❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters

Metal carbonyl clusters are the metal clusters (two or more metal centers directly bonded to each other) having carbonyl groups as the ligand species. The metal centers in these cluster geometries are actually present in low oxidation state (+1, 0, −1) that can be stabilized by carbonyl ligands. Metal carbonyl clusters are mainly formed by some end-group metal (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) of the *d*-block elements. The primary domain of carbonyl clusters is composed of neutral carbonyls, carbonyl anions, metal carbonyl hydrides. The carbonyl hydride clusters can be obtained from neutral carbonyls by replacing one of the CO groups with two H-groups; while carbonyl anions are derived by replacing CO with one H-atom and one negative charge, or with two negative charge. Metal carbonyl clusters can be classified into two types; low nuclearity carbonyl clusters (LNCC) and high nuclearity carbonyl clusters (HNCC), depending upon the number of metal centers involved in the skeletal framework. If the number of metal centers is in the range of 2–4, they are generally labeled as low nuclearity; while on the other hand, a metal-center number of 5 and above makes them designable as high nuclearity carbonyl cluster system. Owing to the difference of electron counting scheme from high nuclearity carbonyl clusters, this section will exclusively deal with low nuclearity carbonyl clusters. The rationalization of bonding and structural profile of some important low nuclearity carbonyls clusters on the basis 18-electron scheme is discussed below.

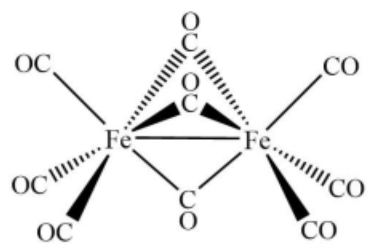
- ***Dinuclear Carbonyl Clusters:***

The structural framework of dinuclear metal carbonyl clusters is comprised of two metal centers connected by 1 metal-metal bond, and therefore, linear in geometry. The CO groups can be terminal, bridging or both. The most common examples of these are $Co_2(CO)_8$, $Fe_2(CO)_9$, Mn_2CO_{10}, Tc_2CO_{10}, and Re_2CO_{10}.

1. $Co_2(CO)_8$: This cluster is known to exist in two isomers; the first one has a D_{3d} symmetry with one metal-metal bond with zero bridging carbonyl, the second one is of C_{2v} symmetry and has two bridging CO ligands along with one metal-metal bond. The 18-electron count for $Co_2(CO)_8$ is 2×9 + 8×2 = 34. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).

Figure 26. Structures and bonding in $Co_2(CO)_8$.

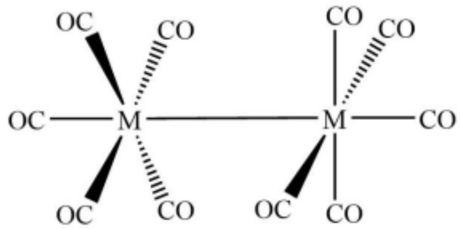
2. $Fe_2(CO)_9$: The structure of $Fe_2(CO)_9$ exist with D_{3h} symmetry, and contains three bridging CO ligands and six terminal CO groups attached. The 18-electron count for $Fe_2(CO)_9$ is 2×8 + 9×2 = 34. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).



$Fe_2(CO)_9$

Figure 27. Structures and bonding in $Fe_2(CO)_9$.

3. $M_2(CO)_{10}$: M_2CO_{10} (M = Mn, Tc, Re) exists with D_{4d} symmetry with one metal-metal bond and four CO ligands attached to each of the metal centre. The 18-electron count for M_2CO_{10} (M = Mn, Tc, Re) is 2×7 + 10×2 = 34. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).



