

TRANSITION METAL CLUSTERS CONTAINING FERROCENYL DIPHOSPHINE

A Dissertation

FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

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CERTIFICATE

This is to certify that the dissertation entitled “**TRANSITION METAL CLUSTERS CONTAINING FERROCENYL DIPHOSPHINE**” being submitted by **Suvendu Kumar Barik** 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)

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Rourkela

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DECLARATION

I hereby declare that the research work incorporated in this dissertation entitled “**TRANSITION METAL CLUSTERS CONTAINING FERROCENYL DIPHOSPHINE**” is an original research work carried out by me in Chemistry department, Nation Institute of Technology Rourkela under the supervision of Dr. Saurav Chatterjee.

Date:

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CHAPTER 1

INTRODUCTION

1.1. Transition Metal Clusters

A transition metal cluster contains two or more transition metal atoms bonded by direct or substantial metal-metal bonding and forms a three dimensional polyhedral geometry. The transition metals bridged by main group elements form especially robust cluster and they constitute link between homogeneous and heterogeneous catalysis. Transition metal clusters show high activity in heterogeneous catalysis and selectivity in the homogeneous catalysis [1]. Literature survey shows the presence of some cluster complexes in various enzymes such as hydrogenase and their activity in biocatalysis [2] (Figure 1.1). Clusters have also been used as potential candidate in the area of material science and in advanced opto-electronic materials for their non-linear optical property [3].

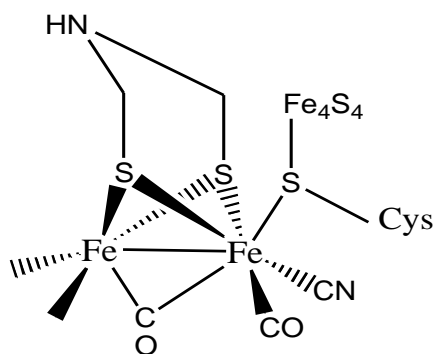


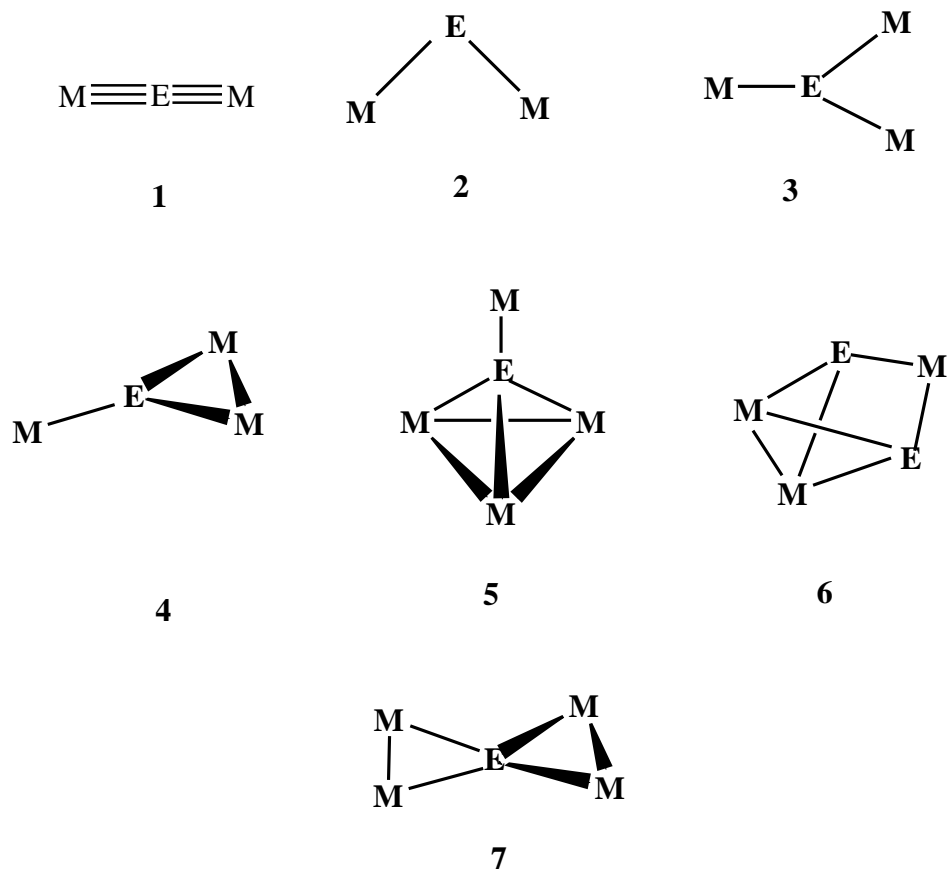
Figure 1.1: Proposed active site structure of the [Fe-Fe] hydrogenase enzyme

Some metal cluster contains π -donor ligands like cyclopentadienyl, alkene, alkyne, known as π -donor cluster having high oxidation state metal atom. The transition metal cluster which contains π -acceptor ligands like CO, PPh₃ are known as π -acceptor clusters with low oxidation state metal fragments. The transition metal clusters containing the CO ligand are found to bind with metals in a variety of bonding modes and other ligands like phosphine, halides, isocyanides, alkenes and hydrides also stabilizes the clusters. The clusters act as "electron reservoirs" and can access to multiple redox states as the number of metals increases. It has been seen that clusters can undergo rearrangement through the breaking of the metal-metal bond thereby allowing for the organic substrate to react with an accessible coordination site on the metal leading to organic transformations [4]. It has been studied that clusters can effectively catalyze reactions in

biphasic medium so that the fragments remains in the aqueous phase and the organic substrates remain in the organic phase [5].

