

Isolability, direct linkage to valence

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ABSTRACT

The isolability concept utilized to explain cluster chemistry may simply be regarded as being synonymous to valence. By assigning a valence to organometallic fragments, many structures of organometallic compounds can readily be explained. The valence of a fragment is deduced from the octet rule or the 18 electron rule. This paper briefly reflects and reviews the isolability concept and points out the its direct linkage to the valence concept. This approach will greatly improve and simplify the teaching of molecular cluster systems at both undergraduate and postgraduate levels. Ample examples of molecules to illustrate the application of valence concept to explain molecular geometry are given.

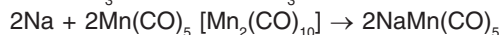
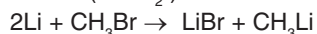
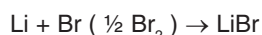
Key words: Isolability, direct linkage.

INTRODUCTION

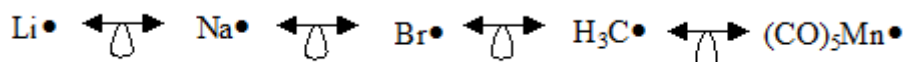
Since the introduction of the isolability concept in early 80's by Hoffman¹⁻², it has been widely utilized to explain clusters found in organic, inorganic and organometallic chemistry³⁻⁸. Also hole formalism has been used to relate to isolability⁹. However after some scrutiny, it is quite clear that we can readily correlate the isolability to valence. This makes the isolability linkage to molecular geometry much smoother and easier.

Isolability and valence

Let us consider the following simple reactions



The chemical species Li, Na, Br, CH_3 , $\text{Mn}(\text{CO})_5$ can be regarded as being monovalent. That is, having one available valence electron to participate in a chemical reaction. Hence, these species are isolobal. This can be symbolized as follows:



Just like Br, the CH_3 fragment has 7 valence electrons (4 from C and 3 from the 3 H atoms). The methyl fragment while it has one unpaired electron, it is short of 1 electron to attain the octet rule. Similarly, the $(\text{CO})_5\text{Mn}$ fragment has 17 electrons (10 from the five COs and 7 from Mn). It is short of 1 to attain the 18 electron rule. Thus, the $(\text{CO})_5\text{Mn}$ fragment can be considered to

carry 1 unpaired electron in its participation on bond formation to form simple or complex molecules. Similar fragments can be considered as being monovalent as is the case with Group 1 elements (alkali metals) or Group 7 elements (halogens). A removal of one hydrogen atom from the CH_3 fragment produces H_2C : radical. It has a total of 6 electrons and can be regarded as a divalent

species. In this way it has a resemblance to Group 2 elements (alkaline earth elements) or Group 6. The metal carbonyl fragment $(\text{CO})_4\text{Fe}$ has 16 electrons (8 from the 4 COs + 8 from Fe). It is short of 2 electrons to attain the 18 electron rule. Just like an oxygen atom, it can be regarded as a divalent fragment, $[(\text{CO})_4\text{Fe}]$ with two electrons to share and form compounds. Removal of H atom from the CH_2 radical generates the CH fragment which

may be regarded as being trivalent. Likewise, the fragment $(\text{OC})_3\text{Ir}$ can be regarded being trivalent. The carbon itself will be considered to be quadrivalent. This is illustrated in Table 1. The classification of selected fragments into valence types is also given in Table 2. The chemical species which have the same valence (isovalent) are isolobal.

Table 1: Shows the linkage between isolobality and valence for selected species.

