

# **Synthesis and characterization of transition metal cluster containing diphosphine ligands**

*A Dissertation*

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

By

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## **CERTIFICATE**

This is to certify that the dissertation entitled **“Synthesis and characterization of transition metal cluster containing diphosphine ligands”** being submitted by Arnab Bhowmick 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 her 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

NIT Rourkela

Dr Saurav Chatterjee

Date:

(Supervisor)

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Rourkela

Date:

Arnab Bhowmick

# Abstract

Various metal complexes containing transitional metal elements have been prepared. Using shlenk line technique . Spectroscopic analysis by IR and NMR shows that two types of diphosphine co-ordinated metal clusters have been obtained,one having chelating mode of binding  $[\text{Fe}_3\text{SeTeCO}]_7\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}$  ,and the another is having mono dentate co-ordination  $[\text{Fe}_3\text{Te}_2(\text{CO})_8\{(\text{PPh}_2) (\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}]$ .

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# **Chapter-1**

## **Introduction**

## 1.1 Metal clusters

A metal cluster is defined as a group of two or more metal atoms held together by direct or indirect substantial metal-metal bonding. Cluster compounds constitutes an area of great interest because of their vast structural diversity, various modes of bonding and their potential application in the field of catalysis. These compounds play an important role in catalysis in bridging the gap between homogeneous and heterogeneous catalysis,<sup>1</sup> showing high activity generally associated with heterogeneous systems and high selectivity of homogeneous catalysis. Clusters containing two or more metal atoms are 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>

## 1.2. Properties of Clusters

Cluster science is one of the most active and evolving fields of research in chemistry. These cluster system bridge the domains of atomic and molecular physics on one part and condensed matter physics on the other. Cluster show discrete spectroscopy due to their finite size.<sup>4</sup> Some of the points which illustrates the importance of cluster are as follows:

1. Cluster properties are influenced by electron delocalization. Quantum mechanical degrees of freedom help to give rise to shell structure and magic numbers in clusters. In metal and semiconductor cluster, the electronic shell structure and geometric shell structure determines the shape and stability.

2. The existence of spherical shells in a metal clusters, phase change into amorphous of clusters and their thermal stability determines the cluster geometry.

3. The magnetic behavior differs in the size regime from bulk behavior. The enhancement in magnetic moment is due to strong d-electron localization.

4. Interaction of cluster with external fields like strong lower fields has to be evaluated which is quite important now a days.

Metal cluster have several properties that suggest they are useful catalysts. The absence of large bulk phases leads to high surface to volume ratio, which is advantageous in catalysts applications as this maximizes the reaction rate per unit amount of catalyst material, and minimizes the cost.<sup>5</sup>

Metal cluster are characterized by high degree of fluxionality of surface ligand and adsorbates associated with low energy barrier to rearrangement of the species on the surface .<sup>6,7</sup>

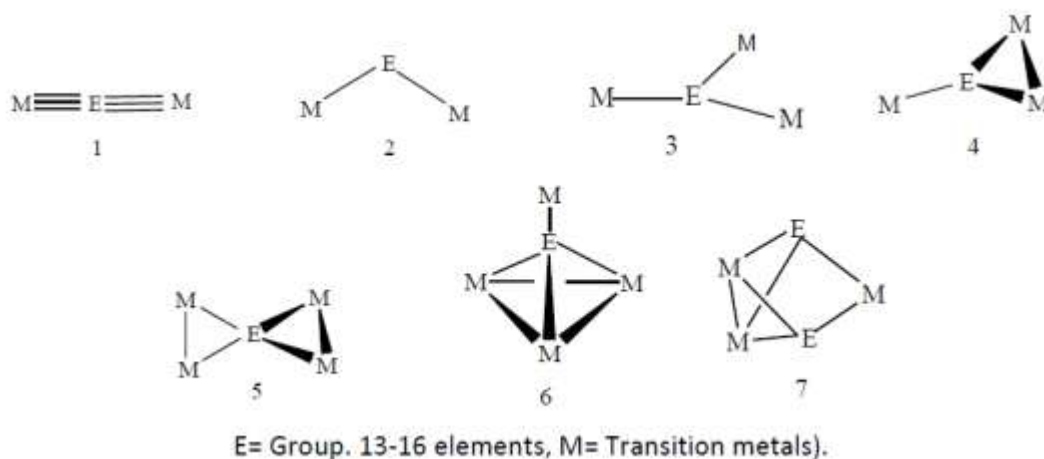
### **1.3. Main group and Transition metal clusters**

The last decade has witnessed a tremendous development in the chemistry of transition metal clusters stabilized by single atom ligand derived from main group elements.<sup>8</sup> These main group elements actually acts as bridging ligands and ultimately serves to maintain the framework of the whole cluster body. Therefore, their synthesis is demanding much attraction for cluster growth reaction. Recent research in the field of cluster chemistry has proved that these materials consists of non linear optical properties for their probable application in optoelectronics.<sup>9</sup> It has been also proved that large third order non linearity could be obtained in these clusters and thus they become attractive in such optical devices as optical limiting.<sup>10,11</sup>

Clusters are regarded as intermediates in catalysis and for use as catalyst themselves. Interest in cluster catalysis arises because of their striking resemblance in the structures and



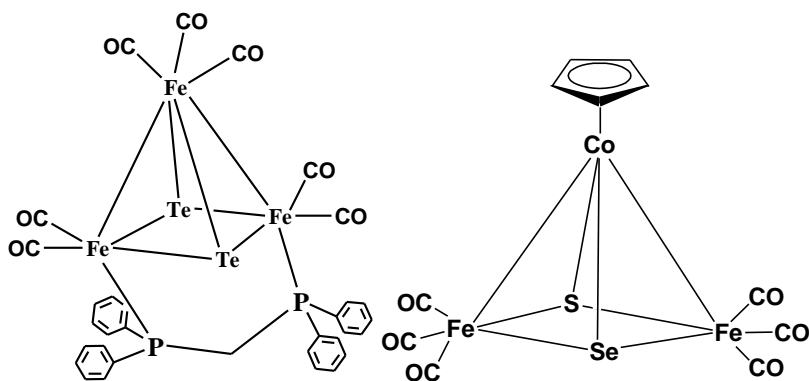
stoichiometric transformation to those of metal particles and metal surfaces. Many transition metal clusters are unstable and undergo degradation to mononuclear species under forced reaction conditions required to be used for studies related to catalysis and organic transformations. Heteronuclear transition 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, hetero-metal clusters can often stabilize the cluster framework considerably and the bridging ligands, particularly main group atoms, 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>12-15</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 Figure. 1



**Figure 1 – Structural geometries of transitional metal clusters with bridging ligands**

## 1.4. Mixed Transition Metal Clusters

Mixed metal clusters are of interest because of their application as precursors for the preparation of bimetallic and multimetallic heterogeneous catalysts. This has become possible by allowing the clusters to adsorb on to catalyst supports such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, 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>16</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, multimetallic 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 2.<sup>17,18</sup>



