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CHEMISTRY	11. Inorganic Chemistry–III (Metal π-Complexes and Metal Clusters)
	Module 33: Preparation, structure and bonding of compounds having M-M multiple bonds

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**CHEMISTRY****11. Inorganic Chemistry–III (Metal π -Complexes and Metal Clusters)****Module 33: Preparation, structure and bonding of compounds having M-M multiple bonds**

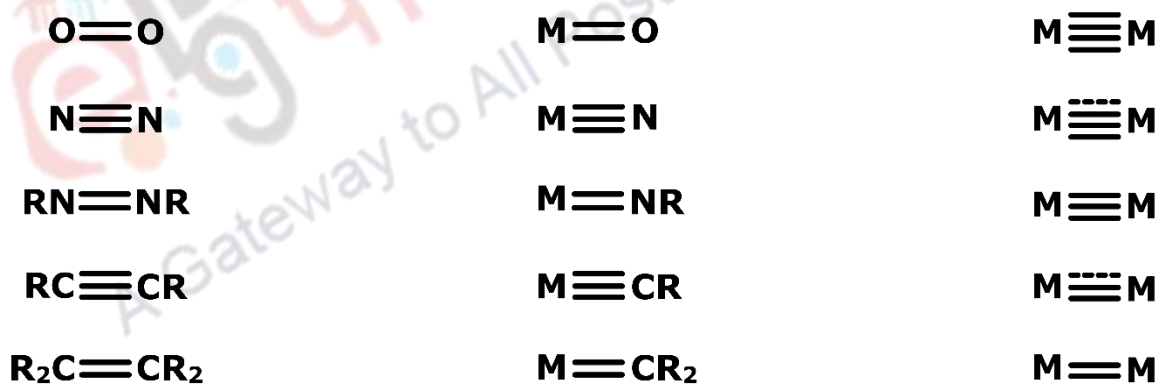
1. Learning Outcomes

After studying this module, you shall be able to know about

- Metal cluster compounds.
- Preparative methods for metal cluster compounds containing single and multiple metal-metal bonds.
- Type of bonding and molecular orbital picture of the M-M bonds in such cluster.

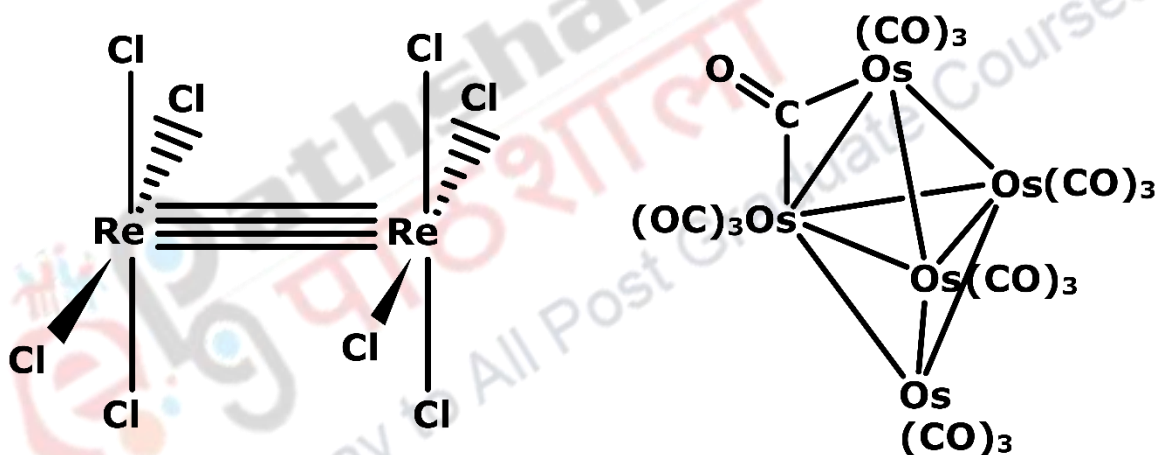
2. Introduction

Metal-metal multiple bonding is an important feature of the chemistry of many transition elements and is very important to the field of metal cluster chemistry. They constitute an important class of multiple bonds unlike multiple bonds between the main group elements and multiple metal-ligand bonds. Multiple metal-metal bonds of the order 2, 2.5, 3, 3.5 and 4 are well-known.



