SYNTHESIS, CHARACTERIZATION AND APPLICATION OF PINCER COMPLEXES FOR C – C COUPLING

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

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DECLARATION

by the Ph.D. Research Scholar

I hereby *declare* that the Research Thesis entitled **“SYNTHESIS, CHARACTERIZATION AND APPLICATION OF PINCER COMPLEXES FOR C – C COUPLING”** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** in Chemistry is a *bonafide report of the research work carried out by me.* The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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CERTIFICATE

This is to *certify* that the Research Thesis entitled **“SYNTHESIS, CHARACTERIZATION AND APPLICATION OF PINCER COMPLEXES FOR C – C COUPLING”** submitted by Lolakshi Mahesh Kumar (Register Number: 135060CY13F02) as the record of the research work carried out by her is *accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of **Doctor of Philosophy**.

Research Guide
(Name and Signature
with Date and Seal)

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Dedicated to my Parents and

Parents in-law

Acknowledgments

A tree to bear fruits has to witness several wet and dry seasons and its worthiness lies in enduring all the nourishment and hardships evenhandedly. It is the contributions of several which makes a sapling grow into a plant and then into a tree which over a period of time becomes fruitful. Though this dissertation appears with my name, there are many contributors to this success who have lent their share in making this thesis possible and cherishable.

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ABSTRACT

Inorganic chemistry has gone through a colossal transformation and breakthroughs in the scientific field. The work of Alfred Werner in the development and understanding of coordination chemistry helped significantly to establish the importance of ligands in defining the properties of a central metal ion. Phosphine donor ligands and their chelates were developed as efficient new catalysts for organic transformations. In the midst of these developments, a meridional tridentate ligand emerged out of the initial work of Shaw and van Koten which unveiled and paved way to the pincer ligand as a strong contributor to the then established field of Inorganic chemistry. Pincer complexes possess unique metal bound structures which defines their desirable catalytic activity in organic transformations. Pincer compounds find major application as homogeneous catalysts and forms a major and an important segment of organometallic and coordination compounds.

The present research work is focused on synthesizing non-palladium pincer complexes with ‘P’ and ‘N’ based donors for cross-coupling of aryl halides with phenylboronic acid. In our effort to provide an alternative to the costly Pd-catalyzed reactions, this study has credited a substantial materialization of nonprecious metal catalysts for the Suzuki cross coupling reactions. The basic approach of research study was to synthesize pincer complexes as homogeneous catalysts for Suzuki coupling reactions. A very good catalytic efficiency was observed with the four series of pincer complexes synthesized and their fruitfulness motivated us to heterogenize the selective complexes to achieve recovery and reusability of the otherwise disposable active components. Six of the complexes displaying high catalytic activity were chosen and immobilized on aminofunctionalized solid substrate of graphene oxide and applied again as catalysts in the coupling reaction and their recovery and reusability was demonstrated. The ease of synthesis, use of nonprecious metals as an alternative to the expensive palladium metal, low catalyst loading, mild reaction conditions, good coupling yield, catalyst recovery through immobilization are few of the key attractions of the proposed catalytic system.

Keywords: Pincer complexes, Suzuki Miyaura cross coupling, biaryls.

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CHAPTER 1

INTRODUCTION

Chapter 1 covers a general introduction and literature review on catalysis which is inclusive of both the homogeneous and heterogeneous aspects. The basic properties of the pincer complexes, their immobilization on solid substrates and their role as catalysts in the cross-coupling reactions are addressed. Scope and objectives of the present work are also covered in this chapter.

1.1 CATALYSIS

1.1.1 Introduction to Catalysis

Catalysis is the phenomenon where an additive can alter the reaction rate without itself being consumed. The reaction rate is increased through a lowering of the activation barrier of the reaction. It can often catalyze the reaction in very small quantities. The current definition of catalyst in use is "*A catalyst is a* substance which alters the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved".

Substances that can reduce the action of catalysts are of two types. If reversible, they are called catalyst inhibitors and when irreversible, they are catalyst poisons. Due to the inhibitors decreasing the reaction rate, they are sometimes referred to as "negative catalysts". Promoters are those substances which can cause an increase in the catalytic activity, even though they are not catalysts by themselves.

1.1.2 History

In a general sense (Lindström and Pettersson, 2003), anything that increases the rate of a process is a "catalyst", a term derived from Greek 'καταλύειν', meaning "to annul," or "to untie," or "to pick up." JönsJakob Berzelius first used the term 'catalysis' in 1835 to describe the acceleration of the reaction by a substance without itself changing after the reaction. Further, the use of platinum in catalysis was proposed by Humphry Davy. A discovery by Wilhelm Ostwald in the 1880s won him the Nobel Prize in Chemistry for the year 1909. He investigated the reactions that were catalyzed in the presence of acids and bases where he observed the chemical reactions occurring at finite rates. It was further suggested by him that the strength of the acids and bases could be determined using these reaction rates (Roberts 2000).

1.1.3 Technical perspective of catalysis

A catalyst need not involve itself in a single chemical transformation, instead can participate in multiple of them. The effect of a catalyst can vary positively in the presence of promoters or negatively when inhibitors or poisons are present. When we compare the catalyzed reactions to an uncatalyzed one, it is observed that the catalyzed ones have lower activation energy, E_a (rate-limiting free energy of activation) when compared to the corresponding uncatalyzed one. This results in the catalytic action which is a higher reaction rate at both the temperature and concentration of reactants remaining the same. The mechanistic approach of a catalytic process is quite complex and difficult to explain. Catalysts are expected to affect positively on the reaction environment, or sometimes get bound to the reagents and polarize the chemical bonds (e.g. acid catalysts for reactions of carbonyl compounds). They can also form certain intermediates that are otherwise not produced, such as osmate esters in osmium tetroxide-catalyzed dihydroxylation of alkenes; or cause the reagents to dissociate to reactive forms, such as chemisorbed hydrogen in catalytic hydrogenation (McNaught 1997).

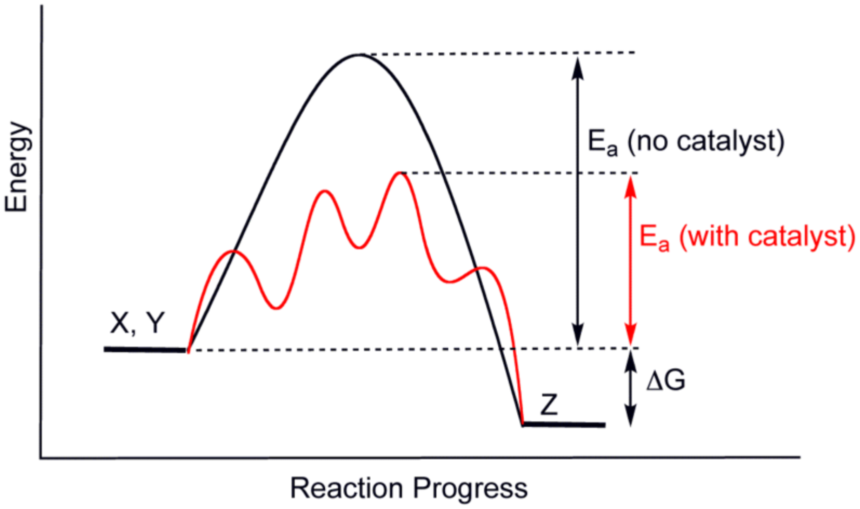


Figure 1.1 Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. [Source: Wikipedia]

To specify in terms of reaction kinetics, catalysts exert their activity by providing a pathway or mechanism which is alternative to the uncatalyzed one, where the transition state differs and the activation energy is lowered. As a consequence, the molecular collisions happening in the reaction have the energy needed to reach the transition state. In this way, the catalysts enable the reactions which are otherwise blocked or slowed by a kinetic barrier. The catalyst in its course of action may increase the reaction rate or selectivity of the reaction or facilitate the reaction at lower temperatures. Overall, it can be said that in the presence of a catalyst, a different reaction pathway is opened (Figure 1.1) which has a lower activation energy. The end result of the reaction and its overall thermodynamics do not change. In terms of reaction kinetics, catalytic reactions are the usual chemical reactions where the rate of a reaction depends on the rate of the reactants colliding with each other in the rate-determining step. Generally, the catalyst takes part in this slowest step, and the rates are limited by the amount of catalyst and its "activity". For example, both the diffusion of reagents to the surface and the diffusion of products from the surface can be rate determining in heterogeneous catalysis. Corresponding events related with binding to the substrate and product dissociation are applicable to homogeneous catalysts.

Characteristic feature of the catalysts does not allow them to be consumed by the reaction itself. However, there are possibilities of them getting inhibited, deactivated, or destroyed by secondary processes. Leaching of the catalytically active components into the reaction impedes the catalyst recovery in a homogeneous catalytic process. In heterogeneous catalysis, this can happen by certain secondary processes like coking where the polymeric side products happen to cover the catalyst blocking their activity. They can also dissolve into the solution in a solid-liquid system or undergo sublimation in a solid–gas system.

1.1.4 Importance of catalysis

A catalyst enables the establishment of reaction equilibria and can also enhance the selectivity of product greatly. An ideal catalyst would allow the chemical transformations to be carried out with improved productivity, minimal waste and at a significantly lower energy. A positive catalyst accelerates the reactions and allows them to be performed under the most beneficial thermodynamic regime at a lower temperature and pressure.

Efficient catalysts, in combination with the optimized reactor and the production design, are the fundamental factor in lowering both the investment and operation costs of chemical processes with profitable production point of view in the industry. Also, a “green” technology is one where the raw materials are used in a resourceful manner, taking care to avoid toxic and hazardous materials while the chemical wastes or adverse byproducts are minimized. Catalytic routes mange to fulfill these criteria mostly and hence are coined under the purview of ‘Green Chemistry’.

The biological importance of catalysis is often signified by the massive role and ability of enzymes, which proficiently carry out most of the chemical transformations in our bodies with neither much requirement of maintenance nor with a lot of breakdowns. Owing to all its beneficial uses, history has evidenced the attempts of mankind to harness the enormous potential of catalysts throughout the years.

1.1.5 Types of catalysts

Catalysts can either be heterogeneous or a homogeneous one, depending on it existing in the same phase of the substrate or in a different phase. Biocatalysts (enzymes) are considered to be a separate group as they possess and exhibit some additional features to the classified ones. In the heterogeneous category, where the catalyst acts in a different phase than the reactants include some important examples like the catalytic converters in cars for conversion and toxicity reduction of automobile exhaust gases or the Haber-Bosch process for the production of fertilizers. The second category is the homogeneous catalysis, wherein the catalyst acts in the same phase as the reactants and this is where most of the transition metal catalysis occurs.

1.1.5.1 Heterogeneous Catalysis

Heterogeneous catalysis is the class of catalysis where the phase of the catalyst and the reactants are not the same. Here phase refers not only to the three states of matter - solid, liquid, or gas but also the immiscible liquids (e.g. oil and water). The heterogeneous catalysts applicable in day to day life are majorly solids while most of the reactants are gases or liquids. This class of catalysts is of significance and principally finds application in numerous areas of the chemical and energy industries.

Heterogeneous catalysis generally occurs through adsorption mechanism and these adsorptions can be of two types, however some of the processes come under an indistinct range between the two limits. The first type is physisorption which brings about only small changes to the adsorbate with respect to their electronic structure. In the second type, i.e chemisorption, the adsorbate is strongly discomposed and involves bond-breaking commonly. van der Waals forces guides the physisorption mechanism where as in chemisorption, there is a sharing of electrons between the adsorbate and the adsorbent. Chemisorption are of two types, the molecular adsorption and dissociation adsorption. In the first type, adsorbate remains intact and in second, one or more bonds break along with adsorption.

The reactants diffuse into the surface of the catalyst and get adsorbed to it through chemical bonds in heterogeneous catalysis. Once the reaction is done, the products get desorbed from the catalyst surface and then diffuse away. The surface area of a solid heterogeneous catalyst is significant as it defines the availability of catalytic sites. These surface areas can be very large as in some mesoporous silicates which have area measuring up to 1000 m^2/g on their surface. The spread or grafting of the catalyst on the catalyst supports maximizes the surface areas relatively.

1.1.5.2 Homogeneous Catalysis

A sequence of reactions in which the catalyst works in the same phase (solid, liquid, or gas) as reactants is the homogeneous catalysis. A homogeneous catalyst along with the reactant is co-dissolved in a solvent. Homogeneous catalysts include few examples like Bronsted and Lewis acids, which is widely used in organic synthesis, metal complexes, metal ions, organometallic complexes, organic molecules. Hydroformylation, transfer hydrogenation, certain kinds of Ziegler-Natta polymerization and hydrogenation are the well-known examples of homogeneous catalysis. Industrial processes such as the Wacker process for formation of acetaldehyde from ethylene, the Monsanto process and the Cativa process for the conversion of methanol and CO to acetic acid also involve homogeneous catalysis.

The homogeneous catalytic process involves different steps such as

- Association/dissociation of a ligand
- Insertion and elimination reactions
- Nucleophilic attack on a coordinated ligand
- Oxidation and reduction of a metal center
- Oxidative addition / reductive elimination

1.1.5.3 Comparison of Homogeneous and Heterogeneous Catalysis

A heterogeneous catalytic process is very obviously a surface phenomenon, therefore the atoms or species only on the surface are catalytically active. This leads to the reactions to be carried out at moderately high temperatures and contains low specificities. Also, the study of catalysis mechanism is a complex process in this type. However, the best feature of a heterogeneous process will be the recovery of the catalyst which is relatively easier compared to the homogeneous one. On the other hand, it is possible to design a homogeneous catalyst by ligand variation with high reproducibility. High specificity and low temperature reactions are the characteristic features of homogeneous processes depending upon the catalyst employed. Their mechanism can be better explained compared to the surface reactions of heterogeneous systems. Major drawback in this category would be the recovery of the catalyst as there is leaching of catalyst observed. This problem could be tackled by attaching a catalyst which is homogeneously active to a polymeric support and used in the reaction. When used this way, cleaving of the catalyst from the support after the reaction becomes easier and thus catalyst recovery is not affected.

1.1.6 Catalysis by Transition Metals

The transition metal complexes have been studied significantly and extensively from the past century due to their promising capability as dynamic catalysts in the field of organic and polymer chemistry. Transition metal catalyzed transformations form a major tool for synthesis in the organic chemistry owing to their green approach in terms of their efficiency and selectivity. An economical use of reactants is another feature aspiring the use of these metal complexes as catalysts. The environmental concerns gaining increasing emphasis and the need for the efficient and less expensive processes have benefitted the application of transition metal complexes as homogeneous catalysts in wide organic reactions (Nakamura and Tsutsui 1980).

The versatility and resourcefulness of the transition metals as catalysts find major applications such as the Ziegler-Natta polymerization, the Wacker process, the Monsanto process, alkene hydrogenation through Wilkinson’s catalyst which has been used for several decades in large scale. Foundation for the development of homogeneous catalysis was laid by the revolutionary work of Ziegler and coworkers.

The Wilkinson's catalyst which is nothing but the square planar rhodium complex, chlorotris(triphenyl phosphine)rhodium(I), used in hydrogenation has been the first effective homogeneous catalyst. A variety of homogeneous metal carbonyl complexes like $[HFe(CO)_4]^-$ $[Rh(CO)_2I_2]^-$ and $[Ru(bpy)_2(CO)Cl]^+$ are used in the conversion of CO to CO_2. Use of cobalt or rhodium complexes in the hydroformylation reaction successfully produces annually about 5 million tons of aldehydes and aldehyde (Antolovic and Davidson 1987). Another important landmark in homogeneous catalysis is in the conversion of methanol to acetic acid by the famous Monsanto acetic acid process which uses the rhodium complex, $[Rh(CO)I_2]^-$. Wacker process which uses palladium catalysts for the production of acetaldehyde from ethylene is another noted achievement in the catalytic field (Smidt, et al. 1959). Today, transition metal catalyzed reactions comprise a major portion of organic synthesis. The rich chemistry provided by the accessible d-orbitals make the complexes of transition metals favorite aides in the never-ending quest for ways to build new molecules. The significance and glory of the field have been acknowledged by the several Nobel prizes awarded to transition metal catalyzed reactions in the last decade.

The oxidation state and coordination environment of the central metal ion and the ligand is subjected to change in a catalytic reaction. During complexation, the coordination environment surrounding the central metal ion will influence the features of the complexes formed which is why the role of different ligands in complexation of transition metal atoms is significant. There exist nine orbitals in total in the transition metal atoms of which one is a ‘s’ orbital, three are ‘p’ orbitals and the remaining five are ‘d’ orbitals. All the nine orbitals of the metal atom may or may not participate in formation of bonds with ligands during complexation. The central transition metal atom exists in different oxidation states which is a direct benefit and a promising virtue in the catalytic studies. The multi-oxidation state of a central transition metal is a property which largely guides the development of coordination chemistry. A ligand gets added through S_N1 type of substitution reaction, when the nine orbitals of the metal atom are completely filled. Here, one ligand gets dissociated from the complex, thus forming a coordinatively unsaturated species which contains only sixteen valence electrons. As a result of unsaturation, it tries to increase its electron count to eighteen by binding with the incoming ligands and thus attains a saturated state. The transition metal ion is believed to be shifting between these two states in a catalytic process (Parshall and Ittel 1992).