**Figure 2: Homonuclear and Heteronuclear cluster**

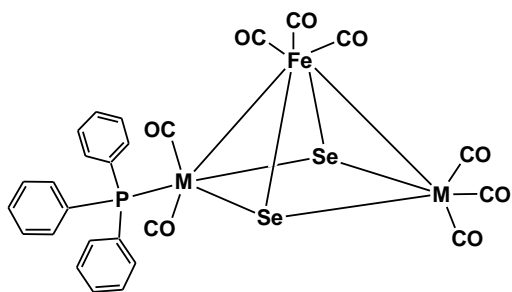
## 1.5. Transition metal phosphine cluster

A large variety of transition metal phosphine clusters have been known in the literature in which the phosphine ligands are bound to metal centers with different bonding modes. For example (a) monodentate and terminal phosphines, where ligands are bonded to one metal center, (b) diphosphine ligand or bidentate phosphines which can bind with one or two metal centers in chelating or bridging modes. Examples are known where the bridging phosphine can coordinate with metal atoms of the same cluster or can bridge two different cluster units.

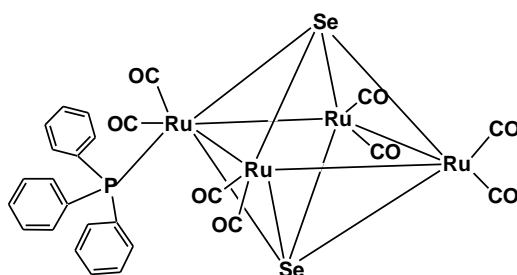
Phosphine ligands bind well to most of the transition metals, especially those in the middle and late transition metal groups. In terms of steric bulk,  $\text{PPh}_3$  has a cone angle of  $145^\circ$ , which is intermediate between those of  $\text{P}(\text{C}_6\text{H}_{11})_3$  ( $170^\circ$ ) and  $\text{P}(\text{CH}_3)_3$  ( $115^\circ$ ). 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>19</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>20</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.

Reaction of  $\text{Ph}_3\text{PSe}$  with  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_{12}$  produces a variety of  $\text{Ph}_3\text{P}$  substituted selenido carbonyl clusters, whose structural frameworks are represented in (Figure 3) and (Figure 4).<sup>21</sup>

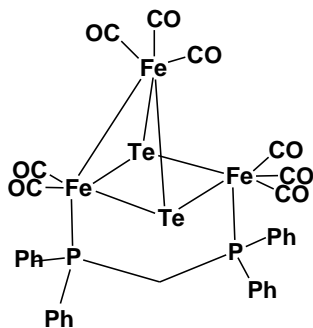


**Figure 3:**  $[\text{FeM}_2(\text{CO})_8(\text{PPh}_3)]$  ( $\text{M} = \text{Fe}, \text{Ru}$ )



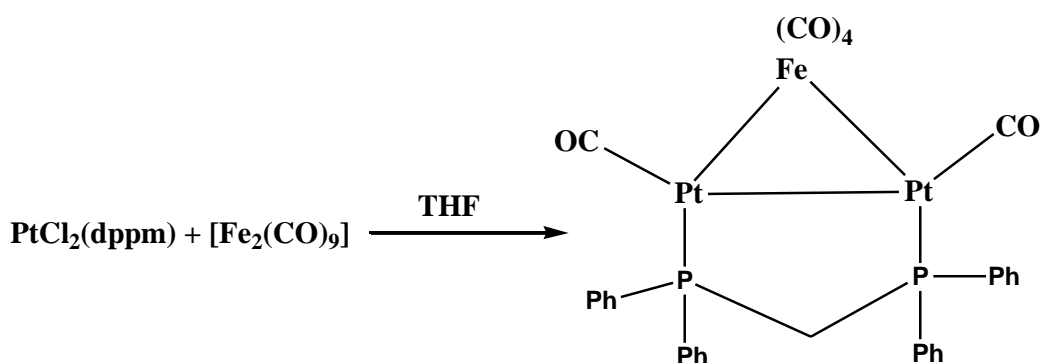
**Figure 4:**  $[\text{Ru}_4\text{Se}_2(\text{CO})_8\text{PPh}_3]$

Room temperature reaction of  $[\text{Fe}_3\text{Te}_2(\text{CO})_8(\text{PPh}_3)]$  with Bis-(diphenylphosphino)methane in dichloromethane solvent results in the formation of a dppm bridged triiron tellurium cluster,  $[\text{Fe}_3\text{Te}_2(\text{CO})_8(\mu\text{-dppm})]$  (Figure 5).<sup>22</sup>



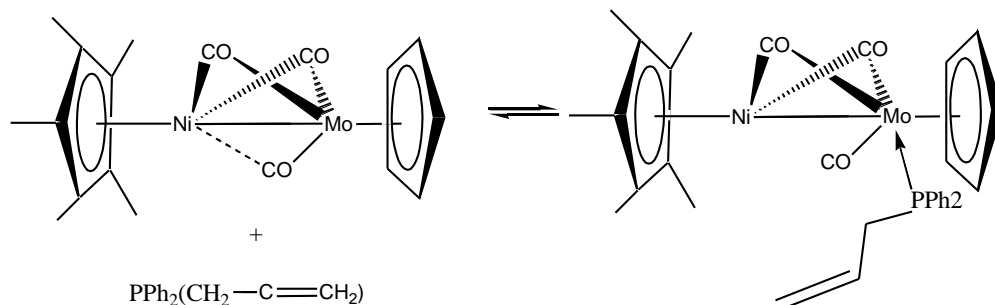
**Figure 5:**  $[\text{Fe}_3\text{Te}_2(\text{CO})_8(\text{PPh}_2)_2]$

In one of the recent synthesis  $\text{PtCl}_2(\text{dppm})$  reacts with  $\text{Fe}_2(\text{CO})_9$  in tetrahydrofuran at room temperature to form a diphosphine substituted hetero-metallic cluster,  $[\text{FePt}_2(\mu\text{-dppm})(\text{CO})_6]$  where dppm is bridged between the two platinum metal atoms ( Scheme 1.1).<sup>23</sup>



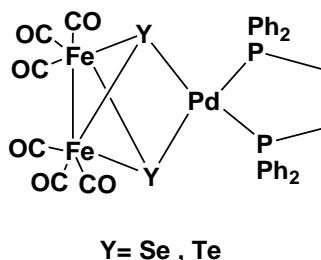
**Scheme 1.1**

Another very interesting example of phosphine containing metal cluster has been observed when unsaturated nickel-molybdenum complex  $[(\eta\text{-C}_5\text{Me}_5)\text{Ni}=\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ , reacts with allyldiphenylphosphine to give the phosphine complex  $[(\eta\text{-C}_5\text{Me}_5)\text{Ni}(\mu\text{-CO})_2\text{Mo}(\text{CO})(\text{PPh}_2\text{CH}_2\text{CH}=\text{CH}_2)(\eta\text{-C}_5\text{H}_5)]$  which is in equilibrium with the reactant at ambient temperature. In this compound the phosphine ligand is attached to the Molybdenum atom via the phosphorus atom (Scheme 1.2).<sup>24</sup>