	Valence (V) = 0	Monovalent 1	Divalent 2	Trivalent 3	Quadrivalent 4
	CH_4	$\text{H}_3\text{C}.$	$\text{H}_2\text{C}:$	$\text{HC}:$	$\text{C}:$
#Es	8	7	6	5	4
	$(\text{OC})_6\text{Cr}$	$(\text{OC})_5\text{Mn}$	$(\text{OC})_4\text{Fe}$	$(\text{OC})_3\text{Ir}$	$(\text{OC})_3\text{Fe}$
#Es	18	17	16	15	14

#Es = Number of electrons around the central atom

Table 2: Shows a selected collection of chemical species of the same valence

MONOVALENT, V = 1

CH_3 : Li, Na, K, Rb, Cs, F, Cl, Br, I; $\text{M}(\text{CO})_5$, M = Mn, Tc, Re; $\text{M}(\text{CO})_4$, M = Co, Rh, Ir; $\text{C}_p\text{M}(\text{CO})_2$, M = Fe, Ru, Os; $\text{C}_p\text{M}(\text{CO})_3$, M = Cr, Mo, W

DIVALENT, V = 2

CH_2 : Be, Mg, Ca, Sr, Ba; O, S, Se, Te; $\text{M}(\text{CO})_4$, M = Fe, Ru, Os; $\text{M}(\text{CO})_5$, M = Cr, Mo, W; $\text{C}_p\text{M}(\text{CO})$, M = Co, Rh, Ir; $\text{C}_p\text{M}(\text{CO})_2$, M = Mn, Tc, Re; $\text{C}_p\text{M}(\text{CO})$, M = Co, Rh, Ir

TRIVALENT, V = 3

CH; B, Al, Ga, In, Tl; N, P, As, Sb, Bi; $\text{M}(\text{CO})_3$, M = Co, Rh, Ir; $\text{MH}(\text{CO})_3$, M = Fe, Ru, Os; $\text{C}_6\text{H}_6\text{M}$, M = Co, Rh, Ir; $\text{C}_5\text{H}_5\text{Ni}$; $[\text{M}(\text{CO})_3]^-$, M = Fe, Ru, Os; $\text{C}_p\text{M}(\text{CO})$, M = Fe, Ru, Os; $\text{C}_p\text{M}(\text{CO})_2$, M = Cr, Mo, W

QUADRIVALENT, V = 4

C, Si, Ge, Sn, Pb; $\text{M}(\text{CO})_3$, M = Fe, Ru, Os; $\text{C}_p\text{Mn}(\text{CO})$, M = Mn, Tc, Re; $\text{M}(\text{CO})_4$, M = Cr, Mo, W

Interaction of fragments to form molecules and clusters

The formation of simple molecules and clusters can simply be viewed as involving the interactions of appropriate fragments. This is illustrated by the following selected examples given in Figs 1 to 6.

Monovalent fragments

The interaction of monovalent fragments to form molecules are illustrated by $\text{M}(\text{CO})_4$ (M = Co, Rh, Ir) and $\text{M}(\text{CO})_5$ (M = Mn, Tc, Re) in Fig. 1. below.

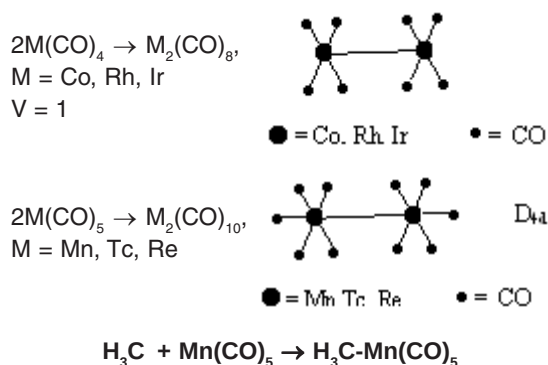


Fig. 1: The interaction of selected monovalent fragments to form molecules

Divalent fragments

Interaction of two divalent fragments are expected to produce a double bonded molecule. This is illustrated in Fig. 2.