1.2. Main group elements in Transition metal clusters

Clusters are described as models for intermediate in catalysis and are also used as catalysts. From the recent research development it has been found that many transition metal clusters are unstable and degrade when studied for organic transformation and catalysis. The main group elements can be used as bridging elements forming the framework of the clusters which are necessary for catalysis. The main group elements can be used as promoters to give higher yields and better selectivity in many commercial catalytic reactions and also act as sites for reactivity. Various research groups have proved in the field of cluster chemistry that these materials consists of nonlinear optical properties for their probable application in optoelectronics [6]. The formation of metal-metal bond is related to the size of the central main group element which helps in their stability. The smaller main group elements helps in metal-metal bonding while heavier main group elements generally bridge more open structures. The substituent on main group elements and the mode of binding are responsible for the number of electrons contributed to the clusters by main group fragments necessary for stabilizing the clusters. The bridging ligand is preferred to promote the formation and stabilization of transition metal cluster complexes [7-10]. The main-group elements incorporated into transition-metal carbonyl clusters enhance the structural and reactivity features. The main-group-element ligand can be used to bridge between different metal fragments in cluster growth reactions.



E=Group,13-16 elements,M=Transition metals

Figure 1.2: Structural geometries of transition metal cluster with main group elements.

Adams et. al. had reported recently the main group element containing rhenium cluster $[\text{Re}(\text{CO})_4-(\mu\text{-BiPh}_2)]_3$ by heating $[\text{Re}_2(\text{CO})_8\text{Bi}_2\text{Ph}_4]$ (Figure 1.3) [11].

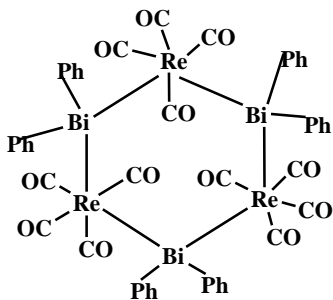


Figure 1.3. $[\text{Re}(\text{CO})_4(\mu\text{-BiPh}_2)]_3$

1.3. Chalcogenide metal clusters

Incorporation of the chalcogen as bridging ligand into the clusters unit results in the formation of unique structural features and unusual reactivities [12]. Chalcogen elements and transition-metal combine together to form cluster units showing interesting geometries and forming new coordination and thereby acting as precursors for synthesis of new materials [13-15]. Chalcogen ligand show a wide variety of bonding modes when these are incorporated into transition metal carbonyl cluster frameworks. Chalcogen are used in metal cluster as these ligand bridges with metals thereby preventing the degradation of the fragments as the clusters are usually susceptible during catalytic processes [16]. The clusters containing the bond between transition metal and group-16 elements such as S, Se, and Te are subjected to recent studies as these main group elements act as bridges between different metal atoms in clusters and also helps in stabilizing ligand which prevent their fragmentation. Chatterjee et al very recently discussed room temperature reactions of dppe with metal clusters $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9]$, $[\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_8\text{PPh}_3]$ to obtain different types of chalcogenide metal-phosphine clusters, one of them showing the bridging mode where two cluster unit are attached by the dppe unit $[(\text{CO})_{18}\text{Fe}_6(\mu_3\text{-Te})_4\{\mu\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$ (Figure 1.4) [17].

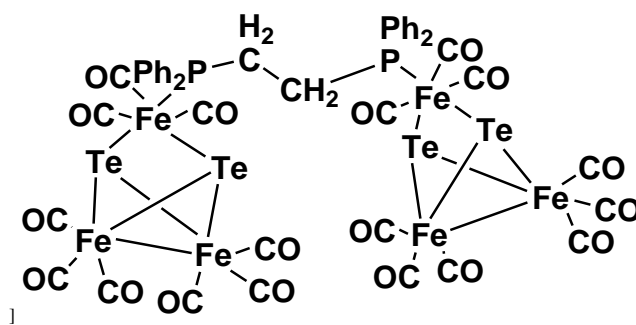


Figure 1.4. $[(\text{CO})_{18}\text{Fe}_6(\mu_3\text{-Te})_4\{\mu\text{-PPh}_2(\text{CH}_2)_2\text{PPh}_2\}]$

1.4. Phosphine incorporated transition metal cluster

Phosphines, PR_3 , are the ligands in which the electronic and steric properties can be adjusted in a desired way over a wide range by varying the organic group (R) [18]. Various

research groups were involved in the synthesis of transition metal clusters containing phosphine ligands by ligand substitution reaction of the carbonyl containing metal clusters [19-23]. Several metal catalysts contain mono and bidentate phosphine ligands which are very important in Heck, Suzuki and Buchwald-Hartwig cross coupling reactions as the choice of proper phosphines at the metal centers of the catalysts influences the reactivity of the participating species in the catalytic cycle [24-27]. The phosphines are classified into monodentate phosphine with only one phosphorus atom binding to the metal center of the cluster unit, bidentate phosphines when two phosphorus atoms are linked to metal atoms of the cluster unit and polydentate phosphines with more than two phosphorus atoms binding to the metal centres of the cluster unit. The common monodentate ligands like triarylphosphines, tricyclohexylphosphine, tri(*tert*butyl)phosphine and trimethyl phosphine are of much interest as the chiral monodentate phosphines are found to be very effective in asymmetric homogenous catalysis [28](Figure 1.5). The tertiary phosphine ligands co-ordinate with the late metal centers of the metal complexes as they stabilize the low-valent metal intermediates thus allowing high activity of the catalysts. They react with the metal clusters and possess simple terminal, edge-bridged and face-capped positions for facile P-C bond formation and cleavage, so that metal skeletal transformations can be understood. Hence, the bonding modes adopted by phosphine ligand upon co-ordination are explored largely.