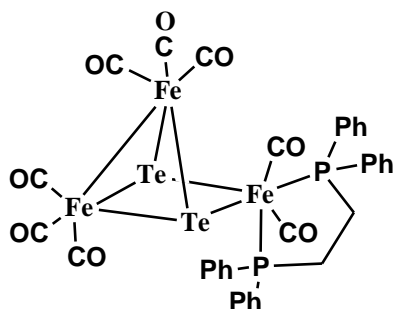
**scheme 1.2**

The dppe ligand can serve as bidentate chelate and often tends to form bridging ligands between two metal atoms. When an equimolar amounts of  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}(\text{PPh}_3)_2]$  ( $\text{Y} = \text{Se}, \text{Te}$ ) and bis-(diphenylphosphino)ethane (dppe) was stirred in dichloromethane solvent at room temperature for 1 hr under argon atmosphere the dppe ligand chooses to form a bidentate chelating coordination and forms a diphosphine coordinated heterometallic iron-palladium clusters,  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$  ( $\text{Y} = \text{Se}, \text{Te}$ ) (Figure 6).<sup>25</sup>

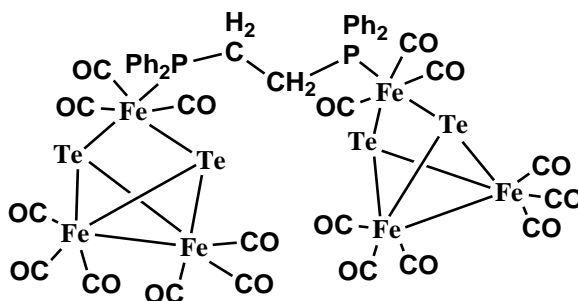


**Figure 6:**  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$

A hexametallc cluster,  $[(\text{CO})_{18}\text{Fe}_6(\mu_3\text{-Te})_4\{\mu\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$  and a tri iron diphosphine cluster,  $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_8\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$  have been obtained by the reaction of  $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_8\text{PPh}_3]$  with dppe at room temperature and inert atmospheric condition (Figure-7 and Figure 8). In compound  $[(\text{CO})_{18}\text{Fe}_6(\mu_3\text{-Te})_4\{\mu\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$  a diphosphine ligand (dppe) is acting as a bridge between two  $\text{Fe}_3\text{Te}_2$  cluster fragments (Figure 8), whereas in  $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_8\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$  the diphosphine ligand is acting as a chelate forming a bidentate coordinated with a basal iron atom.<sup>26</sup>



**Figure 7:**  $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_8\{\text{PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$



**Figure 8:**  $[(\text{CO})_{18}\text{Fe}_6(\mu_3\text{-Te})_4\{\mu\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$

## 1.6 Ferrocene and its derivative

Ferrocene or di( $\eta^5$ -cyclopentadienyl) iron(II) was accidentally discovered by Peter L. Pauson and his graduate student Tom Kealy in 1951 when they attempted the reductive coupling of the Grignard reagent cyclopentadienyl magnesium bromide in the presence of ferric chloride. The unique sandwich structure of ferrocene was first predicted by infrared and nuclear magnetic resonance spectroscopies and later confirmed by X-ray crystallography in 1954.<sup>27</sup>

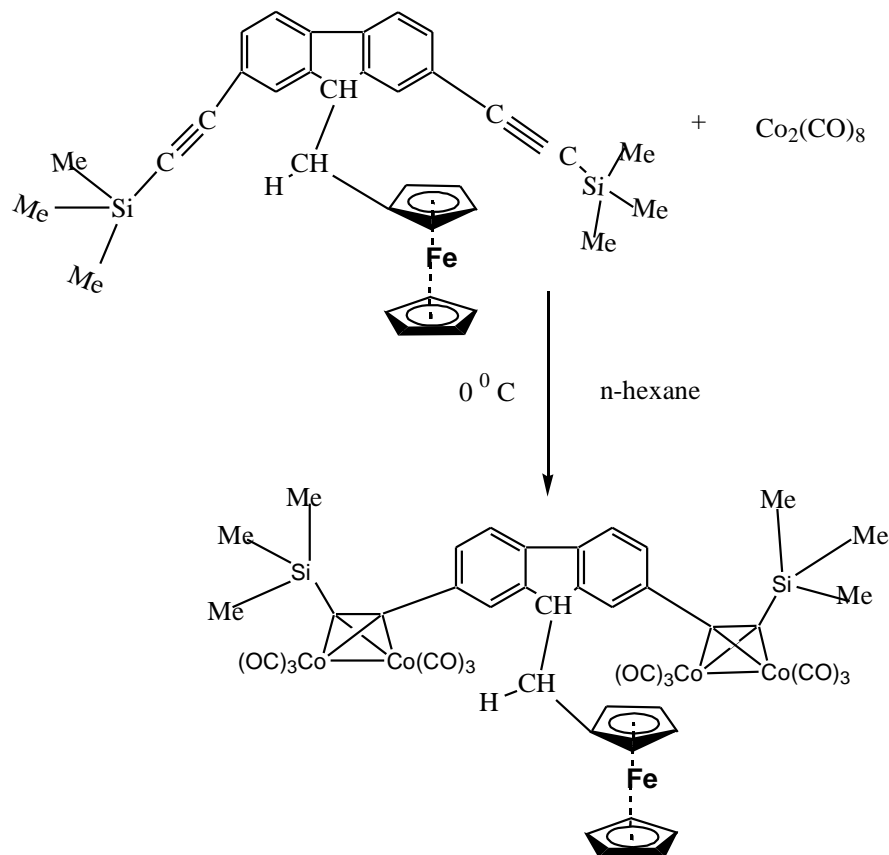
Ferrocene behaves like an aromatic compound. It is susceptible to direct electrophilic substitution reactions, giving rise to a variety of substituted ferrocenes. Ferrocene has provided a very rich chemistry as a super aromatic compound and had led to multiple applications in the field of materials and molecular engineering, molecular ferromagnets,<sup>26</sup> modified electrodes for redox catalysis (titration of glucose in blood), polymers and dendritic electrochemical sensors for molecular recognition and antitumor drugs due to its interesting redox properties. At room

temperature ferrocene is an air stable orange colored solid and it can be oxidized to blue-green ferrocenium cation,  $[(C_5H_5)_2Fe]^+$ . The inter-ring spacing in ferrocene is 332 pm and the distance between the Fe—C bond is 204 pm. The inter-ring spacing in ferrocene is 332 pm and the distance between the Fe—C bond is 204 pm. Ferrocene at room temperature crystallizes in a monoclinic form, at  $T < 164K$  in a triclinic form and in an orthorhombic modification at  $T < 110K$ . In the monoclinic form disorder phenomena feign a staggered conformation ( $D_{5d}$ ) of individual sandwich molecules. In the triclinic form, the molecules deviate from the eclipsed conformation ( $D_{5d}$ ) by  $9^\circ$  while in the orthorhombic form the rings are fully eclipsed ( $D_{5h}$ ). In the gas phase ferrocene also adopts an eclipsed conformation, the rotational barrier being small.