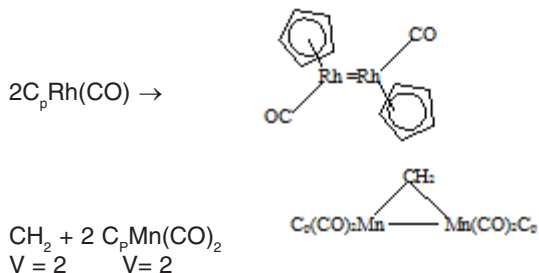
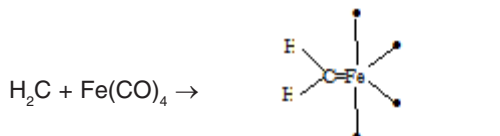
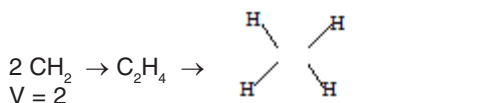


Fig. 2: The interaction of selected examples of divalent fragments

Cluster formation

More than two fragments can interact to form a cluster. For example, 3 $\text{M}(\text{CO})_4$ fragments with Fe, Ru and Os do interact to generate $\text{M}_3(\text{CO})_{12}$ cluster complexes as shown in Fig.3. Cyclopropane may be considered to consist of 3 CH_2 fragments(see Fig. 3).

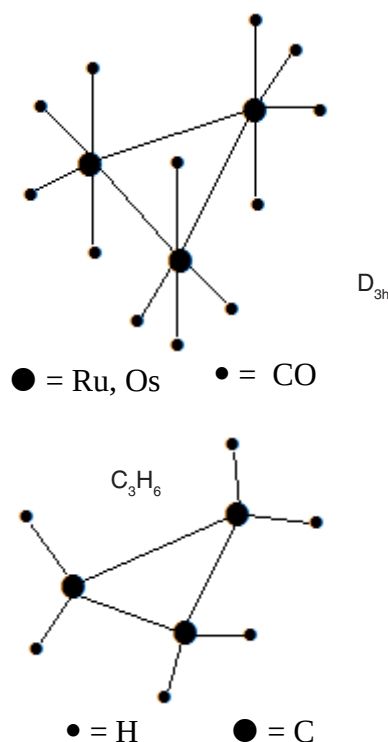
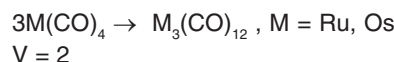
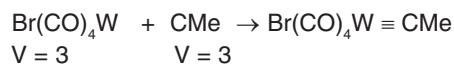


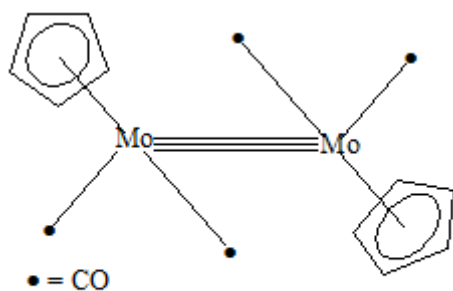
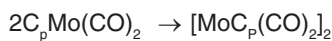
Fig. 3: Selected clusters involving divalent fragments

Trivalent fragments

Trivalent fragments interact in the same way as divalent fragments. For instance, $\text{Br}(\text{CO})_4\text{W}$ a "CMe complex may be considered to arise from the interaction of $\text{Br}(\text{CO})_4\text{W}$ and CMe fragments. While the dimerization of $\text{C}_p\text{Mo}(\text{CO})_2$ fragment produces a triply bonded $[\text{MoC}_p(\text{CO})_2]_2$ complex. More examples of molecules and clusters formed from trivalent clusters are given in Figs. 4a-4c.



