



Preparation & Reactions of Metal Clusters

Mr.Kale D.V.

Dept. of Chemistry,
Shrimant Babasaheb Deshmukh
Mahavidyalay, Atpadi, Sangli (MS)

Dr. Rathod S. D.

Dept. of Chemistry
Milind College of Science,
Aurangabad (MS)

Abstract:

Metal groups are atomically precise sets of metal atoms. When preparing metal clusters in the gas phase, only certain sizes (or "magic numbers") are observed. This can be explained with electron counting rules (superatoms). In short, the valence electrons of the metal are counted (in the case of gold, 6 s electrons). If the number of valence electrons N_e corresponds to a magic number (2, 8, 18, 20, 34, 40, 58, 92, ... in globular groups), then electron shell closing is observed. In particular, the properties of metal clusters are non-scalable, i.e. the geometric and electronic structures dominate the properties. It is summarized under the claim "every atom counts". Valence electrons are denoted on the volume of the cluster and form orbitals whose shape, angular momentum and degeneracy are similar to those of atomic orbitals. Thus, for example, an electron count of 8 may be associated with a noble gas configuration.

Introduction:

A metal–metal bond is a bond between two metal centers, specifically between two transition metal atoms, that ranges from a single to a quadruple bond. The existence of metal–metal bonding in transition metals is mainly due to the presence of $(n+1)s$, $(n+1)p$ and nd orbitals as valence shell electronic configurations. Transition metals can form three general types of bonds namely covalent bonds, basic bonds and weak metal–metal symmetry interactions where covalent bonds are strongest and symmetry interactions are weakest. Compounds containing a large number of metal–metal bonds forming triangular and larger structures are called cluster compounds, although these also include linear M–M bonds. Metal groups can also be defined as any units that have a metal-metal bond. The journey began with the identification of Hg–Hg in the Hg_{22} ion (Hg_2Cl_2), the first d-block metal–metal bonded species. Most of these cluster compounds are homo-metallic; There are however some exceptions with hetero-metallic cluster complexes. Molecular complexes containing metal–metal bonds that form triangular or larger structures are called metal groups, although linear



metal–metal bonds also fall under the category of metal groups. Therefore, any metal complex containing a bond between two metal ions is called a metal group.

Initially, metal complex clusters were obtained either as side products in other reactions or by unplanned routes. Eventually, efficient synthetic methodologies were developed to prepare various cluster complexes containing different types of bonds. Later, specific methods were also developed for the synthesis of heterogeneous metal–metal bonds and the formation of cluster complexes. Now, well-defined and highly efficient methods are known for synthesis of desirable metal-metal bond for specific application.

Methods of Preparing Metal Clusters:

1. By pyrolysis of metal carbonyl complexes:

Metal carbonyls are coordination complexes of transition metals with a carbon monoxide ligand. Metal carbonyls are useful as catalysts or catalytic precursors in organic synthesis and in homogeneous catalysis, such as hydroformylation and Repe chemistry. This method is mainly applicable to metal carbonyls where the lower carbonyl complexes are heated to precipitate some carbon monoxide molecules. The unsaturated fragments thus formed can rearrange and react to form higher metal carbonyl complexes containing metal–metal bonds.

In some cases, these reactions can also be carried out by photolysis of the lower metal carbonyls.

2. By nucleophilic attack of metal carbonyl ion:

A nucleophilic attack often occurs when an electron-rich species (nucleophile) "attacks" an electron-deficient species (electrophile, usually a carbocation), forming a new bond between the nucleophile and the carbocation. A metal carbonyl ion such as the pentacarbonylmanganese (I) ion can show a nucleophilic substitution reaction with bromopentacarbonyliranium (I) containing a replaceable bromide. The reaction results in the formation of a Mn-Re covalent bond.

3. Binuclear Reductive Elimination:

Reductive elimination occurs at high oxidation state metal centers, where the oxidation state of the metal ion undergoing the reaction is reduced by two units to the product. Reductive



elimination is the reverse of oxidative addition and reduces both the oxidation state and the coordination number by two.

The addition of a synergistically saturated cluster to an unsaturated cluster via a bridging group. In this method, hydrides are used to co-ordinately link saturated species to unsaturated clusters.

4. Addition of m-Si multiple bond in a metal compound.

Oxidative addition reactions (and their reverse, reductive elimination) are among the most important elementary transformations in organometallic chemistry and also play an important role in many stoichiometric and catalytic processes. Oxidative additions usually involve a neutral molecule (X–Y) in a single metal center (M), resulting in the formation of new M–X and M–Y bonds and an increase of two units in the metal's oxidation state, electron count, and coordination number. Although oxidative addition and reductive elimination are in principle reversible reactions, the state of equilibrium, which is governed by the overall thermodynamics of the species involved (i.e., the relative strength of bonds broken and formed), is often completely shifted in one Goes side. This method was developed based on the isolabel analogy. The M=C double bond that is the metal carbene is isolobular with the C=C double bond, so metals that are capable of forming alkene complexes can also be expected to form complexes with metal carbenes.

5. By joining metal to metal-metal multiple bonds.

Metal–metal multiple bonding is an important feature of the chemistry of many transition elements and is of great importance to the field of metal cluster chemistry. They form an important class of multiple bonds as opposed to multiple bonds between main group elements and multiple metal–ligand bonds. This method was developed by Green and coworkers and was based on the isolobal analogy between an M = M multiple bond and an alkene. Like the addition reactions shown by alkanes, metal–metal multiple bonding (M = M) can also exhibit addition reactions with other metal precursors.