1.2 PINCER COMPLEXES

Pincer compounds find major application as homogeneous catalysts and form an important class of organometallic and coordination compounds. The last two decades have witnessed the continuous growth in the development of pincer complexes. They possess exceptional metal bound structures which make them the most sought-after catalysts for many organic transformations. The research work of Shaw and van Koten in 1976 caused the invent of the pincer ligand. Pincer complexes are formed when an electron-rich chemical moiety binds to a metal atom forming at least one carbon-metal bond. The structure formed resembles a pincer having three bonds from the metal atom to the ligand. (Figure 1.2). The resulting structure is responsible for the unique properties of the complex and it also protects the metal atom by the unique enclosure. It should be pointed out that the term ‘‘pincer’’ has never been explicitly defined in the literature. The consensus is that the first set of pincer complexes reported (but not originally called ‘‘pincer’’) by Shaw in 1976 features a C-M bond with two flanking phosphine groups (Moulton and Shaw 1976). Over the years, the scope of pincer ligands has been extended in various ways, with the broadest definition of ‘‘pincer’’ including any tridentate ligand that binds a metal in a meridional configuration (Choi, et al. 2011).

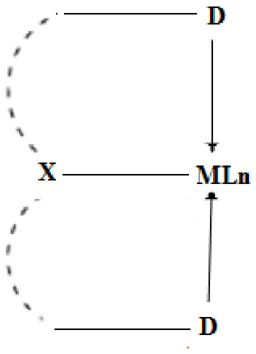


Figure 1.2 General representation of a pincer ligand (MLn = Metal complex, X, D = Donor atoms P, O, N, S, C etc

Pincer ligands have gained tremendous popularity, largely due to their high tunability and their general tendency to make the metal complexes thermally robust and, in some cases, their ability to stabilize unusual metal oxidation states. Their unique stability is owed to the σ metal-carbon bond. Due to their stability, metal does not easily dissociate from the ligand avoiding decomposition of the complex. The donor atoms along with their substituents can refine the steric and electronic properties of the complex effectively.

The pincer ligands generally favor meridional coordination; however facial binding is also observed in some cases. Most often, these ligands contain a central aryl ring possessing two ortho-substituted arms containing donor ligands (Bhattacharya and Guan 2011). The central attachment on the aryl ring is classically through its carbon atom on the center, and the pendant arms can be donor atoms like C, N, P, O, S, or Se. Few other architectures of pincers are known which contain a central pyridine or phosphinine ring or a central N-heterocyclic carbene. Seldomly, these can be a phospha-barrelene, a cycloheptatriene, an anthracene, or a simple divalent carbene carbon groups also. Groups on the pendant arms can be a wide variety of chemical functionalities like phosphines, amines, thiols, ethers, selinides, phosphine-sulfides, iminophosphoranes, and N-heterocyclic carbenes (Figure 1.3).

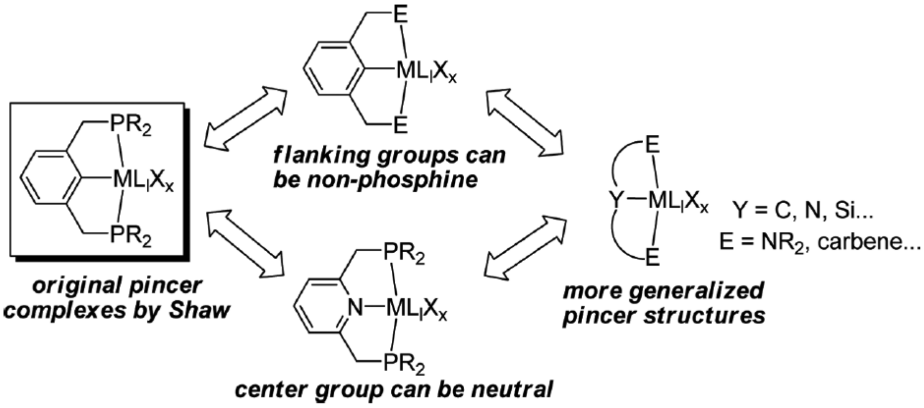


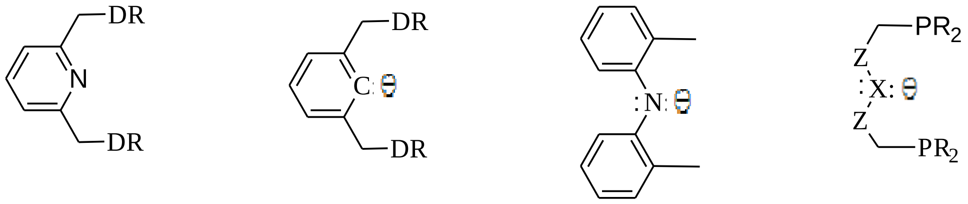
Figure 1.3 Variation of pincer complexes (Bhattacharya and Guan 2011)

1.2.1 Nomenclature

The pincer ligands are classified by the nature of donor atoms in the ligand skeleton. These flanking donors are used to abbreviate them as ‘DXD’ pincer (Figure 1.2). ‘D’ constitutes neutral species of chemical groups such as NR_2, PR_2, SR, and SeR.

These neutral species and their spacer atoms form the side arms of the pincer skeleton which control the stability and electronic properties of the complexes formed.

A sensible method of classifying the pincer ligands is based on the three donor atoms which are found to coordinate to the central metal ion, and resultingly abbreviated as 'DXD'. For instance, if a pincer complex is resulted with amino ligands (D = NR_2) as main donors, then it would be called an NCN complex and if formed with phosphines (D = PR_2), then it would be a PCP complex. If an unsymmetrical pincer complex is formed with two different donors in the side arms, then it would be a DXD' pincer complex. These types are strategically synthesized to improve the catalytic activity and are sometimes used. But the symmetrical pincer complexes find major application, one reason being the relatively easy synthesis of these species. DXD type pincer complexes with carbon as the X group find wide applications in organic synthesis. Figure 1.4 displays a small sample of various charge-neutral and anionic pincer frameworks (van der Vlugt and Reek 2009).



D = S; [SNS]
D = NR'; [NNN]
D = PR'; [PNP]

D = S; [SCS]
D = NR'; [NCN]
D = PR'; [PCP]

D = NR_2; [NNN]$^-$
D = PR_2; [PNP]$^-$
D = O; [ONO]$^{3-}$
D = NR; [NNN]$^{3-}$

X = N, Z = $SiMe_2$; [PNP]$^-$
X = C, Z = CH_2; [PCP]$^-$
X = Si, Z = CH_2; [PSiP]$^-$

(R, R' – Organic derivative)

Figure 1.4 Selected examples of pincer ligands in literature

1.2.2 Basic Properties

Most of the advantageous properties of the pincer complexes in catalytic transformations are mainly due to their unique architecture. They show a high thermal stability because of their firm tridentate coordination. Other consequential properties are their high stability toward moisture and air, thus making them easy to store and handle. These characteristics define their high durability and provide with a broad reaction scope. The pincer architecture is also responsible for causing product selectivity in the catalytic process. The rigid tridentate coordination imparts the complex its exclusive stability making the metal and ligand remain together under each catalytic step, and therefore, the ligand effects are efficiently transmitted to the metal atom.

The pincer ligand is generally meridional oriented and it is coplanar with the coordination site available for catalysis. This causes the efficient transfer of the steric and electronic properties of the pincer ligand to the metal center. Different donor groups can be used to vary the side arms (D) of the pincer ligand which directly impacts on the reactivity of the resulting complex. The aromatic backbones provide an opportunity of inducing electronic effects depending on the substituents on the aromatic ring. (Dijkstra, et al. 2003). Additionally, dendrimers (Pijnenburg, et al. 2011) and polymer supported (McDonald, et al. 2009) pincer complexes have also been reported, thus enriching the field of environmentally benign and sustainable catalysis.

The remarkable stability of metal pincer complexes due to their tridentate chelation and availability of a stable σ bond between carbon and metal atom connects them more to the normal organic moieties than to the organometallic species. The terdentate coordination results in the number of free coordination sites on the metal to reduce by three. This factor appreciably facilitates to increase the regio- and stereoselectivity of the organic conversions or to change the metal reactivity. Their stoichiometry and the bonding structure are well-defined, thus enabling the sensible design of the catalytic transformations in addition to their catalytic properties being efficiently tuned (van Koten, et al. 2013). When a pincer type ligand was reported in 1976 by Moulton and Shaw, there was no much claims made on their unique properties. They rather represented a few novel diphosphine derivatives at that time (Moulton and Shaw 1976) and was completely forgotten for over a decade. Then in the late 80’s, when their properties were scrutinized carefully, it was revealed that these compounds possess an exceptional thermal stability. They have very high melting points and can sublime without getting decomposed. This remarkable property of the pincer complexes could be exploited advantageously and used potentially in homogeneous catalysis.

In 1989, van Koten first coined the term ‘pincer’ for the terdentate ligands (van Koten 1989). He reported the firm bis-ortho chelation of the tridentate ligand to provide the central metal in the complex with a set of extraordinary features by restricting the number of coordination sites in the complex for incoming reagents and other ligands. In his work, he reported the organometallic complexes with N-donor ligands (instead of P-donor ligands) coordinating to the metal and construed that this particular binding could lead to new stability patterns of complexes with new reaction patterns in homogeneous catalysis. Baldovino-Pantaleón and coworkers pursued their continuous interest in the use of pincer ligands and their complexes with transition metal for novel transformations in organic field using aromatic fluorinated substituents. Fluorinated substituents were used with the intention of tuning the steric and electronic properties of the complexes by varying the fluorine substitution in the aromatic ring (Baldovino-Pantaleón, et al. 2005). In pursue of fervent interest in the development of bis(oxazoline) and azabis(oxazoline) ligands for catalysis, bis(oxazoles) were explored as an ancillary and a stable ligand scaffold to form metal complexes (Luo, et al. 2007).

A series of new PCN pincer Pd(II) complexes with phosphinito donors were reported which were suitably prepared through a one-pot phosphorylation/palladation reaction. Pyrazolyl or amino-containing m-phenol derivatives were reacted with chlorophosphines and $PdCl_2$ to obtain the Pd complexes (Gong, et al. 2007). NHC (N-heterocyclic carbene)-derived CNC-type pincer complexes of nickel(II) were reported which were presented as four coordination complexes and the geometry was established as a slightly distorted square-planar structure (Inamoto, et al. 2009). The reported method asserts the synthetic approach to be highly applicable wherein the complexes can be easily prepared from cheaper and commercially available raw materials. A sterically demanding dbf bis(phosphinimine) ligand was used to prepare a cationic complex of zinc which was unsaturated electronically in the work reported by Wheaton and Hayes. These cationic compounds were synthesized using the neutral bis(phosphinimine) ligand 4,6-$(MesN{=}PPh_2)_2$dibenzofuran in a resourceful methodology (Wheaton and Hayes 2010).

Non-symmetric pincer compounds were synthesized by a group of workers where they included a oxygen (hard) atom and a sulfur (soft) atom in the spacer between the main donor atom ‘P’ and the aromatic ring (Serrano-Becerra, et al. 2010). Two novel nickel complexes $[(2\text{-}(CH{=}NR)\text{-}6\text{-}(OPR'_2)C_6H_3)NiCl]$ ($R = 2,6\text{-}{}^{i}Pr_2C_6H_3$, $R' = Ph$ or ${}^{i}Pr$), bearing unsymmetrical PCN-type iminophosphinite pincer ligands were prepared in good yields under mild conditions (Sanford, et al. 2011). PCP pincer ligands were easily synthesized from 1,3-phenylenediamine, followed by its complex formation with Pd(COD)Cl_2 through the ligand substitution reaction in toluene media (Feng and Cai 2013). SNS, SeNSe and TeNTe pincer ligands possessing central non-aryl group and their Pd complexes were reported (Kumar, et al. 2013), which stands aside from the classic definition of pincer complexes having central aryl ring. Ethanol was the solvent used in the synthesis asserting a green approach to the method for its choice of solvent. Nickel pincer complexes were developed in a one-pot procedure (Vabre, et al. 2013), which was reported to be an alternative to the conventional methods for the synthesis of (POCOP)NiCl complex. The approach was reported as ‘green’ for being a one-pot protocol involving an inexpensive source of Ni element.

If tuning the structures of the pincer arms and substituents on the backbone of the pincer skeleton can modify the coordination geometries and electronic properties of a complex, then the reactivity of the metal center can also be varied. On using the pyrazolyl-imine system which is supported by a pyridyl group, it is expected that the π-system can increase the Lewis-acidity of the metal center which in turn accelerates the metal-reactant interactions, thereby enhancing the activity. This factor led to the synthesis of a new class of cobalt complexes with unsymmetrical pincer type ligands (Gong, et al. 2013). [Ru(CO)H(PNN)] pincer complex based on a dearomatized PNN ligand (PNN: 2-di-tert-butylphosphinomethyl-6-diethylaminomethylpyridine) was synthesized and reported (Perdriau, et al. 2014). A group of cobalt chloride, methyl, acetylide and hydride complexes with bis(phosphino)pyridine pincer ligands were synthesized (Semproni, et al. 2014). They were structurally characterized and evaluated for their electronic structures in the research study. A series of six-coordinate neutral $16e^-$ halocarbonyl Mo(II) complexes of the type [Mo(PNP^{Me}-*i*Pr)(CO)X_2] (X = I, Br, Cl), with a PNP pincer ligand N,N′-bis(diisopropylphosphino)-N,N′-dimethyl-2,6-diamino pyridine (PNP^{Me}-*i*Pr), were prepared by a group of researchers. (de Aguiar, et al. 2014). These complexes were synthesized using various methods depending on the halide ligands.

1.3 IMMOBILIZATION OF METAL COMPLEXES

Deactivation is the major drawback of the homogeneous catalyst. Immobilization on suitable substrates provides a strong interaction between the support and the homogeneous catalyst. Thus, it prevents leaching of homogeneous counterparts during the catalytic reactions. Various synthesis protocols for immobilization of homogeneous catalyst have been established. This majorly encompasses the covalent and non-covalent attachments on various organic and inorganic supports. Other methods developed include a) encapsulated method, b) coordination method, and c) ion interaction method. Covalent approaches are in generally more favored because of their superior stability and applicability. The choice of support, linkers and the appropriate point of anchoring play a crucial role in immobilization of the catalyst.

Attachment of metal complexes to a surface by immobilization methods may be by physical adsorption (non-covalent interactions) or through chemical bonding where the complex gets covalently bonded on the chemically functionalized activated supports. Non-uniformity of the catalyst getting loaded on the support, use of excess of the complex for immobilization or the use of harsh reaction conditions are few of the drawbacks in the immobilization methods. This lacuna promotes the researchers to determine the advances in the immobilization strategy by various methods and thereby take care of the shortcomings of the existing system.

1.3.1 Graphene oxide as a substrate

Graphene and its derivatives are the group of materials showing promising potential in the field of nanotechnology. From a theoretical point of view, graphene and graphene oxide are the definitive two-dimensional structures forming an ideal catalytic support. The outstanding properties of these material in terms of their physical and mechanical appearance or their chemical structure makes them ideal for preparing the composite-materials with unprecedented features. Graphene derivatives are also characterized by their large specific surface area and a well-known biocompatibility. Given their unique surface area, they possess high adsorption capacity and can be used as constructive substrates to interact with a diverse species. Application of these composites can then wide ranged varying from catalysis to electrochemical applications. Graphene oxide which is a graphene product has its own pros when compared with the graphene. It is oxygen rich and there are hydroxyl and epoxide groups on its basal planes while the sheet edges possess carbonyl and carboxyl groups.

These functional groups of oxygen present graphene oxide with its immobilization strength. Homogeneous materials can be immobilized on graphene oxide support to form active sites. The oxygen functionalities present on graphene oxide ensures their dispersion in organic solvents, water and different matrixes. This is a property which is advantageous when combining the material with a polymer or ceramic matrixes to enhance their mechanical and electrical properties (Julkapli and Bagheri 2015).

Investigation on the immobilization and intercalation of Pd nanoparticles using oxygen functional groups present in graphene oxide were conducted and reported (Scheuermann et al. 2009). When compared to conventional Pd supported on activated carbon catalysts, activity shown by graphene oxide and graphene-based catalysts were much higher. Also, very low Pd leaching (<1 ppm) was observed in the Suzuki–Miyaura coupling reaction. Recovery and reuse of the catalysts was shown with some activity loss. In a simple method, gold nanoparticles were fabricated on graphene oxide and the nanocomposites obtained displayed unusual catalytic activity for the cross-coupling of chlorobenzene and phenylboronic acid with yield as high as 98% (Zhang et al. 2011). In another study, highly active Pd nanoparticles were supported on graphene by taking an aqueous mixture of palladium nitrate and dispersed graphite oxide sheets and reducing it in microwave condition. (Siamaki et al. 2011). High stability of the catalyst along with their easy recovery and reusability were the highlights of this research work in addition to their better performance when compared to the reputed, commercial Pd/C catalyst. The usefulness of the catalyst in Heck coupling reactions was also demonstrated in this study.

