

# **Synthesis of Transition metal carbonyl clusters with phosphine ligands**

*A Dissertation*

*Submitted in partial fulfillment*

**FOR THE DEGREE OF  
MASTER OF SCIENCE IN CHEMISTRY**

*Under Academic Autonomy*

**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

*By*

**Deepak Ranjan Mandal**

Under the Guidance of

*Dr. Saurav Chatterjee*



**DEPARTMENT OF CHEMISTRY**

**NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA**

**ORISSA-769008**



## CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis of Transition metal carbonyl clusters with phosphine ligands**” being submitted by Deepak Ranjan Mandal to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela.

Date:

*Dr. Saurav Chatterjee*

**(Supervisor)**

# ACKNOWLEDGEMENT

I owe this unique opportunity to place on record my deep sense of gratitude & indebtedness to Dr Saurav Chatterjee, Department of Chemistry National Institute of Technology, Rourkela for his scholastic guidance, for introducing the present project topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I most gratefully acknowledge his constant encouragement and help in different ways to complete this project successfully.

My sincere gratitude is to Mr. Sumanta Kumar Patel for his overall guidance, immense help, valuable suggestions, constructive criticism & painstaking efforts in doing the experimental work.

I express my profound gratitude to Vijaylakshmi, Sagarika, Subhashree, Saswati and Purabi for their ceaseless encouragement, immense help, hearty encouragement during my project work.

Lastly I express my abysmal adoration & heartfelt devotion to my beloved parents for their countless blessings, unmatched love, affection & incessant inspiration that has given me strength to fight all odds & shaped my life, career till today.

In the end I must record my special appreciation to GOD who has always been a source of my strength, inspiration & my achievements.

Rourkela

Date:

(Deepak Ranjan Mandal)

# Chapter 1

## **Introduction**

## 1.1. Transition metal carbonyl cluster

Transition metal cluster contains two or more metal atoms held together by direct and substantial metal-metal bonding. These cluster compounds are of immense interest because of their structural diversity and potential applications in the field of catalysis. Transition metal clusters are also important for their role in bridging the gap between homogeneous and heterogeneous catalysis, showing high activity and selectivity of the homogeneous catalysts.<sup>1</sup> Di- and poly-nuclear metal clusters have also proved to be useful precursors for the preparation of novel catalysis. Some cluster complexes has been reported for their presence in various enzymes such as nitrogenase and their activity in biocatalysis.<sup>2</sup> Interest has also been currently known in the area of material science and in advanced electronic materials which exhibit good non-linear optical activity.<sup>3</sup>

Some transition metal clusters contains  $\pi$ -donor ligand, and hence, these clusters are termed  $\pi$ -donor cluster or high oxidation state clusters as the metal are in the high formal oxidation state, whereas some other transition metal cluster with Group 7-10 metals with  $\pi$ -accepter ligands, like the carbonyl and phosphine ligands are either termed as  $\pi$ -accepter clusters or low oxidation state clusters. The  $\pi$ -accepter ligand helps to produce the most favorable condition for metal-metal bond formation of the Group 8-10 elements by including the greatest overlap between the atomic orbital of the metals. In addition, overlap between atomic orbitals increases as the principle quantum number increases. Therefore as the transition metal sub-group is descended the metal-metal bond increases in strength.<sup>4</sup> The metal ligand and metal-metal bond with the  $\pi$ -accepter ligand must also be kinetically inert towards bond dissociation otherwise fragmentation or colloid formation can take preference over clustering. The balance between the metal ligand and metal-metal bond strengths has allowed clusters with nuclearities ranging from three to around fifty to be isolated in the laboratory. These constitute clusters in between mononuclear complex and colloids. Figure 1.1 shows the relative particle size from a single metal complex to bulk metallic state.<sup>5</sup>

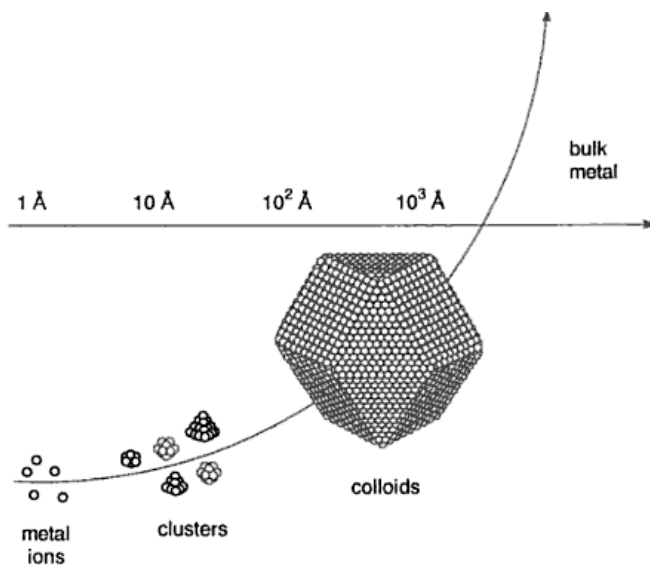


Figure 1.1

## 1.2. Transition metal phosphine cluster

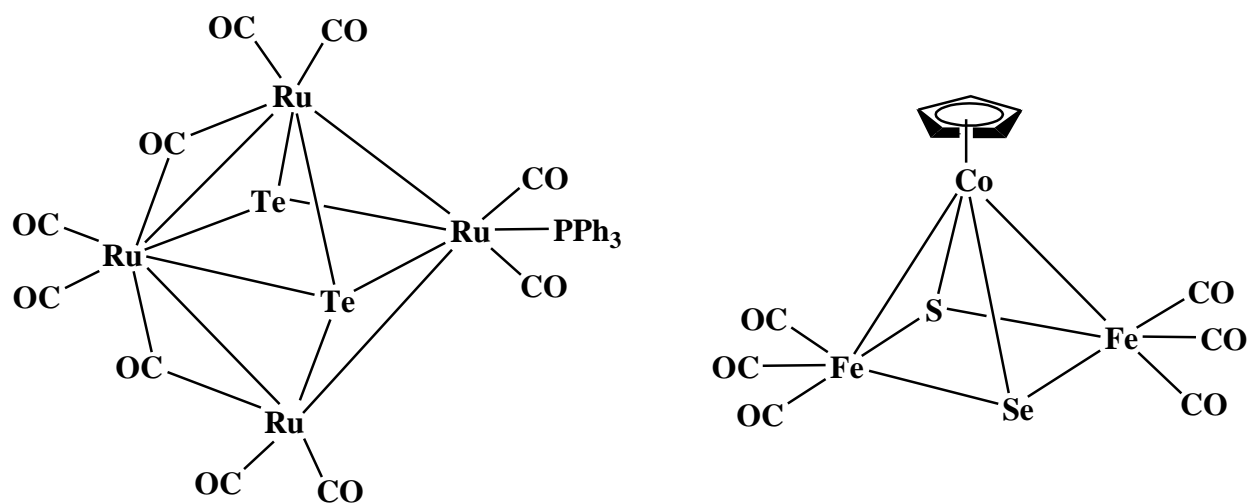
Phosphine ligands binds well to most transition metals, especially those in the middle and late transition metals of groups 7-10.<sup>6</sup> In terms of steric bulk,  $\text{PPh}_3$  has a cone angle of  $145^\circ$ , which is intermediate between those of  $\text{P}(\text{C}_6\text{H}_{11})_3$  ( $170^\circ$ ) and  $\text{P}(\text{CH}_3)_3$  ( $115^\circ$ ). In an early application in homogeneous catalysis,  $\text{NiBr}_2(\text{PPh}_3)_2$  was used by Walter Reppe for the synthesis of acrylate esters from alkynes, carbon monoxide, and alcohols.<sup>7</sup> Wilkinson's further popularized the use of  $\text{PPh}_3$ , including the then revolutionary hydroformylation catalyst  $[\text{RhH}(\text{PPh}_3)_2(\text{CO})_2]$ .<sup>8</sup>

An important technique for the characterization of metal-phosphine compounds is  $^{31}\text{P}$  NMR spectroscopy. Substantial shifts occur upon complexation and  $^{31}\text{P}$ - $^{31}\text{P}$  spin-spin coupling can provide insight into the structure of complexes containing multiple phosphine ligands.