$M_2(CO)_{10}$

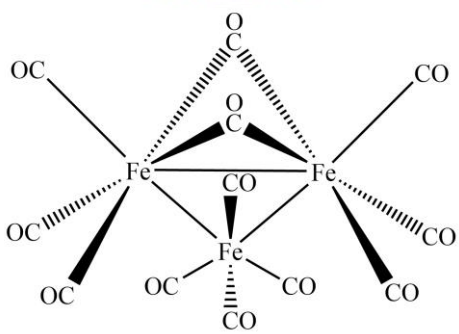
M = Mn, Tc, Re

Figure 28. Structures and bonding in M_2CO_{10} (M = Mn, Tc, Re).

➢ ***Trinuclear Metal Carbonyls***

The structural framework of trinuclear metal carbonyl clusters is comprised of three metal centers connected by three metal-metal bonds, and therefore, usually trigonal in geometry. The CO groups can be terminal, bridging or both. The most common examples of trinuclear carbonyl clusters are Fe_3CO_{12}, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ systems.

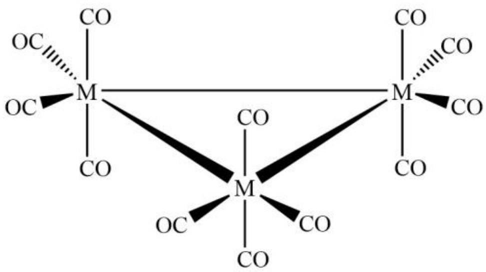
1. Fe_3CO_{12}: $Fe_3(CO)_{12}$ is different, with two bridging CO ligands, resulting in C_{2v} symmetry. The 18-electron count for $Fe_3(CO)_{12}$ is 3×8 + 12×2 = 48. Hence, three metal-metal bonds (6 electrons) are needed to fulfill the requirement of three metal centers (54 electrons).



$Fe_3(CO)_{12}$

Figure 29. Structures and bonding in $Fe_3(CO)_{12}$.

2. $M_3(CO)_{12}$ (M = Os, Ru): For example, the $Ru_3(CO)_{12}$ cluster has D_{3h} symmetry, consisting of an equilateral triangle of Ru atoms, each of which has two axial and two equatorial CO ligands. $Os_3(CO)_{12}$ has the same structure. The 18-electron count for $M_3(CO)_{12}$ (M = Os, Ru) is 3×8 + 12×2 = 48. Hence, three metal-metal bonds (6 electrons) are needed to fulfill the requirement of three metal centers (54 electrons).



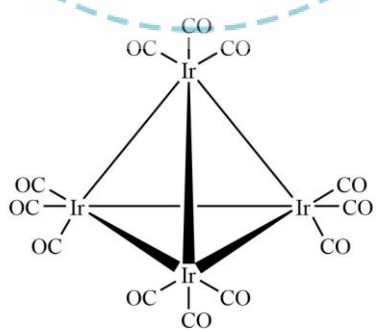
$M_3(CO)_{12}$
M = Os, Ru

Figure 30. Structures and bonding in $M_3(CO)_{12}$ (M = Os, Ru).

➢ ***Tetranuclear Metal Carbonyls***

The structural framework of tetranuclear metal carbonyl clusters is comprised of four metal centers connected by four to six metal-metal bonds, and therefore, usually tetrahedral in geometry. The CO groups can be terminal, bridging or both. The most common examples of tetranuclear carbonyl clusters are $Ir_4(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Re_4CO_{16}^{2-}$, $Ru_3(CO)_{12}$ and $Os_4(CO)_{16}$ systems.

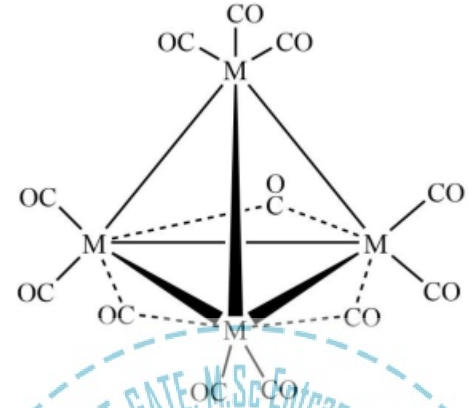
1. $Ir_4(CO)_{12}$: The $Ir_4(CO)_{12}$ has perfect T_d symmetry with no bridging CO ligands groups. The 18-electron count for $Ir_4(CO)_{12}$ is 4×9 + 12×2 = 60. Hence, six metal-metal bonds (12 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).