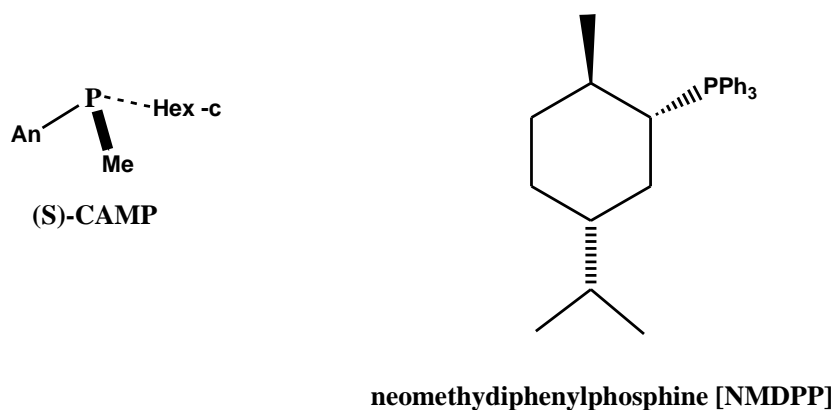


Figure 1.5. Monodentate phosphine

Literature survey shows that phosphine ligands play a major role for the synthesis of polynuclear units of the clusters. Low temperature reaction of PBU₃ with triosmium clusters led to the formation of mononuclear complexes Os(CO)₄(PBU₃) and Os(CO)₃(PBU₃)₂. Adam's et al.

reported a heterometallic platinum-osmium cluster complex, $[\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{P}^t\text{Bu}_3)_2]$ in which two monodentate phosphines are bonded to the platinum metal centres (Figure 1.6) [29].

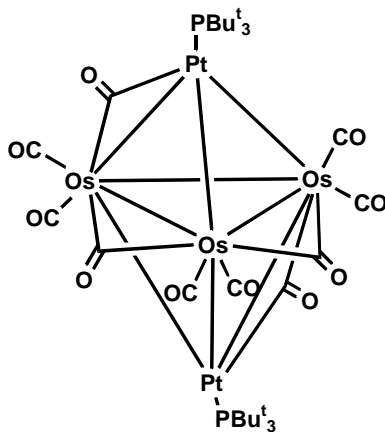


Figure 1.6. $[\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{P}^t\text{Bu}_3)_2]$

Shawkataly et al. recently reported six trinuclear substituted complexes of the type $[\text{Ru}_3(\text{CO})_9(\text{arphos})(\text{L})]$ synthesized from the substitution reaction involving $[\text{Ru}_3(\text{CO})_{10}(\text{arphos})]$ with various monodentate phosphine ligands like PCy_3 , PPh_3 , $\text{P}(\text{C}_6\text{H}_4\text{F-m})_3$, $\text{P}(\text{C}_6\text{H}_4\text{F-p})_3$, $\text{P}(\text{C}_6\text{H}_4\text{Cl-p})_3$ and $\text{PPh}(\text{C}_6\text{H}_4\text{OMe-p})_2$ using the thermal synthetic method (Figure 1.7) [30].

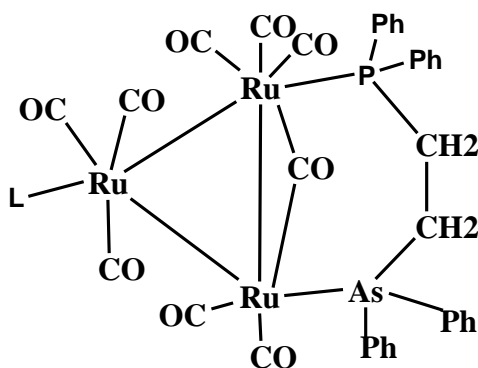


Figure 1.7. $[\text{Ru}_3(\text{CO})_9(\text{arphos})(\text{L})]$

$\{\text{L} = \text{PCy}_3, \text{PPh}_3, \text{P}(\text{C}_6\text{H}_4\text{F-m})_3, \text{P}(\text{C}_6\text{H}_4\text{F-p})_3, \text{P}(\text{C}_6\text{H}_4\text{Cl-p})_3, \text{PPh}(\text{C}_6\text{H}_4\text{OMe-p})_2\}$

Bidentate ligands like diphosphines give support to the multimetallic framework and also help to bind two or more cluster fragments resulting in cluster stability and structural diversity of higher nuclear cluster. Some diphosphine ligands used in cluster substitution reaction have been shown in Figure 1.8.