## 1.3. Mixed Metal Transition Clusters

Mixed metal clusters are of interest because of their application as precursors for the preparation of bimetallic and multimetallic heterogeneous catalysts. This has been possible by

allowing clusters to adsorb on to catalyst supports such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , followed by pyrolysis to remove the ligands. This technique could yield multimetallic catalysts having precisely defined composition and high dispersion, provided that degree of aggregation which occurs during the pyrolysis step is minimal.<sup>9</sup> Secondly mixed-metal clusters may find important applications in homogeneous catalysis. Because of their different activities of the different metal present in mixed-metal clusters, multimetal homogeneous catalysts shows reactivity patterns having significantly different from those of homometallic clusters. Low symmetry of mixed metal clusters makes them useful for probing various aspects of the reactivity and molecular dynamics of clusters. Some examples of mixed metal clusters are given in Figure 1.2.<sup>10,11</sup>



*Figure 1.2 Examples of mixed metal clusters*

#### 1.4. Different Types of Transition Metal Clusters

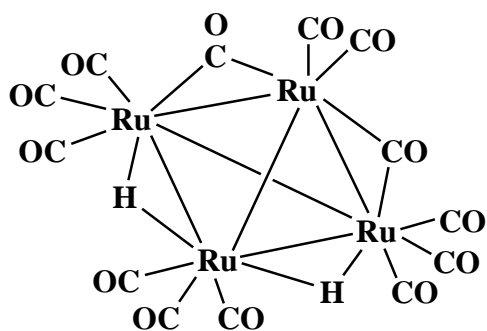
Transition–metal clusters may be divided into different groups:

1. Naked Clusters: These types of clusters don't contain ligands or groups and they are accessible on inert matrices, at low temperatures and studied by physical methods. E.g.  $\text{Ag}_6$ .
2. Metal halides and oxides: Various types of metal in a low oxidation state are known with ligands like chloride, oxide etc. e.g.  $[\text{Mo}_6\text{Cl}_8]^{4+}$ . These are primarily very important in catalysis.

3. Polynuclear metal carbonyls, nitrosyls, phosphines and mixed-ligand complexes containing cyclopentadienyl groups. e.g.  $[\text{CpFe}(\text{CO})_4]_2$ . These are interesting as precursor for cluster growth reactions and the metals exist in low oxidation states.

4. Metal cluster with single atom bridging ligands : An example of single atom bridged metal cluster is  $[\text{Os}_3(\mu_3\text{-S})(\text{CO})_{10}]$  which show catalysis for the transalkylation of amines.

5. Homo-metallic clusters: Homo-metal clusters are the ones which contain only one type of metal in the cluster framework. Some example are  $[(\text{AuPPh}_3)_8]^{2+}$ ,  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Os}_5(\text{CO})_{16}$ ,  $\text{Os}_3\text{H}_2(\text{CO})_{10}$ ,  $\text{Os}(\text{CO})_{15}$ ,  $\text{Co}_4(\text{CO})_{12}$ ,  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and  $\text{Ru}_4(\mu\text{-H})_2(\text{CO})_{13}$  core structures of some homo-metal clusters are shown in Figure-1.3.<sup>12,13,14</sup>



*Figure-1.3*  $\text{Ru}_4(\mu\text{-H})_2(\text{CO})_{13}$

6. Mixed metal clusters: Mixed metal clusters or hetero-metal clusters are the ones which contain two or more different types of metal atom in the cluster. Mixed metal clusters are of interest because of the following properties.

(a) They are valuable as precursors for the preparation of bimetallic and multi-metallic heterogeneous catalysts.

(b) These clusters also find important applications in homogeneous catalysis because of high selectivity.

(c) The low symmetry of mixed metal clusters makes them useful for probing various aspects of the reactivity and molecular dynamics of clusters.

Some examples of mixed metal clusters are shown in Figure 1.4. and Figure 1.5.



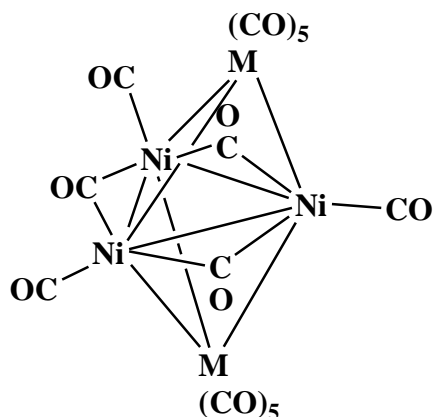


Figure-1.4.  $[M_2Ni_3(CO)_{16}]^{2-}$  ( $M = Cr, Mo, W$ )

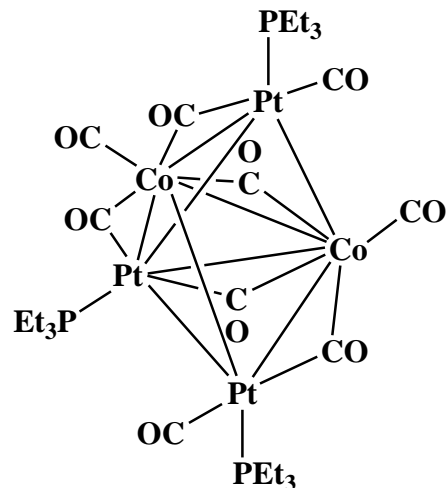


Figure-1.5.  $Pt_3Co_2(CO)_9(PEt_3)_3$

Fig

Further, metal clusters can also be classified in the basis of nuclearity as follows:

1. Dinuclear clusters: A rhenium cluster with metal-metal double bond with each rhenium containing four terminal carbonyl groups and hydride bridging ligand,  $[H_2Re_2(CO)_8]$  (Figure 1.6.).

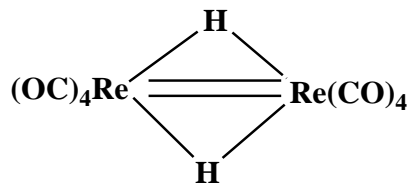
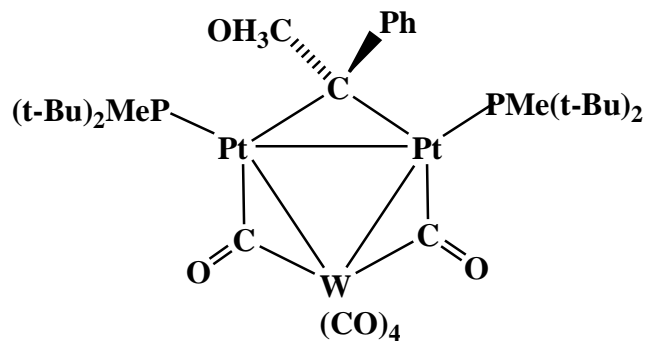


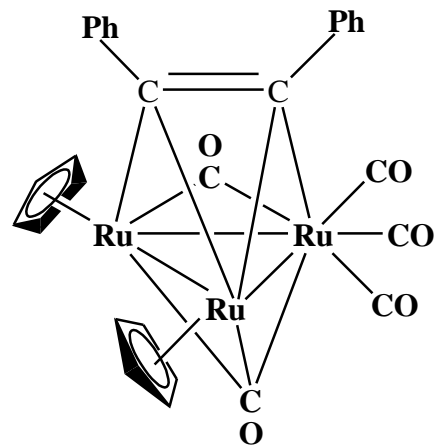
Figure 1.6.  $[H_2Re_2(CO)_8]$

2. Trinuclear clusters:

The trinuclear ruthenium cluster  $[Ru_3(Cp)_2(\mu_3-Ph_2C_2)(CO)_5]$  (Figure 1.8.) has been reported to be a catalyst precursor for the hydrogenation of diphenyle acetylene and for the isomerization of Z-stilbene.<sup>15</sup> Some other trinuclear clusters are  $[WPt_2\{\mu-C(OMe)Ph\}_6\{PMe(t-Bu)_2\}_2]$ ,  $[FeCo_2(CO)_9S]$  shown in the Figure 1.7.