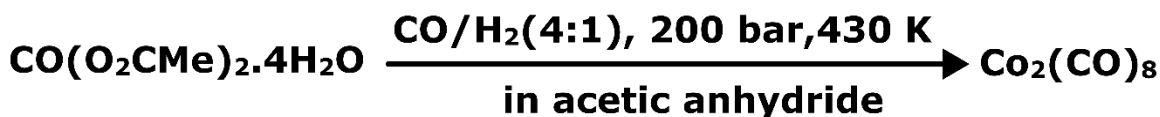
The Re=Re double bond was the first ever observation of a metal-metal multiple bond in $[\text{Re}_3\text{Cl}_{12}]^{3-}$. A typical property of metals is that rather than forming straight chains or rings, metals tend to agglomerate so as to form maximum number of bonds with minimum number of adjacent metal atoms, giving rise to either metal-metal multiple bonds or metal cluster compounds. Metals do so to attain 18-electronic configuration and hence to attain stability. For example, the triangular cluster $\text{Os}_3(\text{CO})_{12}$ can be viewed as a

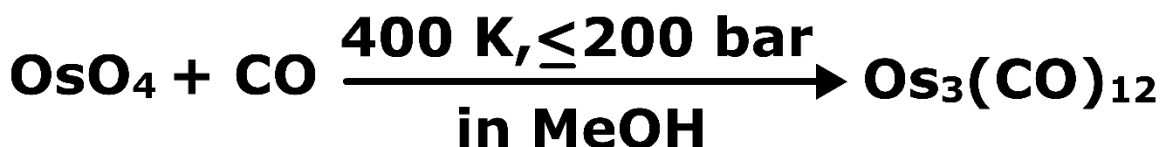
stable trimer of the unsaturated 16 electron fragment $\text{Os}(\text{CO})_4$. The 15 electron $\text{Rh}(\text{CO})_3$ fragment forms the tetramer $\text{Rh}_4(\text{CO})_{12}$ with a tetrahedron of metal atoms. Such kind of compounds may be classified as organometallic clusters. Unsaturated (electron deficient) metal fragments may form multiple bonds with other fragments such as $(\text{RO})_3\text{Mo}\equiv\text{Mo}(\text{RO})_3$, $\text{Cl}_4\text{Re}\equiv\text{ReCl}_4$ and $\text{Mo}_6(\mu^3\text{-Cl})_8^{4-}$ are referred to as inorganic clusters. Organometallic clusters are often low-oxidation species and require ligands such as carbonyl whereas inorganic clusters are often higher valent and have ligands such as chloride. Thus, the term clusters can be applied to a broad class of compounds which include metal-metal single or multiple bonds such as:



3. Preparation of organometallic carbonyl clusters

Metal halides, oxides and other compounds react with carbon monoxide (CO) gas in the presence of a reducing agent (excess of CO acts as reducing agent) at high pressure. The process is called reductive carbonylation. Yields are often poor.

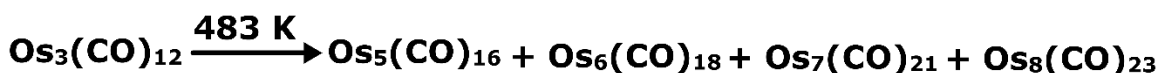
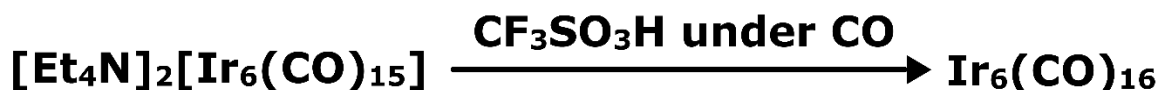
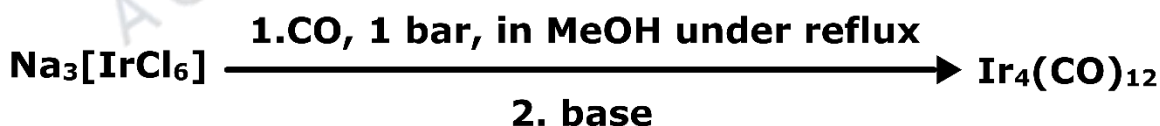
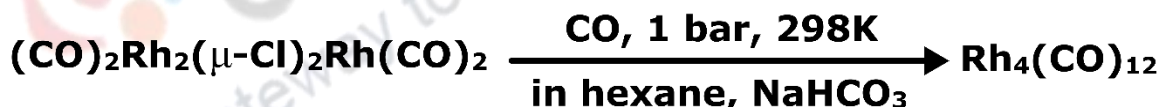




Diiron nonacarbonyl ($\text{Fe}_2(\text{CO})_9$) is usually prepared by photolysis of $\text{Fe}(\text{CO})_5$.