$Ir_4(CO)_{12}$

Figure 31. Structures and bonding in $Ir_4(CO)_{12}$.

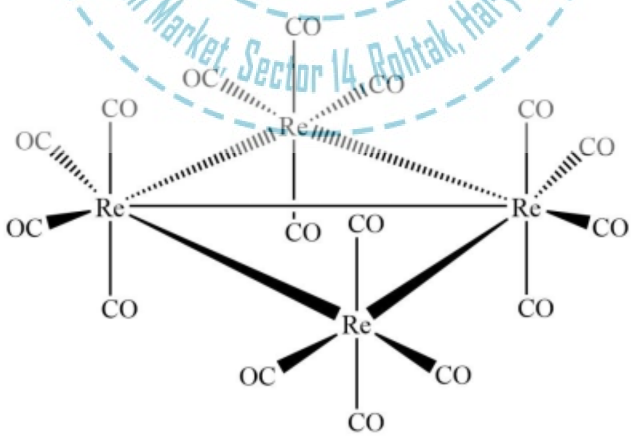
2. M_4CO_{12} (M = Co, Rh): M_4CO_{12} (M = Co, Rh) is consisted of a tetrahedral M_4 core, but the molecular symmetry is C_{3v}. Three carbonyl ligands are bridging ligands and nine are terminal. The 18-electron count for $M_4(CO)_{12}$ (M = Co, Rh) is 4×9 + 12×2 = 60. Hence, six metal-metal bonds (12 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).



$M_4(CO)_{12}$
M = Co, Rh

Figure 32. Structures and bonding in $M_4(CO)_{12}$ (M = Co, Rh).

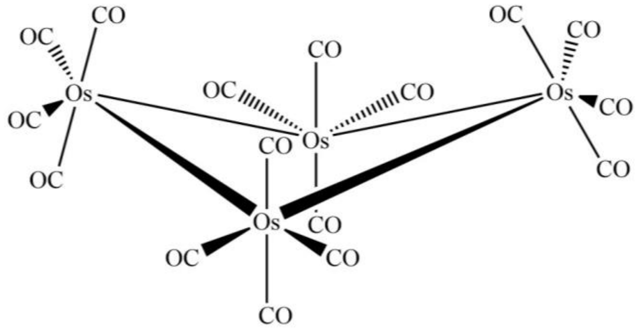
3. $[Re_4(CO)_{16}]^{2-}$: $[Re_4(CO)_{16}]^{2-}$ has D_{2h} symmetry with no bridging carbonyl. The 18-electron count for $[Re_4(CO)_{16}]^{2-}$ is 4×7 + 16×2 + 2 (charge) = 62. Hence, five metal-metal bonds (10 electrons) are needed to fulfil the requirement of four metal centres (72 electrons).



$[Re_4(CO)_{16}]^{2-}$

Figure 33. Structures and bonding in $[Re_4(CO)_{16}]^{2-}$.

4. $Os_4(CO)_{16}$: The tetranuclear $Os_4(CO)_{16}$ is analogs to the cyclobutane with a puckered structure. The X-ray diffraction analysis of $Os_4(CO)_{14}$ unveiled an irregular tetrahedral Os_4 skeleton with four weakly semi-bridging CO groups and four different Os–Os bond lengths. The 18-electron count for $Os_4(CO)_{16}$ is 4×8 + 16×2 = 64. Hence, four metal-metal bonds (8 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).



$Os_4(CO)_{16}$

Figure 34. Structures and bonding in $Os_4(CO)_{16}$.

It is worthy to note that the electron counting scheme in low nuclearity carbonyl clusters is the same as that is used in mononuclear metal carbonyl complexes.

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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