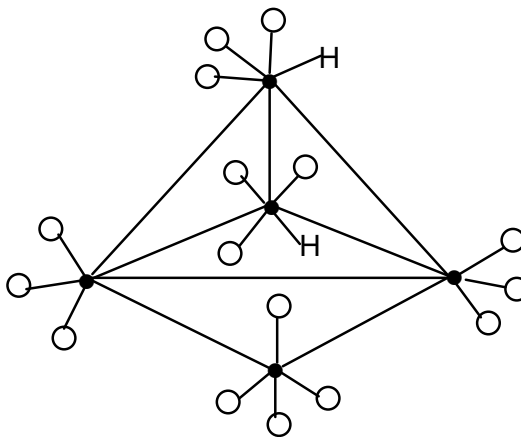
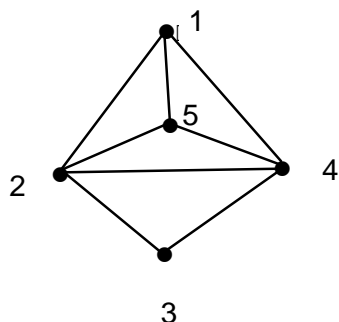
$k_4 = 5 - 4(0.5) = 5 - 2 = 3$



Ex-2

Ex-3. $H_2Os_5(CO)_{16}$ Os($k = 5$), CO($k = -1$), H($k = 0.5$)

$$k = 5(5) - 2(0.5) - 16(1) = 25 - 17 = 8 \quad k_1 = 5 - 1.5 = 3.5, k_2 = 5 - 2 = 3, k_3 = 5 - 1 = 4, k_4 = 5 - 2 = 3, k_5 = 5 - 1.5 = 3.5$$



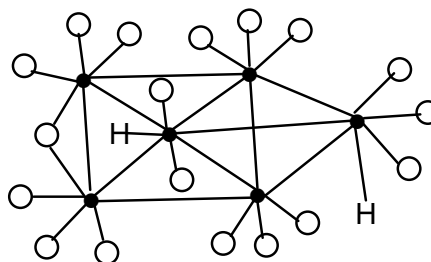
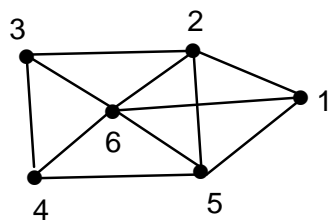
Ex-3

Ex-4. $H_2Os_6(CO)_{18}$ Os($k = 5$), CO($k = -1$), H($k = -0.5$)

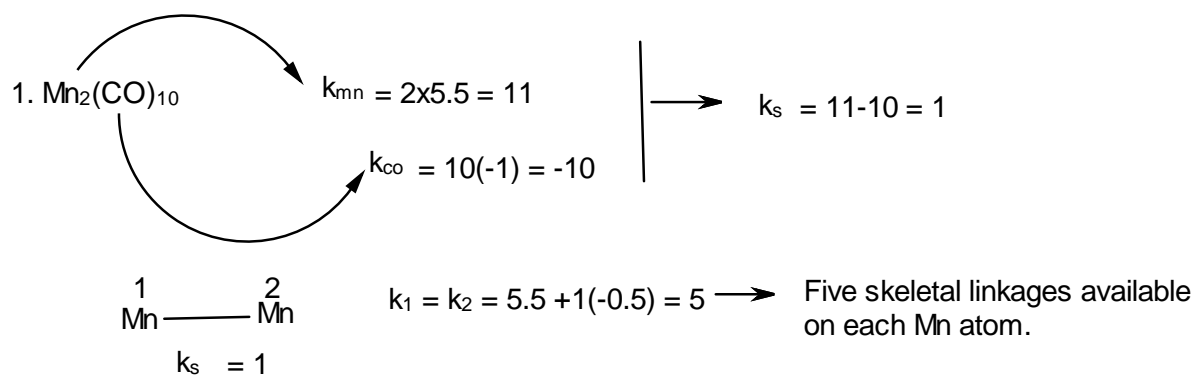
$$k = 6 \times 5 - 18(1) - 2(0.5) = 30 - 19 = 11$$

$$k_1 = 5 - 1.5 = 3.5 \quad k_2 = 5 - 2 = 3 \quad k_3 = 5 - 1.5 = 3.5$$

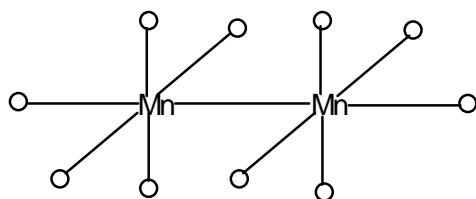
$$k_4 = 3.5 \quad k_5 = 3 \quad k_6 = 5 - 2.5 = 2.5$$



Ex-4

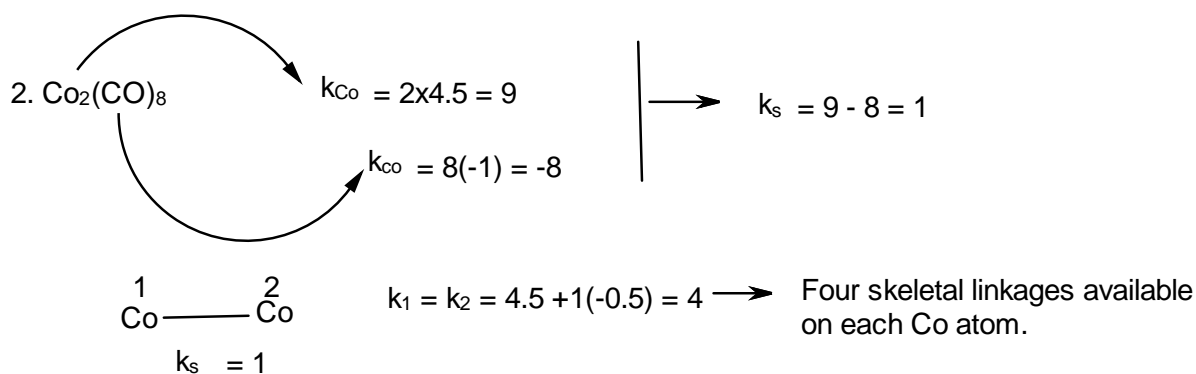


Possible structure shown in F-1.