Metal carbonyl clusters consisting of four or more metal atoms are prepared by a variety of methods such as carbonylation and pyrolysis.

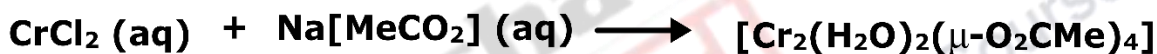


In this reaction, the $\text{Os}_6(\text{CO})_{18}$ is the major product and can be separated by chromatography.

4. Preparation of inorganic metal clusters

Chromium(II) carboxylates exist as dimer with general formula $[\text{Cr}_2(\mu\text{-O}_2\text{CMe})_4]$

and represents a class of compounds containing metal-metal multiple bond. It is prepared by the addition of an aqueous solution of CrCl_2 to an aqueous saturated solution of $\text{Na}[\text{MeCO}_2]$.

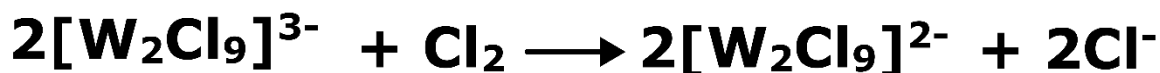


These type of chromium dimers possess Cr-Cr quadruple bond.

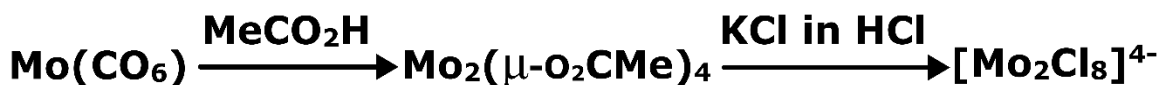
Tungsten dimeric clusters can be synthesized by electrolytic reduction of tungstenoxide in concentrated hydrochloric acid.



The $[\text{W}_2\text{Cl}_9]^{3-}$ ion is diamagnetic and possesses a $\text{W}\equiv\text{W}$ triple bond with bond distance of 242 pm. Oxidation of $[\text{W}_2\text{Cl}_9]^{3-}$ ion produces $[\text{W}_2\text{Cl}_9]^{2-}$ ion which has a lower bond order of 2.4 and increased bond length of 254 pm.



Refluxing an acetic acid solution of molybdenum hexacarbonyl would result in the dimolybdenum tetraacetate intermediate which is a useful synthon for a variety of other Mo cluster variants. Replacement of acetate with chloride ions using a solution of KCl in HCl would give rise to the dimolybdenum octachloride cluster.

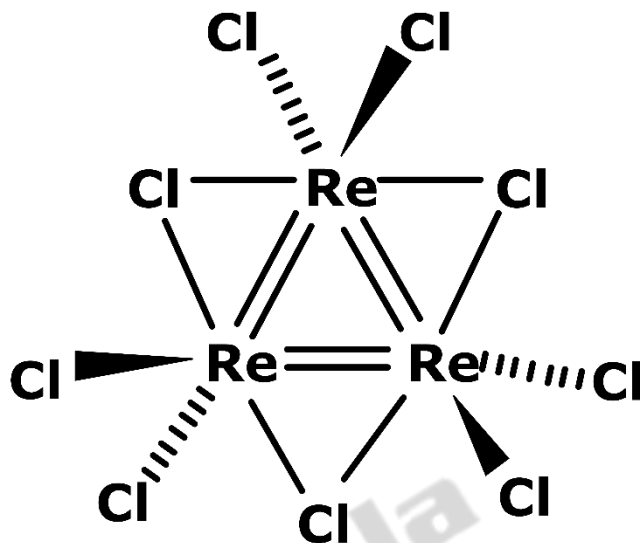


The $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion possess a metal-metal quadruple bond with a bond distance of 214 pm and a bond order of 4.0. The oxidation state of Mo is +2.