*e-1.7.  $WPt_2\{\mu-C(OMe)Ph\}_6\{PMe(t-Bu)_2\}_2$*

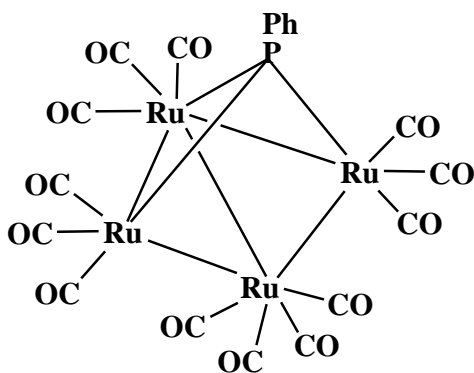


*Figure-1.8.  $Ru_3(Cp)_2(\mu_3-Ph_2C_2)(CO)_5$*

*Figur*

### 3. Tetra nuclear clusters:

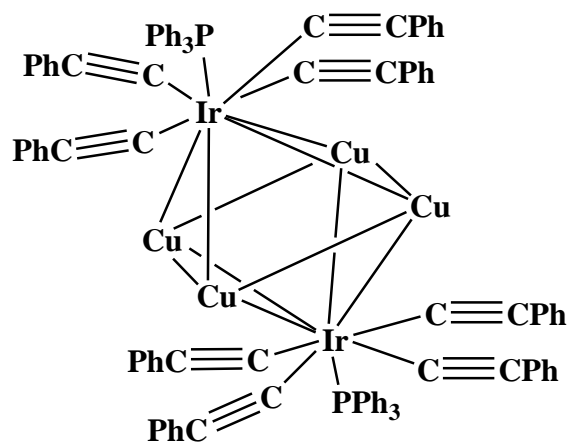
The tetra-nuclear phosphinidene cluster,  $[Ru_4(\mu_3-PPh)(CO)_{13}]$  (Figure 1.9.) is also a catalyst precursor for the homogeneous hydrogenation of diphenyl acetylene under mild condition. The compound contains triply bridged phosphorus and terminal carbonyl ligands.<sup>16</sup>



*Figure-1.9.  $Ru_4(\mu_3-PPh)(CO)_{13}$*

### 4. Polynuclear clusters:

For examples:  $[Ph_3PAuFeCo_3(CO)_{12}]$ ,  $[Os_6(CO)_{18}]$ ,  $[Rh_{13}(CO)_{24}H_3]^{2-}$ ,  $[Ir_2Cu_4(PPh_3)_2(C_2Ph)_8]$  (Figure-1.10.)

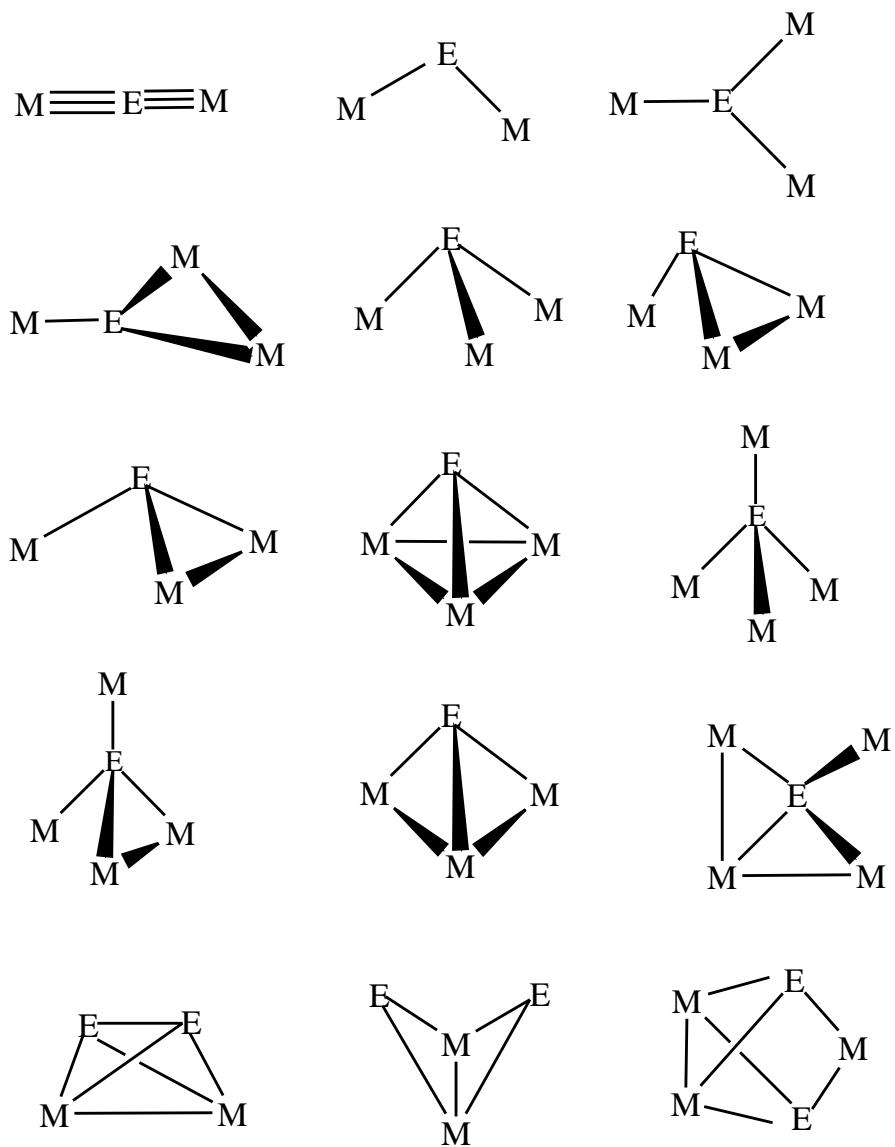


*Figure-1.10. Ir<sub>2</sub>Cu<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>Ph)<sub>8</sub>*

### 1.5. Transition Metal cluster containing main group elements

Clusters are regarded as modes of intermediates in catalysis and for use as catalysis themselves. Interest in cluster catalysis arises because of their striking resemblance in the structures and stoichiometric transformation to those of metal particles and metal surfaces. Many transition metal clusters are unstable and undergo degradation to mononuclear species under forced reaction conditions required to be used for studies related to catalysis and organic transformations. Heteronuclear transition metal cluster complexes have been known to exhibit unusual properties and are of particular interest as models of heterogeneous bimetallic alloy catalysts. Due to the presence of polar metal-metal bonds, heterometal clusters can often stabilize the cluster framework considerably and the bridging ligands thereby serving to maintain cluster integrity.

Single atoms derived from group 13-16 of the Periodic Table have been widely used for supporting cluster growth and stabilization purpose.<sup>17</sup> A large diversity of structural geometries are observed in transition metal clusters containing group 13-16 elements. Some structural geometry for main group bridged clusters are shown in the Figure 1.11.



**Figure 1.11. Structural geometries of transition metal clusters with bridging ligands**

*(E=Gp. 13-16 elements, M=Transition metals)*

## 1.6. Transition metal clusters bridged by main group atoms.

The heterometallic spiro  $M_4E$  type cluster compounds with Ge as a single atom ligand has been reported in  $[\text{Ge}\{\text{Fe}_2(\text{CO})_8\}\{(\text{MeC}_5\text{H}_4)\text{MnFe}(\text{CO})_6\}]^{18}$  and  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})\{\mu\text{-GeCo}_2(\text{CO})_6(\mu\text{-CO})\}_2]^{19}$ . The former is the first example of two different transition metal atoms bonded to Germanium and was prepared from the reaction of  $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Mn}=\text{Ge}=\text{Mn}(\text{CO})_2(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)]$  and  $\text{Fe}_2(\text{CO})_9$  (Figure 1.12).