### **1.7. Homonuclear cluster containing ferrocene**

A metal cluster containing same type of metal in its cluster cage is better known as homoneuclear cluster. In recent days homoneuclear cluster containing ferrocene is going through a tremendous growth due to its potential application in biosensors, catalysis etc. Ferrocene containing cobalt cluster has been prepared from an alkene containing trimethylsilane and a ferrocenyl unit and dicobaltoctacarbonyl (scheme 1.3).





**Scheme 1.3**

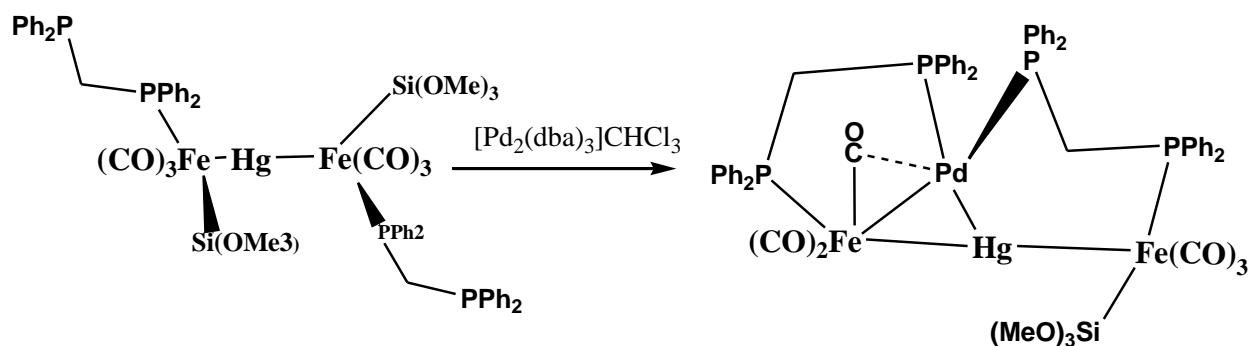
### 1.8 Hetero nuclear cluster containing ferrocene:

One of the basic cluster derivation is ligand substitution of carbonyl clusters generally by phosphine substitution which takes place under facile reaction condition. When chemically equivalent metal clusters create a site for selectivity effect of phosphine then complication arises. Such complication is therefore manifested by four bonding modes- 1) unidentate 2) chelating 3) bridging etc.

In one of the very important cluster synthesis, an unusual Fe-Hg-Pd cluster,

$[\text{Hg}\{\text{Fe}[\text{Si}(\text{OMe})_3](\text{CO})_3(\mu\text{-dppm})\}_2\text{Pd}]$ , with a palladium(0) fragment has been prepared the reaction of the complex  $[\text{Hg}\{\text{Fe}[\text{Si}(\text{OMe})_3](\text{CO})_3(\text{dppm})\}_2]$  with a  $[\text{Pd}_2(\text{dba})_3]$  as shown in

Scheme 1.4. The compound has been stabilized by an unusual heterometallic Pd-Hg bonding with  $d^{10}-d^{10}$  interaction (Scheme 1.4).<sup>28</sup>



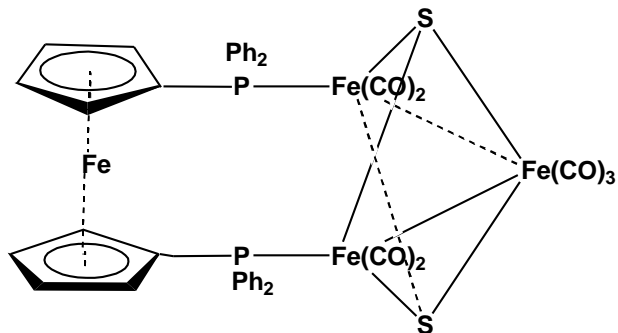
Scheme 1.4

### 1.8. Ferrocene containing chalcogen metal clusters

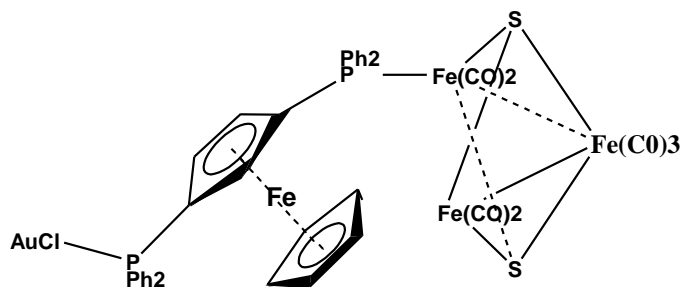
Ferrocene containing metal clusters has undergone rapid development in recent years. Various methodologies and substitution effects has been observed on this cluster moiety with various applications. In order to study the substitution effects on triangular clusters  $M_3(\mu-S_2)CO_9$  based on the stabilizing effect exerted by capping sulfide ligands. The isosceles triangle provides a model for the study of co-ordination mode and side selectivities. The incoming diphosphine is represented by 1,1'-bis (diphenylphosphino)ferrocene(dppf) which has been shown to exhibit a variety of co-ordination modes under very similar conditions . Diphosphine substituted triangular clusters have attracted considerable attention mainly because of their characteristic bonding catalytic value and their electroactivity and thermolytic products.

- 1) Carbonyl exchange of  $Fe_3(\mu-S_2)CO_9$  with 1,1'-bis diphenylphosphino)ferrocene(dppf) in refluxing gives a cluster ligand with a pedant phosphine moiety,  $Fe_3(\mu-S_2)CO_9 (\eta^1-dppf)$

under different conditions gives different substitutions products (Figure 9 & Figure-10).  
 Although bridged cluster forms only in trace quantity (Figure 10).<sup>29</sup>

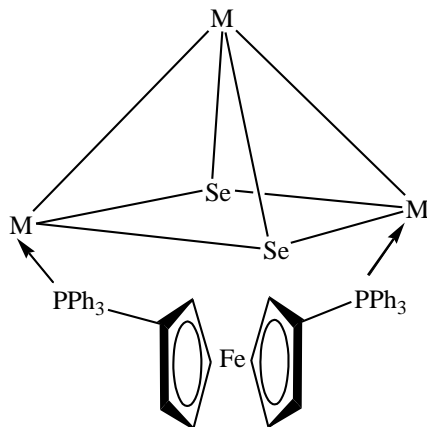


**Figure 9:**  $[\text{Fe}_3\text{S}_2(\text{CO})_8(\text{PPh}_2)_2(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)]$