The trirhenium nonachloride cluster complex can be easily synthesized by heating ReCl_5 .



Interestingly, the trirhenium cluster has a triangular structure with three Re ions forming a triangle where each Re ion is connected to the other by double bond with a bond distance of 245 pm.

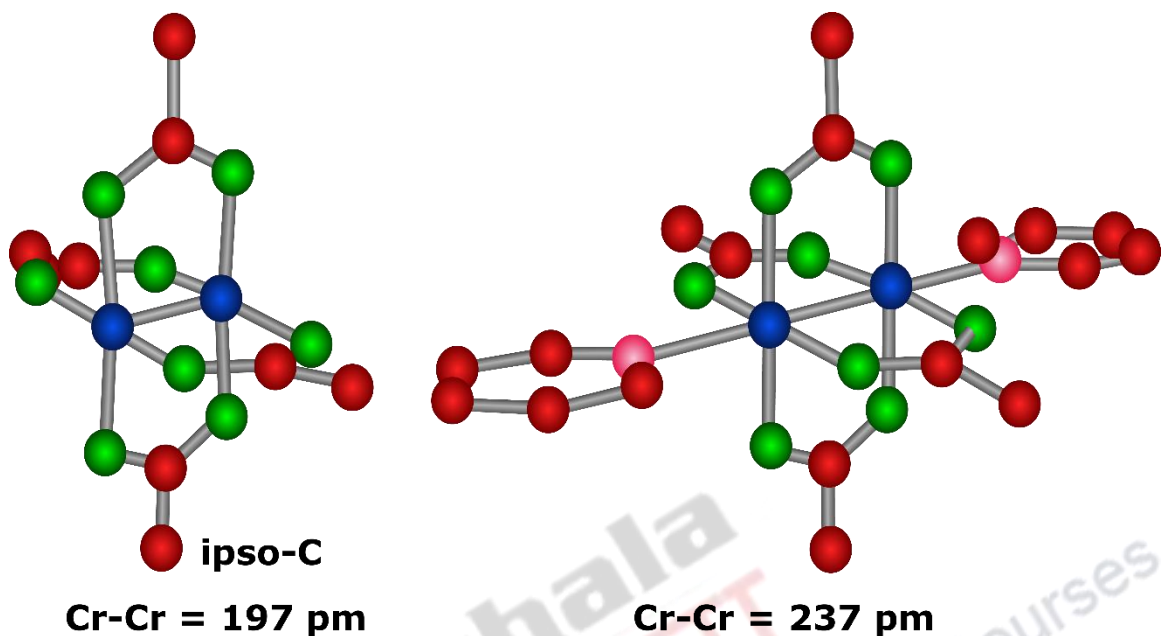


The interesting dirhenium octachloride cluster $[\text{Re}_2\text{Cl}_8]^{2-}$ can be synthesized by the reduction of $[\text{ReO}_4]^-$ anion using hydrogen gas (H_2) or $[\text{HPO}_2]^{2-}$ in the presence HCl. The product possesses a Re-Re quadruple bond with a bond distance of 224 pm.