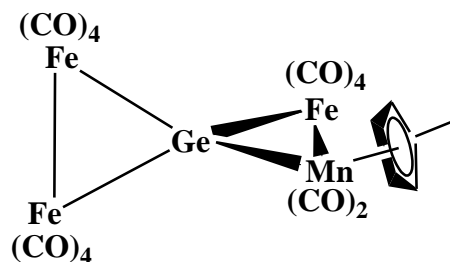


Figure 1.12.  $[\text{Ge}\{\text{Fe}_2(\text{CO})_8\}\{(\text{MeC}_5\text{H}_4)\text{MnFe}(\text{CO})_6\}]$

A Spirocyclic  $EM_4$  type cluster,  $[\text{Ru}_2(\text{CO})_8\text{Bi}\{\text{HRu}_3(\text{CO})_{10}\}]$  was prepared from the reaction of  $\text{Bi}(\text{NO}_3)_5\cdot\text{H}_2\text{O}$  and  $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$  in methanol. The structure consists of a  $[\text{Ru}_2(\text{CO})_8]$  unit connected to a  $[\text{Ru}_3\text{H}(\text{CO})_{10}]$  fragment by a  $\mu_4$ -bismuth atom with a pseudo-tetrahedral coordination geometry. All the carbonyl ligands are terminally bonded and the hydride ligand is bridged between two ruthenium center (Figure 1.13).<sup>20</sup>

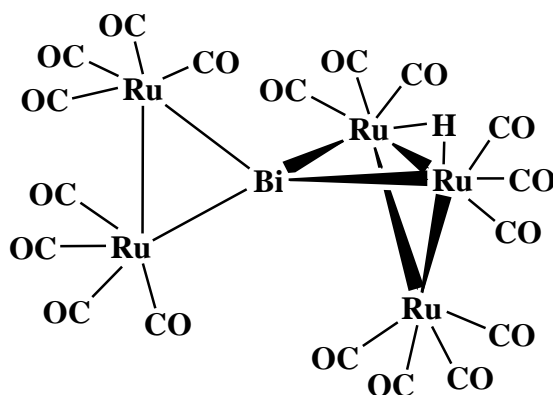
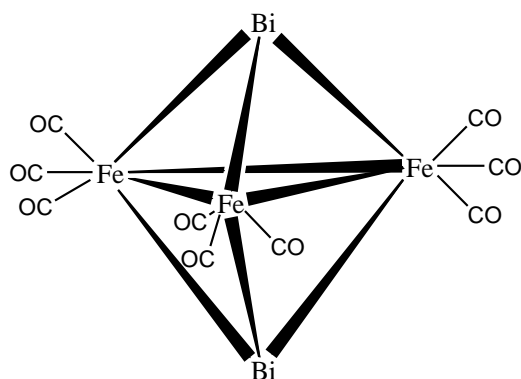


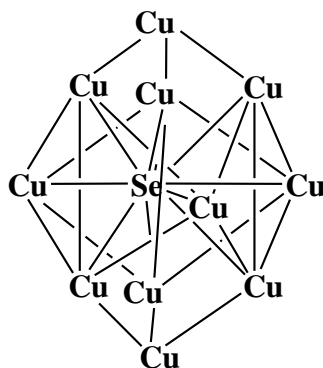
Figure 1.13.  $[\text{Ru}_2(\text{CO})_8\text{Bi}\{\text{HRu}_3(\text{CO})_{10}\}]$

Clusters of the type  $E_2M_3$  with both E being axial in trigonal bipyramidal geometry have been observed in  $[Bi_2Fe_3(CO)_9]$  cluster, synthesised by treatment of  $[HFe(CO)_4]^-$  with  $NaBiO_3$  followed by dilute  $H_2SO_4$ . The structure shows two triply bridging naked bismuth atoms at the apical position of the trigonal bipyramid and terminal carbonyl ligands attached to iron.(Figure-1.14).<sup>21</sup>



**Figure 1.14**  $[Bi_2Fe_3(CO)_9]$

The square pyramid structure with bridging group 16 elements is best represented by  $[M_3(CO)_9(\mu_3-E)_2]$ , (E= S, Se, Te; M=Fe, Ru, Os) clusters.<sup>22,23</sup> Another common structural pattern is that of a cube of metals capped on all the faces with  $\mu_4-E$  ligands. Synthesis of a nanocoordinate bridging selenido ligand in a tricapped trigonal prismatic geometry,  $[Cu_{11}(\mu_9-Se)(\mu_3-Br)_3\{Se_2P(OPr^i)_2\}_6]$  (Figure-1.15) has been reported along with the formation of closed-shell ion-centered  $Cu_8$  cubes,  $[Cu_8(\mu_8-Se)\{Se_2P(OPr^i)_2\}_6]$  and  $[Cu_8(\mu_8-Br)\{Se_2P(OPr^i)_2\}_6(PF_6)]$ , from the low temperature reaction of  $[NH_4Se_2P(OPr^i)_2]$ ,  $[Cu(CH_3CN)_4PF_6]$  and  $Bu_4NBr$ .<sup>24</sup>



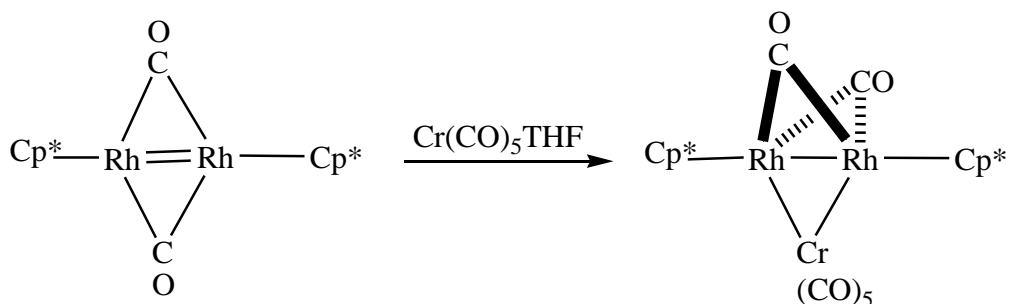
**Figure 1.15** Core structure of  $[Cu_{11}(\mu_9-Se)(\mu_3-Br)_3\{Se_2P(OPr^i)_2\}_6]$

## 1.7. Synthetic approaches to transition metal cluster

Clusters with higher nuclear metal atoms have been prepared with proper synthetic strategies. Except for the heaviest transition elements, metal-metal bonding is not stronger than metal ligand bonding, it becomes obvious that the cluster core itself should participate in many cluster reactions irrespective of the ligand types, sizes and geometries. Basic metal cluster reactions are understood to be those affecting the cluster core, its composition, shape, size, charge, oxidation state or bonding situation. In an attempt to systematic cluster synthesis, the cluster has to be prepared from fragments with distinct frontier orbital with different reaction sequence like metal - ligand bond breaking and metal - metal bond formation.

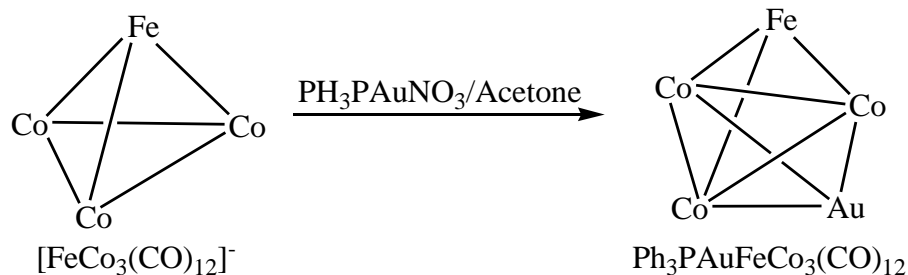
### 1. Use of M-M multiple bonds for Cluster building:

Addition of M=M bond to species with labile ligands.