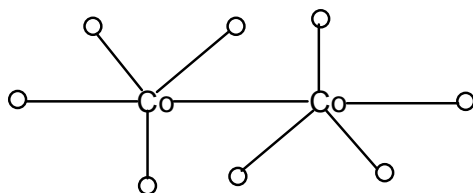


F-1

Scheme 4. Derivation of $Mn_2(CO)_{10}$ structure using skeletal numbers

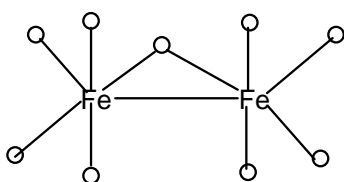
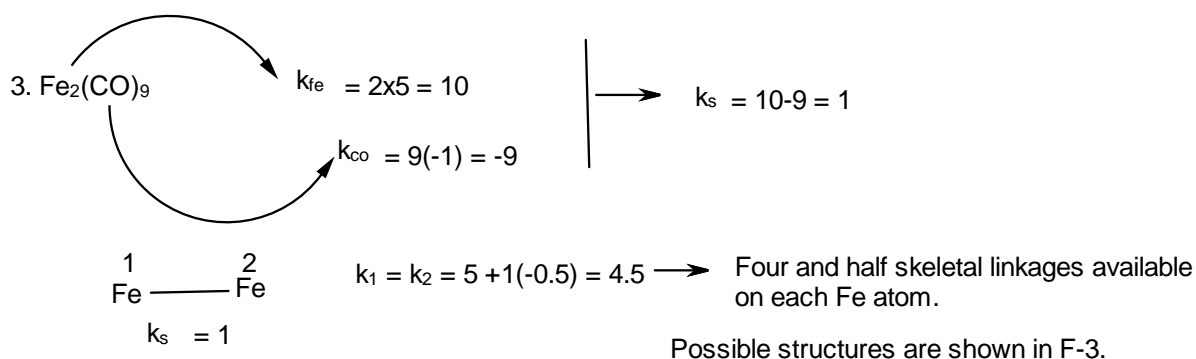


Possible structure shown in F-2.



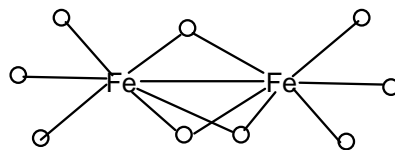
F-2

Scheme 5. Derivation of $\text{Co}_2(\text{CO})_8$ structure using skeletal numbers



F-3a

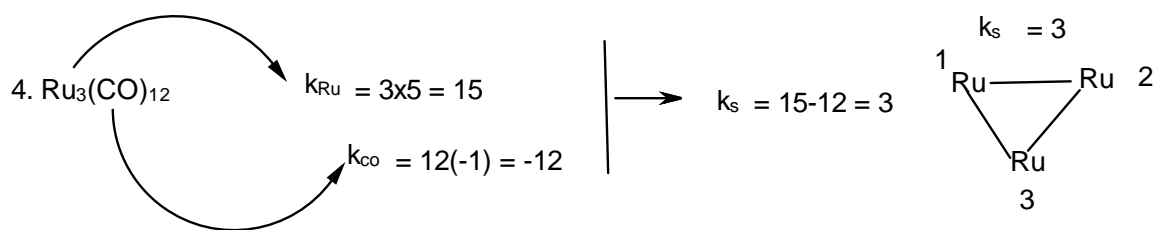
Predicted possible isomer of $\text{Fe}_2(\text{CO})_9$



F-3b

Another possible isomer of $\text{Fe}_2(\text{CO})_9$

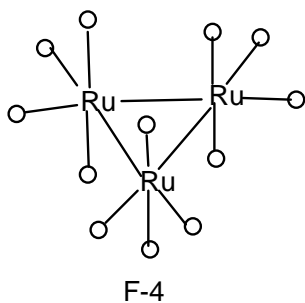
Scheme 6. Derivation of $\text{Fe}_2(\text{CO})_9$ structure using skeletal numbers



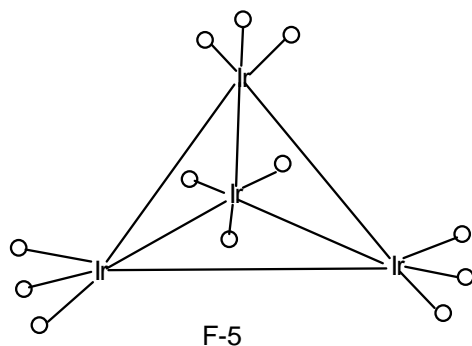
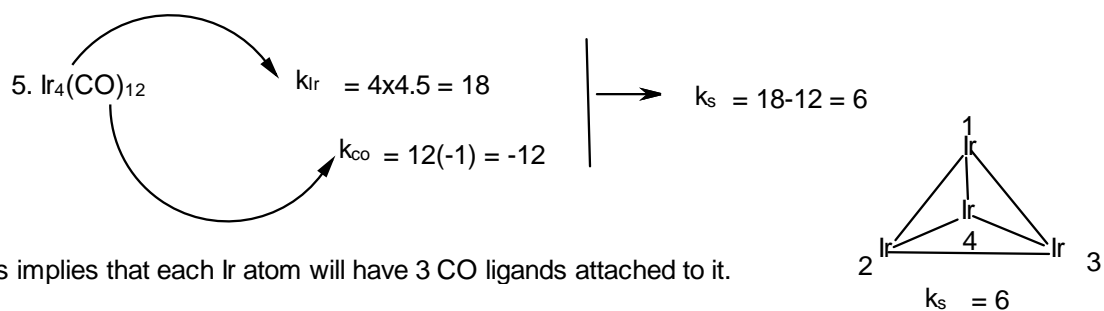
$$k_1 = k_2 = k_3 = 5 + 2(-0.5) = 5 - 1 = 4$$

This implies that each Ru atom will have 4 CO ligands attached to it.

Possible isomer is shown in F-4.

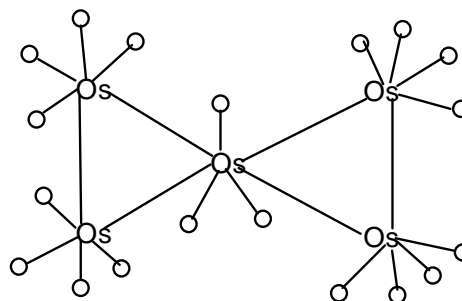
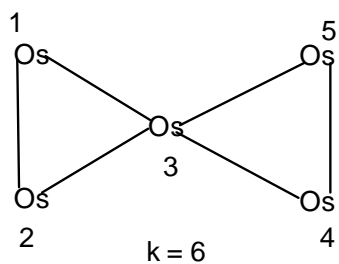
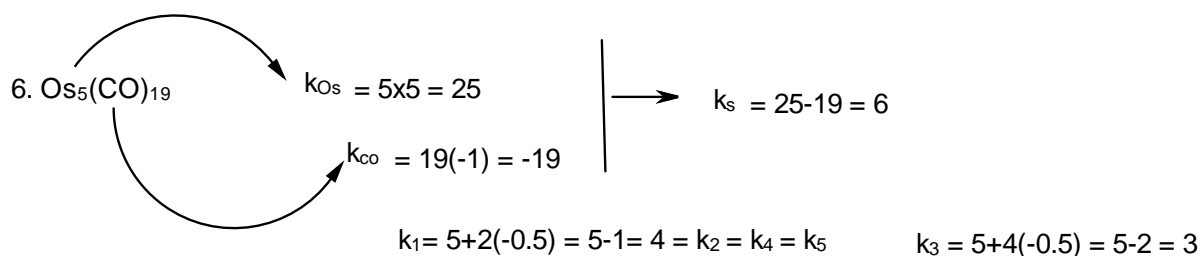


Scheme 7. Derivation of $\text{Ru}_3(\text{CO})_{12}$ structure using skeletal numbers



$k_1 = k_2 = k_3 = k_4 = 4.5 + 3(-0.5) = 4.5 - 1.5 = 3$
 Possible isomer is shown in F-5.