DIMERIZATION



CLUSTER FORMATION

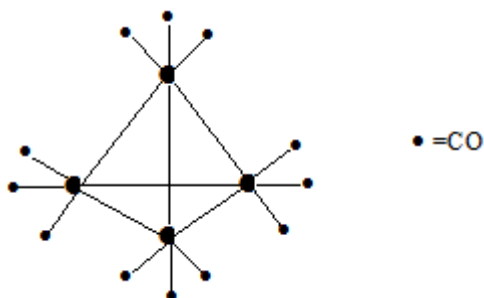


Fig. 4a: Interaction of selected trivalent fragments to form complexes

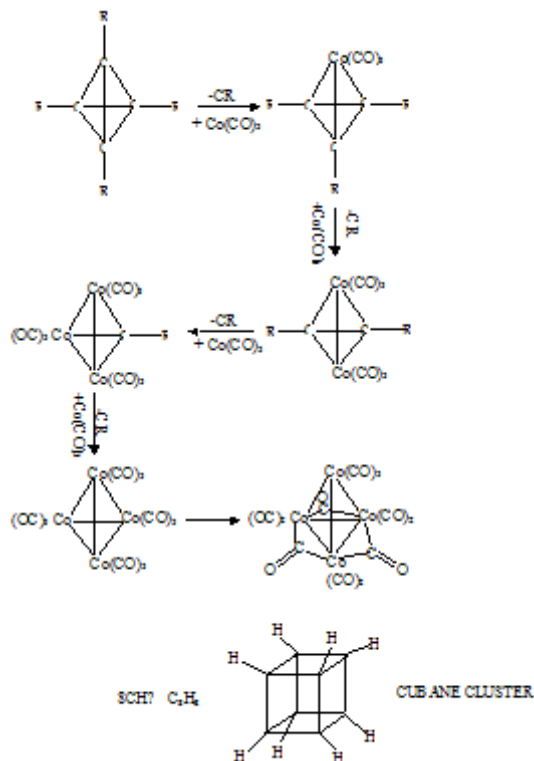


Fig.4b: Cluster formation involving trivalent CR, (OC)₃Co, and CH fragments

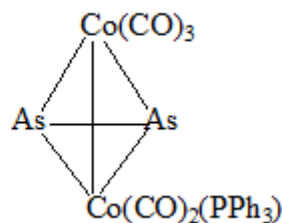
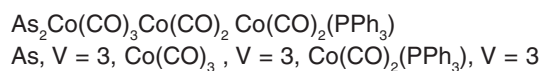
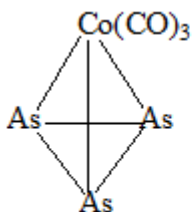
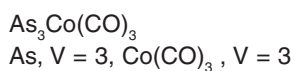
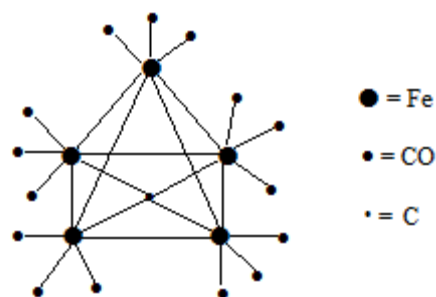
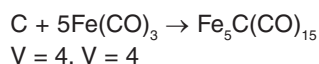


Fig. 4c: Cluster formation involving As, Co(CO)₃, and Co(CO)₂(PPh₃) fragments

Tetravalent fragments

The valence concept is readily applied to clusters involving tetravalent fragments as well. For instance the formation of $\text{Fe}_5\text{C}(\text{CO})_{15}$ complex can be considered to arise from the interaction of C (V=4) with $5\text{Fe}(\text{CO})_3$ (V=4) fragments. Also fragments with different valences can interact to form appropriate clusters. Examples include Sn (V=4) and $\text{Fe}(\text{CO})_4$ (V=2) fragments to form

$\text{Sn}[\text{Fe}(\text{CO})_4]_4$, interaction of $\text{Os}(\text{CO})_3$ (V=4) and 4 $\text{Os}(\text{CO})_4$ (V=2) to produce $\text{Os}_5(\text{CO})_{19}$, formation of $\text{SnMe}_2[\text{Re}(\text{CO})_5]_2$ from Sn, Me, and $\text{Re}(\text{CO})_5$ fragments. Finally, the complex $\text{C}_p(\text{CO})_2\text{FeSnCl}_3$ can be viewed as being formed from the fragments $\text{C}_p(\text{CO})_2\text{Fe}$ (V=1), Sn (V=4) and Cl (V=1). This is summarized in Fig. 5 and more examples are given in Fig. 6.