Grafting of oxovanadium Schiff base on the graphene oxide substrate through a covalent bonding was reported for the oxidation of alcohols. The immobilized complex showed high catalytic activity which was comparable to its homogenous analogue with an advantage of recovery and reusability of the catalyst as the successful runs showed no significant loss in its catalytic activity. Metal complexes immobilized on the graphene surface was also studied for its enhancement of the catalytic activity and its recyclability (Sabater et al. 2014). In this work, they immobilized Pd and Ru complexes of a N-heterocyclic carbene ligand onto the reduced graphene oxide (rGO) substrate by π-stacking. Both the parent complexes and their hybrid materials have been catalytically applied in the hydrogenation of alkenes (Pd) and oxidation of alcohols (Ru). The hybrid materials show an improved yield when compared to their homogeneous analogues. Schiff base complexes of transition metals (Fe^{2+}, Co^{2+}, VO^{2+} or Cu^{2+}) were immobilized onto graphene oxide previously functionalized with 3-aminopropyltriethoxysilane (3-APTES) (Su et al. 2014) and studied for their catalytic activity in the epoxidation of styrene. Composites with copper showed better catalytic performance with above 94% styrene conversion. Also, high (99%) selectivity to the epoxide could be achieved when tert-butyl hydroperoxide (TBHP) was used as an oxidant after 7 h reaction. The catalyst also maintained very high styrene conversion (>93%) and epoxide selectivity (>99%) even after being used for four cycles.

A palladium catalyst supported on graphene was reported for Suzuki coupling reaction by grafting Pd(II) chloride on graphene oxide support through in situ coordination interaction with aminosilane ligand spacers (Bai et al. 2014). Excellent catalytic activities were observed in the Suzuki coupling of various aryl halides and phenylboronic acid. Catalyst recycling and reusability was also studied. In another research study, a core–shell Fe_3O_4@amine-functionalized graphene (Fe_3O_4@GON) composite was prepared and the Pd nanoparticles were immobilized on this support and their catalytic activity was investigated in Sonogashira cross-coupling reactions between various aryl iodides and terminal acetylenes (Kim et al. 2015). Gold nanoparticle and graphene oxide incorporated strontium crosslinked alginate/carboxymethyl cellulose composites were synthesized and studied for o-nitroaniline reduction and Suzuki-Miyaura cross-coupling reactions (Thomas et al. 2017). Solid-supported palladium catalysts was reviewed by Alonso and coworkers who have suitably listed their progression and developments in Sonogashira cross-coupling reactions (Alonso et al. 2018).

Three-dimensional amine-terminated ionic liquid functionalized graphene/Pd composite aerogel was studied in Suzuki cross-coupling reactions by Chinese researchers. They reported the high efficiency, stability and recycling / reusability of these composites for the Suzuki cross-coupling reactions under mild conditions with the catalytic efficiency showing no obvious loss even after ten repeated cycles (Huang et al. 2018). A review article on the newest advances in the preparation of graphene supported metal nanoparticles and their application in the C-C and C-X bond formation gives a large number of examples where these catalysts can be easily and reliably prepared (Nasrollahzadeh et al. 2018). Catalytic properties and the recycling possibilities are discussed elaborately for the Suzuki, Heck, Hiyama, Ullmann, Buchwald and Sonogashira coupling reactions.

1.4 CROSS COUPLING REACTIONS

Cross-coupling reactions have registered their presence invincibly in the field of organic chemistry ever since their emergence in the beginning of the1970s and this fact is further proven by the awarding of the Nobel Prize in 2010 to three of the most influential people in this field. It was Kumada (Tamao, et al. 1972) and Corriu (Corriu and Masse 1972) who pioneered the attempt by showing a possibility to couple an aryl halide with a Grignard reagent using nickel as the active catalyst. Development of other carbon nucleophiles has eventuated the use of organozinc, organotin, organoboron, and organosilicon reagents which show tolerance towards functional groups in comparison to the original Grignard reagent. Considering the less toxicity and higher stability of palladium towards oxygen, this metal catalyst has replaced the original nickel catalyst in most cases (Cassar, 1975). Many new and versatile couplings have materialized following this improvement, the renowned ones being Heck, (Heck and Nolley Jr 1972), Suzuki, (Miyaura, et al. 1979), Negishi, (Negishi, et al. 1977), Hiyama,(Hatanaka and Hiyama 1988), Stille, (Stille, 1985) and Sonogashira (Sonogashira, et al. 1975) coupling reactions.

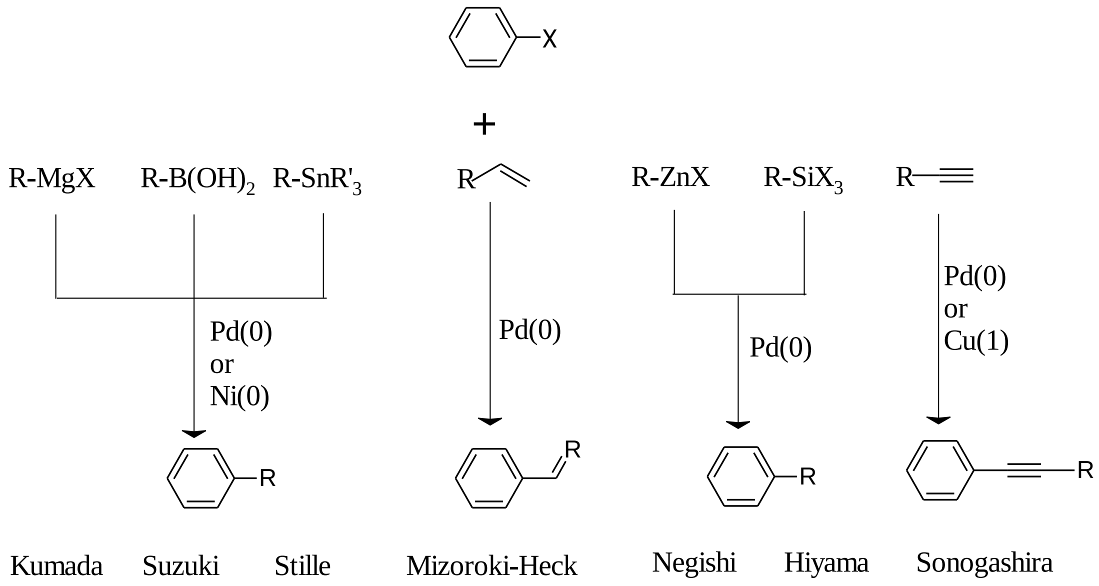


Figure 1.5 The most common named carbon-carbon bond forming cross-coupling reactions

Further development of the cross-coupling reaction includes new ways of performing the reaction, such as employing new ligands or substrates. One other important improvement is the use of other metals as catalysts.

1.4.1 Suzuki-Miyaura coupling

Cross-coupling between organoboron compounds and aryl halides can be efficiently done in the presence of Pd catalyst and a base. This reaction was discovered by Suzuki and coworkers (Miyaura, et al. 1979) and is widely used now in organic laboratories and industrial syntheses.

$$R_1\text{-X} \quad + \quad R_2\text{-B(OY)}_2 \xrightarrow{\text{Pd catalyst, base}} R_1\text{-}R_2$$

Pd is the widely used metal in Suzuki coupling. The chemistry of Suzuki coupling is a thoroughly researched and developed field with an availability of a library of Pd catalysts, even for difficult substrates. In some cases, other metals can be advantageous compared to Pd. Catalysts with nickel are exceptionally good for the reactions with aryl chlorides and mesylates. Inorganic bases like Na_2CO_3 or K_3PO_4, are commonly and efficiently used for this reaction. Water when present in trace amount can accelerate the reaction. It is recommended to add water to anhydrous bases to form the desired products at a faster rate.

1.5 CATALYSTS FOR CROSS-COUPLING REACTIONS

A wide range of organometallic reagents can be used in cross-coupling reactions, starting from very reactive and highly inflammable organo-magnesium or organolithium reagents to moisture and oxygen tolerant organoboron compounds. Figure 1.5 depicts the significant cross-coupling reactions catalyzed by transition metals. Different electrophiles can also be used in cross-coupling reactions. Among them, aryl, alkenyl and alkyl halides, triflates and tosylates are the most popular substrates. Palladium or nickel are the most commonly used transition metals in the cross-coupling reactions. Research study reports the use of many different transition metals as an alternative catalyst for cross-coupling reactions. However, catalytically Pd- and Ni-catalysts have excelled in catalytic activity and thus remains the most competent.

There have been many attempts to interpret the mechanism of coupling reactions. Transformations taking place in the catalytic cycle have been speculated by many researchers and several hypotheses have been reported. The mechanism can vary greatly depending on the catalyst, substrates, additives, solvent, temperature, etc. The catalytic cycle in Figure 1.6 describes the typical mechanism for a palladium catalyzed cross coupling reaction. Initially the precatalyst with Pd(II) metal form gets reduced to a Pd(0) form by the ligands or substrates. The catalytic cycle then begins with an oxidative addition of a aryl halide moiety, Ar-X on the Pd(0) center, producing $Pd^{II}(Ar)(X)$. The next step is the transmetallation with an organometallic reagent to eliminate the halide group and form $Pd^{II}(Ar)(Ar^1)$. In the last step, the metal undergoes reduction and regenerate the catalyst Pd(0) which takes up the next catalytic cycle. The coupled product (Ar- Ar^1) is eliminated in the process (Vechorkin 2011).

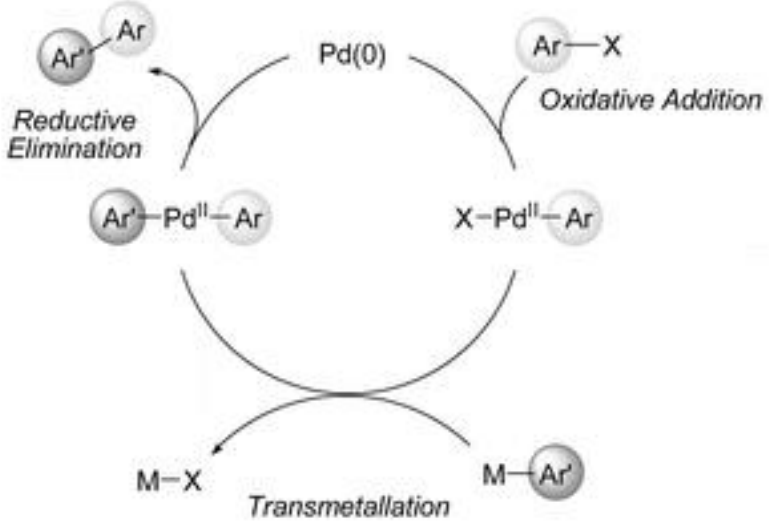


Figure 1.6 General mechanism for Pd-catalyzed cross-coupling reactions

1.5.1 Pincers as catalysts in Suzuki Coupling

Since their introduction to homogeneous catalysis, pincer complexes have been extensively utilized in catalyzing different C-C coupling reactions than any of its analogs. Even though their catalytic activity has been explored comprehensively about two decades over their advent to the field of catalysis, the extent to which they have been employed to catalyze various coupling reactions is well witnessed through hitherto published reports on pincer complexes. Among the named cross-coupling reactions, Suzuki- Miyaura reaction is privileged with the honor of being the most sought-after method of coupling. It is advantageous as it uses commonly available reagents and the reaction conditions are generally mild. Also, the reaction takes place in the presence of variety of functional groups. Even though different organometallic reagents are used in other cross-coupling reactions, the organoboron compounds used in this reaction are interesting because of their thermal stability, nonreactivity to water and oxygen. Also, their easy handling is appreciated and the non-toxic nature of the byproducts makes this coupling reaction most appropriate in the laboratories as well in the industries (Suzuki 1999).

The versatility of N-heterocyclic carbene ligands in organotransition-metal catalysis was studied (Loch, et al. 2002) using a palladium complex with a firm C,N,C-tridentate pincer ligand of carbene which showed exceptional air and thermal stability at higher temperatures and was catalytically active in C-C coupling reactions. The acatalyst was studied in Heck, Suzuki and Sonogashira coupling reactions. The outcome of the study proves the efficacy of the carbene complexes well equivalent to the corresponding catalysts of phosphine donors. In their work on pincer palladacycles, Rosa and coworkers have explained the efficacy of the NCP mixed pincer palladacycle in the coupling of boronic acids with aryl chlorides (Rosa, et al. 2006). The reported catalyst has stood with the best-reported systems in the literature in terms of yield. The study also reported the effective coupling of both electron-rich and -poor aryl chlorides and a wide variety of functional groups could be tolerated in both aryl chloride and aryl boronic acid.

Synthesis of novel bis(oxazole) ligands and their corresponding pincer palladium complexes were reported (Luo, et al. 2007) which were vigorous catalysts for Suzuki-Miyaura cross-coupling reactions. Here, the biaryls were synthesized under aerobic conditions with turnover numbers of up to 790,000 and turn over frequencies of up to 49,000 h^{-1}. The study suggested that bisoxazoles could be an attractive alternative to commonly employed NCN pincer ligands. A convenient synthesis of a series of novel achiral and chiral PCN pincer palladium(II) complexes was described (Zhang, et al. 2009). They successfully employed the obtained complexes as efficient catalysts for the Suzuki and copper-free Sonogashira reactions with good coupling yields. A series of iminophosphinite pincer complexes of palladium were synthesized and their catalytic activity was evaluated in the Suzuki coupling reactions (Yorke, et al. 2010). Their facile synthesis, air and thermal stability were the highlighting features reported. Catalytic activity was high toward 4-bromoanisole and moderate toward aryl chlorides in the coupling reaction. Research interest in the transition metal complexes containing pyrazolyl derivatives as ligands encouraged Hurtado and coworkers to synthesize palladium(II) complexes with the pincer ligand 3,5-bis(indazol-2-ylmethyl)toluene (Hurtado, et al. 2010). Catalytic properties of the palladium complexes were investigated in the polymerization of ethylene and in the Suzuki–Miyaura cross coupling and Heck reactions and the results show that the reported complexes were very active as catalysts.

A POCOP pincer complex of nickel [NiCl{$C_{10}H_5$-2,10-($OPPh_2)_2$}] based on a naphthoresorcinol frame was reported (Estudiante-Negrete, et al. 2012). They were found to be catalytically efficient in Suzuki reaction. An example of unsymmetrical NCN pincer of palladium [2-(2-oxazolinyl)-6-(2-pyridyl)]phenylpalladium (II) chloride via transmercuration was presented and its catalytic activity was assessed in Suzuki coupling reactions (Li, et al. 2013). Catalytic activity reported was very good with the bromo substituted benzenes showing higher reactivity than their chlorides congeners. Also, the coupling of aryl halides possessing electron withdrawing groups was much convenient when compared to the electron-donating groups. POCOP pincer palladium complex based on modified Merrifield resin was reported as a heterogeneous catalyst in Heck, Suzuki, and Sonogashira cross-coupling reactions with different aryl halides including inactive aryl chlorides (Tamami, et al. 2013). The effectiveness of the catalyst was expressed in terms of lesser reaction times and their excellent catalytic yields. The catalyst was successfully re-used up to 10 runs without appreciable change in its activity with a high turnover number.

The published literature accounts the credentials of pincer complexes for their catalytic applications in organic reactions, majorly the C-C coupling. However, the said reactions are predominantly the Pd catalyzed ones, with a small fraction of catalysis being performed with Ni, Ru metals as the active centers. Also, the literature on immobilization of metal complexes on solid substrates pronounces and highlights the attempts towards tackling of the recovery and reusability issues of homogeneously catalyzing transition metal complexes. The review findings prompted us to design transition metal catalysts with cheap, environment affectionate and abundantly available first row transition elements – manganese, iron, cobalt and copper to carry out coupling reactions. Also, the advantage of immobilization technique was harnessed to experiment the recovery aspect of the homogeneous catalysts as a part of the research scheme.

1.6 SCOPE OF THE WORK

Complexes bearing pincer ligands possess unique metal bound structures which make them the most active catalysts for organic transformations. Pincer complexes of palladium and to some extent nickel, have been extensively used as active catalysts in the cross-coupling reactions. A greener approach in the domain of catalysis necessitates the application of catalysts using less expensive and environmentally benign metals. In this regard, use of non-precious metals like cobalt, iron, copper, and manganese in the synthesis of pincer complex and further its catalytic activity study in cross-coupling reactions need a scrutiny and a comprehensive study.