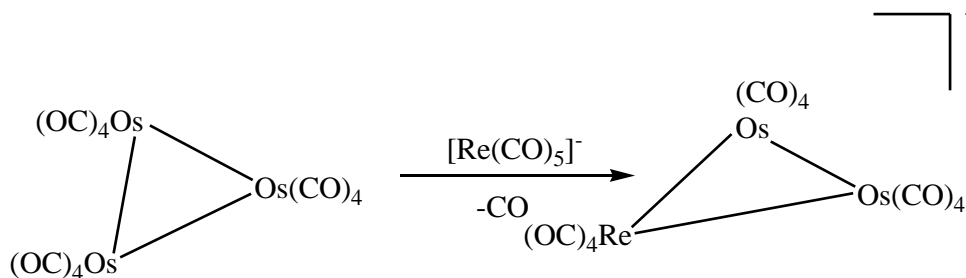


### 2. Cluster expansion reactions

Addition of tetranuclear Cobalt -iron cluster to the fragment  $\text{Ph}_3\text{PAu}$  gave pentanuclear cluster.

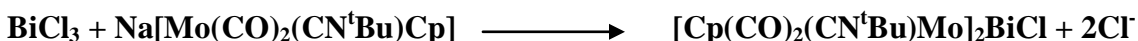


### 3. Metal exchange using isolobal fragments



### 4. Substitution reactions

The reaction of  $\text{BiCl}_3$  with  $\text{Na}[\text{Mo}(\text{CO})_2(\text{CN}^t\text{Bu})\text{Cp}]$  results in the formation of a dinuclear molybdenum cluster with bridging a bismuth atom.<sup>25</sup>



### 5. Pyrolysis and thermolysis reactions

Thermolysis reactions can lead to various bond breaking and bond formation which results in different types of products. Simple ligand loss can occur with the formation of M-M bonds as shown below:



## 1.8. Transition metal cluster to Nanocluster

Small metal particles called colloids or nano-particles have found uses for many years- medieval red stained glass contains colloidal gold, for example. Very striking advances have been made in recent years in their controlled synthesis, better characterization and in the identification of new commercial applications. Traditional aqueous metal colloids were formed by reducing a metal salt in the presence of protective polymer such as polyvinyl alcohol (PVA), which absorbs on the surface. More recently large ligand stabilized particles have been prepared that are intermediate between clusters and nano-particles.



Chaudret has shown that the metal-organic precursor  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  can be reduced by hydrogen in the presence of  $n\text{-C}_{16}\text{H}_{33}\text{NH}_2$  to give iron nano-particles of very similarly shape and size cubes of  $7\text{ \AA}$  edge length. They even “crystallize” into a cube super lattice, as known from the electron micrographs.<sup>26</sup>

A giant palladium cluster was synthesized by Moiseev and co-workers from  $\text{H}_2$  and  $\text{Pd}(\text{OAc})_2$  and dipyriddy was used to protect the Pd colloid formed.<sup>27</sup> The crystallites are catalytically active for  $\text{O}_2$  or peroxide oxidation of ethylene, propylene and toluene to vinyl acetate or benzyl acetate. From electron microscopy we come to know that it has a  $25\text{ \AA}$  particle size distribution. A  $35\text{ \AA}$  Pd colloid was stabilized by a polymeric hydrosilane has substantially different selectivity than either Pd/C or homogeneous Pd catalysts in hydrogenation and hydrolysis reactions. Giant clusters can also be obtained as pure compounds by different synthetic methodology. The largest clusters that can still be crystallized for X-ray studies and are found to be of a defined nuclearity are now in the M100 range, e.g. the closed packed  $\text{Pd}_{69}(\text{CO})_{36}(\text{PEt}_3)_{18}$  shows unusual physical properties.<sup>28</sup>

## 1.9. Application of transition metal cluster

Metal cluster compounds, especially those having numbers of carbonyl ligands, have been evaluated as catalysts for a wide range of reactions, especially related to carbon monoxide utilization, but no industrial applications exist. The clusters  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{12}$  catalyze the water gas shift reaction, also catalyzed by iron oxide, and  $\text{Rh}_6(\text{CO})_{16}$  catalyzes the conversion of carbon monoxide into hydrocarbons, reminiscent of the Fischer-Tropsch process, also catalyzed by iron compounds.

Clusters are common catalysts in nature. Most prevalent are the iron-sulfur proteins, which are involved with electron-transfer but also catalyse certain transformations. Nitrogen is reduced to ammonia at an Fe-Mo-S cluster at the heart of the enzyme nitrogenase. CO is oxidized to  $\text{CO}_2$  by the Fe-Ni-S cluster carbon monoxide dehydrogenase. Hydrogenases rely on  $\text{Fe}_2$  and NiFe clusters.<sup>29</sup>

Metal clusters have also been used as valuable precursors for preparation of bimetallic and multimetallic heterogeneous catalysts. These are very useful for activation of organic molecules - catalysis. Cluster like  $\text{PbMo}_6\text{S}_8$  remain superconducting in very strong magnetic field.<sup>30</sup> Transition metal clusters show photochemical properties with possible relevance for conversion of solar energy. These are of immense interest due to their diverse structural property and potential applications in the field of material science.

## Chapter 2

### **Transition metal phosphine cluster: Synthesis and characterization**

## 2.1. Introduction

Clusters with unique structural features and unusual reactivities have been obtained by using chalcogen atoms as bridging ligands.<sup>31</sup> Chalcogen ligands display a wide variety of bonding modes when these are incorporated in transition metal carbonyl cluster frameworks. The incorporation of main group elements into transition metal clusters introduces novel structural and reactivity features and plays a key role in stabilizing the bonding network in the transition metal, non-metal clusters. These clusters often have the ability to add or remove ligands or electrons while retaining the cluster integrity.<sup>10</sup> The compounds  $[\text{Fe}_3(\text{CO})_9(\mu\text{-E}_2)]$  and  $[\text{Fe}_2(\text{CO})_6(\mu\text{-E})_2]$  (E= S, Se, Te) have been used as convenient starting materials for several cluster growth reactions.<sup>32,33,34</sup>

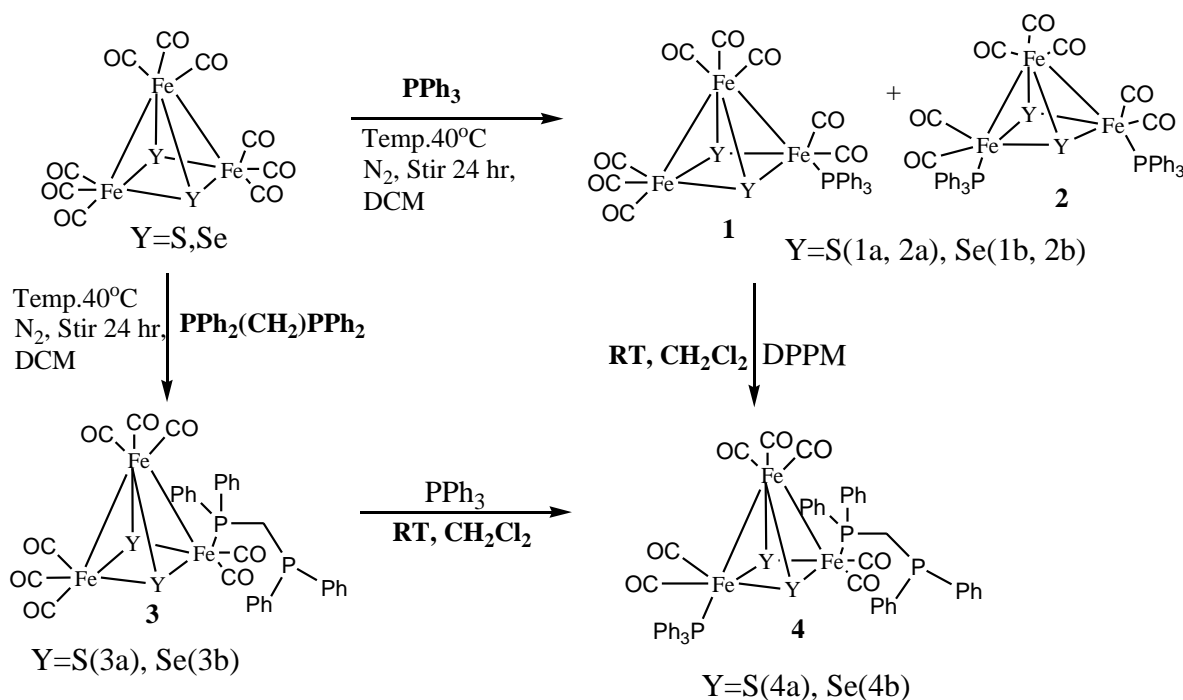
Ligands attached to metals are also important to maintain structural geometries and leads to interesting properties. Carbonyl ligands, one of most common ligands in metal cluster compounds, is an unsaturated ligand by virtue of the C-O multiple bond. They act as  $\pi$  acceptors by accepting metal d- electron by back bonding. CO can act as spectator or actor ligands. Similar type of ligands like Tertiary phosphines,  $\text{PR}_3$  are also important because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a very wide range by varying R. They also stabilize an exceptionally wide variety of ligands of interest to organometallic chemist as their phosphine complexes  $(\text{R}_3\text{P})_n\text{M-L}$ . Phosphines are more commonly spectator than actor ligands.