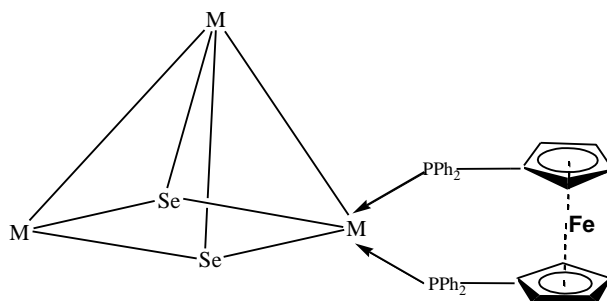


**Figure 10:**  $[\text{Fe}_3\text{S}_2(\text{CO})_8(\text{PPh}_2)_2(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)\text{Au}(\text{PPh}_2)]$

One of the recent synthesis has shown that 1,1'-bis (diphenyl phosphine) ferrocenediselenide (dppfSe<sub>2</sub>) with [Fe<sub>3</sub>(CO)<sub>12</sub>] and [Ru<sub>3</sub>(CO)<sub>12</sub>] under the same reaction condition affording respectively [Fe<sub>3</sub>(μ-Se)<sub>2</sub>(μ-dppf)(CO)<sub>7</sub>] (Figure 11) and [Ru<sub>3</sub>(μ-Se)<sub>2</sub>(dppf)(CO)<sub>7</sub>] (Figure 12) as the main products.<sup>30</sup> Figure 11 shows a bridging ligation whereas Figure 12 depicts a chelation coordination to metal cluster.

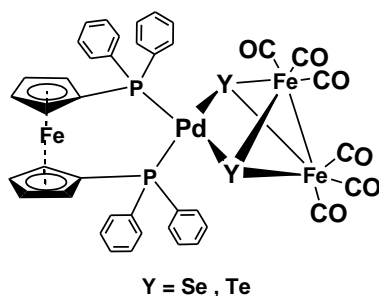


**Figure 11:  $[\text{Fe}_3(\mu\text{-Se})_2(\mu\text{-dppf})(\text{CO})_7]$ , Ferrocene as bridging ligand**



**Figure12:  $[\text{Ru}_3(\mu\text{-Se})_2(\text{dppf})(\text{CO})_7]$ , Ferrocene as chelating ligand**

Another interesting example of unusual chelating coordination by ferrocenyl-diphosphine ligand attached to a particular metal ion has been observed in the room temperature reaction of  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}(\text{PPh}_3)_2]$  ( $\text{Y} = \text{Se}, \text{Te}$ ) with bis(diphenylphosphino)ferrocene (dppf). Resulting in ferrocenyldiphosphine containing iron palladium clusters  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}\{\text{PPh}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2\})]$  ( $\text{Y} = \text{Se}, \text{Y} = \text{Te}$ ), structural characterization reveals an unusual chelating coordination by ferrocenyldiphosphine ligand attached to palladium atom (Figure-20).<sup>25</sup>



**Figure 13:**  $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}\{\text{PPh}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2\})]$

The recently explored phosphine and ferrocene containing metal cluster has shown a variety of application in various field of science. Due to their electroactive properties and their probable applications in the electrochemical reactions and sensors we have concentrated our work on the incorporation of phosphine and ferrocene in cluster moiety so that the various probable application of the synthesized compound could be observed.

## **Chapter 2**

# **Metal clusters containing ferrocenyl diphosphine : Synthesis and Characterisation**

## 2.1. Introduction

The phosphine substitution chemistry of mixed-metal clusters<sup>30, 31</sup> has found significant recent research interest. The electronic environment of the clusters can be tuned by modifying the peripheral ligands, so the more pi acceptor carbonyl ligands can be replaced by the less pi accepting phosphines.

Fe,S,Se cluster complexes are also gaining importance in recent organometallic research as they are finding more and more biometric application models for the active sites of the [NiFe] and [NiFeSe] hydrogenases<sup>32-35</sup>. Li-Cheng Song research group has reported the preparation of linear NiS<sub>2</sub>-bridged diphosphine complexes containing two butterfly [Fe<sub>2</sub>SeS=C] cluster cores, where the dppf chelated to the nickel atom. This structurally unique cluster is prepared by the reaction of [(μ-RSe)(μ-CO)Fe<sub>2</sub>(CO)<sub>6</sub>][Et<sub>3</sub>NH] with excess of carbondisulfide followed by treatment with (dppf)NiCl<sub>2</sub> species Figure 14.<sup>36</sup>

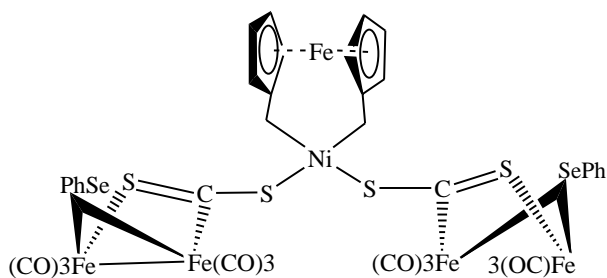


Figure :14

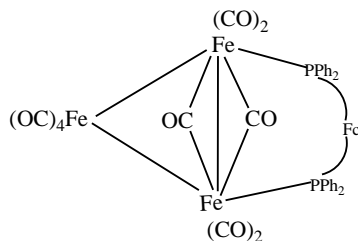


Figure 15:[Fe<sub>3</sub>(CO)<sub>8</sub>(μ-CO)<sub>2</sub>( μ , η<sup>2</sup>-dppf)]

Kim and Heo *et. al.* synthesized a dppf – iron cluster from a reaction between dppf and  $\text{Fe}_3(\text{CO})_{12}$  giving rise to  $\text{Fe}_3(\text{CO})_8(\mu\text{-CO})_2(\mu, \eta^2\text{-dppf})$  (Figure 23)<sup>37</sup>. Stein and Fujiwara have also recently carried out some electrochemical studies on two homonuclear iron-dppf clusters, *viz.*  $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2(\mu\text{-dppf})\text{Fe}(\text{CO})_4]$  and  $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu\text{-dppf})_7\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu\text{-dppf})]$  shows two irreversible waves corresponding to a two-electron reduction to give the radical anion  $[\{\text{Fe}_3(\text{CO})_9(\mu\text{-CO})_2\}_2(\mu\text{-dppf})]^{2-}$  the subsequent decomposition of this radical anion.(Figure16).