Scheme 8. Derivation of $\text{Ir}_4(\text{CO})_{12}$ structure using skeletal numbers

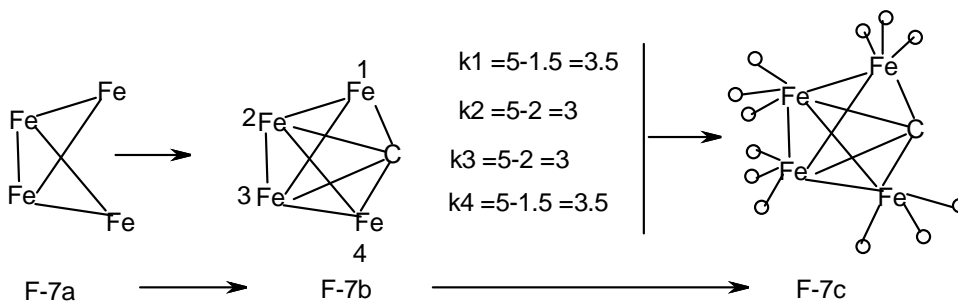


Possible isomer is shown in F-6.

Scheme 9. Derivation of $\text{Os}_5(\text{CO})_{19}$ structure using skeletal numbers

7. $\text{Fe}_4(\text{C})(\text{CO})_{12}^{2-} \longrightarrow k_s = 4(5) - 1(2) - 12(1) - 2(0.5) = 5$. The skeletal shape is sketched in F-7a.

If the carbon atom is taken as a skeletal atom, then $kS = 4(5) + 1(2) - 12 - 1 = 22 - 13 = 9$. This means that the 5 skeletal atoms are linked by 9 lines. The sketch appears as in F-7b. The tentative distribution of carbonyl ligands is shown in F-7c.



The $k_1 = k_4 = 3.5$ means that there 3 carbonyl ligands and the fractions represent the negative charges.

Scheme 10. Derivation of the structure of $\text{Fe}_4(\text{C})(\text{CO})_{12}^{2-}$ using skeletal numbers

Converting the k value of $\text{Fe}_5(\text{C})(\text{CO})_{12}^{2-}$ into series

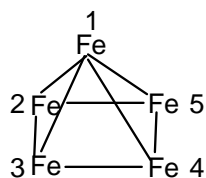
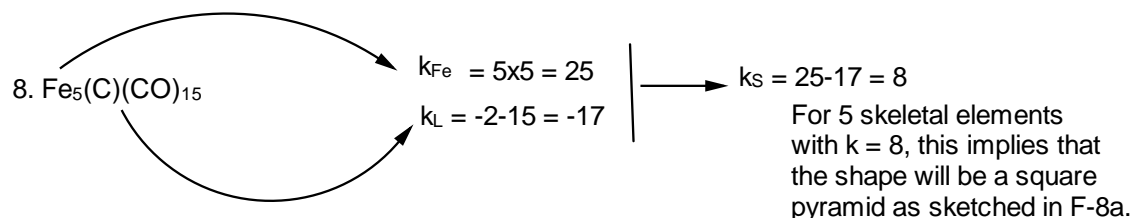
We have learnt that the series $S = 4n+q$ has a corresponding k value given by

$k=2n-q/2$. Since there are 5 skeletal elements if we include the carbon atom, then $n=5$ and $k=9$. Hence, $k=9=2(5)-q/2$; $q/2=10-9=1$. Therefore, $q=2$.

Hence the cluster series $S=4n+2$. This is CLOSO cluster.

Its borane equivalent $F_B=[\text{BH}](5)+2 = \text{B}_5\text{H}_5^{2-}$. The hydrocarbon equivalent cluster will be given by $F_{\text{CH}}=[\text{C}](5)+2\text{H}=\text{C}_5\text{H}_2$.

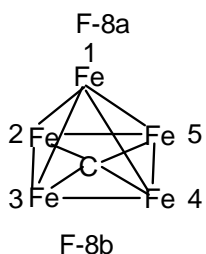
Scheme 11. Transforming the k value of a given cluster into series



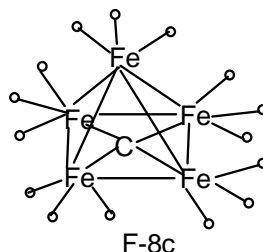
If we include the carbon atom as a skeletal atom, then its contribution to cluster k value is 2. hence, the net $k = 25+2 = 27$. The $k_{\text{L}} = -15$. Hence, $k_{\text{S}} = 27-15 = 12$.

The difference between the k -values = $12-8 = 4$ will be due to the C linkages.

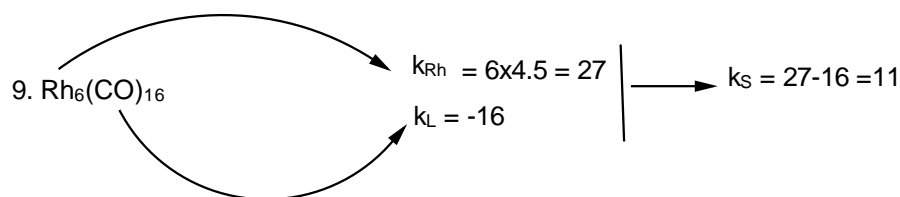
The modified skeletal shape will be as in shown in F-8b.



Using F-8b as a basis, $k_1 = 5-2 = 3$, $k_2 = 5-2 = 3$, $k_3 = 5-2 = 3$, $k_4 = 5-2 = 3$, $k_5 = 5-2 = 3$.



Scheme 12. Derivation of structure of $\text{Fe}_5(\text{C})(\text{CO})_{15}$ cluster using skeletal numbers

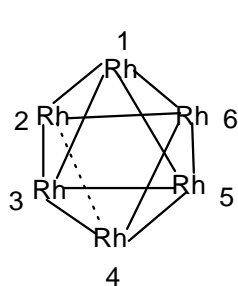


The k-value of 11 for 6 skeletal elements is characteristic of an octahedral geometry. Based on this, we can construct an octahedral sketch as shown in F-9a.