In case of CO, the  $\pi^*$  orbital accepts electrons from the metal. The  $\sigma^*$  orbital of P-R bond play the role of acceptor in  $\text{PR}_3$ ; when the R group becomes more electronegative, this implies that  $\sigma^*$  orbital of the P-R bond becomes more stable and more accessible for back donation.

Chelating ligands such as  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  (e.g. dppm, dppe) series usually enforce a cis arrangement of the chelate effect. Different chelates differ in their preferred bite angle.

## 2.2. Results and discussion:

The sulphur and selenium bridged cluster,  $[\text{Fe}_3\text{Y}_2(\text{CO})_9]$  ( $\text{Y}=\text{S}, \text{Se}$ ) when stirred with equimolar amount of  $\text{PPh}_3$  in dichloromethane solvent at room temperature, mono and di- $\text{PPh}_3$  substituted products (**1** and **2**) are obtained. The dichloromethane solution of **1** was further stirred with diphenylphosphino methane to obtain disubstituted phosphine containing tri iron cluster,  $[\text{Fe}_3\text{Y}_2(\text{CO})_7(\text{PPh}_3)\{(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2\}]$ , ( $\text{Y}=\text{S}, \text{Se}$ ) (**4**) as shown in the scheme-1. In another reaction a dichloromethane solution of  $[\text{Fe}_3\text{Y}_2(\text{CO})_9]$  ( $\text{Y}=\text{S}, \text{Se}$ ) was stirred with equimolar amount of bis-(diphenylphosphino)methane to obtain black colored mono DPPM substituted product,  $[\text{Fe}_3\text{Y}_2(\text{CO})_8\{(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2\}]$  ( $\text{Y}=\text{S}, \text{Se}$ ) (**3**) (scheme-1). Compound **3** when stirred with triphenylphosphine in dichloromethane solvent at room temperature gives rise to the same substituted compound **4**. Compound **1-3** has been characterized by FTIR and compared with the literature value.<sup>33</sup> Compound **4** was characterized by FTIR,  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectroscopy. FTIR spectroscopy reveals the presence of terminal carbonyl ligands with  $\nu_{\text{CO}}$  in the range of 2000-1950  $\text{cm}^{-1}$ . Proton NMR shows multiplet in the region 7.1 – 7.7 for phenyl group and a triplet at 2.8 for  $\text{CH}_2$ - group.



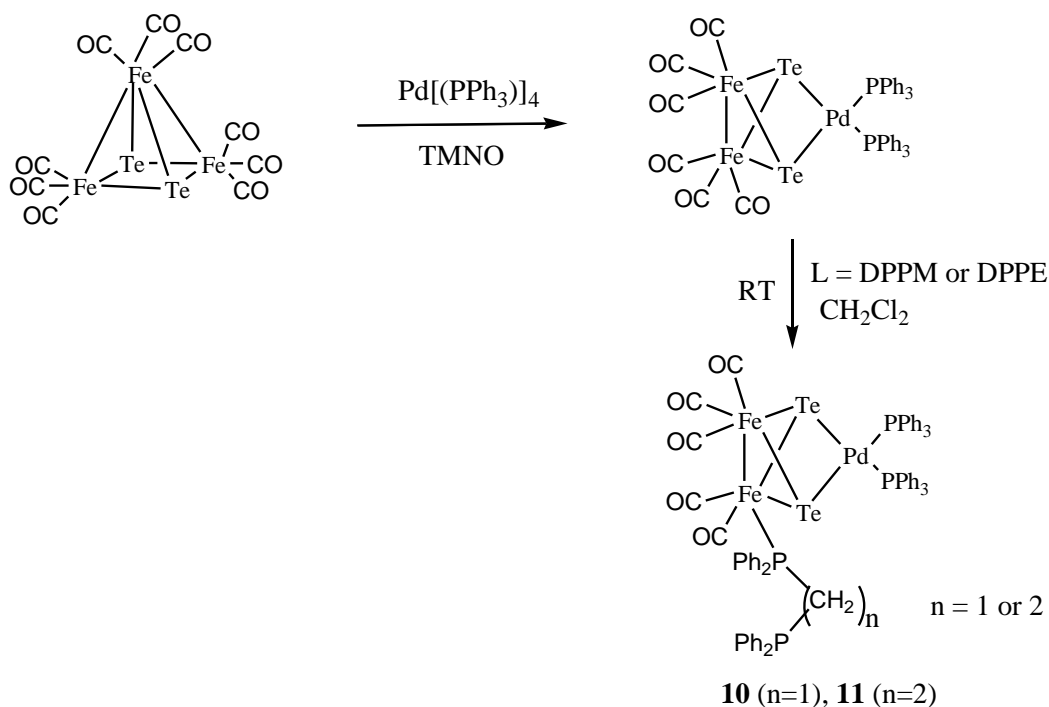
**Scheme-1**

The tellurium analogue,  $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$  when stirred with equimolar amount of  $\text{PPh}_3$  in dichloromethane solvent for 10 minutes at room temperature a product with a open cluster  $[\text{Fe}_3\text{Te}_2(\text{CO})_9(\text{PPh}_3)]$  (**5**) was obtained. Compound **5** was further stirred for 20 hrs at room temperature giving rise to a new product  $[\text{Fe}_3\text{Te}_2(\text{CO})_8\text{PPh}_3]$  (**6**) as shown in the scheme-2. The products (**5** & **6**) was isolated after completion of the reaction and characterized by FTIR, which shows the presence of terminal bonded metal carbonyl groups and compared with the literature value to predict the struture.<sup>32</sup>

Room temperature reaction of  $\text{Fe}_3\text{Te}_2(\text{CO})_9$  with equimolar amount of bis-(diphenylphosphino)methane results in the formation of a open cluster,  $[\text{Fe}_3\text{Te}_2(\text{CO})_9\{(\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2\}]$  (**8**) which transforms to  $[\text{Fe}_3\text{Te}_2(\text{CO})_8\{\mu\text{-}((\text{Ph})_2\text{PCH}_2\text{P}(\text{Ph})_2)\}]$  (**9**) after 20 hrs of stirring at room temperature as shown in the scheme-3. Compound **8** was characterized by FTIR and compared with the literature<sup>32</sup> and compound **9** was characterized by FTIR and  $^{31}\text{P}$  NMR as containing terminal carbonyl groups and bridging DPPM ligands.