Graphene oxide acts as a strong support to the metallic catalysts. The plenty oxygen functional groups in graphene oxide could immobilize various homogeneous materials as active sites. Immobilizing the metal complexes on GO substrate may provide some significant advantages in the area of C–C cross-coupling chemistry. Cross-coupling reactions such as Suzuki–Miyaura have been typically performed under homogeneous conditions using Pd catalysts. Unfortunately, catalyst recovery and recyclability remain a challenge, with several attempts being made to overcome this difficulty. One of the obvious method is the heterogenization of the catalyst. Although heterogeneous supports do allow a more efficient recovery, the activity of the immobilized catalysts frequently decreases. Development of metal catalysts that combine high activity, stability, and recyclability is an important goal in catalytic research. In this aspect, graphene-based substrates may be considered as potential supports for otherwise homogenously catalyzed C–C coupling reactions.

The research work is proposed on the synthesis of pincer ligands and their complexation with transition metals like cobalt, iron, copper and manganese. These complexes were characterized and studied for their catalytic applications in cross-coupling of aryl halides and organoboron compounds. The best performing pincer complexes will be further immobilized on graphene oxide support and studied for their catalytic application.

1.7 OBJECTIVES

The main objectives of the proposed research plan are as follows.

- To synthesize pincer complexes of Mn, Fe, Co and Cu transition elements.
- To characterize the synthesized complexes using elemental analysis and spectral (UV-Vis, FTIR, NMR and Mass spectral) studies.

- To study the catalytic activity of pincer complexes for cross-coupling of aryl halides and organoboron compounds as a homogeneous catalyst.
- To immobilize selected pincer complexes on the graphene oxide and their characterization.
- To study the catalytic activity of immobilized pincer complexes on graphene oxide for cross-coupling of aryl halides and organoboron compounds as a heterogeneous catalyst.
- To investigate the effect of solvent, the effect of time, the effect of catalyst amount in the coupling reaction.
- To study the scope of the catalytic system to various aromatic substrates and the effect of substituents in the activities of catalysts.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF PINCER COMPLEXES

Chapter 2 outlines the experimental procedures for the synthesis of the pincer complexes and their characterization using various physicochemical analytical methods.

Pincer complexes have emerged over the last two decades as a potential class of organometallic compounds capable of having extended utility in the field of homogeneous catalysis (Van der Boom and Milstein 2003). Their exceptional thermal stability often accompanied with the unique chemical stability of the σ-M-central atom and the rigid tridentate pincer motif, avoids the dissociation of the metal from the ligand. This in turn, makes the pincer metal interaction retain throughout the catalytic reactions and can attribute to the enhanced catalytic activity of the pincer complexes (Morales 2004), (Poverenov and Milstein 2013). Research studies reported hitherto emphasize the use of pincer complexes with mostly palladium (Selander and J. Szabó 2011) (Singleton 2003) and some instances, with nickel (Tu et al. 2010) (Inamoto et al. 2009), ruthenium (Na et al. 2004) (Kumar et al. 2009) as a catalyst, which is either an expensive affair due to the less abundance and consequently heavy cost of the metal or they may not be appreciably environmentally benign. Therefore, if quite an analogous outcome in terms of yield and efficiency can be obtained using less expensive and substantially benevolent metal complexes, the effort positively renders an economical and a green approach towards the research study.

In this chapter, we report the synthesis of PCP, PNP and NNN pincer complexes using cobalt, iron, copper and manganese as the active metal. Characterization of the synthesized complexes using various analytical methods is also being discussed in this chapter.

2.1 EXPERIMENTAL

2.1.1 Materials

Cobalt (II) acetate, copper (II) acetate, ferrous sulphate, manganese sulphate, iron (II) chloride, manganese (II) chloride were purchased from Merck, India and used as received. m-aminophenol, m-phenylenediamine, 2,6-diaminopyridine, chlorodiphenylphosphine, 2-amino-4-nitrophenol, pyridine-2,6-diol, phenylboronic acid and aryl halides were purchased from Sigma-Aldrich and tetrahydrofuran (THF), triethylamine (Et_3N), acetonitrile (ACN) were purchased from Alfa-Aesar and used without further purification.

2.1.2 Experimental techniques

A variety of physicochemical methods were employed to characterize the structure of organic pincer ligands and their metal complexes. A brief account of these methods is given below.

(a) Elemental analysis

The C, H, and N contents of the ligands and their metal complexes were determined by microanalysis using Thermoflash EA1112 series elemental analyzer.

(b) Magnetic measurements

The magnetic susceptibilities of the complexes were done at room temperature on a Sherwood UK magnetic balance using ($HgCo(NCS)_4$) as solid calibrant. The solid sample was tightly packed into a weighed sample tube to suitable length (*l*) and noted the sample weight (*m*). Then the packed sample tube was placed into tube guide of the balance and noted the reading (R). The mass susceptibility, χ_g, is calculated using the formula,

$$\chi_g = [C_{bal} \times l \times (R\text{-}R_0)] \div [10^9 \times m]$$

where: *l* = the sample length (cm)

m = the sample mass (g)

R = the reading for the tube plus sample

R_0 = the empty tube reading

C_{Bal}= the balance calibration constant

The molar susceptibility was calculated as, $\chi_m = \chi_g \times$ molecular formula of the complex. The molar susceptibility was then corrected with diamagnetic contribution. The effective magnetic moment, μ_{eff}, was calculated using the following expression:

$$\mu_{eff} = 2.83\sqrt{T * X_A}$$

Where χ_A is the corrected molar susceptibility.

The theoretical magnetic moments were calculated using the formula

$$\mu_{\mathrm{eff}} = \sqrt{n(n + 2)}\ \mathrm{BM}$$

Where n is the number of unpaired electrons.

(c) NMR spectra

^{1}H NMR spectrum was recorded in Bruker AV 400 instrument using TMS as internal standard. The spectra of the ligands were recorded in $CDCl_3$.

(d) Infrared spectra

FT-IR spectra were recorded on a Bruker-Alpha ECO-ATR FTIR spectrometer.

(e) Electronic spectra

Electronic spectra of ligands and complexes were measured on analytikjena SPECORD S600UV – Vis spectrophotometer in the 200 – 800 nm range. Electronic spectral studies were carried out mainly in a structural diagnostic perspective so as to supplement any information obtained from magnetic studies and as a confirmatory observation of the complex formation.

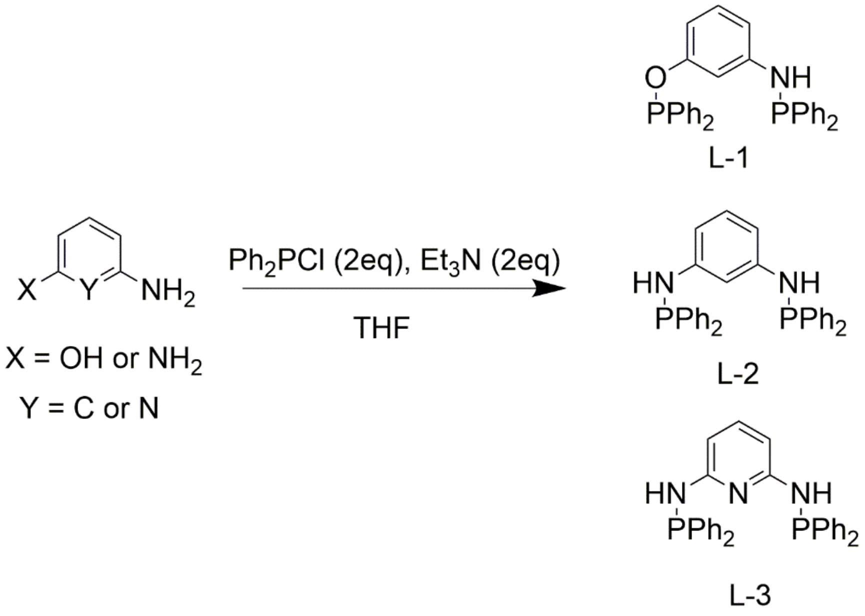
(f) Thermogravimetric analysis

The Thermogravimetric measurements were performed on (EXSTAR-6000) using nitrogen as the carrier gas (flow rate: 50 mL/min). The heating rate was 10°C/min. Samples were heated in air atmosphere from 30°C to 800°C. Thermogravimetric analysis (TGA) was used to determine the purities and structure stabilities of the complexes.

(g) Mass spectra

Molecular mass of the compounds was determined using a Waters Q-ToF micro mass spectrometer with an ESI source. Methanol was used as a solvent for the ligands. The complexes were analyzed with methanol/DMSO mixture of solvents.

2.1.3 Synthesis of ligands *(L-1, L-2 and L-3)*

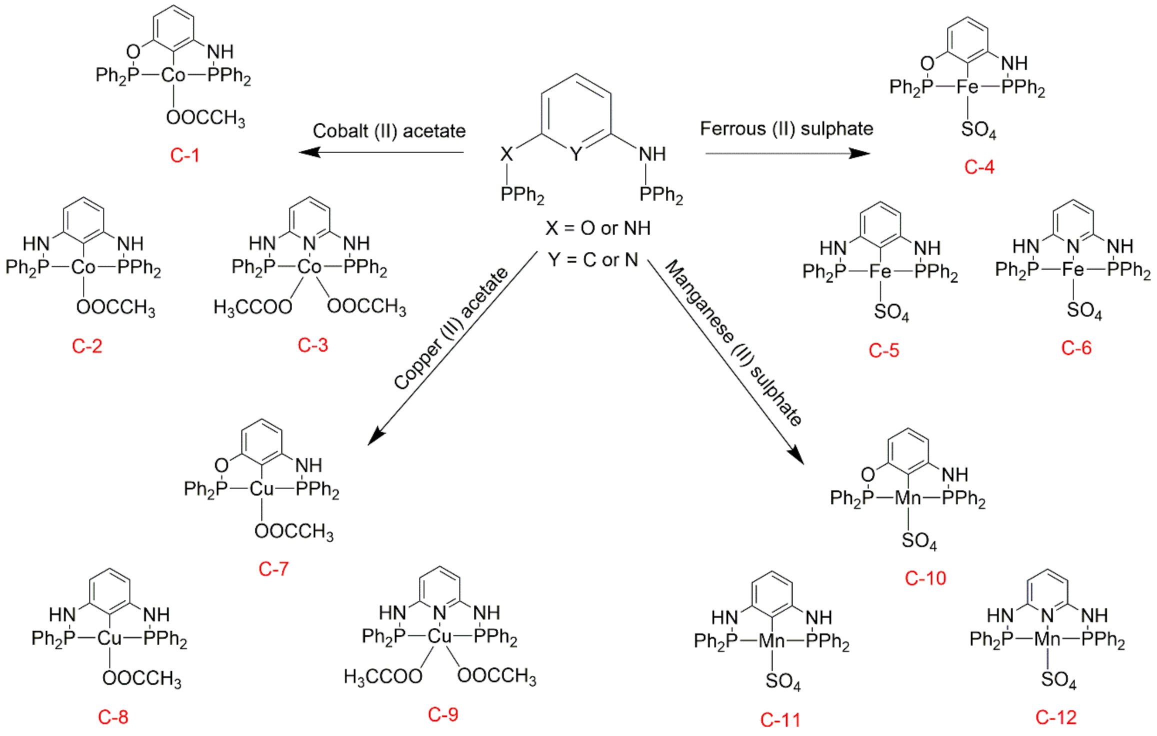


Scheme 2.1: Synthesis of ligands: a) L-1; b) L-2; c) L-3

The ligands were synthesized as per the reported procedure (Feng and Cai 2013) with certain modifications. In a typical synthesis process, triethylamine (1.85 g, 18.3 mmol) was dissolved in THF (20 mL) with the respective amine (1 g, 9.2 mmol). The mixture was cooled to 0°C followed by drop wise addition of chlorodiphenylphosphine (4.04 g, 18.3 mmol) under stirring. The solution was brought to room temperature and refluxed overnight. The solution was then filtered, washed with anhydrous hexane (2 x 10 mL), and the solvent was removed under vacuum to afford the ligands, **L-1, L-2 and L-3** (Scheme 2.1).

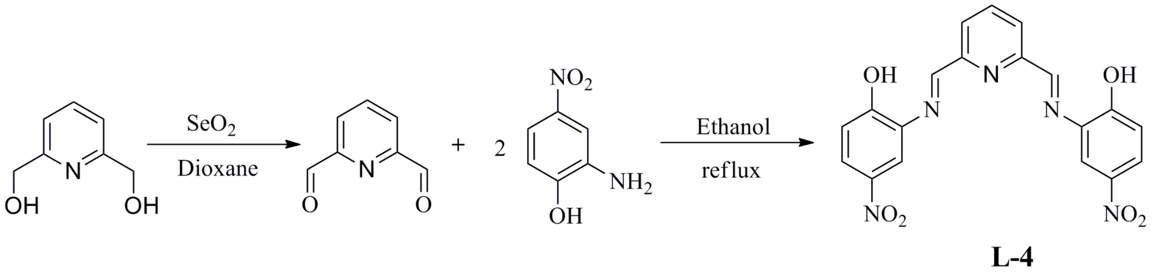
2.1.4 Synthesis of complexes *(C-1 to C-12)*

Metal salts were refluxed for 4h with ligands L-1, L-2, L-3 in 1:1 ratio in THF. The precipitates obtained were filtered and washed with ether (Scheme 2.2).



Scheme 2.2: Synthesis of complexes C-1 to C-12

2.1.5 Synthesis of NNN ligand (*L-4*)



Scheme 2.3: Synthesis of NNN pincer ligand (L-4)

Pyridine-2,6-diol was oxidized to pyridine-2,6-dialdehyde as per the reported procedure (Alam 2011). 0.2 g of the aldehyde obtained was stirred in ethanol (10 mL). 0.48g of 2-amino-4-nitrophenol was added and the mixture was refluxed to obtain the Schiff base ligand (L-4). The solution was then filtered, washed with anhydrous hexane (2 x 10 mL) and the yellow solid was isolated (Scheme 2.3). Yield: 92 %.

2.1.6 Synthesis of complexes (*C-13, C-14, C-15 and C-16*)

Ligand (L-4) was refluxed with metal salts, cobalt (II) acetate, copper (II) acetate, iron (II) chloride and manganese (II) chloride respectively for 8 h in 1:1 ratio in THF. The precipitates obtained were filtered and washed with ether (Figure 2.1).

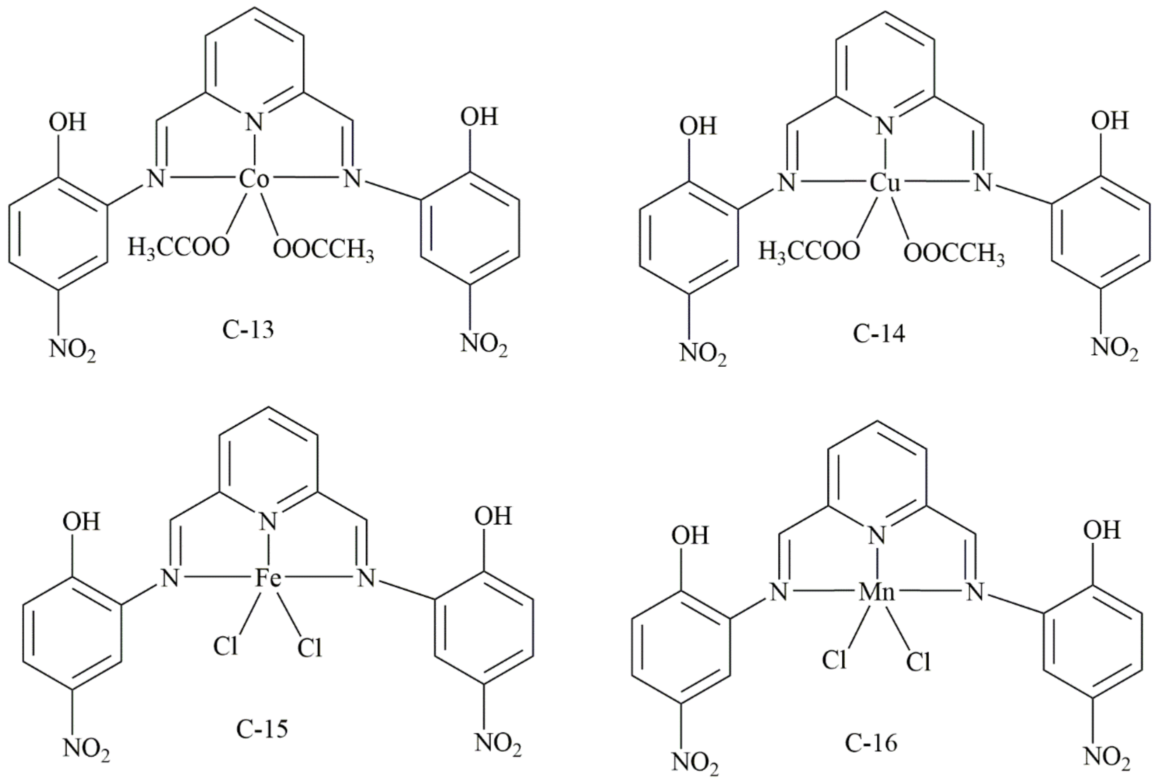


Figure 2.1: Complexes C-13, C-14, C-15 and C-16

2.2 RESULTS AND DISCUSSION

The ligands and the complexes were characterized by FTIR, mass spectra and elemental analysis. All the results were in full agreement with the proposed structure. ^{1}H NMR spectral analysis of the ligands also substantiates the structures proposed for the ligands. TGA spectra of the complexes further support the structures of the complexes.