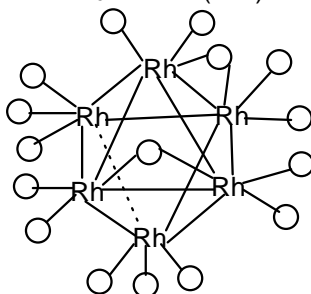
$$k_1 = 4.5 + 4(-0.5) = 4.5 - 2 = 2.5, k_2 = 4.5 + 3(-0.5) = 4.5 - 1.5 = 3, k_3 = 4.5 - 4(0.5) = 4.5 - 2 = 2.5,$$

$$k_4 = 4.5 + 3(-0.5) = 4.5 - 1.5 = 3, k_5 = 4.5 + 4(-0.5) = 4.5 - 2 = 2.5,$$

$$k_6 = 4.5 + 4(-0.5) = 4.5 - 2 = 2.5$$



F-9a

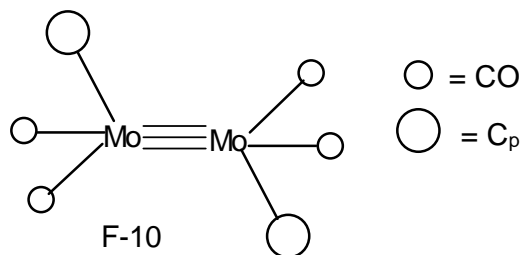
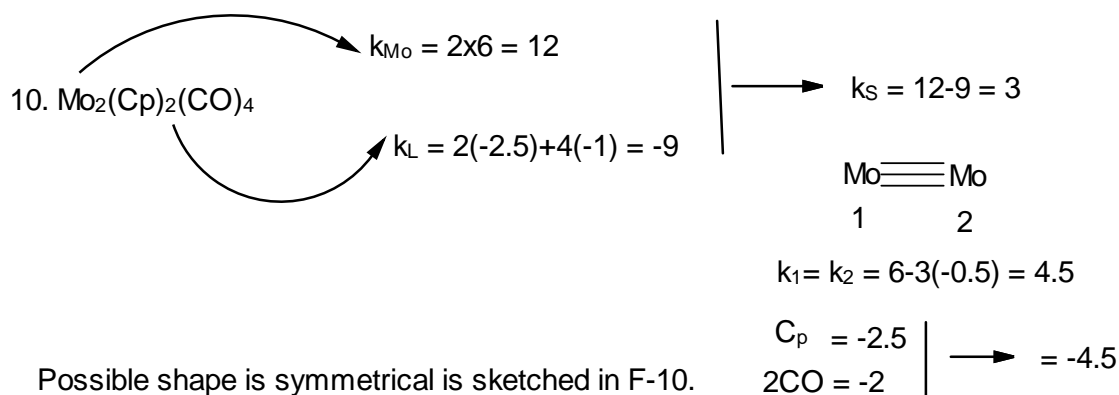


F-9b

The dotted line is not used in the calculation since we are using $k = 11$ for an O_h symmetry.

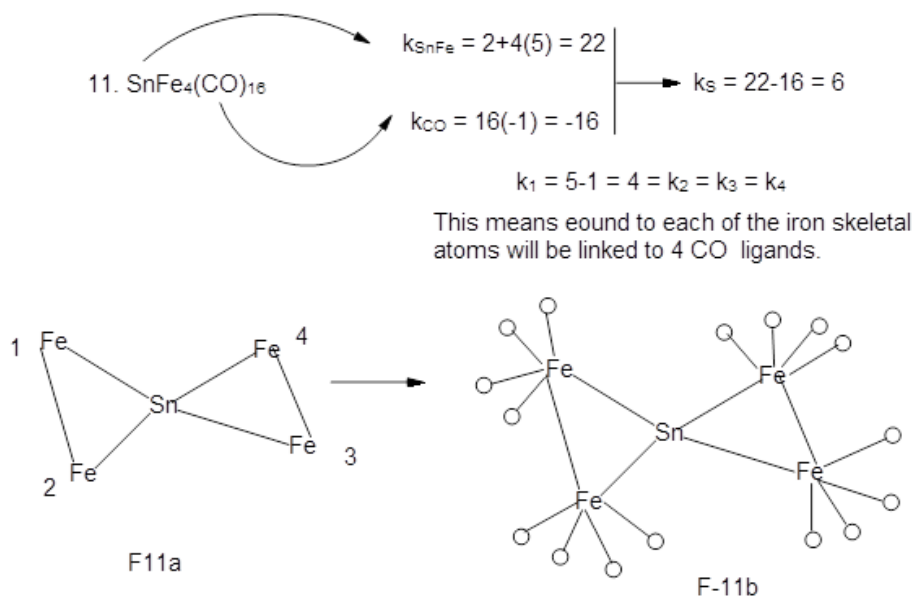
Final sketch of one of the possible isomer is given in F-9b.

Scheme 13. Derivation of structure of $Rh_6(CO)_{16}$ cluster using skeletal numbers



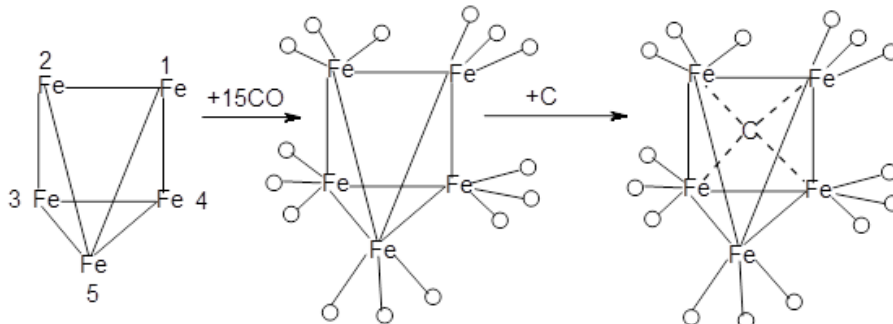
F-10

Scheme 14. Derivation of structure of $Mo_2(Cp)_2(CO)_4$ using skeletal numbers

Scheme 1 Derivation of possible structure of $\text{Mo}_2(\text{Cp})_2(\text{CO})_4$ using skeletal numbers12. Another way of Redistributing Ligands in $\text{Fe}_5(\text{C})(\text{CO})_{15}$

$$\text{Fe}(k = 5), \text{C}(k = -2), \text{CO}(k = -1)$$

$$k = 5(5) - 2 - 17 = 8 \quad k_1 = 5 - 1.5 = 3.5 \quad k_2 = k_1 = k_3 = k_4 \quad k_5 = 5 - 2 = 3$$