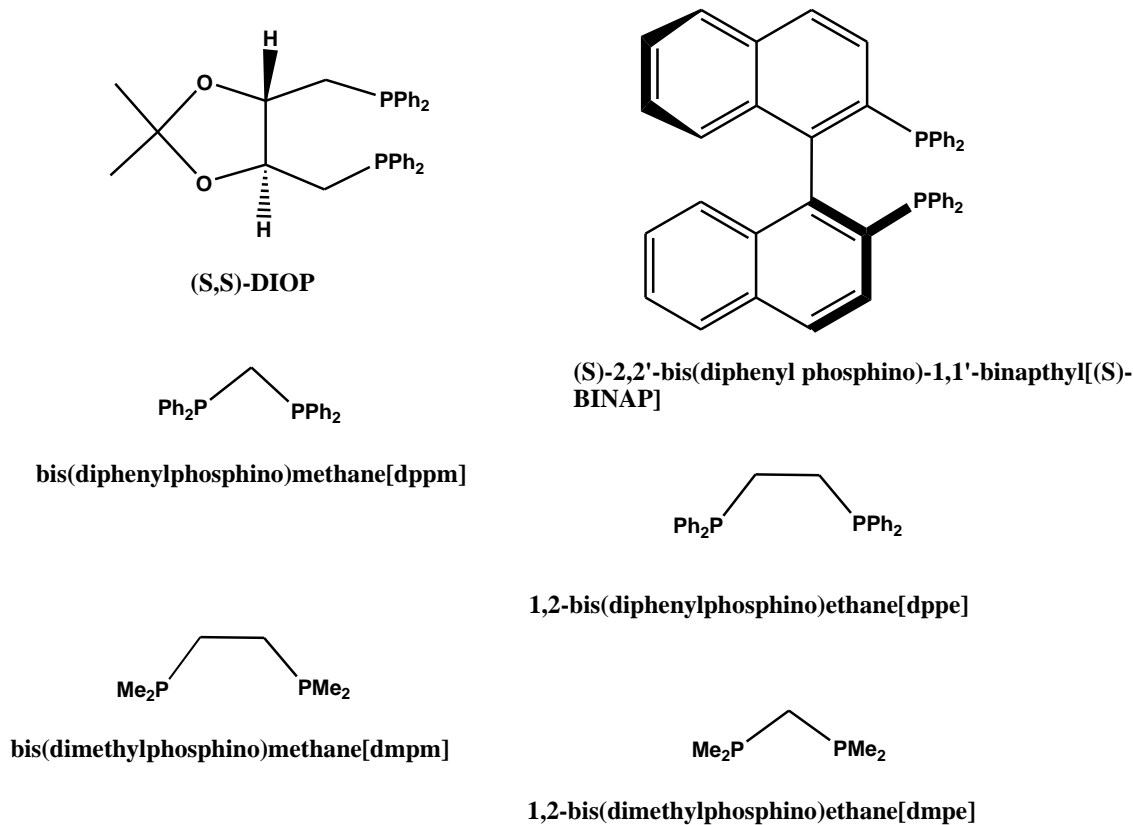


Figure 1.8. Different types of bidentate phosphine ligands

Research group of Zavras reported the structure of $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3-Cl)(\mu-H)]BF_4$ in which $[Ag(\mu-Cl)(\mu_3-H)]$ core is found to be tetrahedral and the two phosphorus atoms of the dppm ligands binds the Ag metals in intra-bridging mode (Figure 1.9) [31].

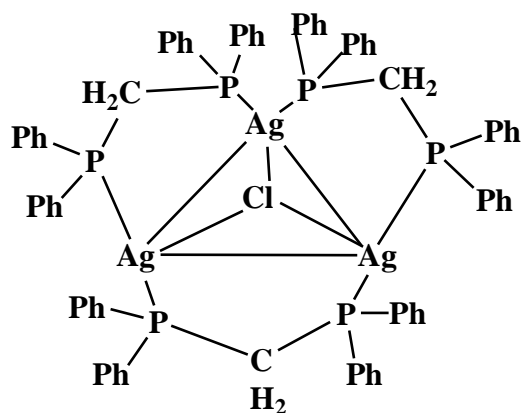


Figure 1.9. $[\text{Ag}_3\text{-}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}_3(\mu_3\text{-Cl})(\mu\text{-H})]\text{BF}_4$

Zhang et al. studied the tricobalt cluster, $[\text{PhCCO}_3(\text{CO})_9]$ which undergoes facile ligand substitution with 1,8-bis(diphenylphosphino)naphthalene (dppn) forming the cluster containing a chelating dppn ligand, $[\text{PhCCO}_3(\text{CO})_4(\mu\text{-CO})_3(\text{dppn})]$ involving three bridging CO groups in the solid state structure (Figure 1.10) [32].

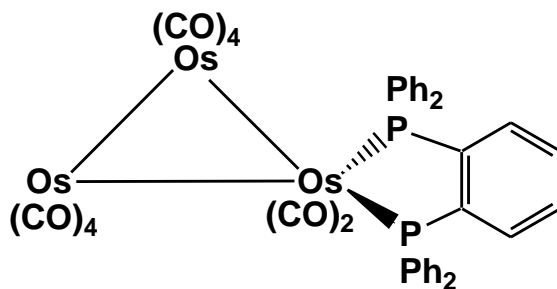


Figure 1.10: $[1,1\text{-Os}_3\text{-(CO)}_{10}(\text{dppbz})]$

1.5. Cluster containing ferrocenyl diphosphine

(a) *Homonuclear*

Homonuclear clusters contain same type of metal in its cluster cage. These homonuclear cluster containing ferrocene have very important due to its potential application in biosensors, catalysis etc. The complex $[\text{Pd}_3(\mu\text{-dppf})(\text{dppf})(\mu_3\text{-S})_2\text{Cl}_2]\cdot 2\text{CH}_2\text{Cl}_2$ reported by Yeo and group

shows dppf coordinating the cluster unit in both the chelating and bridging mode (Figure 1.11) [33].

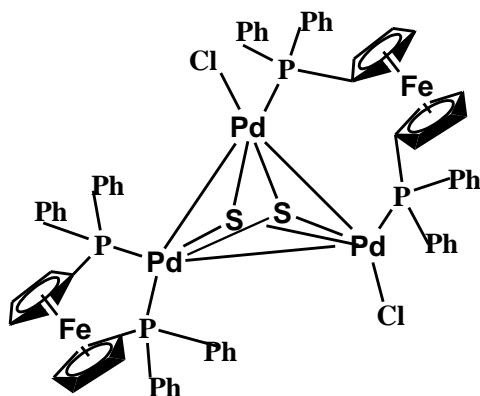


Figure 1.11. $[\text{Pd}_3(\mu\text{-dppf})(\text{dppf})(\mu_3\text{-S})_2\text{Cl}_2] \cdot 2 \text{CH}_2\text{Cl}_2$

The complex $[\text{Co}_2(\eta^1\text{-dppf})(\mu^2\text{-(MeO}_2\text{C)}_2\text{C}_2)(\text{CO})_5]$ is the sole structure containing an η^1 -coordinating dppf reported by McAdam group [34]. Zhuravel group discussed the diphosphine ligand which has an anticlinal eclipsed arrangement, with an angle of 154.9° in $[\text{Pt}_2(\text{dppf})_2(\mu\text{-H})(\mu\text{-pms})]\text{Br}$, which is a dinuclear μ -alkylidene μ -hydride cation, where each dppf behaves as η^2 -chelating and assumes a synclinal staggered conformation (Figure 1.12) [35].