MIXED VALENCE COMPLEXES

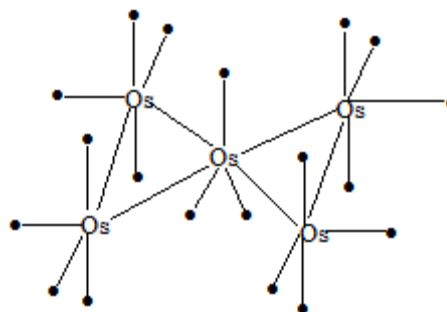
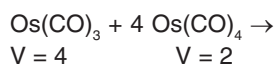
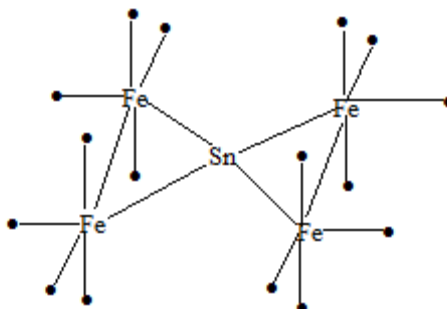
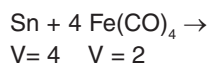


Fig. 5: Interaction of quadrivalent and mixed valence fragments to form clusters

Conclusion

The relatively recently introduced isolobal concept appears to be shrouded in mystery when teaching it at undergraduate level. This mystery

vanishes when it is simply regarded as synonymous to valence. In so doing, many geometries of clusters can readily be explained with pleasure.

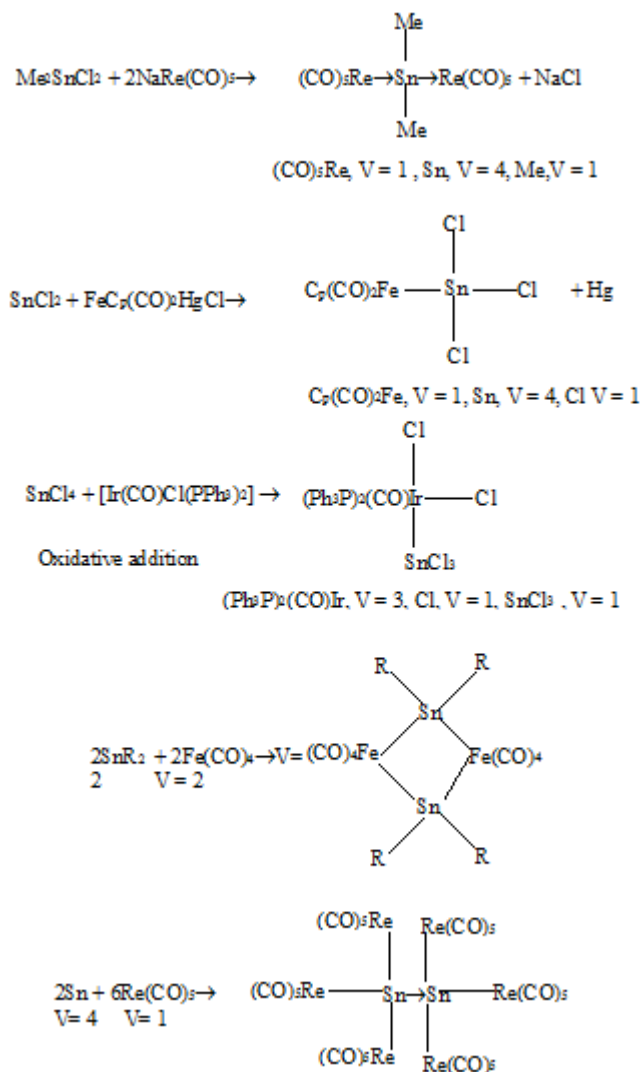


Fig. 6: Interaction of mixed valence fragments to form clusters

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