2.2.1 Physical and analytical studies

The physical properties and analytical data of the ligands and the complexes are given in the Table 2.1. The elemental analysis (C, H, and N) data were in good agreement with the proposed empirical formulae of the complexes, respectively.

Table 2.1 Physical properties and analytical data

Sample	Yield (%)	Elemental analysis data*		
		C	H	N
L-1	83	74.90 (75.46)	5.30 (5.28)	2.59 (2.93)
L-2	78.9	75.01 (75.62)	5.41 (5.50)	5.69 (5.88)
L-3	87.2	72.15 (72.95)	5.03 (5.28)	8.56 (8.80)
C-1	79.6	63.95 (64.66)	4.41 (4.58)	2.18 (2.36)
C-2	77.4	63.89 (64.76)	4.52 (4.76)	4.43 (4.72)
C-3	82.3	59.85 (60.56)	4.43 (4.77)	6.28 (6.42)
C-4	80.4	57.02 (57.34)	3.76 (3.85)	2.17 (2.23)
C-5	79.1	57.02 (57.43)	4.04 (4.02)	4.23 (4.47)
C-6	80.9	55.15 (55.34)	3.92 (4.00)	6.51 (6.68)
C-7	73.6	63.91 (64.16)	4.43 (4.54)	2.19 (2.34)
C-8	72.4	64.08	4.58	4.60

Sample	Yield (%)	Elemental analysis data*		
		C	H	N
		(64.26)	(4.72)	(4.68)
C-9	75.3	59.85 (60.13)	4.47 (4.74)	6.12 (6.38)
C-10	71.5	57.11 (57.42)	3.72 (3.86)	2.14 (2.23)
C-11	73.9	57.07 (57.52)	3.92 (4.02)	4.29 (4.47)
C-12	74.2	54.89 (55.42)	3.88 (4.01)	6.50 (6.69)
L-4	91	55.90 (56.02)	3.18 (3.22)	17.08 (17.19)
C-13	83	47.10 (47.27)	3.20 (3.28)	11.89 (11.98)
C-14	78	46.68 (46.90)	3.19 (3.25)	11.72 (11.89)
C-15	81	42.48 (42.73)	2.39 (2.45)	13.03 (13.11)
C-16	75	42.56 (42.80)	2.41 (2.46)	13.08 (13.14)

*** Found (calculated)**

2.2.2 FTIR spectra

FTIR analysis of the ligands L-1, L-2 and L-3 showed medium intensity secondary N-H stretching at 3350, 3360 and 3250 cm^{-1}, respectively (Figure 2.2 to Figure 2.4).

Formation of bond between O and P in L-1 is indicated by the absence of broad peak for O-H stretching and appearance of a peak at 750 cm^{-1} for P-O stretching. A sharp peak at 694 cm^{-1} is assigned to the P-N stretching in both the ligands and the complexes (Shagidullin et al. 1985).

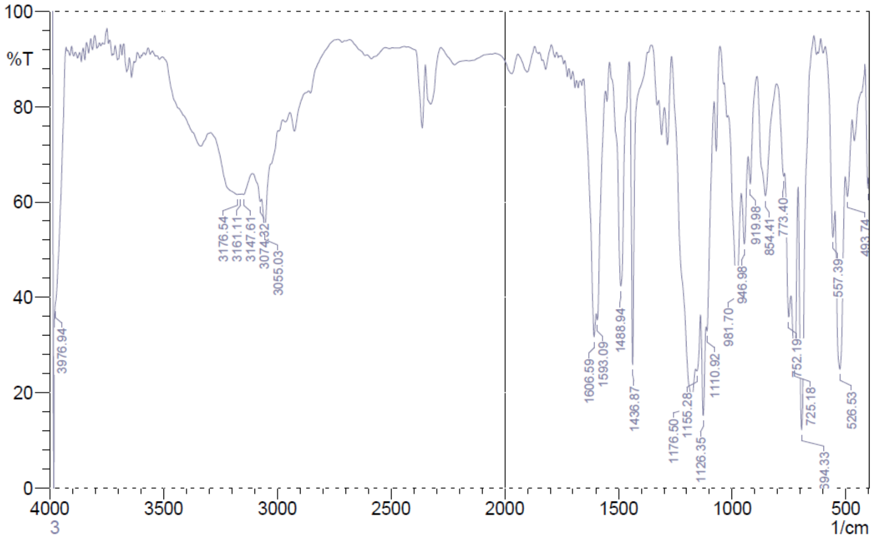


Figure 2.2 FTIR spectrum of L-1

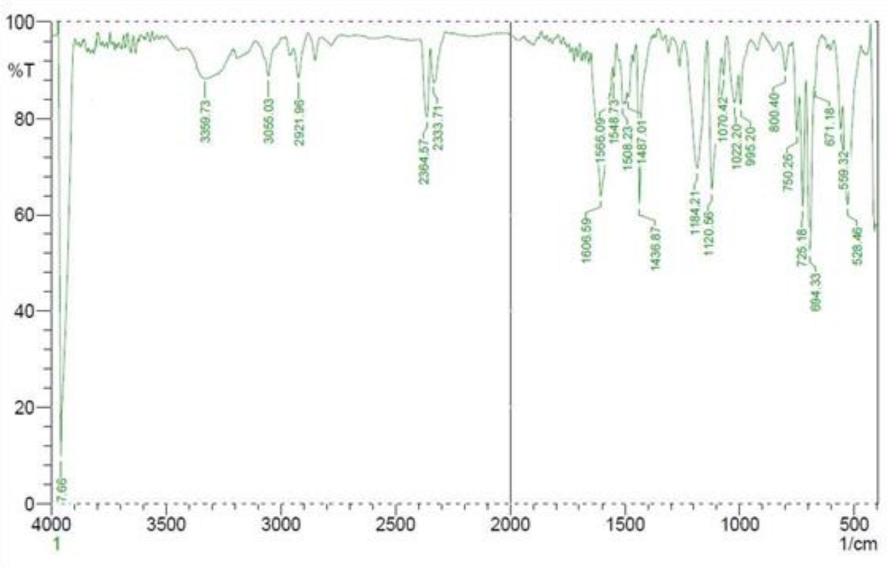


Figure 2.3 FTIR spectrum of L-2

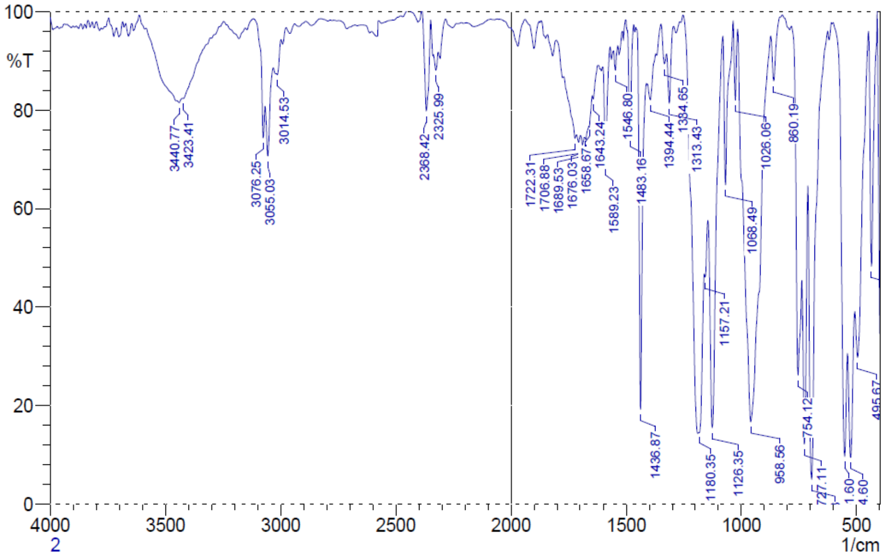


Figure 2.4 FTIR spectrum of L-3

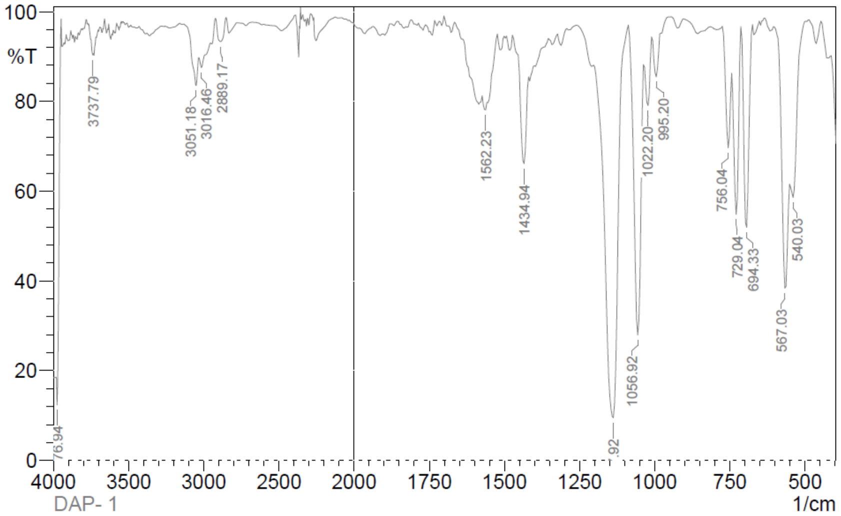


Figure 2.5 FTIR spectrum of C-3

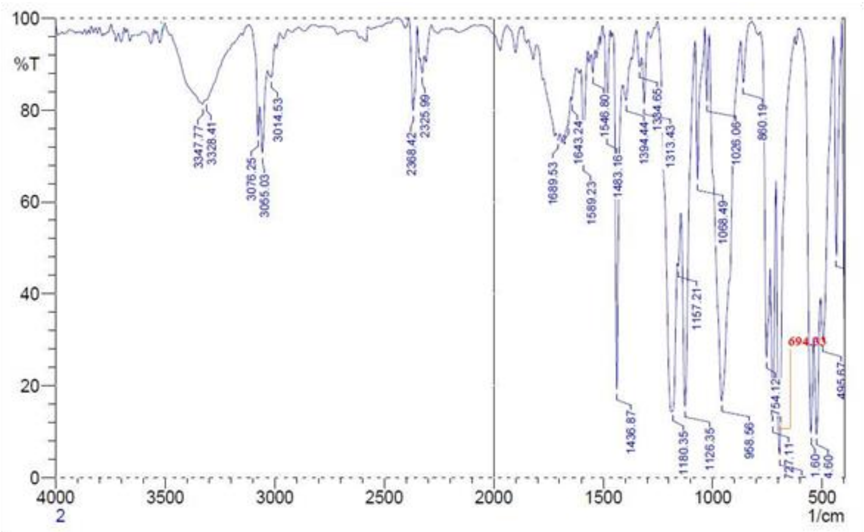


Figure 2.6 FTIR spectrum of C-4

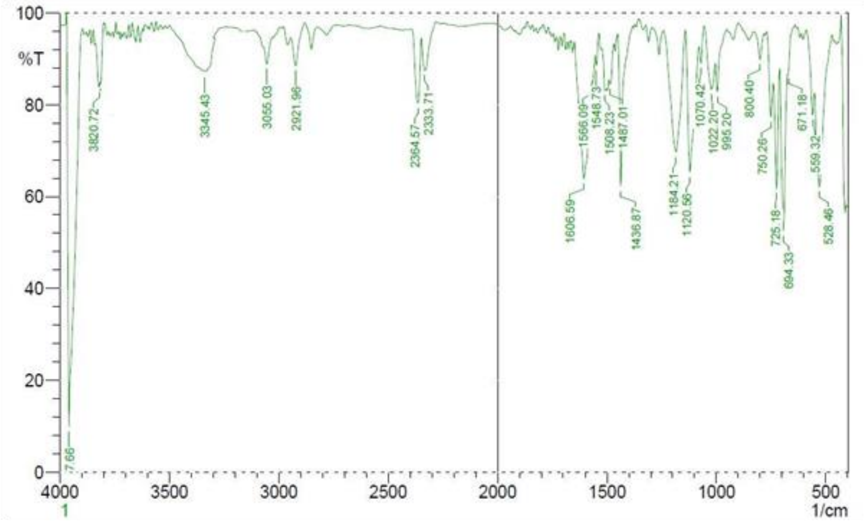


Figure 2.7 FTIR spectrum of C-7

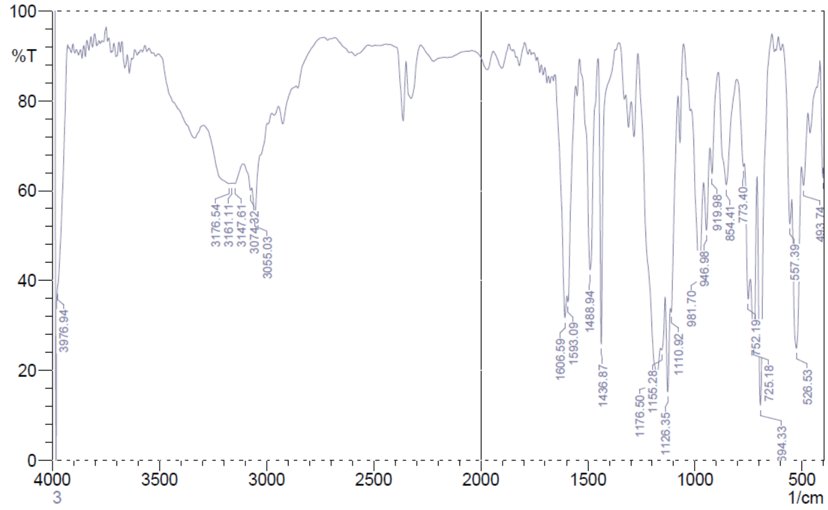


Figure 2.8 FTIR spectrum of C-10

Figure 2.9 represents the FTIR spectra of the complexes C-13 to C-16 in comparison with the ligand, L-4. A strong, broad O-H stretching is present in all the spectra in the region of 3300-3400 cm^{-1}. Also, medium absorption around 3080-90 cm^{-1} corresponds to the aromatic C-H stretching in the spectra. A medium absorption at 1686 cm^{-1} in L-4 corresponding to imine stretching appears to have shifted to lower frequency on complexation in the spectra of complexes (Sreekanth and Kurup 2003).

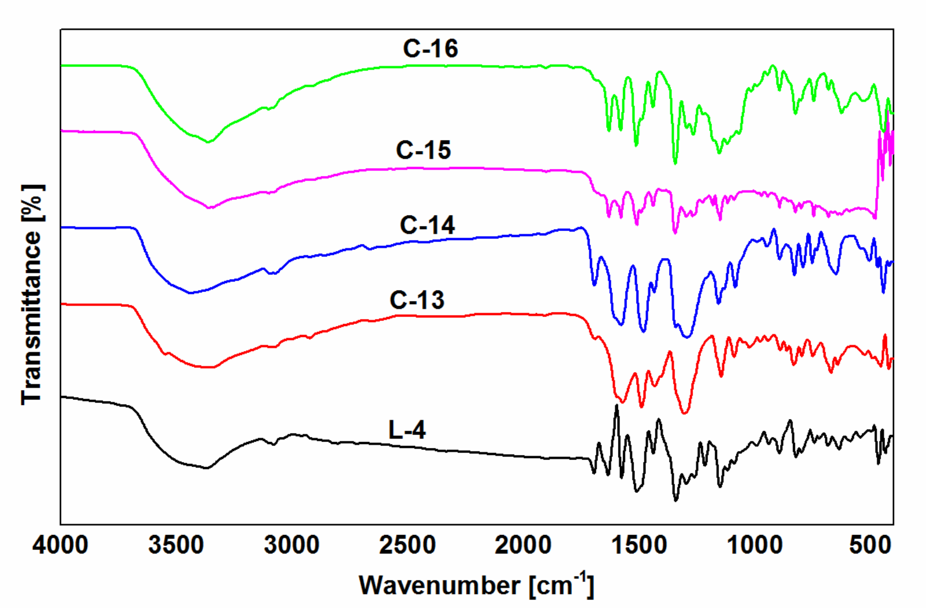


Figure 2.9 FTIR spectra of L-4 and its complexes

2.2.3 Electronic spectra

Electronic spectra of the complexes along with their corresponding ligands were recorded using methanol as a confirmatory measure to imply the complex formation (Figure 2.10 to Figure 2.13). In all the spectra recorded, there is a shift in the absorption band from the ligand to the complex perceptibly indicating the complex formation. The absorption bands observed in the spectrum of the free ligand have shifted to lower energy region in the spectra of complexes due to the coordination of the ligand with metal ion. Bathochromic shift observed from the free ligand to the complexes indicates a charge transfer phenomenon and it can be inferred that the transitions observed in the spectra are majorly due to intra ligand charge transfer transitions in the ultraviolet region and ligand to metal charge transfer transitions in the visible region of the spectra (Garcia et al.2004).