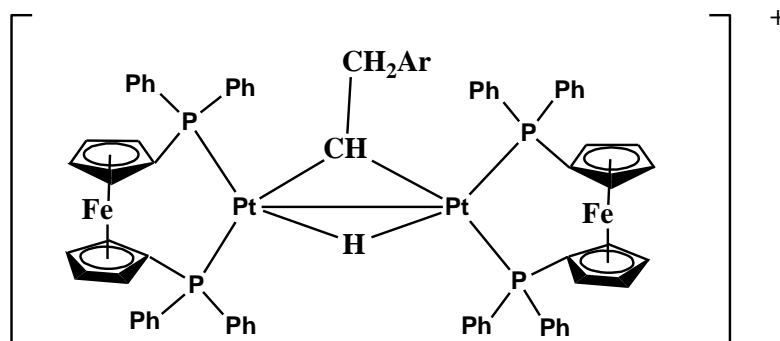


Figure 1.12. $[\text{Pt}_2(\text{dppf})_2(\mu\text{-H})(\mu\text{-pms})]^+$

The complex, $[\text{Au}_2(\text{dppf})(\mu\text{-pdt})]$, is an η^1, η^1 -intra-bridging cluster complex, although the Au–Au separation in this molecule (3.060(1) Å,) is considered a bond, it is very much long as compared to other clusters (Figure 1.13) [36].

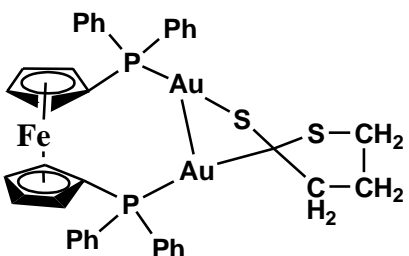


Figure 1.13. $[\text{Au}_2(\text{dppf})(\mu\text{-pdt})]$

(b) Hetero nuclear

Heterometallic clusters are compounds having two or more different metals forming the cluster core. Group 14 element containing transition metal clusters have been studied by Mackay v, Lewis and Braunstein [37-39]. The heterometallic clusters are interesting due to their synthetic studies and structural bonding pattern and their application in the field of catalysis. Nyholm et al. described the first heterometal gold cluster, $[\text{Au}_2\text{Fe}(\text{CO})_4(\text{PPh}_3)_2]$, Collins et al. synthesised $[\text{Au}_2\text{Ru}_3(\mu_3\text{-S})(\mu\text{-dppf})(\text{CO})_9]$ having the metal framework containing trigonal bipyramidal or distorted trigonal bipyramidal Au_2Ru_3 groups (Figure 17) [40].

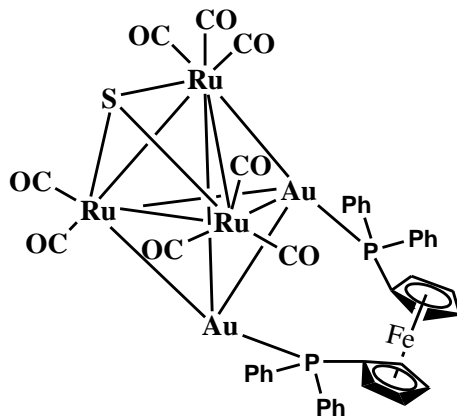


Figure 1.14. $[\text{Au}_2\text{Ru}_3(\mu_3\text{-S})(\mu\text{-dppf})(\text{CO})_9]$

In one of the very recent cluster $[\text{Hg}\{\text{Fe}[\text{Si}(\text{OMe})_3](\text{CO})_3(\text{dppm})\}_2\text{Pd}]$, an unusual Fe-Hg-Pd bond, with a palladium (0) fragment has been observed. The cluster was prepared from the reaction of complex $[\text{Hg}\{\text{Fe}[\text{Si}(\text{OMe})_3](\text{CO})_3(\text{dppm})\}_2]$ with $[\text{Pd}_2(\text{dba})_3]$. The compound has been stabilized by an unusual heterometallic Pd-Hg bonding with d10–d10 interaction (Figure 1.15) [41].

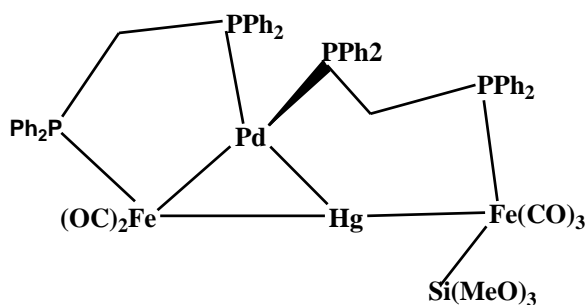


Figure 1.15. $[\text{Hg}\{\text{Fe}[\text{Si}(\text{OMe})_3](\text{CO})_3(-\text{dppm})\}_2\text{Pd}]$,

1.6. Ferrocenyl diphosphine substituted metal chalcogen clusters

Ferrocene containing chalcogen metal clusters has shown a rapid interest. Various methodologies and substitution effects has been observed on this cluster moiety in order to study the substitution effects on triangular clusters $\text{M}_3(\mu\text{-S}_2)(\text{CO})_9$ based on the stabilizing effect exerted by capping sulfide ligands. The isosceles triangle provides a model for the study of coordination 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 catalytic value and their electroactivity and thermolytic products. Hor and coworkers isolated a tripalladium compound with an Pd_3S_2 core shaped in an intriguing 'Mexican-hat like' arrangement [42]. The Pd_3S_2 core can be obtained through metallation of a Pd_2S_2 nucleus, similar to the one obtained for $[\text{Pd}_2\text{Ag}_2(\text{dppf})_2(\mu_3\text{-S})_2\text{Cl}_2]$ [43]. The dppf ligand exhibits fluxional behavior, despite its large steric bulk and the stability is

imposed on the Pd₃S₂ core by the triply bridging sulfides. This allows the cooperative rearrangement of the two dppfs on the Pd₃ triangle.