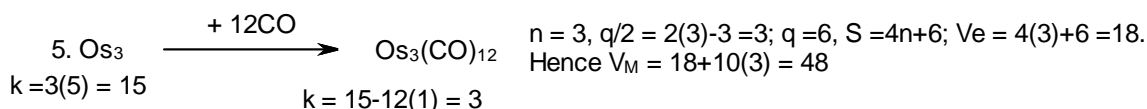
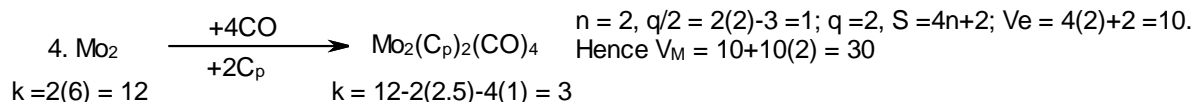
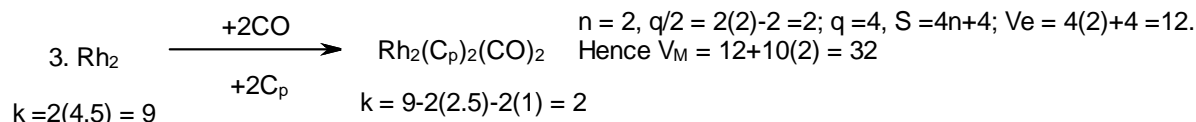
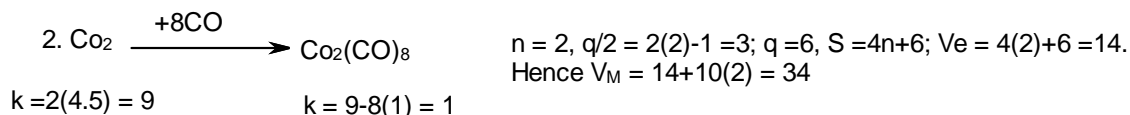
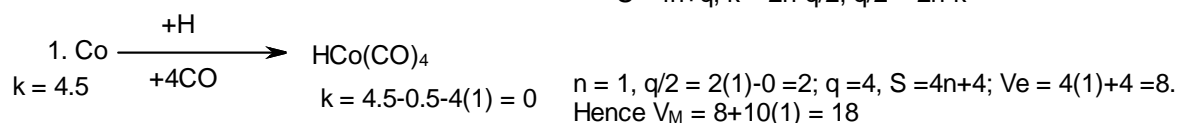
Scheme 1 . Stepwise derivation of the structure of $\text{Fe}_5(\text{C})(\text{CO})_{15}$ using skeletal numbers

2.8 Consolidation of the Skeletal Linkages Principle

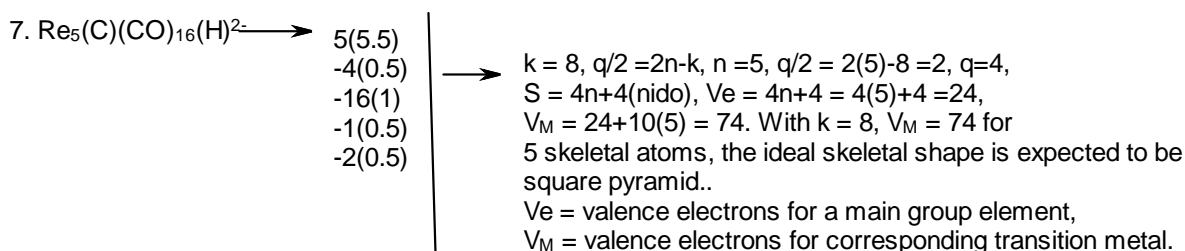
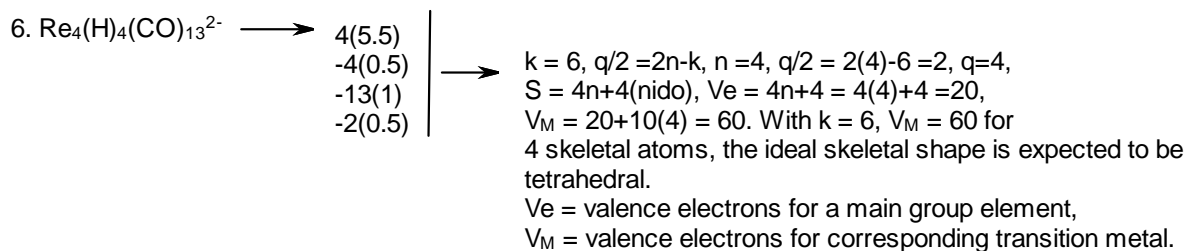
Arising from the analysis of the series of generated from adding carbonyl ligands to transition metal fragments, that we can regard the parent skeletal metal fragment as the provider of the total skeletal numbers (see Table 2) of the cluster in question. When the carbonyl and other ligands are added to the parent skeletal metal fragment, they use up some of the skeletal numbers. The remaining skeletal numbers or linkages hold the skeletal fragment of the cluster together. Take a mono-skeletal fragment such as rhodium Rh with skeletal value of $k = 4.5$. When the ligands, CO, 2PPh₃, and Cl are added, to form the Vaska's complex (Cotton, et al, 1980), $\text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{CO})$, the CO utilizes one(1) skeletal value, the 2 PPh₃ use up two(2) and the Cl takes (0.5) skeletal numbers. Hence, the k value of the cluster will be given by $k = 4.5 - 1(1) - 2(2) - 1(0.5) = 1$. This means the cluster is missing a pair of valence electrons to complete the 18-electron rule. Thus, the cluster is a 16-valence electron system. Hence, it is no surprise to see the Vaska's complex undergo the oxidative addition reactions such as $\text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{CO}) + \text{H}_2 \rightarrow \text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{CO})(\text{H})_2 (k=0)$, and $\text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{CO}) + \text{MeI} \rightarrow \text{Rh}(\text{Cl})(\text{PPh}_3)_2(\text{CO})(\text{Me})(\text{I}) (k=0)$. The addition of 8CO ligands to $\text{Co}_2 (k=2 \times 4.5=9)$ skeletal fragment produces $\text{Co}_2(\text{CO})_8$ complex with $k=9-8=1$. This means that the 8 carbonyl ligands use up 8 of the 9 skeletal values of Co_2 leaving behind $k=1$. Therefore the cobalt carbonyl complex $\text{Co}_2(\text{CO})_8$ is held by one Co-Co bond. This