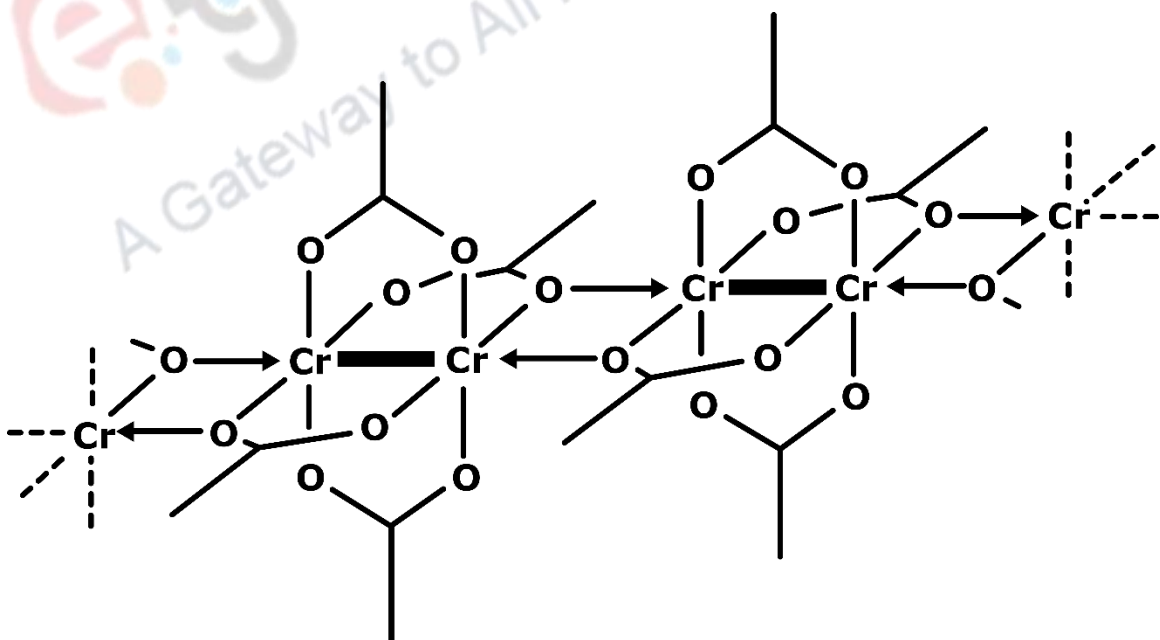


5. Structure and bonding of metal-metal multiple bond containing clusters

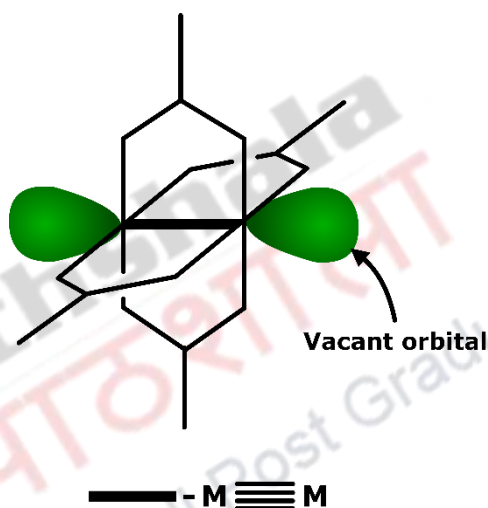
The chromium based dinuclear cluster containing metal-metal multiple bond has the general formula as $[\text{Cr}_2(\mu\text{-O}_2\text{CMe})_4]$. The chromium ions share a quadruple bond. Sometimes the ipso carbon is coordinated with ligands such as H_2O and pyridine.



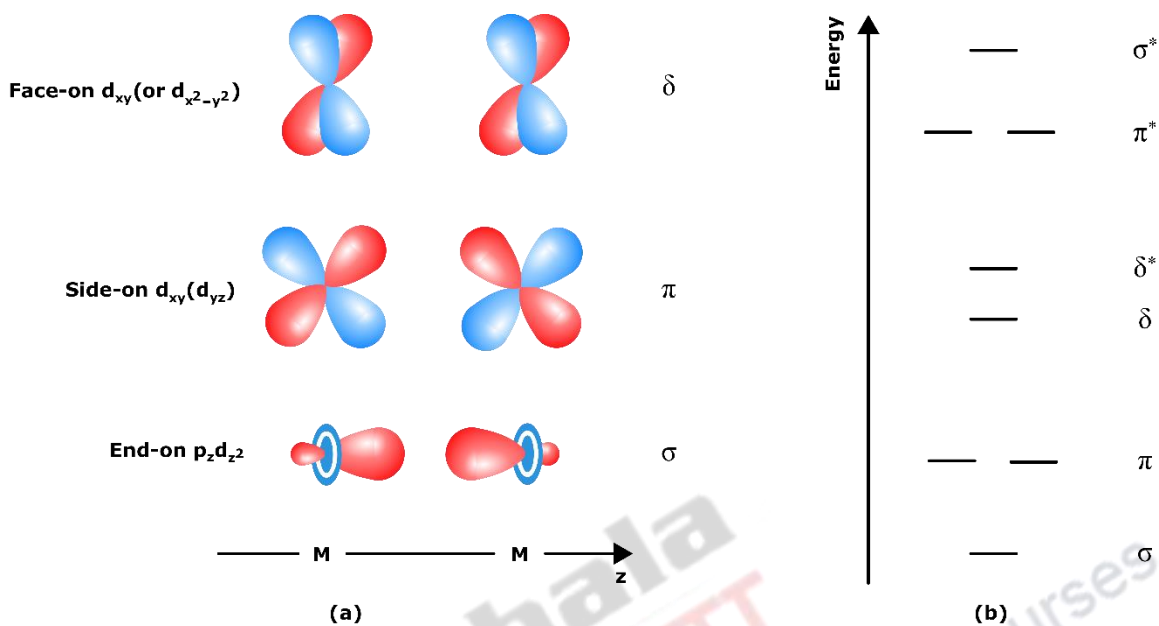
The Cr-Cr bond length is normally 197 pm whereas this bond distance increases to 237 pm with ipso substitution by H₂O and pyridyl ligand due to elongation of the Cr-Cr bond. In the absence of ipso substitution i.e. in the absence of an axial ligand, the chromium cluster associates to form a 2-dimensional structure.