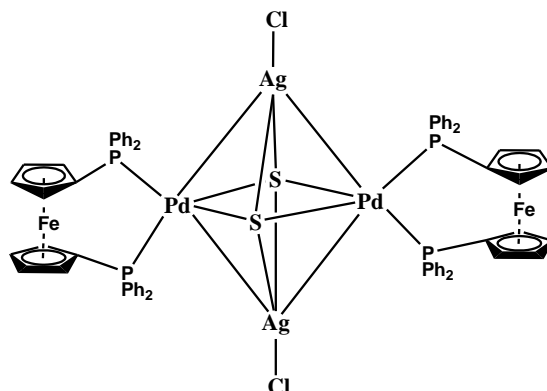


Figure 1.16: [Pd₂Ag₂(dppf)₂(μ₃-S)₂Cl₂] showing dppf in chelating mode

The carbonyl exchange reaction of Fe₃(μ-S₂)CO₉ with 1,1'-bis(diphenylphosphino)ferrocene (dppf) in refluxing solvent gives a cluster ligand with a pedant phosphine moiety, [Fe₃(μ-S₂)CO₉(η¹-dppf)]. It has also been observed that under different reaction conditions, a variety of different substitutions products are obtained, although bridged cluster forms only in trace quantity (Figure 1.17) [44]

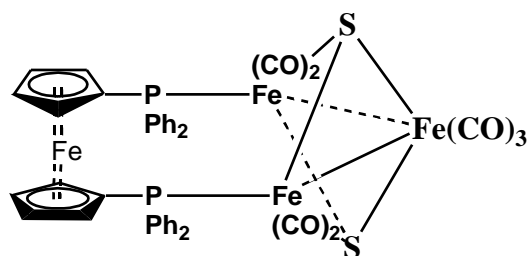


Figure 1.17. [Fe₃S₂(CO)₈(PPh₂)₂(C₅H₄)Fe(C₅H₄)]

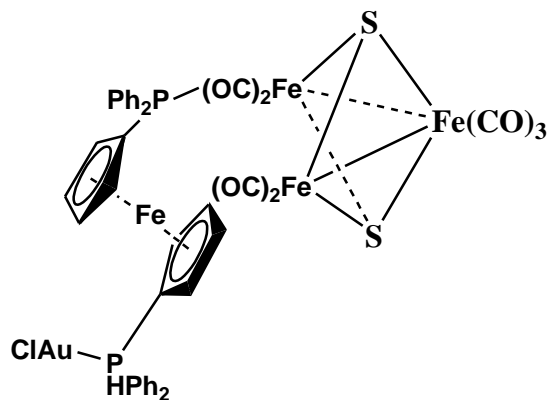


Figure 1.18. $[\text{Fe}_3\text{S}_2(\text{CO})_8(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Au}(\text{PPh}_2)]$

One of the recent synthesis has shown that 1,1'-bis(diphenyl phosphine)ferrocene diselenide (dppfSe_2) with $[\text{Fe}_3(\text{CO})_{12}]$ and $[\text{Ru}_3(\text{CO})_{12}]$ under the same reaction condition afforded $[\text{Fe}_3(\mu\text{-Se})_2(\mu_2\text{-dppf})(\text{CO})_7]$ and $[\text{Ru}_3(\eta^2\text{-Se})_2(\text{dppf})(\text{CO})_7]$ respectively [45]. Figure 1.19 shows a bridging ligation whereas Figure 1.20 depicts a chelation coordination to metal cluster.

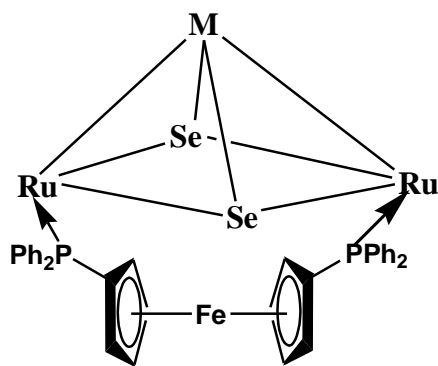


Figure 1.19. Bridging mode of $[\text{Fe}_3(\mu_2\text{-Se})_2(\mu\text{-dppf})(\text{CO})_7]$

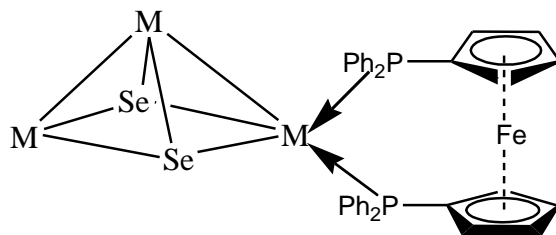


Figure 1.20. Chelating mode of $[\text{Ru}_3(\eta^2\text{-Se})_2(\text{dppf})(\text{CO})_7]$

Another interesting example of unusual chelating coordination by ferrocenyl-diphosphine ligand attached to a particular metal ion has been reported by Chatterjee et al. in which it is observed that 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 ferrocenyl diphosphine 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 ferrocenyl diphosphine attached to palladium atom (Figure 1.21) [25].

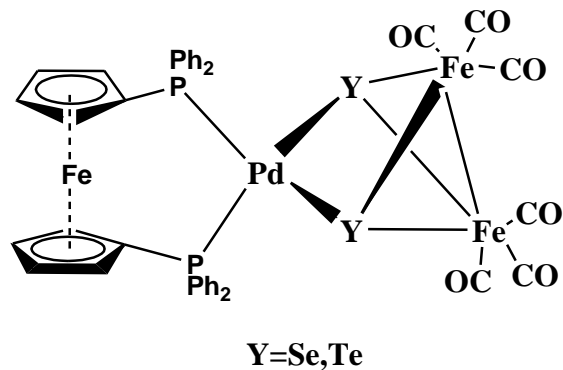


Figure 1.21. $[(\text{CO})_6\text{Fe}_2(\mu_3\text{-Y})_2\text{Pd}\{\text{PPh}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{PPh}_2\}]$ (Y=Se, Y=Te)