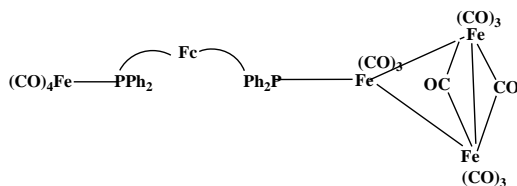


Figure: 16

In addition to those clusters that possess homonuclear iron core, Hor *et. al.* reported the sulfido-capped clusters  $[\text{Fe}_3(\text{CO})_7(\mu\text{-dppf})(\mu_3\text{-S})_2]$ ,  $[\text{Fe}_3(\text{CO})_8(\eta^1\text{-ddpf})(\mu_3\text{-S})_2]$ ,  $[\{\text{Fe}_3(\text{CO})_8(\mu_3\text{-S})_2\}_2(\mu\text{-dppf})]$ . (Figure 17,18 & 19)

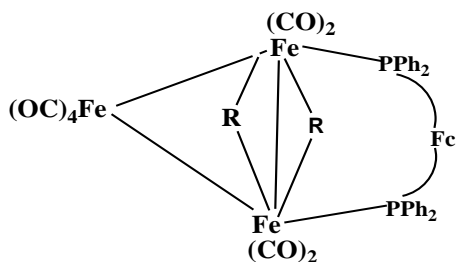


Figure: 17(R=S)  $\text{Fe}_3(\text{CO})_8(\mu_2\text{-dppf})(\mu_2\text{-S})_2$

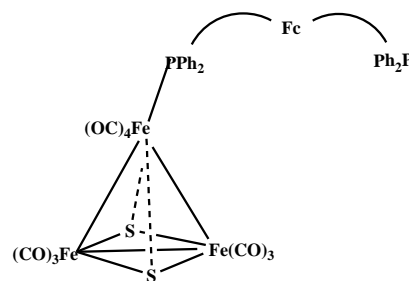
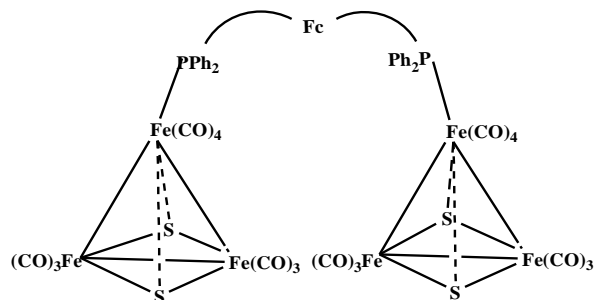


Figure: 18  $[\text{Fe}_3(\text{CO})_{10}(\eta^1\text{-ddpf})(\mu_3\text{-S})_2]$ ,





**Figure-19**  $[\text{Fe}_3(\text{CO})_8(\mu_3\text{-S})_2]_2(\mu\text{-dppf})$

The selenido-capped  $\{\text{Fe}_3\}$  clusters of dppf revealed their structural similarity with the sulfido-capped clusters,<sup>38</sup>

The ferrocenyl diphosphine unit incorporated into organometallic clusters are important due to their redox active properties associated with ferrocene fragment, as well as due their magnetic and optical properties<sup>39</sup>. Dppf has also been explored of possible applications in catalysis and materials science. The intrinsic skeletal flexibility of dppf as a ligand relieves some excessive strain imposed by complex formation and also it supports geometrically and structurally strained cluster molecules.

## 2.2. Experimental

### 2.2.1. General Procedures

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified argon using standard schlenk line techniques. Solvents were purified, dried and distilled under argon atmosphere prior to use. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I spectrometer as dichloromethane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a 400 MHz Bruker spectrometer in  $\text{CDCl}_3$ . Elemental analyses were performed on a Vario El Cube analyser. TLC plates (20x20 cm, Silica gel 60 F254) were purchased from Merck. Dppf and dppe were purchased from Sigma Aldrich.  $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$ ,  $[\text{Fe}_3\text{TeSe}(\text{CO})_9]$ , were prepared following reported procedures .

### 2.2.2 Synthesis of $Fe_3Te_2(CO)_8PPh_3$ (2)

A dichloromethane solution of  $[Fe_3Te_2(CO)_9]$  (1) (70mg, 0.127mmol) was reacted with Triphenyl phosphine (30 mg, 0.11mmol) at room temperature under continuous stirring condition and nitrogen atmosphere for 15 hours. The reaction was monitored by TLC. On completion of the reaction the solution was dried under vacuum and the residue was dissolved in dichloro methane solvent and subjected to chromatographic work-up using preparative TLC. Elution with dichloromethane/hexane (20:80v/v) solvent mixture separated the following compounds: unreacted  $[Fe_3(\mu_3-Te)_2(CO)_9]$  and a red compound  $[Fe_3(\mu_3-Te)_2(CO)_8\{PPh_3\}]$  (2). (Yield = 51mg , 60%). Trace amount of decomposition was also observed during the work-up.

2.. IR( $\nu_{CO}$ ,  $cm^{-1}$ ), 2052.11 (vs), 2012.73(vs), 1983.86( br), 1933.59(br)

### 2.2.3 Reaction of $Fe_3Te_2(CO)_8PPh_3$ with Dppf (Diphenylphosphinoferrocene)

A dichloromethane solution of  $[Fe_3(\mu_3-Te)_2(CO)_8 PPh_3]$  (60mg, 0.065 mmol) was reacted with bis-(diphenylphosphino) ferrocene (36 mg, 0.065mmol) at room temperature under continuous stirring condition and nitrogen atmosphere for 12hours. The reaction was monitored by TLC. On completion of the reaction the solution was dried under vacuum and the residue was dissolved in dichloromethane solvent and subjected to chromatographic work-up using preparative TLC. Elution with dichloromethane/hexane (30:70v/v) solvent mixture separated the following three compounds: Black product (3) (Trace), red,  $[Fe_3Te_2(CO)_8\{(PPh_2)(C_5H_4)Fe(C_5H_4)(PPh_2)\}]$  (4) (Yield = 24 mg, 25%) and red,  $[Fe_3Te_2(CO)_7\{(PPh_2)$

$(C_5H_4)Fe(C_5H_4)(PPh_2)\}$ ] (**5**) (Yield =37mg, 40%) and unreacted  $[Fe_3(\mu_3-Te)_2(CO)_8PPh_3]$ . Trace amount of decomposition was also observed during the work-up.

**4** :IR( $\nu_{CO}$ ,  $cm^{-1}$ ,  $CH_2Cl_2$ ): 2052.47(br), 2035.16(vs), 2009.46(vs), 1991.71(br),1968.23(br)}

**5**. IR( $\nu_{CO}$ ,  $cm^{-1}$ , $CH_2Cl_2$ ): 2037.7 (s), 1995.57 (vs), 1964.17 (s,br), 1953(s,br)

#### **2.2.4. Reaction of $Fe_3Te_2(CO)_9$ with Dppf (Diphenylphosphinoferrocene)**

A dichloromethane solution of  $[Fe_3(\mu_3-Te)_2(CO)_9]$  (**1**) (60mg,0.1 mmol) was reacted with bis-(diphenylphosphino) ferrocene(55 mg, 0.1 mmol) at room temperature under continuous stirring condition and nitrogen atmosphere for 12h. The reaction was monitored by TLC. On completion of the reaction the solution was dried under vacuum and the residue was dissolved in dichloromethane solvent and subjected to chromatographic work-up using preparative TLC. Elution with dichloromethane/hexane (30:70v/v) solvent mixture separated a red compound,  $[Fe_3Te_2(CO)_7\{(PPh_2)(C_5H_4)Fe(C_5H_4)(PPh_2)\}]$  (**5**) (Yield =56mg, 60%) along with unreacted  $Fe_3Te_2(CO)_9$  and trace amount of decomposition during the work-up.