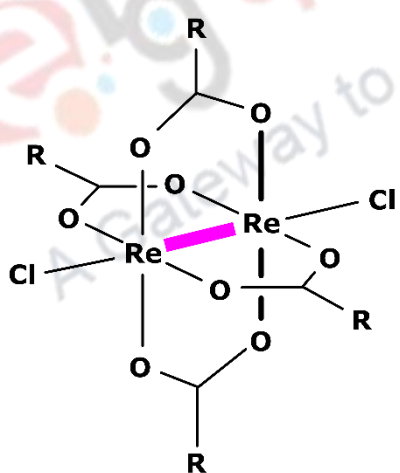
The Cr(II) ion is diamagnetic in these structures where the d -electrons being involved in the quadruple bonding. The Cr atoms can be defined to lie on the z -axis and out of its nine atomic orbitals each Cr atom uses four orbitals (s , p_x , p_y and $d_{x^2-y^2}$) to form Cr-O bonds. The p_x and d_z^2 orbital mix together to give two hybrid orbitals directed along the z -axis ($p_x d_z^2$ bonding and $p_x d_z^2$ non-bonding). This bonding orbital overlaps to form a σ -bond whereas the $d_{xz} - d_{xz}$ and the $d_{yz} - d_{yz}$ overlaps to degenerate a pair of π -orbitals and finally the overlapping of the d_{xy} orbitals leads to a δ -bond.



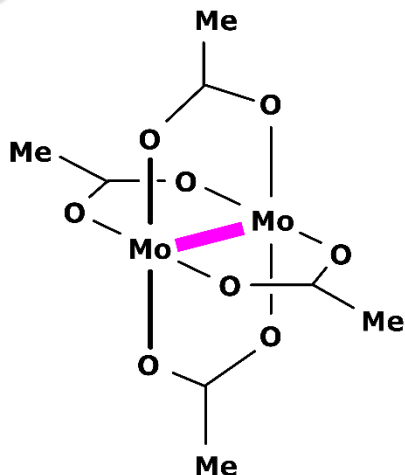
The degree of overlapping is in the order $\sigma > \pi > \delta$ as shown in the MO diagram below.



The quadruple bond formation in the dimolybdenum and dirhenium clusters (given below) can also be explained on the basis of similar MO explanations.



— = quadruple bond



— = quadruple bond

6. Summary

- Cluster compounds contain metal-metal single or multiple bonds and form rings or linear chains. Apart from containing σ and π bonds, cluster complexes also display δ bonds.
- Cluster complexes can be synthesized by various methods such as pyrolysis of carbonyl clusters, nucleophilic attack on clusters, reductive elimination and attack of metal precursors on multiple bond containing clusters.
- Cluster compounds can be divided into two types namely the organometallic clusters containing the metal-metal single bonds and the inorganic metal clusters containing the metal-metal multiple bonds.
- Inorganic clusters may contain quadruple bonds due to the formation of an extra bond called δ bond which is formed by the overlapping of the $d_{x^2-y^2}$ or d_{xy} orbitals.
- The degree of overlapping and hence the bond strength is in the order $\sigma > \pi > \delta$.