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CHAPTER 2

TRANSITION METAL CLUSTERS CONTAINING FERROCENYL DIPHOSPHINE

2.1. Introduction

Transition metal cluster containing non-metal atoms as bridging element are gaining a lot of research interest, as they show unique structures and novel chemical reactivity, and also they find application in the field of material science and catalysis [1-4]. When the chalcogens are incorporated in transition metal carbonyl cluster frameworks a wide variety of bonding modes are observed which help them to obtain novel structural and reactivity features [5,6]. The iron chalcogenide clusters, $[\text{Fe}_3(\text{CO})_9(\mu\text{-E}_2)]$ and $[\text{Fe}_2(\text{CO})_6(\mu\text{-E})_2]$ (E= S, Se, Te) are used as the starting materials for several cluster growth reactions [7-10]. Carbonyl ligands are one of most common ligands in metal cluster chemistry leading to stabilization of low oxidation state metal cluster compounds. Other ligands like phosphines attached to the transition metals are found to be very important in maintaining the electronic and steric properties over a very wide range by varying the organic group (R) [11]. So the researchers in the field of metal clusters focus more on the synthesis of transition metal clusters containing phosphine ligands, obtained mostly by ligand substitution reaction of the carbonyl analogue [12-16]. The diphosphines help in maintaining the multimetallic framework as well as help in attaching two or more cluster fragments resulting in cluster stability and structural diversity of higher nuclear cluster. Some of these phosphine ligands play a major role for the synthesis of polynuclear metal clusters by linking two or more cluster fragments [17-18]. 1,1'-bis(diphenylphosphino)ferrocene (dppf) was first synthesized in 1965 by the lithiation of ferrocene with n-butyllithium followed by condensation with chlorodiphenylphosphine in the presence of *N, N, N', N'*-tetramethylethylenediamine (TMEDA). The intimate relationship of clusters with polymetallic aggregates and oligomers has been extensively studied which enables dppf to find a place in stabilizing the clusters as well as in attaching two or more cluster fragments. The flexible diphosphine is an important member of the ferrocenylphosphine family. Dppf forms chelates to a single metal atom, but it can also act as a monodentate ligand or as a bridge across a metal-metal bond. F.F. de Biani et al. reported two isomeric nido-clusters $[\text{Ru}_3(\mu_3\text{-Se})_2(\text{dppf})(\text{CO})_7]$ and $[\text{Ru}_3(\mu_3\text{-Se})_2(\text{CO})_7(\mu\text{-dppf})]$ containing a dppf ligand in chelating and bridging mode and also these kinetically controlled chelated compounds can be converted to the more stable bridged cluster at high temperature (Figure 2.1) [19].

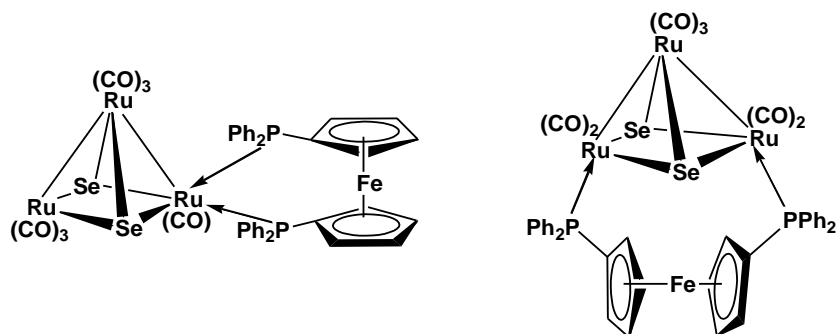


Figure 2.1 $[\text{Ru}_3(\mu_3\text{-Se})_2(\text{dppf})(\text{CO})_7]$ in chelating and bridging mode

Cauzzi et al. reported $[\text{Fe}_3(\mu_3\text{-Se})_2(\text{CO})_7\text{dppf}]$, it is described to have the bicapped open triangular structure with Fe_3Se_2 core and regarded as nido cluster with seven skeletal electron pairs (Figure 2.2) [20].

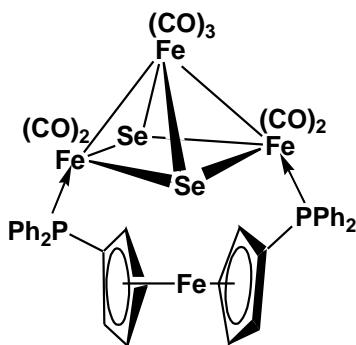


Figure 2.2: $[\text{Fe}_3(\mu_3\text{-Se})_2(\text{dppf})(\text{CO})_7]$ in bridging mode

Housecroft and Rheingold *et al.* described $\{\text{Ru}_4\text{B}\}$ -dppf cluster in which dppf adopts distinct pendant coordination modes in $[\text{Ru}_4(\text{CO})_{11}(\eta^1\text{-dppf})(\mu_4\text{-BH}_2)(\mu\text{-H})]$ (Figure 2.3) [21].

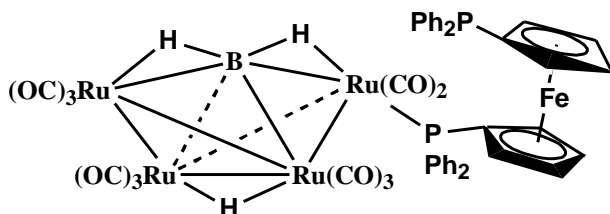


Figure 2.3: $[\text{Ru}_4(\text{CO})_{11}(\eta^1\text{-dppf})(\mu_4\text{-BH}_2)(\mu\text{-H})]$

Hor *et al.* discussed the cluster $[\text{Fe}_3(\text{CO})_8(\eta^1\text{-dppf})(\mu_3\text{-S})_2]$ containing a sulfido-bicapped $\{\text{Fe}_3\}$ triangular core, with dppf adopting pendant coordination mode. The cluster was synthesized from the respective $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})]$ by means of carbonyl exchange reactions in the presence of dppf (Figure 2.4) [22].