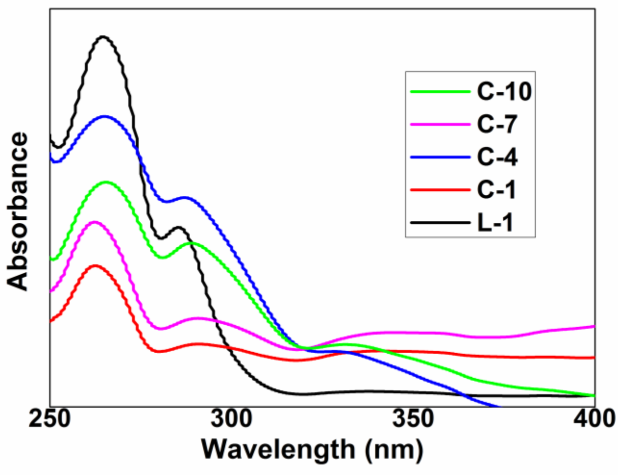


Figure 2.10 Electronic absorption spectra of complexes with ligand L-1

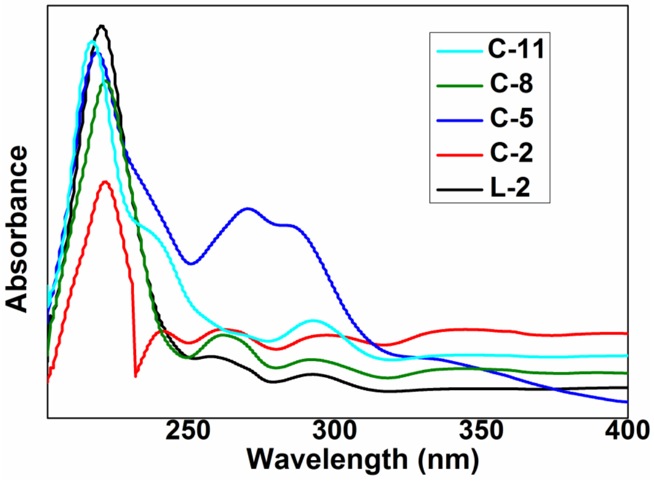


Figure 2.11 Electronic absorption spectra of complexes with ligand L-2

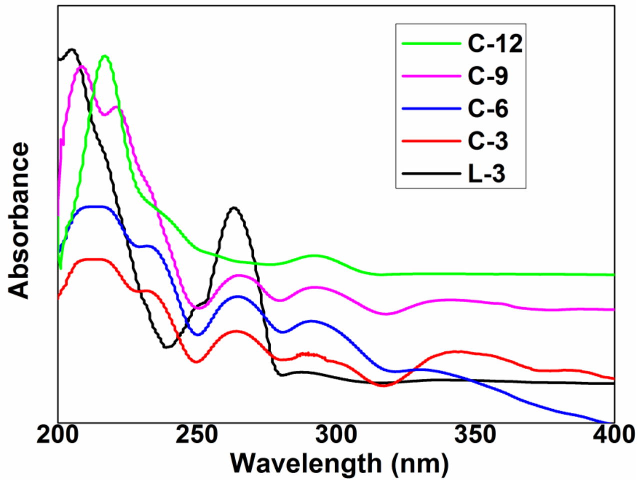


Figure 2.12 Electronic absorption spectra of complexes with ligand L-3

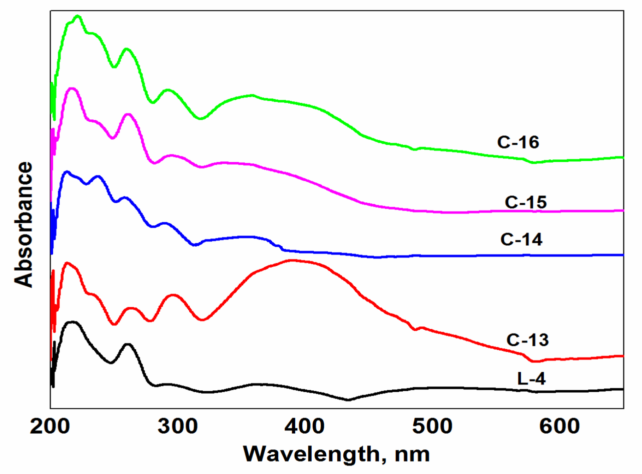


Figure 2.13 Electronic absorption spectra of complexes with ligand L-4

2.2.4 Thermal analysis

To determine the thermal behavior and stability of the complexes, TGA analysis was performed from room temperature to 700 °C at a heating rate of 10 °C/min for complexes C-1, C-2, C-3, C-6, C-9 and C-12. The cobalt complexes, C-1, C-2 and C-3 with ligands L-1, L-2 and L-3 respectively show typical TGA curves (Figure 2.14) representing single step dissociation of the complexes. The dissociation of the ligands is observed well after the temperature of 500 °C indicating the exceptional stability of the pincer complex formed. TGA curves for C-3, C-6, C-9 and C-12 corresponding to cobalt, iron, copper and manganese complexes of ligand L-3 are shown in Figure 2.15. Iron complex, C-6 closely follows C-3 in the structural decomposition showing major dissociation w.r.t the ligand moiety removal at 501 °C. This type of dissociation is attributed to the excellent thermal stability expected of a pincer complex. Thermogram of copper complex, C-9 represents a two-step dissociation, wherein the first dissociation begins at 130 °C and continues up to 230 °C showing a cumulative weight loss of about 22%, constituting the dissociating acetate ligands along with water of crystallization. C-12, which is a manganese complex, shows two-step dissociation of the ligand moieties and the initial dissociation starting at 260 °C corresponds to the loss of sulphate ligand. The structural decomposition reflects on the inferior stability of the complexes formed and suggests C-9 and C-12 complexes to have coordination environment with lower stability compared to their cobalt and iron analogues.

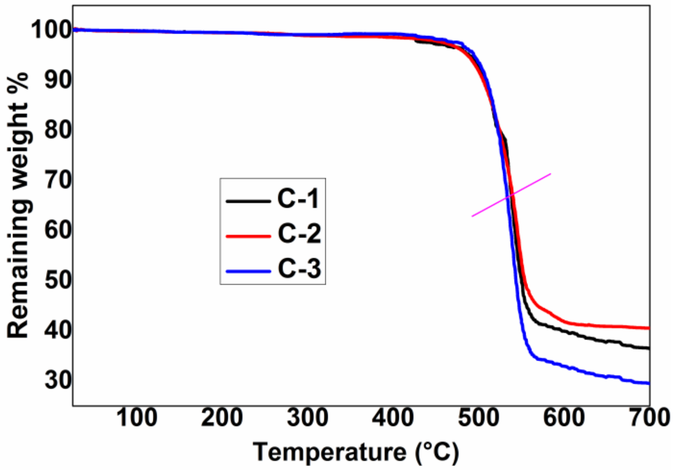


Figure 2.14 TGA curve of complexes C-1 to C-3

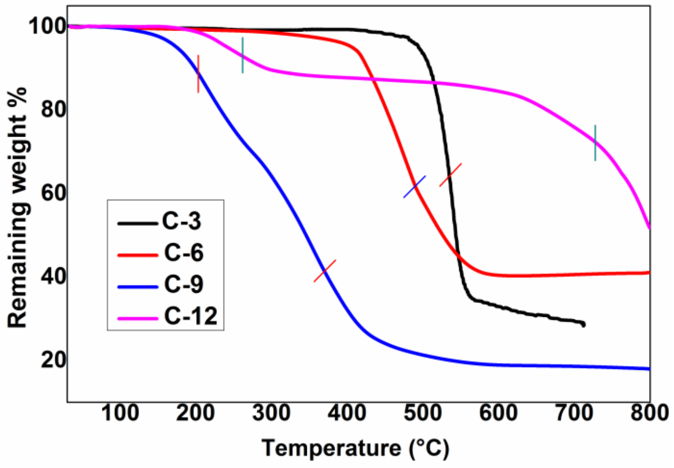


Figure 2.15 TGA curve of complexes C-3, C-6, C-9 and C-12

Complexes C-13 to C-16, were subjected to thermal analysis in order to interpret the stability as well as their structural information and is shown in Figure 2.16. Thermograms of C-13 and C-15 show high temperature, single step dissociation curves which basically reflects very strong on the stability of the complexes with cobalt and iron as the coordinated metals respectively. The dissociation of both these complexes begins well after 400 °C which strongly signifies the stable complexes formed of these two metals with the ligand, L-4. Thermograms corresponding to copper and manganese complexes of the same ligand, C-14 and C-16 however show low temperature and multi-step dissociation of the ligand moiety. This TGA dissociation pattern reflects on the lesser stability of these complexes when compared to their cobalt and iron analogues. From the thermograms, C-16 which is a manganese coordinated complex is expected to be least stable. With respect to the thermograms being a characteristic tool confirming the structure of the complexes, all the dissociation curves clearly indicate the absence of any coordinated water molecules and seconds the structures proposed for the complexes.

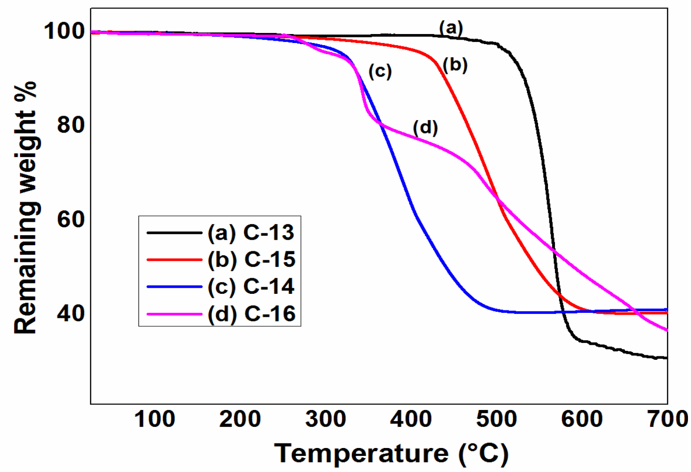


Figure 2.16 TGA curve of complexes C-13 to C-16

2.2.5 Magnetic susceptibility measurements

The spin-state of the complexes is generally related in close to the properties of the donor groups and to the resulting geometry of the complexes. Spin-state of a metal complex is determined by the strength of the ligand field, which is the deciding factor in the magnitude of splitting. The softness and the π-bonding ability of the donor atoms largely determine the spin-state of the complexes. Additionally, the nephelauxetic effect of the donor atoms also accounts to the splitting, since it can reduce the separation between the free ion terms by as much as 50%. Consequently, the crossover points between high- and low-spin ground terms may occur at relatively small values of 10Dq. The nephelauxetic reduction is a function of the electronic delocalization on the ligand and the covalency of the metal-ligand bond, both properties related to the softness and π-bonding ability of the donor atoms. High-spin complexes are generally formed with hard donors (N, O, Cl, etc.) and low-spin complexes are formed with soft donors (P, As, C, I, etc.) (Morassi et al. 1973). Ligands with P, As, and C as donor atoms generally give low-spin complexes (Sacconi 1968). PCP and the PNP ligands used in this research work have in accordance resulted low spin complexes. The magnetic susceptibility measurements of the complexes, C-1 to C-12 in the solid state are given in Table 2.2.

Table 2.2 Magnetic moments of complexes C-1 to C-12

Compound	μ_{eff} (BM)	Geometry		Compound	μ_{eff} (BM)	Geometry
C-1	2.34	square planar		**C-7**	1.70	square planar
C-2	2.41	square planar		**C-8**	1.81	square planar
C-3	1.96	trigonal bipyramidal		**C-9**	1.77	trigonal bipyramidal
C-4	1.82	square planar		**C-10**	2.98	square planar
C-5	1.93	square planar		**C-11**	3.19	square planar
C-6	2.97	square planar		**C-12**	2.18	square planar

Cobalt complexes, C-1 to C-3 are paramagnetic low-spin complexes with magnetic moment values 2.34, 2.41 and 1.96 BM respectively suggesting the presence of metal in Co^{2+} state with an unpaired electron. The ligands which give low-spin complexes usually have donor atoms of low electronegativity such as P, As or C capable of forming π bonds (Sacconi 1968). Complexes, C-1 and C-2 are low spin four coordinate complexes whose magnetic moments very well matches to the calculated range of 2.1-2-9 B.M for square planar Co(II) species and magnetic moment of C-3 very much lies in the specified range for five co-ordinate cobalt(II) complexes (Barefield et al. 1968), (Higginson et al. 1975).

Among iron complexes, paramagnetism corresponding to one unpaired electron is recorded for C-4 and C-5 supporting the formation of Fe(III) complexes whereas the observed magnetic moment value of 2.97 BM in C-6 supports the formation of Fe(II) complex (Barefield et al. 1968). Paramagnetism corresponding to one unpaired electron indicates C-7 to C-9 to be Cu(II) complex (El-Bindary and El-Sonbati, 2000). Presence of Mn(III) in C-10 and C-11 is confirmed by their magnetic susceptibility measurements. μ_{eff} recorded for C-10 and C-11 are 2.98 and 3.19 B.M respectively which corresponds to Mn in d^4 state having two unpaired electrons. C-12 with Mn(II) metal centre shows paramagnetism corresponding to one unpaired electron with magnetic moment of 2.18 B.M.

Complexes synthesized with ligand L-4 have displayed higher paramagnetism with the magnetic moment values indicating them to be high spin complexes. The magnetic susceptibility measurements of the complexes in the solid state are given in Table 2.3.

Table 2.3 Magnetic moments of complexes C-13 to C-16

Compound	**μ_{eff} (BM)**	**Suggested Geometry**
C-13	4.67	trigonal bipyramidal
C-14	1.87	trigonal bipyramidal
C-15	5.31	trigonal bipyramidal
C-16	5.99	trigonal bipyramidal

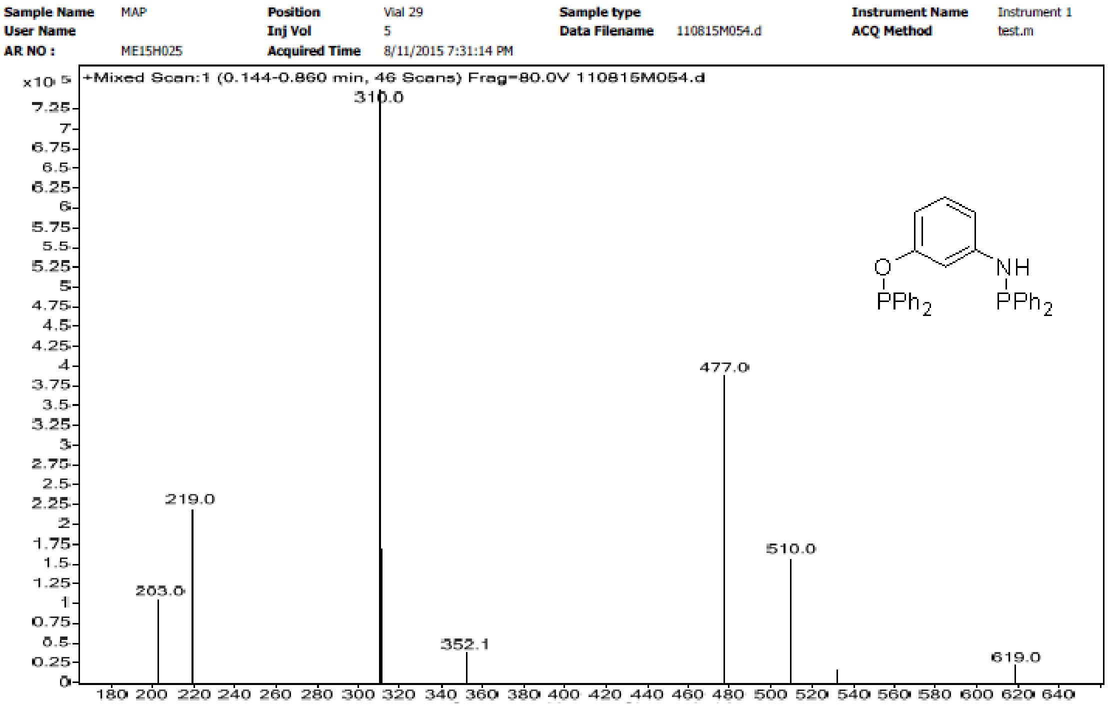
Room temperature magnetic moment values plainly suggest the metal ions to be in their (II) oxidation state in complexes, C-13 to C-16. Cobalt complex, C-13 shows a magnetic moment of 4.67 BM against the expected 4.2 – 4.6 BM for five co-ordinate Co(II) complexes (Barefield et al. 1968). C-14 which is a Cu(II) complex shows paramagnetism of 1.87 BM with respect to one unpaired electron (Hu et al. 2003). Magnetic moment value of 5.31 BM suggests the presence of 4 unpaired electrons in C-15 against the expected magnetic moment of 5.1 to 5.5 BM for Fe(II) five coordinated geometry (Barefield et al. 1968). Manganese in C-16 has a magnetic moment of 5.99 BM against the expected moment of 5.9 to 6.2 for Mn(II) geometry (Chandra and Gupta 2002).