**5**:IR( $\nu_{CO}$ ,  $cm^{-1}$   $CH_2Cl_2$ ): 2038.41.7(vs),1995.47(s,br), 1964.17(br).

## 2.3 Results and Discussions

The Tellurium, bridged cluster,  $[\text{Fe}_3\text{Te}(\text{CO})_9]$  (**1**) when stirred with equimolar amount of  $\text{PPh}_3$  in dichloromethane solvent at room temperature, mono substituted product (**2**) is formed. (Scheme- 1a) The product was isolated in PET:DCM solvents by TLC plates. The cluster (**2**)  $[\text{Fe}_3\text{Te}_2(\text{CO})_8(\text{PPh}_3)]$  was stirred with equimolar amount of bis-(diphenylphosphino) ferrocene in DCM solvent overnight in nitrogen atmosphere to obtain three products (black(**3**), red(**4**) and red (**5**) products are formed (Scheme- 1b). They are also isolated in PET: DCM solvents by TLC plates.

A possible reaction pathway can also be proposed for the transformation of compound **1** to compound **5** (Scheme- 2). It is formed by the substitution of triphenylphosphine group and one carbonyl group of the same basal Iron atom by the two phosphorus atom of the dppf ligand.

The selenium and tellurium, bridged cluster,  $[\text{Fe}_3\text{SeTe}(\text{CO})_9]$  (**7**) when stirred with equimolar amount of dppf in dichloromethane solvent at room temperature, in nitrogen atmosphere to obtain three products black(**8**), red(**9**) and red (**10**) products are formed. They are also isolated in PET: DCM solvents by TLC plates .

The diphosphine compound of the mixed chalcogen compound is obtained by the reaction of selenium & tellurium compound,  $[\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-Te})(\text{CO})_9]$  (**7**) with bis(diphenylphosphino)ferrocene for 15 h under inert atmospheric condition results in the formation of grey (**8**), red  $[\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-Te})(\text{CO})_8\{\text{PPh}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2\}](\mathbf{9})$  and red  $[\text{Fe}_3(\mu_3\text{-Se})(\mu_3\text{-Te})(\text{CO})_7\{\text{PPh}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2\}](\mathbf{10})$  (Scheme 3)

## 2.4. Conclusion

Coordination behaviour of diphosphine ligands for different types of metal clusters have been studied resulting in the control synthesis of clusters containing unique diphosphine attachment to either one metal or two metal of a cluster unit. Two types of diphosphine coordinated metal clusters have been obtained, one having chelating mode of bonding and the other is normal monodentate co-ordination. Synthesis and characterization of ferrocene containing mixed chalcogen atoms,  $[\text{Fe}_3\text{SeTeCO}]_7\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}$  has been achieved in which a diphosphine ligand is attached forming a chelating coordination with the iron atoms of the cluster. Compounds **4-8** have been formed possibly by the substitution of the  $\text{PPh}_3$  groups by one of the phosphorus atoms of the diphosphine ligands resulting in the formation of monodentate phosphine cluster and subsequently substitutes a carbonyl group to form chelating type of coordination around the iron metal centre.

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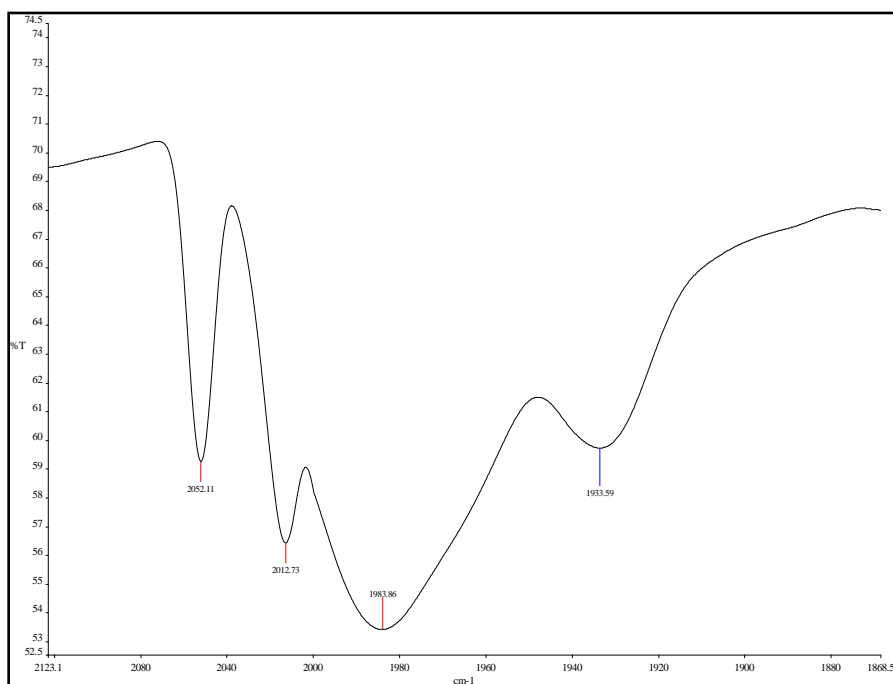


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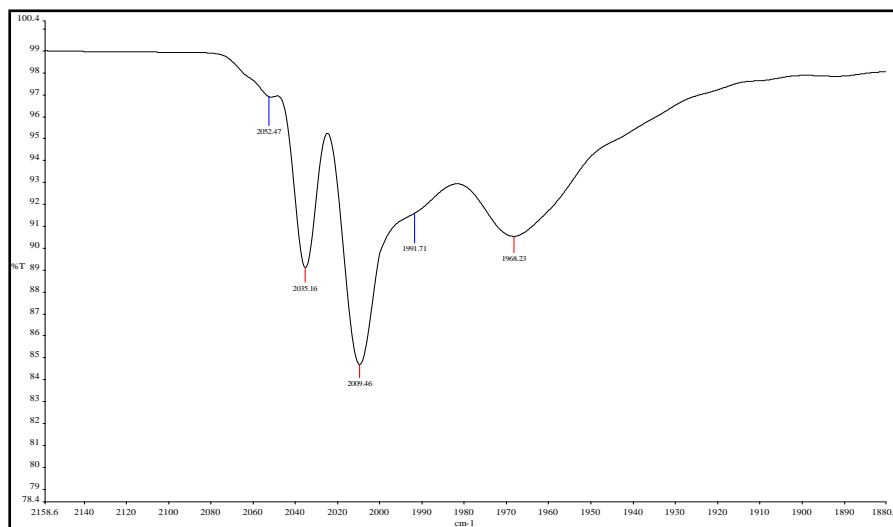
## Annexure