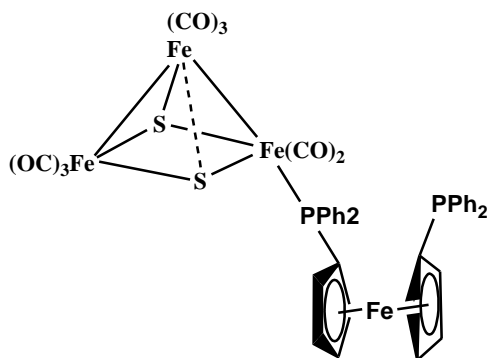


Figure 2.4: $[\text{Fe}_3(\text{CO})_8(\eta^1\text{-dppf})(\mu_3\text{-S})_2]$

Onaka *et al.* reported the structure of the $[\text{Co}_3(\text{CO})_8(\eta^1\text{-dppf})(\mu^3\text{-CCH}_3)]$ clusters which possess the trinuclear μ_3 -ethylidyne-capped $\{\text{Co}_3\}$ core, having a dppf in pendant mode [23]. It also functions as “filler” among different cluster fragments and helps in the design of multimetallic cluster (Figure 2.5).

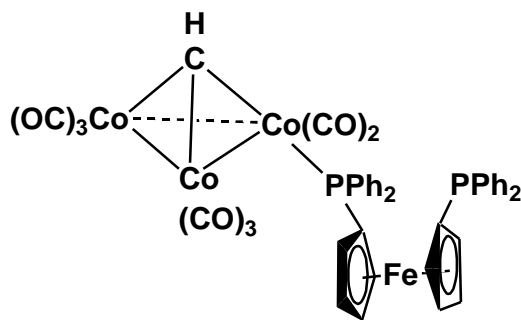


Figure 2.5. $[\text{Co}_3(\text{CO})_8(\eta^1\text{-dppf})(\mu^3\text{-CCH}_3)]$

In $[\text{Pd}_3(\mu\text{-dppf})(\text{dppf})(\mu^3\text{-S})_2\text{Cl}_2]$ the structure shows dppf coordinating the Pd metals in both chelated and bridging mode (Figure 2.6) [24].

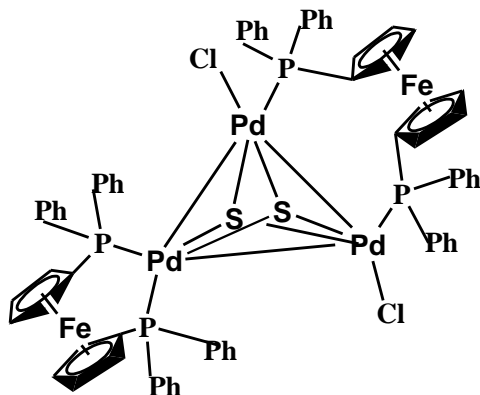


Figure 2.6. $[\text{Pd}_3(\mu\text{-dppf})(\text{dppf})(\mu^3\text{-S})_2\text{Cl}_2]\cdot$

In view of these interesting bonding features of ferrocenyl diphosphine in cluster chemistry, we focused our study on the synthesis of homo and heterometallic transition metal cluster containing chalcogen atoms and ferrocenyl diphosphine ligands in different bonding modes. We have also been able to use ferrocenyl diphosphine containing cluster for cluster growth reaction and obtained heterometallic cluster system.

2.2. Experimental Section

2.2.1. 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 dichloromethane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a 400 MHz Bruker spectrometer in CDCl_3 . TLC plates (20x20 cm, Silica gel 60 F254) and $\text{W}(\text{CO})_6$ were purchased from Merck. $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ and $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$, were prepared following reported procedures

2.3. Results and Discussion

The reaction of $[\text{Fe}_3\text{Te}_2(\text{CO})_9]$ with dppf at room temperature and under argon atmosphere results in the formation of trinuclear iron - chalcogenide ferrocenyl diphosphine clusters, $[\text{Fe}_3\text{Te}_2(\text{CO})_9\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}]$ (Te2Red3), while reaction at low temperature gave another red cluster $[\text{Fe}_3\text{Te}_2(\text{CO})_9\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}]$ (Te2Red1) containing a ferrocenyl diphosphine unit with monodentate coordination. The cluster (Te2Red1) has been observed to convert to the stable cluster (Te2Red3) on room temperature stirring. This shows that (Te2Red1) is an intermediate to the cluster (Te2Red3).

Similar reaction of $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ with dppf at room temperature gave only one black coloured cluster compound, $[\text{Fe}_3\text{Se}_2(\text{CO})_8\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}]$ (Se2Black1).

Further reaction of $[\text{Fe}_3\text{Se}_2(\text{CO})_8\{(\text{PPh}_2)(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_4)(\text{PPh}_2)\}]$ (Se2Black1) with $\text{W}(\text{CO})_5\text{THF}$ results in the formation $[\text{Fe}_3\text{Se}_2(\text{CO})_8(\eta^2\text{-dppf})\text{W}(\text{CO})_5]$.

2.4. Conclusion

Coordination behavior of ferrocenyl diphosphine ligands for different types of transition metal chalcogenide clusters and metal carbonyls have been studied resulting in the control synthesis of clusters containing unique diphosphine attachment to one metal of a cluster unit as well as with different metals. Three types of diphosphine coordinated metal clusters have been obtained, one having hanging uncoordinated phosphorus and other coordinated to the metal, chelated mode of bonding and the other is interbridging mode of bonding. Synthesis and characterization of ferrocene containing chalcogenide transition metal clusters (Te2Red1) and (Te2Red3), (Se2Black1) and (Se2BlackW(CO)₅) has been achieved in which (Te2Red1) and (Se2Black1) shows a diphosphine ligand attached to the metal cluster where one phosphorus is coordinated with the iron atoms of the cluster and the other phosphorus is hanging uncoordinated. Compound (Te2Red3) shows the diphosphine ligands in chelating type of bonding around the iron metal centre. Heterometallic cluster (Se2BlackW(CO)₅) shows a diphosphine ligand attached to the metal cluster where one phosphorus is coordinated with the iron atoms of the cluster and the other phosphorus is coordinated to the tungsten atom.

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