### **2.2.3 Synthesis of $\text{Fe}_2\text{Te}_2\text{Pd}(\text{PPh}_3)_2(\text{L})$ , $\text{L} = \text{Bis-}(\text{Diphenylphosphino})\text{methane (DPPM)}$ , $\text{Bis-}(\text{Diphenylphosphino})\text{ethane (DPPE)}$**

The iron-palladium cluster,  $[\text{Fe}_2\text{Te}_2\text{Pd}(\text{PPh}_3)_2]$  was prepared by treating  $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$  with  $\text{Pd}(\text{PPh}_3)_4$  in presence of TMNO as described in the literature.<sup>35</sup> Equimolar amount of  $[\text{Fe}_2\text{Te}_2\text{Pd}(\text{PPh}_3)_2]$  when stirred with L (L=DPPM, DPPE) in dichloromethane solvent at room temperature gives rise to substituted cluster,  $\text{Fe}_2\text{Te}_2\text{Pd}(\text{PPh}_3)_2(\text{L})$ , L = DPPM, DPPE (**10-11**) as shown in scheme-4. The product is isolated after completion of reaction and is characterized by FTIR and  $^{31}\text{P}$  NMR. The infrared spectral data shows terminally bonded metal carbonyl groups and  $^{31}\text{P}$  NMR shows two different types of phosphorous.



**Scheme-4**

## 2.3. Experimental Sections:

### 2.3.1. General Procedures:

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified argon or nitrogen using standard schlenk line techniques. Solvents were purified, dried and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I spectrometer as hexane or dichloromethane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a 400 MHz Bruker spectrometer in  $\text{CDCl}_3$ . TLC plates (20x20 cm, Silica gel 60 F254) were purchased from Merck.  $[\text{Fe}_3\text{YY}'(\text{CO})_9]$  ( $\text{YY}' = \text{S}_2, \text{Se}_2, \text{Te}_2$ ),  $\text{Fe}_3\text{Te}_2\text{Pd}(\text{PPh}_3)_2$  were prepared following reported procedures.<sup>33,35</sup>

### 2.3.2. Reaction of $[\text{Fe}_3\text{YY}'(\text{CO})_9]$ ( $\text{YY}' = \text{S}_2, \text{Se}_2$ ) with triphenylphosphine and Bis-(diphenylphosphino-methane)

In a typical reaction, Triphenylphosphine or Bis-(diphenylphosphino-methane) (0.1 mmol) was added to a dichloromethane solution of  $[\text{Fe}_3\text{Y}_2(\text{CO})_9]$  ( $\text{Y}_2 = \text{S}_2, \text{Se}_2$ ) (0.1 mmol) under stirring condition. The reaction mixture was stirred for 10 hrs at room temperature under

nitrogen atmosphere. The reaction was monitored by TLC. After the completion of the reaction the solution was vacuum dried and the residue was subjected to chromatographic work-up in silica gel column using dichloromethane / hexane (20:80 v/v) solvent mixture as eluant. The compound obtained on subsequent elution are trace amount of unreacted  $[\text{Fe}_3\text{Y}_2(\text{CO})_9]$  ( $\text{Y}_2 = \text{S}_2, \text{Se}_2$ ) followed by the product  $[\text{Fe}_3\text{Y}_2(\text{CO})_8(\text{PPh}_3)]$ , (1a, b) ( $\text{Y} = \text{S}, \text{Se}$ ) or  $[\text{Fe}_3\text{Y}_2(\text{CO})_8(\text{dppm})]$ , (3a, b) ( $\text{Y} = \text{S}, \text{Se}$ ) and  $[\text{Fe}_3\text{Y}_2(\text{CO})_7(\text{PPh}_3)_2]$ , (2a, b) ( $\text{Y} = \text{S}, \text{Se}$ ).

**1a**,  $[\text{Fe}_3\text{S}_2(\text{CO})_8(\text{PPh}_3)]$  IR( $\text{cm}^{-1}$ ): 2071(s), 2030(s), 2007(br), 1971(w)

**1b**,  $[\text{Fe}_3\text{Se}_2(\text{CO})_8(\text{PPh}_3)]$  IR( $\text{cm}^{-1}$ ): 2065(s), 2024(s), 2003(s), 1966(m), 1946(m)

**2a**,  $[\text{Fe}_3\text{S}_2(\text{CO})_7(\text{PPh}_3)_2]$  IR( $\text{cm}^{-1}$ ), 2037(br), 1998(s), 1972(s), 1935(br)

**2b**,  $[\text{Fe}_3\text{Se}_2(\text{CO})_7(\text{PPh}_3)_2]$  IR( $\text{cm}^{-1}$ ): 2033(br), 1990(s), 1969(s), 1938(br)

**3a**,  $[\text{Fe}_3\text{S}_2(\text{CO})_8\text{dppm}]$  IR( $\text{cm}^{-1}$ ): 2069(s), 2043(s), 2029(br), 1998(br), 1979(w), 1942(w), 1926(br)

**3b**,  $[\text{Fe}_3\text{Se}_2(\text{CO})_8\text{dppm}]$  IR( $\text{cm}^{-1}$ ): 2039(s), 1984(br), 1940(br).

### ***2.3.3. Reaction of 1-3 with Bis-(diphenylphosphino-methane) or Triphenylphosphine (0.1 mmol)***

In a typical reaction, Bis-(diphenylphosphino-methane) or Triphenylphosphine (0.1 mmol) was added to a dichloromethane solution of  $[\text{Fe}_3\text{Y}_2(\text{CO})_8(\text{PPh}_3)]$  ( $\text{Y} = \text{S}_2, \text{Se}_2$ ) (0.1 mmol) or  $[\text{Fe}_3\text{Y}_2(\text{CO})_8(\text{dppm})]$  ( $\text{Y} = \text{S}_2, \text{Se}_2$ ) (0.1 mmol) respectively under stirring condition. The reaction mixture was stirred for 10 hrs at room temperature under nitrogen atmosphere. The reaction was monitored by TLC. After the completion of the reaction the solution was vacuum dried and the residue was subjected to chromatographic work-up using preparative TLC with dichloromethane / hexane (20:80 v/v) solvent mixture. The compound obtained on subsequent elution are trace amount of unreacted  $[\text{Fe}_3\text{Y}_2(\text{CO})_8(\text{P})]$  ( $\text{Y}_2 = \text{S}_2, \text{Se}_2$ ;  $\text{P} = \text{PPh}_3, \text{dppm}$ ) followed by the product  $[\text{Fe}_3\text{Y}_2(\text{CO})_7(\text{PPh}_3)(\text{dppm})]$ , (**3a,b**) ( $\text{Y} = \text{S}, \text{Se}$ ).

### ***2.3.4. Reaction of $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$ with triphenylphosphine and Bis-(diphenylphosphino-methane)***

A dichloromethane solution of  $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$  (0.1 mmol) and triphenylphosphine or Bis-(diphenylphosphino-methane) was subjected to room temperature reaction under stirring



condition and N<sub>2</sub> atmosphere for 20 hrs. After the completion of the reaction the solution was vacuum dried and the residue was subjected to chromatographic work-up using preparative TLC with dichloromethane / hexane (20:80 v/v) solvent mixture. The compound obtained on subsequent elution are trace amount of unreacted [Fe<sub>3</sub>Te<sub>2</sub>(CO)<sub>9</sub>] followed by the product [Fe<sub>3</sub>Te<sub>2</sub>(CO)<sub>8</sub>(PPh<sub>3</sub>)], (**6**) or [Fe<sub>3</sub>Te<sub>2</sub>(CO)<sub>8</sub>(μ-dppm)], (**9**). The intermediate compounds **5** and **8** have also been isolated by preparative TLC.

### **2.3.6. Reaction of [Fe<sub>2</sub>PdTe<sub>2</sub>CO]<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub> with Bis-(diphenylphosphino)-methane or Bis (diphenylphosphino)ethane**

A dichloromethane solution of [Fe<sub>2</sub>Te<sub>2</sub>Pd(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.1 mmol) was taken in a one necked round bottomed flask and Bis-(diphenylphosphino)methane or Bis-(diphenylphosphino)ethane was added under stirring condition and N<sub>2</sub> atmosphere. The reaction was carried out for 20 hrs with continuous stirring and N<sub>2</sub> atmosphere. After the completion of the reaction the solution was vacuum dried and the residue was subjected to chromatographic work-up using preparative TLC with dichloromethane / hexane (40:60 v/v) solvent mixture. The compound obtained on subsequent elution are trace amount of unreacted [Fe<sub>2</sub>Te<sub>2</sub>Pd(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>] followed by the product [Fe<sub>2</sub>Te<sub>2</sub>Pd(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)], (L = dppm (**10**); L = dppe (**11**)).