2.2.6 ESI-Mass analysis

The structure of the ligands and the complexes were further confirmed by ESI mass spectra. The expected molecular weight and the observed molecular weight of the complexes are given in the Table 2.4. Selected mass spectra of ligands and complexes are depicted in Figure 2.17 to Figure 2.27.

Table 2.4 ESIMS data

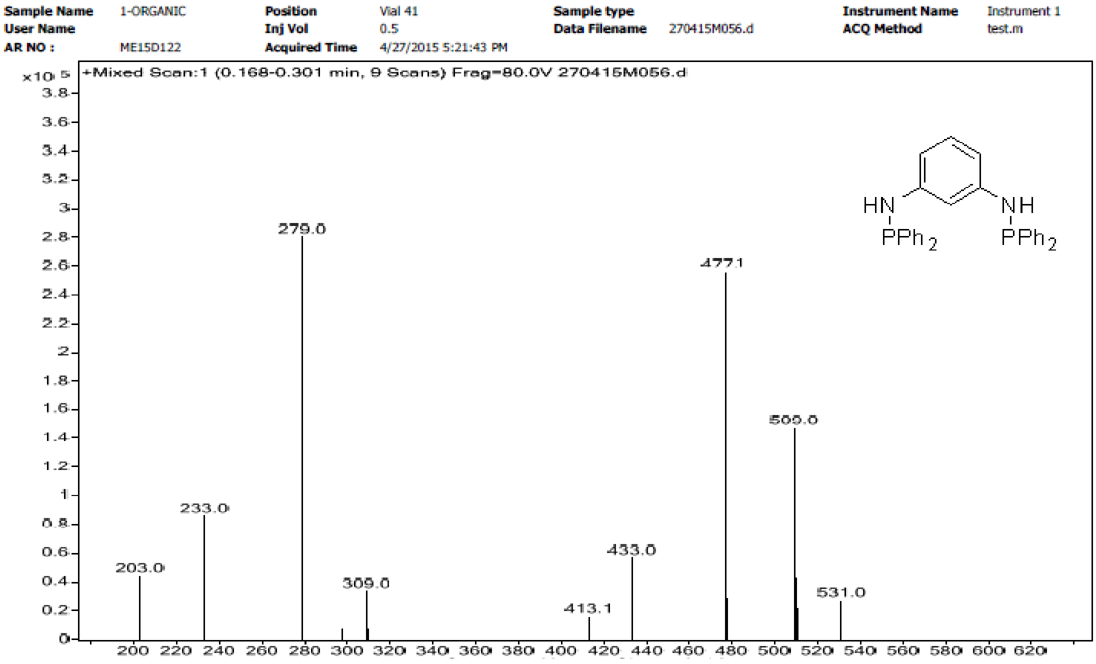
Compound	Expected mass	Observed mass	Compound	Expected mass	Observed mass
L-1	477.1	477.0	C-6	629.1	630.3
L-2	476.1	477.1	C-7	598.1	599.0
L-3	477.1	478.4	C-8	597.1	597.8
C-1	594.1	595.4	C-9	658.1	659.5
C-2	593.1	594.2	C-10	627.0	627.9
C-3	654.1	655.1	C-11	626.0	627.4
C-4	628.0	628.9	C-12	628.0	629.3
C-5	627.0	628.1			
L-4	407.1	407.0	C-15	532.9	533.7
C-13	584.1	585.3	C-16	531.9	532.5
C-14	588.0	588.8			



Sample Name MAP **Position** Vial 29 **Sample type** **Instrument Name** Instrument 1
User Name **Inj Vol** 5 **Data Filename** 110815M054.d **ACQ Method** test.m
AR NO : ME15H025 **Acquired Time** 8/11/2015 7:31:14 PM

+Mixed Scan:1 (0.144-0.860 min, 46 Scans) Frag=80.0V 110815M054.d

Figure 2.17 ESI mass spectrum of L-1



Sample Name 1-ORGANIC **Position** Vial 41 **Sample type** **Instrument Name** Instrument 1
User Name **Inj Vol** 0.5 **Data Filename** 270415M056.d **ACQ Method** test.m
AR NO : ME15D122 **Acquired Time** 4/27/2015 5:21:43 PM

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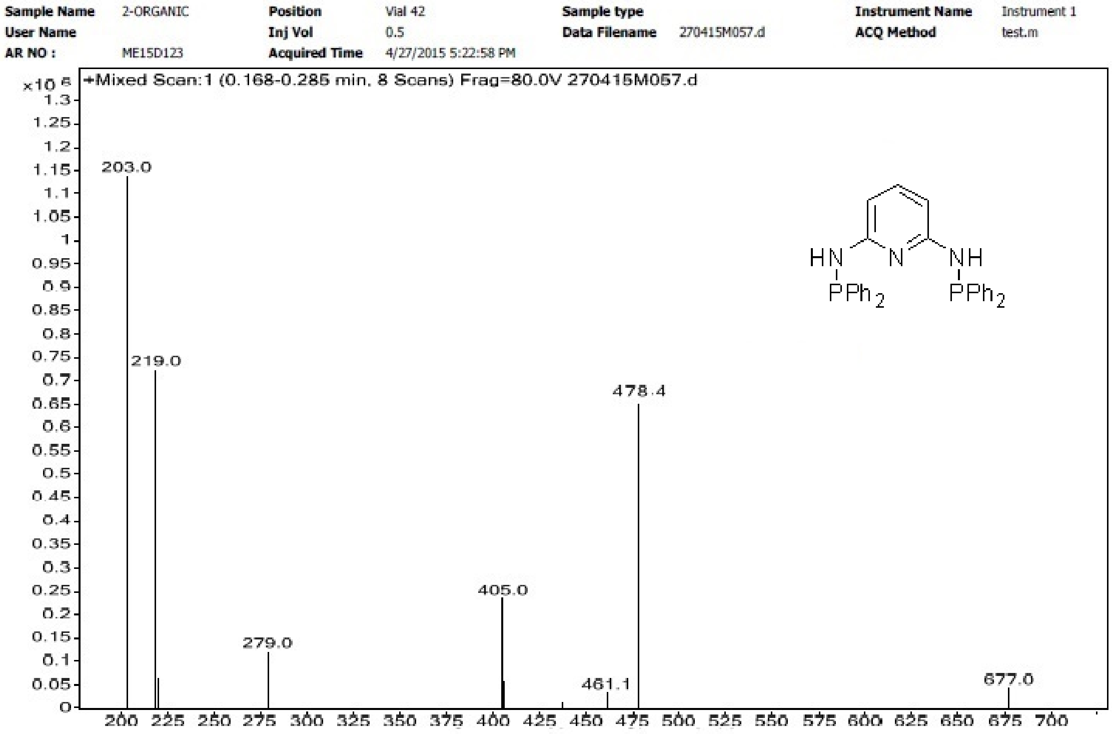
Figure 2.18 ESI mass spectrum of L-2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Acquired Time 4/27/2015 5:22:58 PM
Sample type
Data Filename 270415M057.d
Instrument Name Instrument 1
ACQ Method test.m

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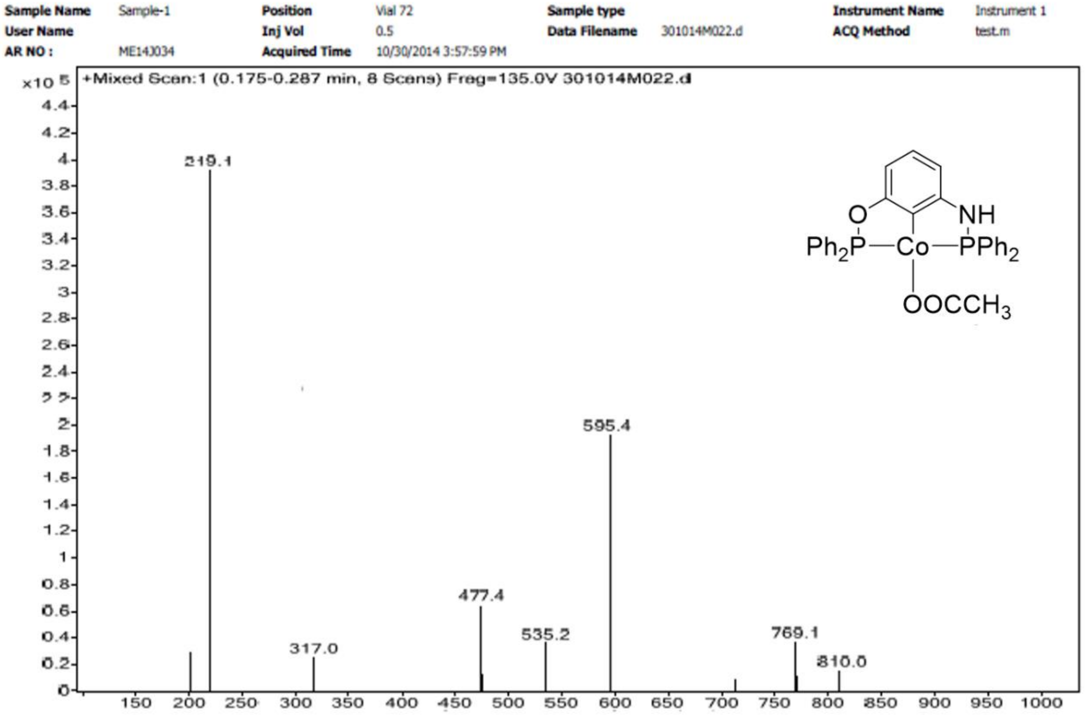
Figure 2.19 ESI mass spectrum of L-3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User Name
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Inj Vol 0.5
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Sample type
Data Filename 301014M022.d
Instrument Name Instrument 1
ACQ Method test.m

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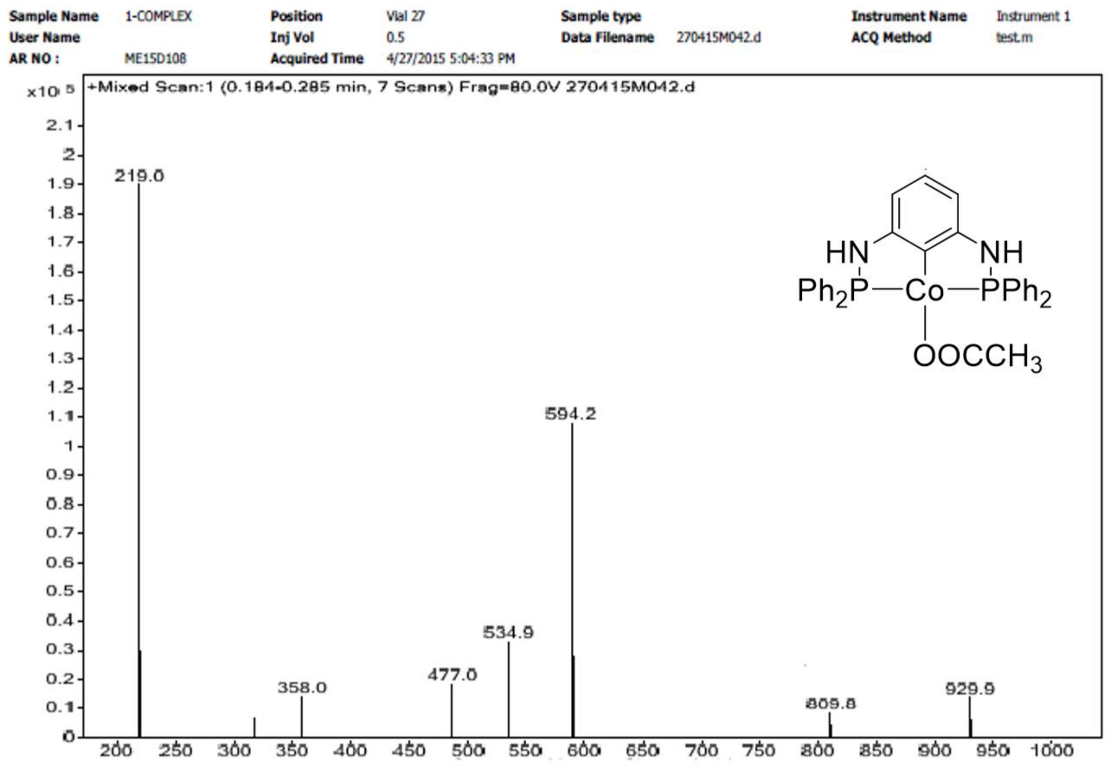
Figure 2.20 ESI mass spectrum of C-1



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User Name
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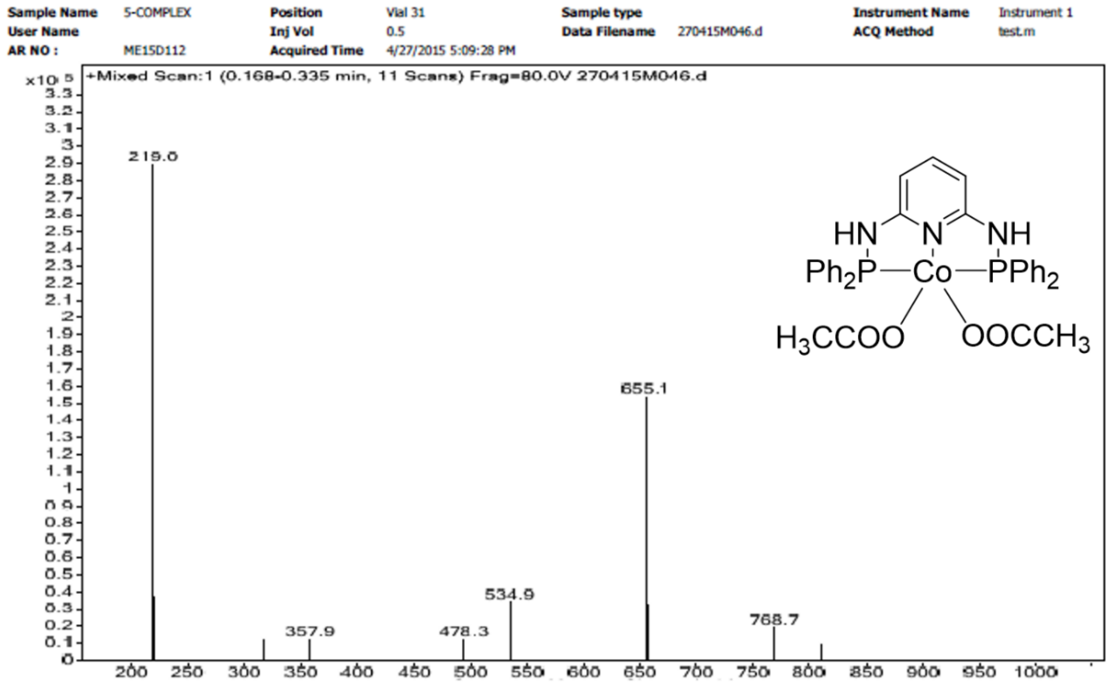
Inj Vol 0.5
Acquired Time 4/27/2015 5:04:33 PM
Sample type
Data Filename 270415M042.d
Instrument Name Instrument 1
ACQ Method test.m

Figure 2.21 ESI mass spectrum of C-2



Sample Name 5-COMPLEX
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Inj Vol 0.5
Acquired Time 4/27/2015 5:09:28 PM
Sample type
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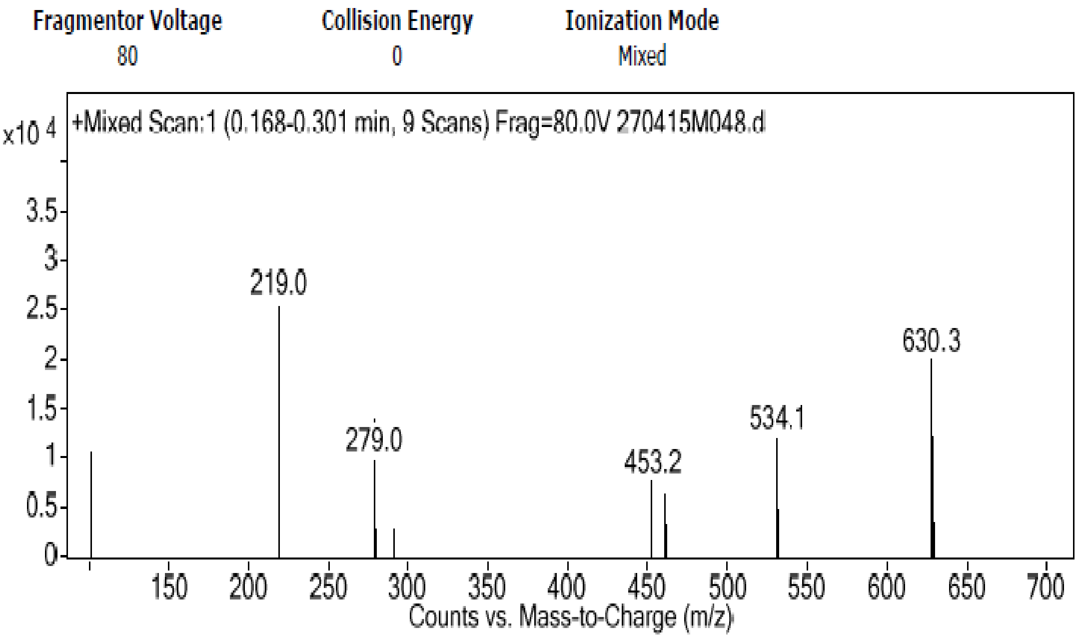
Instrument Name Instrument 1
ACQ Method test.m