approach is indirectly applying equation (i). That is, in order to determine the number of skeletal linkages (k_s) of a given cluster, the equation (i) becomes extremely useful. The k_s value is thus given by $k_s = k_T - k_L$. This equation simply means that if the k values utilized by the ligands are subtracted from the original k values of the naked skeletal elements, the remaining k values represent the skeletal linkages of the cluster. Let us illustrate this using the following few examples. Consider the complex, $\text{Re}_2(\text{Cp})_2(\text{CO})_5$. Since Re has the skeletal number, $k=5.5$, the skeletal number $k_s = 2(5.5) - 2(2.5) - 5(1) = 11 - 10 = 1$ and $S = 4n + q$, $k = 2n - q/2$. Hence, $q/2 = 2n - k = 2(2) - 1 = 3$, $q = 6$ and $S = 4n + 6$. The number of valence electrons, $\text{Ve} = 4n + 6 = 4(2) + 6 = 14$. Since $S = 4n + 6 \Leftrightarrow 14n + 6$, the corresponding valence electrons for the transition metal cluster V_M will be given by $V_M = 14 + 10(2) = 34$. This means that the rhenium complex will have a single Re-Re bond around which the 5CO and the 2 cyclopentadienyl ligands will be bound. For the complex, $\text{Ir}_4(\text{CO})_{12}$, Ir, $k=4.5$ (see Table 2), hence $k_s = 4(4.5) - 12(1) = 6$. Using this value of $k = 6$, we can derive the series and then use the series to deduce the number of valence electrons. Thus, $k=6$, $q/2 = 2(4) - 6 = 2$, $q=4$, $S = 4n + 4$, $\text{Ve} = 4(4) + 4 = 20$, and $V_M = 20 + 10(4) = 60$. The k value of 6 for 4 iridium skeletal atoms implies that they will take up an ideal tetrahedral skeletal shape. Let us consider the rhenium complex $\text{Re}_5(\text{C})(\text{CO})_{16}(\text{H})^{2-}$. Its cluster number is given by $k = 5(5.5) - 1(2) - 16(1) - 1(0.5) - 2(0.5) = 8$, $q/2 = 2(5) - 8 = 2$, $q=4$ and $S = 4n + 4$ (nido series), $\text{Ve} = 4n + 4 = 4(5) + 4 = 24$. Hence, the valence electrons of the corresponding transition metal carbonyl cluster will be given by $V_M = 24 + 10(5) = 54$. The k value of 8 for 5 five skeletal elements is characteristic of a square pyramid geometry. Another example is $\text{Re}_6(\text{C})(\text{CO})_{19}^{2-}$; $k = 6(5.5) - 2 - 19 - 1 = 11$, $q/2 = 2(6) - 11 = 1$, $q=2$, $S = 4n + 2$ (closo series), $\text{Ve} = 4n + 2 = 4(6) + 2 = 26$, and $V_M = 26 + 10(6) = 86$. The k value of 11 for 6 skeletal elements and closo series is characteristic of an octahedral geometry. Applying the same concept of assuming that all the skeletal values are supplied by the skeletal elements and that the carbonyl and other ligands consume some of the skeletal values and that the remaining k values hold the skeletal atoms together, then we can calculate the k values of clusters, derive their corresponding series and valence electrons and predict the shapes of some of the cluster complexes. The following examples in Schemes 17 and 18 illustrate this concept. Due to the fact that the use of skeletal numbers is so easy and flexible, it has been extended to many more clusters carbonyl complexes taken mainly from various reviews (King, 1986; Lewis and Johnson, 1982; Zanello, 2002; Teo and Zhang, 1990, 1991; Belyakova and Slovokhov, 2003; Hughes and Wade, 2000; Rossi and Zanello, 2011). The results are given in Table 10. The table summarizes the analysis of nearly 50 complexes. In addition, 15 more examples are illustrated in Schemes 17 and 18 in order to enable the readers be exposed to a wide range of clusters analyzed using the skeletal numbers. Furthermore, these examples clearly demonstrate the fact that the valence electron counts can readily be derived from the corresponding $4n$ series of the clusters. The results agree with many of the known clusters but also provide more insights on clusters and new interpretations based on the type of $4n$ series and k values. Let us look at some few examples of categorization of a cluster using its k value. These include (Greenwood, et al, 1998) $\text{Co}_2(\text{CO})_8$; $k = 2(4.5) - 8 = 9 - 8 = 1$ (single metal-metal bond), $q/2 = 2n - k$, $n=2$, $q/2 = 2(2) - 1 = 3$, $q=6$, $S = 4n + 6$ (arachno series), $\text{Ve} = 4n + 6 = 4(2) + 6 = 14$, $V_M = 14 + 10(2) = 34$, $\text{Ir}_4(\text{CO})_{12}$; $k = 4(4.5) - 12 = 6$ (six skeletal linkages, tetrahedral skeletal shape), $q/2 = 2n - k$, $n = 4$, $q/2 = 2(4) - 6 = 2$, $q=4$, $S = 4n + 4$ (nido series), $\text{Ve} = 4n + 4 = 4(4) + 4 = 20$, $V_M = 20 + 10(4) = 60$, $\text{M}_6(\text{CO})_{16}$, $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$; $k = 6(4.5) - 16 = 11$, $q/2 = 2n - k$, $n=6$, $q/2 = 2(6) - 11 = 1$, $q=2$, $S = 4n + 2$ (closo), for $n=6$ and cluster belongs to closo series, this corresponds to $\text{B}_6\text{H}_6^{2-}$ cluster which has an ideal octahedral skeletal shape. This is what is observed (Greenwood, et al, 1998). The valence electron count for the octahedral system, $\text{Ve} = 4n + 2$, $n=6$, $\text{Ve} = 4(6) + 2 = 26$ and $V_M = 26 + 10(6) = 86$. The $\text{Ve} = 26$ is the valence electron count of the main group octahedral geometry and $V_M = 86$ is the corresponding valence electron count for a transition metal complex. Hence, $\text{B}_6\text{H}_6^{2-}$ will have $\text{Ve} = 26$. However its counterpart transition metal complex will have its valence electron count of $V_M = 26 + 10(6) = 86$. This is a consequence of a type of isolobal relationship $S = 4n + q$ (Main Group Element cluster) $\Leftrightarrow S = 14n + q$ (Transition Metal Cluster). The difference between the two systems is simply $\pm 10n$. The examples in Table 10 and Schemes 17 and 18 have included the valence electron counts of clusters to demonstrate that valence electron counts are a direct consequence of $4n$ series. The valence electron counts which are associated with skeletal shapes of clusters are also a direct consequence of the $4n$ series (Fehlner, et al, 2007).

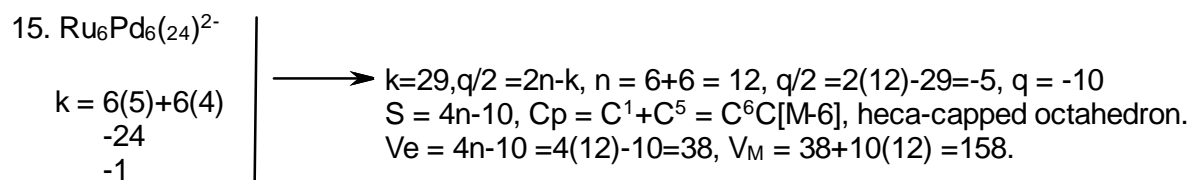
$$S = 4n + q, k = 2n - q/2, q/2 = 2n - k$$



Scheme 17. Examples showing Derivation of series and Valence Electron Counts using the series