(For clarity carbonyl region has been shown)

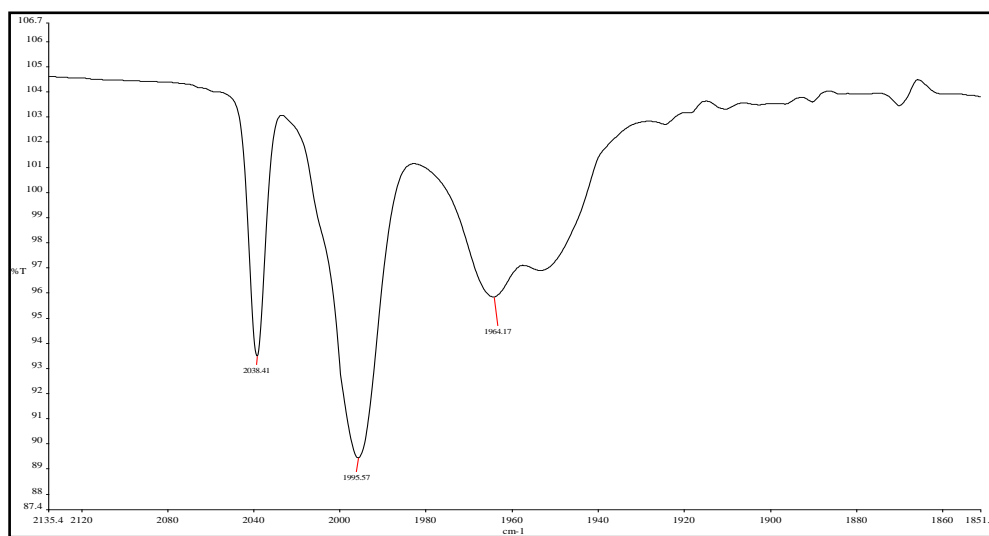
IR spectra of  $[\text{Fe}_3\text{Te}_2(\text{CO})_8(\text{PPh}_3)]$  (2)



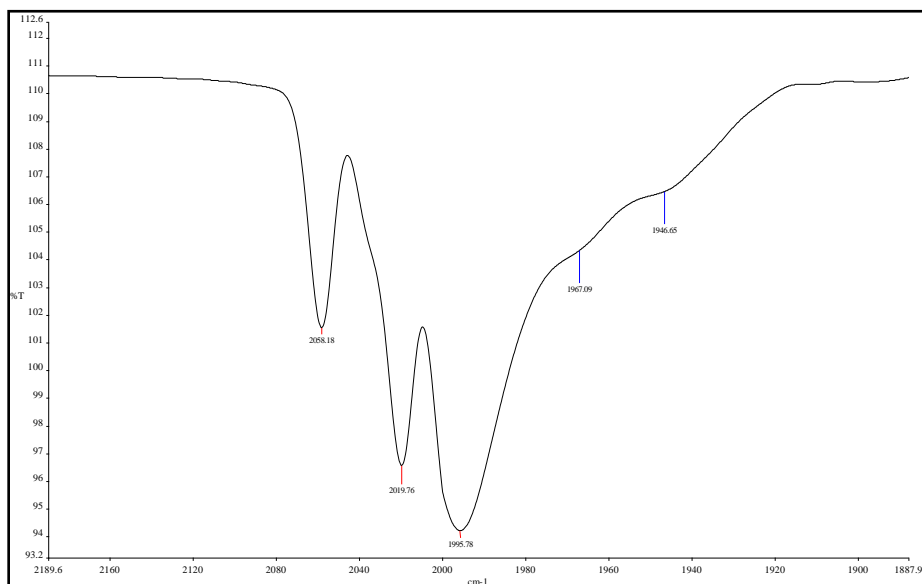
IR spectra of  $\text{Fe}_3\text{Te}_2(\text{CO})_8\{(\text{Ph}_2\text{P})\text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\text{Ph}_2\text{P})\}$  (4)



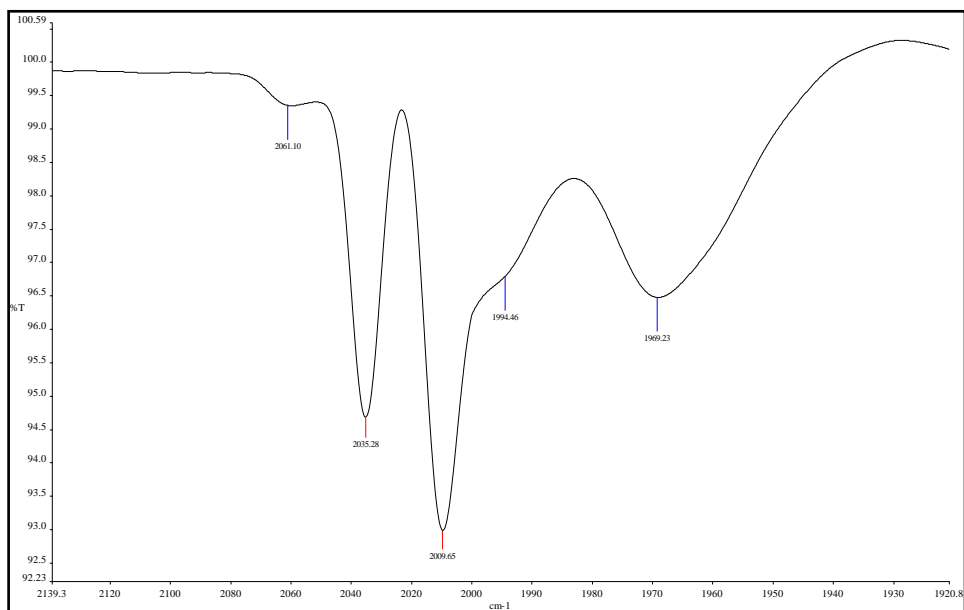
**IR spectra of  $\text{Fe}_3\text{Te}_2(\text{CO})_7\{(\text{Ph}_2\text{P})_2\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{Ph}_2\text{P})\}$  (red) (5)**



**Grey 8**



$\text{Fe}_3\text{SeTe}(\text{CO})_8 \{(\text{Ph}_2\text{P})\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{Ph}_2\text{P})\}$  red (9)



Ir spectra of  $\text{Fe}_3\text{SeTe}(\text{CO})_7 \{(\text{Ph}_2\text{P})\text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2(\text{Ph}_2\text{P})\}$  red (10)