**10**, [Fe<sub>2</sub>Te<sub>2</sub>Pd(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(dppm)], IR (cm<sup>-1</sup>): 2033 (s), 1990(vs), 1953(s, br).NMR: <sup>31</sup>P (δ, ppm): -19.9, 42.6, 48.3; <sup>1</sup>H (δ, ppm): 2.8 (t, 2H), 7.1-7.7 (m, 50H)

**11**, [Fe<sub>2</sub>Te<sub>2</sub>Pd(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(dppe)], IR (cm<sup>-1</sup>): 2031(s), 1989(vs), 1952(s, br).NMR: <sup>31</sup>P (δ, ppm): -19.95, 42.63, 48.34;

## **2.4. Conclusions**

Sulphur, Selenium and tellurium bridged tri-iron transition metal clusters with mono and bidentate phosphine ligands have been synthesized and characterized by various spectroscopic

techniques like FTIR and NMR. The reactivity pattern of sulphur and selenium are similar but the different product was obtained with the tellurium analogue. The bis(diphenylphosphino)methane (dppm) ligand has been used to form bridging unit between the metals, but in compounds **3**, **4**, **8**, **10** the dppm ligand is acting as a monodentate ligand whereas in compound **9** the ligand is acting as a chelate between two iron centers. Synthesis of Fe-Pd heteronuclear clusters with different phosphine ligands have been carried out and characterized. <sup>31</sup>P NMR has been used as a probe to characterize different types of phosphine incorporated clusters.

### 3. References

1. (a) K. H. Whitmire, *J.Coord.Chem.* **1988**, 17, 95; (b) G. Huttner, K.Knoll, *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 743.
2. (a) B. K. Burgess, D. J. Lowe, *Chem. Rev.*,**1996**, 96, 2983; (b) B. E. Smith, *Adv. Inorg. Chem.*, **1999**, 47, 159.
3. (a) H. S. Nalwa, *Appl. Organomet. Chem.*, **1991**, 5, 349; (b) S. Banerjee, G. R. Kumar, P. Mathur, P. Sekar, *Chem. Commun.*,**1997**, 299; (c) P. Mathur, S. Ghose, M. M. Hossain, C. V. V. Satyanarayana, S. Banerjee, G. R. Kumar, P. B. Hitchcocks, J. F. Nixon, *Organometallics*, **1997**, 16, 3815.
4. P. Macchi, A. Sironi, *Coord. Chem. Rev.*, **2003**, 238, 383.
5. Cristina Femoni, M. Carmela Iapalucci, Francesco Kaswalder, Giuliano Longoni, Stefano Zacchini, *Coord. Chem. Rev.*, **2006**, 250, 1580.
6. C. Elschenbroich, A. Salzer "Organometallics : A Concise Introduction" (2nd Ed) **1992** from Wiley-VCH: Weinheim.
7. W. Reppe, W. J. Schweckendiek, *Comp. Rendus* , **1948**, 560 ,104.
8. D. A. Evans, G. C. Fu and A. H. Hoveyda, *J. Am. Chem. Soc.*,**1988**, 110, 6917.
9. Massimo Di Vaira, Piero Stoppioni, *Coord. Chem. Rev.*, **1992**, 120, 259.
10. P. Mathur, B. H. S. Thimmappa, A. L. Rheingold, *Inorg. Chem.*, **1990**, 29 , 4658.
11. P. Mathur, P. Sekar, C. V. V. Satyanarayana, *Organometallics*, **1995**, 14, 2115.
12. P. Michelin-Lausarot, G. A. Vaglio, M. Valle, *J. Organomet. Chem.*, **1984**, 275, 233.
13. P. Michelin-Lausarot, G. A. Vaglio, M. Valle, *Inorg. Chem. Acta.*, **1977**, 25, L104.
14. R. Giordano, E. Suppa, *J. Organomet. Chem.*, **1993**, 448, 157.
15. R. Giordano, E. Suppa, S. A. R. Knox, *J. Cluster Sci.*, **1996**, 7, 179.
16. M. Castiglioni, R. Giordano, E. Sappa, *J. Organomet. Chem.*, **1991**, 407, 377.
17. (a)K. H. Whitmire, *Adv. Organomet. Chem.*, **1998**, 42, 1; (b) P. Mathur, *Adv. Organomet. Chem.*, **1997**, 41, 243; (c) K. H. Whitmire, *J. Coord. Chem.*, **1988**, 17, 95.
18. D. Melzer, E. Weiss, *J. Organomet. Chem.*, **1983**, 255, 335.
19. S. G. Anema, K. M. Mackay, L. C. Mcleod, B. K. Nicholson, J. M. Whittaker, *Angew. Chem.*, **1986**, 98, 744.

20. B. F. G. Johnson, J. Lewis, P. F. Raithby, A. J. Witton, *Chem. Commun.*, **1988**, 401.
21. M. R. Churchill, J. C. Fettinger, K. H. Whitmire, *Inorg. Chem.*, **1985**, 284, 13.
22. (a) R. D. Adams, L-W. Yang, *J. Am. Chem. Soc.*, **1984**, 106, 1869; (b) L. F. Dhal, P. W. Sutton, *Inorg. Chem.*, **1963**, 2, 1067; (c) P. Mathur, I. J. Mavunkal, V. Rugmini, *Inorg. Chem.*, **1989**, 28, 3616.
23. W. Heiber, J. Gruber, *Z. Anorg. Allg. Chem.*, **1958**, 296, 91.
24. K. Guo, C. W. Liu, C-m. Huang, H-C. Chen, J-C. Wang, T-C. Keng, *Chem. Commun.*, **2000**, 1897.
25. W. Clegg, T. Kochi, Z. Tang, Y. Ishii, Y. Mizobe, M. Hidai, *J. Organomet. Chem.*, **1987**, 335, C1.
26. B. Chaudret, *J. Organomet. Chem.*, **2005**, 16, 233.
27. (a) B. M. Trost, *Pure. Appl. Chem.*, **1996**, 68, 779; (b) J. W. Faller et al., *Organometallics*, **1984**, 3, 927; (c) G. Helchen et al., *Pure Appl. Chem.*, **1997**, 69, 513.
28. Nguyet T. Tran, Lawrence F. Dahl, *Angew. Chem. Int. Ed.*, **2003**, 42, 3533.
29. L. Kabir, A. R. Mandal, S. K. Mandal, *J. Magnetism & Magnetic Materials*, **2010**, 322, 934.
30. M. Marezio, P.D. Derniera, J.P. Remeikaa, E. Corenzwita, B.T. Matthias, *Materials Res. Bulletin*, **1973**, 8, 657.
31. (a) L. C. Roof, J. W. Kolis, *Chem. Rev.*, **1993**, 93, 1037. (b) P. Mathur, D. Chakrabarty, I. J. Mavunkal, *J. Cluster Sci.*, **1993**, 4, 351. (c) K. H. Whitmire, *J. Coord. Chem.*, **1988**, 17, 95. (d) N. A. Compton, R. J. Errington, N. C. Norman, *Adv. Organomet. Chem.* **1990**, 31, 91.
32. David A. Lesch, Thomas B. Rauchfuss, *Organometallics*, **1982**, 1, 499.
33. P. Math, Ipe J. Mavunkal, V. Rugmini, *J. Organomet. Chem.*, **1989**, 367, 243.
34. P. Baistrocchi, D. Cauzzi, M. Lanfranchi, G. Predieri, A. T. Camellini, *Inorg. Chem. Act.* **1995**, 235, 173.
35. Manuscript under preparation