8. $\text{Re}_6(\text{C})(\text{CO})_{19}^{2-}$ \rightarrow $\begin{array}{l} 6(5.5) \\ -4(0.5) \\ -19(1) \\ -2(0.5) \end{array}$ \rightarrow $k = 11, q/2 = 2n - k, n = 6, q/2 = 2(6) - 11 = 1, q = 2,$
 $S = 4n + 2(\text{closo}), \text{Ve} = 4n + 2 = 4(6) + 2 = 26,$
 $V_M = 26 + 10(6) = 86.$ With $k = 11, V_M = 86$ for
 6 skeletal atoms, the ideal skeletal shape is expected to be
 octahedral..
 $\text{Ve} =$ valence electrons for a main group element,
 $V_M =$ valence electrons for corresponding transition metal.
9. $\text{Re}_7(\text{C})(\text{CO})_{21}^{3-}$ \rightarrow $\begin{array}{l} 7(5.5) \\ -2 \\ -21 \\ -1.5 \end{array}$ \rightarrow $k = 14, q/2 = 2n - k, n = 7, q/2 = 2(7) - 14 = 0, q = 0,$
 $S = 4n + 0(\text{mono-capped closo}, \text{C}^1\text{C}[\text{M}-6]),$
 $\text{Ve} = 4n + 0 = 4(7) + 0 = 28,$
 $V_M = 28 + 10(7) = 98.$ With $k = 14, V_M = 98$ for
 7 skeletal atoms, the ideal skeletal shape is expected to be
 a mono-capped octahedral..
 $\text{Ve} =$ valence electrons for a main group element,
 $V_M =$ valence electrons for corresponding transition metal.
10. $\text{Re}_8(\text{C})(\text{CO})_{24}^{2-}$ \rightarrow $\begin{array}{l} 8(5.5) \\ -2 \\ -24 \\ -1 \end{array}$ \rightarrow $k = 17, q/2 = 2n - k, n = 8, q/2 = 2(8) - 17 = -1, q = -2,$
 $S = 4n - 2(\text{bi-capped closo}, \text{C}^2\text{C}[\text{M}-6]),$
 $\text{Ve} = 4n - 2 = 4(8) - 2 = 30,$
 $V_M = 30 + 10(8) = 110.$ With $k = 17, V_M = 110$ for
 8 skeletal atoms, the ideal skeletal shape is expected to be
 a bi-capped octahedral..
 $\text{Ve} =$ valence electrons for a main group element,
 $V_M =$ valence electrons for corresponding transition metal.
11. B_5H_9 \rightarrow $\begin{array}{l} 5(2.5) \\ -9(0.5) \end{array}$ \rightarrow $k = 8, q/2 = 2n - k, n = 5, q/2 = 2(5) - 8 = 2, q = 4,$
 $S = 4n + q = 4n + 4(\text{nido}).$ With $k = 8$ for 5 skeletal atoms of nido
 series, the expected ideal shape is square pyramid.
12. $\text{B}_6\text{H}_6^{2-}$ \rightarrow $\begin{array}{l} 6(2.5) \\ -6(0.5) \\ -2(0.5) \end{array}$ \rightarrow $k = 11, q/2 = 2n - k, n = 6, q/2 = 2(6) - 11 = 1, q = 2,$
 $S = 4n + q = 4n + 2(\text{closo}).$ With $k = 11$ for 6 skeletal atoms of closo
 series, the expected ideal shape is octahedral.
13. $\text{C}_2\text{B}_{10}\text{H}_{12}$ \rightarrow $k = 2(2) + 10(2.5) - 12(0.5) = 23$
 $q/2 = 2n - k, n = 2 + 10 = 12, q/2 = 2(12) - 23 = 1, q = 2$
 $S = 4n + q = 4n + 2$ (closo series).
 Since $n = 12$ and belongs to closo series, the ideal
 shape of the cluster will be similar to $\text{B}_{12}\text{H}_{12}^{2-}$.
 $\text{Ve} = 4n + 2 = 4(12) + 2 = 50$
14. $(\text{Cp})_3\text{Co}_3\text{B}_3\text{H}_5$ \rightarrow $k = 3(4.5) + 3(2.5) - 3(2.5) - 5(0.5) = 11, q/2 = 2n - k = 2(6) - 11 = 1,$
 $S = 4n + 2$ (closo). For $k = 11$ and cluster belongs to closo series
 with $n = 6$. the predicted shape of the cluster will be similar to
 that of that of $\text{B}_6\text{H}_6^{2-}$ which is octahedral.



Scheme 18. Using skeletal numbers to derive series and valence electrons

Table 10. Derivation of 4n Series and Valence Electron Counts Using the k-Values of Clusters