6. By using a bridging ligand.

Ligands that have two lone pairs that can bond to two different metals are called bridging ligands because they can bridge two metals. Ligands (A) (cyanide ions) and (B) bridge with bond angles of 180°, while ligands (C) (chloride ions) can bridge with bond angles of ~109°.



Some chelating ligands such as common diphosphine ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) have the ability to either act as a chelating ligand to bind a metal ion or to act as a bidentate ligand to coordinate with two metal ions. It occurs. This is due to the geometrical factors of the ligand allowing different chelate ring sizes in the two cases. A large number of other chelating ligands exhibit the ability to behave as both a chelating ligand and a bidentate ligand.

Reactions of metal cluster compounds

Metal clusters exhibit a large variety of chemical reactions and therefore display rich and unusual organometallic chemistry. However, it is difficult to predict the outcome of reactions and to rationalize the reaction pathway. Reactions on metal groups with multiple metal–metal bonds often occur over multiple bonds. Metal clusters with M–M single bonds exhibit a variety of reactions which are discussed below:

• Reactions with Electrophoresis:

Electrophoresis is a laboratory technique used to separate DNA, RNA or protein molecules based on their size and electrical charge. Electric current is used to move molecules through a gel or other matrix. The proton (H) can be considered as the simplest electrophile because it is a zero-electron species and the smallest in size. Therefore, it can easily undergo addition reactions with a variety of compounds. The binding of a proton to a metal cluster is expected without much change in the cluster geometry. It can be easily deduced that ionic groups are preferentially easier to protonate and these often result in hydride complexes where a hydride bridges two or more metal ions. For example, a re-carbonyl trinuclear cluster can undergo sequential protonation to form a tri-hydride cluster, where the basic structure of the trinuclear cluster remains largely unchanged and the rhenium ion is joined by three hydride bridges connecting the two rhenium ions.

Bulkier electrophiles, on the other hand, are hesitant to act as bridging species and often exhibit reactions on carbonyl ligands in reaction with metal carbonyl clusters. For example, the reaction of $\text{Ru}_3(\text{CO})_{12}$ with aluminum compounds (AlR_3) resulted in the conversion of $\text{Ru}_3(\text{CO})_{12}$ from a normal CO-dissociated structure to a bridged $\text{Ru}_3(\mu\text{-COAlR}_3)\text{CO}_{10}$.

• Reactions with Nucleophiles:

Nucleophile is a term used to refer to substances that donate electron pairs to electrophiles to form chemical bonds with them. Any ion or molecule that has an electron pair that is free or a



π bond consisting of two electrons has the ability to behave like a nucleophile. The addition of a nucleophile adds two electrons to the metal cluster. Adding two electrons to the metal cluster should either rearrange or loosen the two electron ligand. On addition of a nucleophile, the unsaturated cluster $(\mu_2\text{-H})_2\text{Os}_3(\text{CO})_{10}$ does not lose a ligand and one of the M–H–M bridges opens and generates a vacant site. There is always the possibility of cluster fragmentation in different substitutions. For example, $\text{Ru}_3(\text{CO})_{12}$ gives a variety of products such as $\text{Ru}_3(\text{CO})_9\text{L}_3$, $\text{Ru}(\text{CO})_3\text{L}_2$ and $\text{Ru}(\text{CO})_4\text{L}$ as the substitution product on reaction with Pph_3 .

Nucleophiles can also attack coordinate ligands. On reaction of amines with $\text{Os}_3(\text{CO})_{12}$, a metalla-amide is formed. This metal can label the complex by bridging the coordinated COs.

• **Oxidative Addition:**

Oxidative addition is the reaction that adds two electrons to a cluster upon reaction. In a carbonyl cluster, the loss of a carbonyl is required to keep the cluster structure intact. Oxidative addition reactions occur with different ligands by different mechanisms. For example, adding Cl_2 to the $\text{Os}_3(\text{CO})_{12}$ cluster does not require prior dissociation of any carbonyls. Cl_2 oxidizes the cluster by taking two electrons from the metal–metal bonds which causes the cyclic metal–metal ring to break and leads to a linear cluster with only two M–M bonds.

• **Reactions on Metal-Metal Multiple Bonds:**

Like carbon–carbon multiple bonds, metal–metal multiple bonds are central to the reaction. However, metal–metal multiple bonds exhibit a variety of chemical and unpredictable products compared to carbon–carbon multiple bonds. For example, HI can add to Mo–Mo multiple bonds where both H and I are bridging metal atoms. Such a product is most likely formed with a carbon-carbon multiple bond.

Large and heterogeneous metal clusters can also be formed by similar reactions on metal-metal multiple bonds with suitable metal precursor complexes. For example, $\text{Pt}(\text{PPH}_3)_4$ can combine with the loss of two triphenylphosphine units in the 4 Mo–Mo triple bond, resulting in three metal clusters.



Cluster compounds can also show catalytic activity with a variety of molecules. For example, one of the major purposes of cluster carbonyl chemistry is to activate carbon monoxide and facilitate the addition of various alkane or alkene.

Conclusion:

Cluster compounds contain metal–metal single or multiple bonds and form rings or linear chains. In addition to containing and bonding, clusters also exhibit complex bonds. Those compounds are almost all formed by metal atoms, with transition metals being known to contain a large number of metal groups. These metal-metal bonds with complexes can be homo-nuclear, i.e. one type of metal atom, and hetero-nuclear containing two or more types of metal atoms. 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 clusters containing multiple bonds. Cluster compounds exhibit a variety of reactions. The products of these reactions are sometimes unpredictable. The types of reactions that cluster complexes undergo are reactions with electrophiles and nucleophiles, oxidative addition reactions and reactions on the metal-metal multiple bonds.

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