Cluster	k Value	q value	Series (S)	Category	n value	Borane equivalent	Valence Electrons
Fe ₄ (C)(CO) ₁₂ ²⁻	5	6	4n+6	arachno	4	B ₄ H ₁₀	22+40 =62
(H)Os ₃ (CO) ₁₀ (AuL)	7	2	4n+2	closa	4	B ₄ H ₄ ²⁻	18+40 =58
(H)FeCo ₃ (CO) ₉ L ₃	6	4	4n+4	nido	4	B ₄ H ₈	20+40 =60
Re ₄ (H) ₄ (CO) ₁₂	8	0	4n+0	C ¹ C[M-3]	4	B ₄ H ₄	16+40 =56
Fe ₄ (CO) ₄ (η ⁵ -C ₅ H ₅) ₄	6	4	4n+4	nido	4	B ₄ H ₈	20+40 =60
Ir ₄ (CO) ₁₂	6	4	4n+4	nido	4	B ₄ H ₈	20+40 =60
Fe ₅ (N)(CO) ₁₄ ⁻	8	4	4n+4	nido	5	B ₅ H ₉	24+50 =74
Ni ₅ (CO) ₁₂ ²⁻	7	6	4n+6	arachno	5	B ₅ H ₁₁	26+50 = 76
Rh ₅ (CO) ₁₅ ⁻	7	6	4n+6	arachno	5	B ₅ H ₁₁	26+50 = 76
Ni ₃ Cr ₂ (CO) ₁₆ ²⁻	7	6	4n+6	arachno	5	B ₅ H ₁₁	26+50 = 76
Os ₅ (CO) ₁₆	9	2	4n+2	closa	5	B ₅ H ₅ ²⁻	22+50 =72
Se ₂ Cr ₃ (CO) ₁₀ ²⁻	9	2	4n+2	closa	5	B ₅ H ₅ ²⁻	22+30 =52
PtRh ₄ (CO) ₁₂ ²⁻	9	2	4n+2	closa	5	B ₅ H ₅ ²⁻	22+50 =72
Se ₂ Fe ₃ (CO) ₉	8	4	4n+4	nido	5	B ₅ H ₉	24+30 =54
Ru ₆ (CO) ₁₈ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Fe ₆ (C)(CO) ₁₆ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Os ₆ (P)(CO) ₁₈ ⁻	9	6	4n+6	arachno	6	B ₆ H ₁₂	30+60 = 90
Os ₆ (CO) ₁₈	12	0	4n+0	C ¹ C[M-5]	6	B ₆ H ₆	24+60 = 84
Os ₄ (CO) ₁₂ (H) ₂ (AuL) ₂	12	0	4n+0	C ¹ C[M-5]	6	B ₆ H ₆	24+60 = 84
Se ₂ Mn ₄ (CO) ₁₂ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+40 =66
Ru ₆ (C)(CO) ₁₇	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Os ₆ (CO) ₁₈ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Rh ₆ (C)(CO) ₁₅ ²⁻	9	6	4n+6	arachno	6	B ₆ H ₁₂	30+60 = 90
Pt ₆ (CO) ₁₂ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Co ₆ (C)(CO) ₁₅ ²⁻	9	6	4n+6	arachno	6	B ₆ H ₁₂	30+60 = 90
Ru ₆ (C)(CO) ₁₆ ²⁻	11	2	4n+2	closa	6	B ₆ H ₆ ²⁻	26+60 =86
Os ₇ (CO) ₂₁	14	0	4n+0	C ¹ C[M-6]	7	B ₇ H ₇	28+70 = 98
Co ₇ (N)(CO) ₁₅ ²⁻	13	2	4n+2	closa	7	B ₇ H ₇ ²⁻	30+70 =100
Ru ₄ (CO) ₁₂ (AuL) ₃ (H)	15	-2	4n-2	C ² C[M-5]	7	B ₇ H ₅	26+70 = 96
Rh ₇ (CO) ₁₆ ³⁻	14	0	4n+0	C ¹ C[M-6]	7	B ₇ H ₇	28+70 = 98
Os ₈ (CO) ₂₂ ²⁻	17	-2	4n-2	C ² C[M-6]	8	B ₈ H ₆	30+80 = 110
Ru ₈ (P)(CO) ₂₂ ⁻	15	2	4n+2	closa	8	B ₈ H ₈ ²⁻	34+80 =114
Re ₈ (C)(CO) ₂₄ ²⁻	17	-2	4n-2	C ² C[M-6]	8	B ₈ H ₆	30+80 = 110
Cu ₂ Ru ₆ (C)(CO) ₁₆	19	-6	4n-6	C ⁴ C[M-4]	8	B ₈ H ₂	26+80 = 106
Co ₈ (C)(CO) ₁₈ ²⁻	15	2	4n+2	closa	8	B ₈ H ₈ ²⁻	34+80 =114
Ni ₈ (C)(CO) ₁₆ ²⁻	13	6	4n+6	arachno	8	B ₈ H ₁₄	38+80 =118
Bi ₈ ²⁻	13	6	4n+6	arachno	8	B ₈ H ₁₄	38+80 =118
Co ₆ Ni ₂ (C) ₂ (CO) ₁₆ ²⁻	14	-4	4n-4	C ³ C[M-5]	8	B ₈ H ₄	28+80 =108
Ni ₈ (L) ₆ (CO) ₈	12	8	4n+8	hypho	8	B ₈ H ₁₆	40+80 =120
Ni ₈ (CO) ₁₈ ²⁻	13	-2	4n-2	C ² C[M-6]	8	B ₈ H ₆	30+80 = 110
Ge ₉ ²⁻	17	2	4n+2	closa	9	B ₉ H ₉ ²⁻	38
Ni ₉ (CO) ₁₈ ²⁻	17	2	4n+2	closa	9	B ₉ H ₉ ²⁻	38+90=128
Rh ₉ (CO) ₁₉ ³⁻	20	-8	4n-8	C ⁵ C[M-4]	9	B ₉ H ₁	28+90 =118
Ni ₉ (C)(CO) ₁₇ ²⁻	16	4	4n+4	nido	9	B ₉ H ₁₃	40+90 =130
Ni ₉ (CO) ₁₈ ²⁻	17	2	4n+2	closa	9	B ₉ H ₉ ²⁻	38+90=128
L = PPh ₃							
Ru ₁₀ (P)(CO) ₂₄ ²⁻	23	-6	4n-6	C ⁴ C[M-6]	10	B ₁₀ H ₄	34+100 =134
Os ₁₀ (C)(CO) ₂₄ ²⁻	23	-6	4n-6	C ⁴ C[M-6]	10	B ₁₀ H ₄	34+100 = 134
Rh ₁₀ (P)(CO) ₂₂ ³⁻	19	2	4n+2	closa	10	B ₁₀ H ₁₀ ²⁻	42+100=148

3. Conclusion

A skeletal transition metal atom possesses inherent skeletal linkages. The linkages are derived from the valence electrons of the element. They correspond to the number of pairs of electrons needed to enable the metal atom obey the eighteen electron rule. The k-values derived are as follows: Group 3, Sc family, $k=7.5$; Group 4, Ti family, $k=7.0$; Group 5, V family, $k=6.5$; Group 6, Cr family, $k=6$; Group 7, Mn family, $k=5.5$; Group 8, Fe family, $k=5$; Group 9, Co family, $k=4.5$; Group 10, Ni family, $k=4$; Group 11, Cu family, $k=3.5$ and Group 12, Zn family, $k=3$. Ligands have been assigned negative k values as deduced from the $4n$ series. It is proposed that a single electron donor be assigned a k value of -0.5 and a two electron donor $k=-1$. The use of skeletal numbers greatly facilitates the categorization of simple to medium large clusters in a simple manner. Furthermore, it is possible to predict the shapes of some clusters. The skeletal numbers can also be utilized as a guide to assigning the ligands and charges to specific skeletal elements of clusters. The method makes the testing of the 18-electron rule, the understanding of some catalytic processes and the isolobal principle much easier. The skeletal values which have now been introduced for the first time in chemistry and the atoms of the main group and transition metal elements can be arranged into groups based on k values. Nearly 80 clusters of different types have been analyzed using skeletal numbers to demonstrate the ease and flexibility of applying skeletal numbers. This paper introduces a fundamental principle of viewing a naked skeletal cluster of elements as being a reservoir of inherent skeletal linkages which are subject to change when it is gets bound to electron donor ligands. The observed linkages or bonds are just remnants of those skeletal linkages which were not utilized by the ligands. This could be viewed as a form of conservation of skeletal cluster linkages.

Acknowledgements

The author wishes to express gratitude to the University of Namibia for the provision of facilities and NAMSOV, Namibia for the financial support, Mrs Merab Kambamu Kiremire for proof-reading the paper.

Dedication

This work is dedicated to Prof. Charles Alfred Coulson, (UK) whose brief teaching at Makerere University, Uganda in the late 1960s has had a life-long inspiration. His style of teaching valence in chemistry in a simple and inspiring manner left inerasable fond memories. I also wish to dedicate this work to Prof. Frank Bottomley who was my enthusiastic PhD mentor in inorganic chemistry at the University of New Brunswick, Fredericton, Canada in the late 1970s.

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