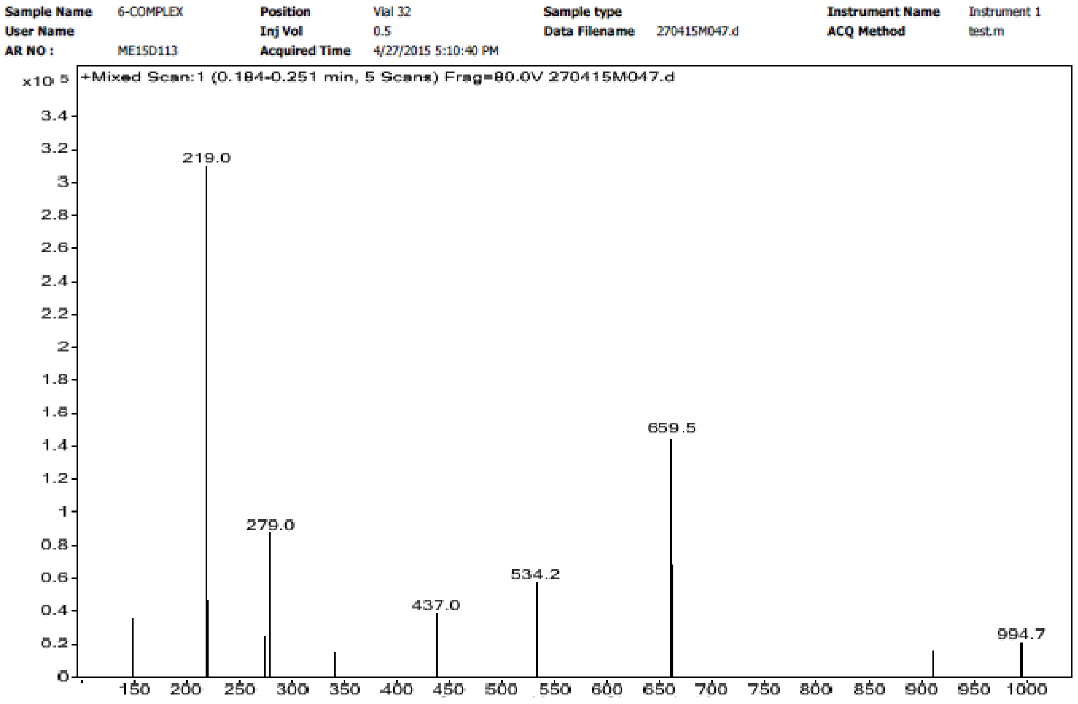
Figure 2.22 ESI mass spectrum of C-3


Fragmentor Voltage 80

Collision Energy 0

Ionization Mode Mixed

Figure 2.23 ESI mass spectrum of C-6


Sample Name 6-COMPLEX

User Name

AR NO : ME15D113

Position Vial 32

Inj Vol 0.5

Acquired Time 4/27/2015 5:10:40 PM

Sample type

Data Filename 270415M047.d

Instrument Name Instrument 1

ACQ Method test.m

Figure 2.24 ESI mass spectrum of C-9

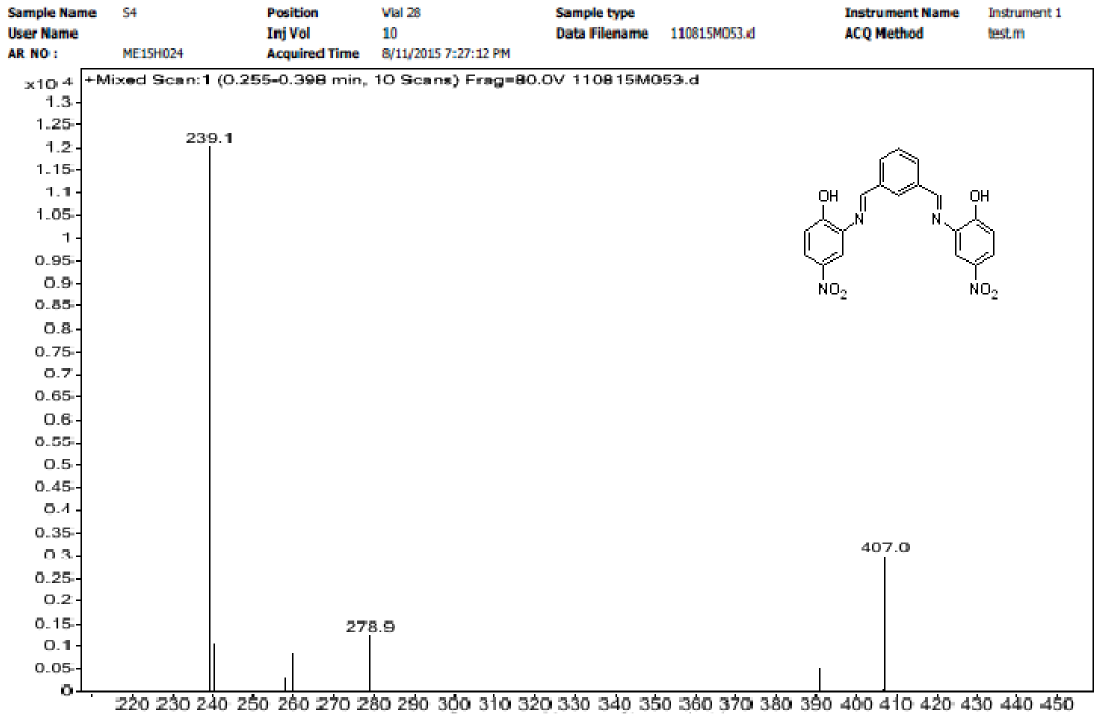


Figure 2.25 ESI mass spectrum of L-4

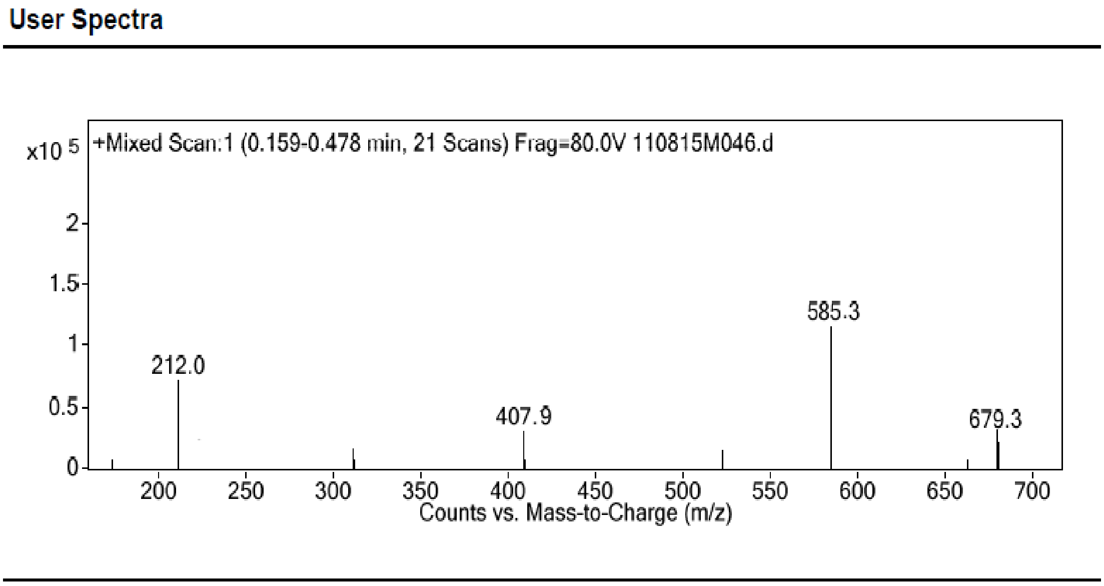


Figure 2.26 ESI mass spectrum of C-13

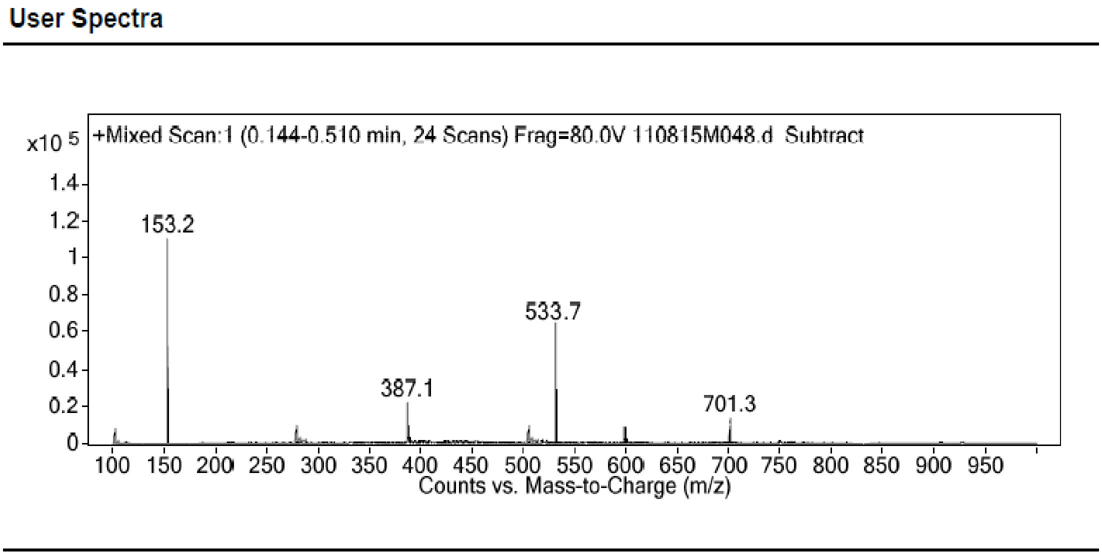


Figure 2.27 ESI mass spectrum of C-15

2.2.7 NMR analysis

^{1}H NMR spectra at 400 MHz were recorded for the ligands L-1, L-2, L-3 and L-4 and ^{31}P NMR spectra at 161.8 MHz were recorded for the ligands L-1, L-2 and L-3 which further provided their structural confirmation (Table 2.5 & 2.6).

Table 2.5 ^{1}H NMR shifts of ligands

Compound	**Chemical shift (ppm)**
L-1 (Figure 2.28)	δ 7.89 – 7.75 (m, 9H), 7.65 – 7.43 (m, 15H), 4.02 (br s, 1H, NH)
L-2 (Figure 2.29)	δ 7.82 – 7.62 (m, 8H), 7.61 – 7.54 (m, 4H), 7.53 – 7.40 (m, 12H), 4.02 (br s, 2H, NH)
L-3 (Figure 2.30)	δ 7.82 – 7.62 (m, 9H), 7.61 – 7.54 (m, 3H), 7.53 – 7.40 (m, 8H), 7.40 – 7.27 (m, 3H), 3.78 – 3.49 (br s, 2H, NH)
Pyridine-2,6-dialdehyde (Figure 2.31)	δ 10.16 (s, 2H, CHO), 8.19 (m, 2H), 8.10 (m, 1H)
L-4 (Figure 2.32)	δ 8.82 (s, 2H), 8.24 (m, 1H) 8.17 – 8.05 (m, 4H), 7.78 (s, 2H), 7.08 (m, 2H), 5.18 (br s, 2H, OH)

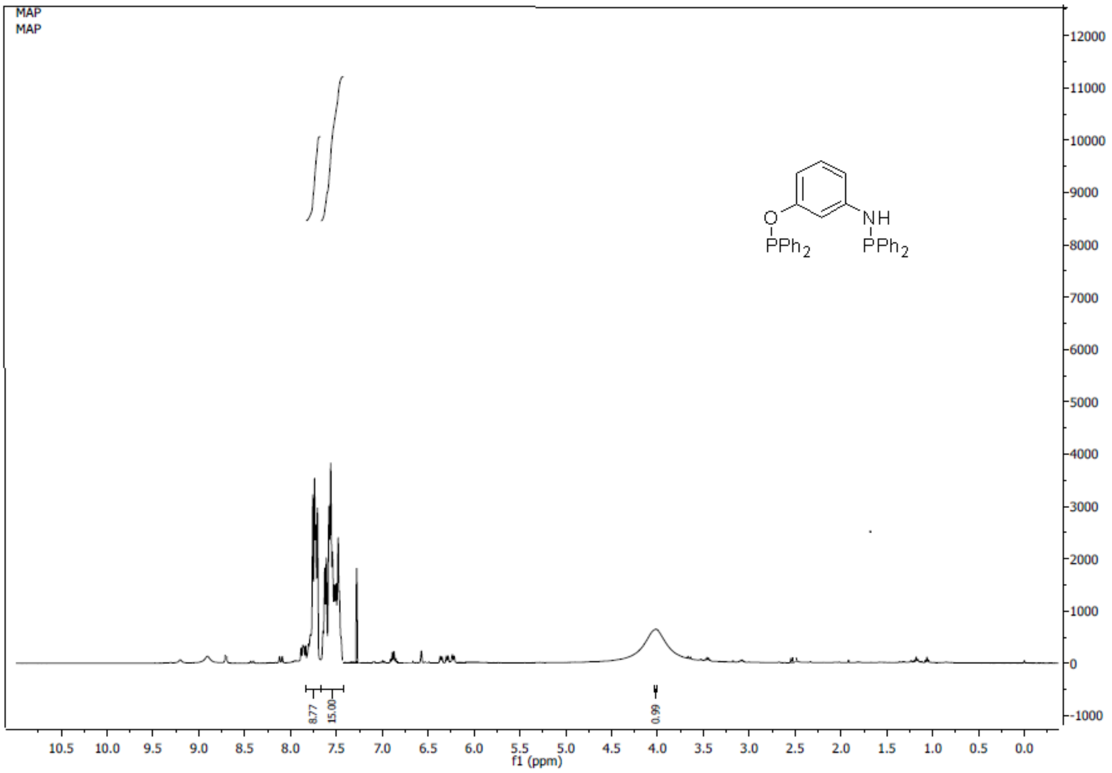


Figure 2.28 ^{1}H NMR spectrum of ligand L-1

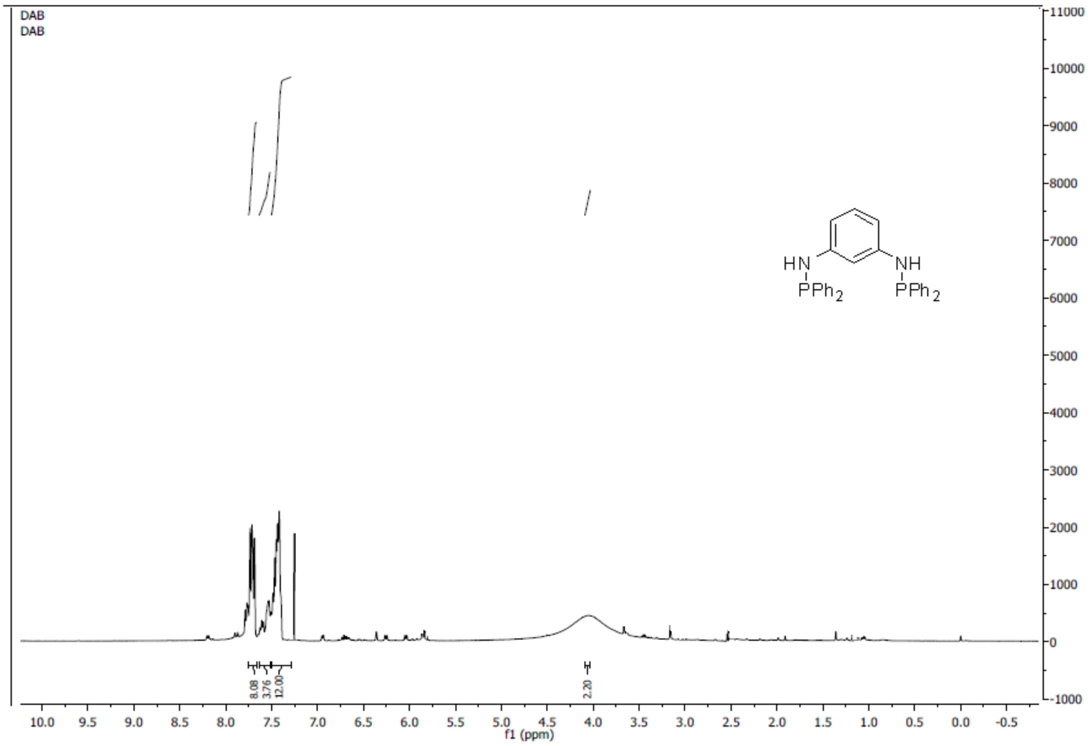


Figure 2.29 ^{1}H NMR spectrum of ligand L-2

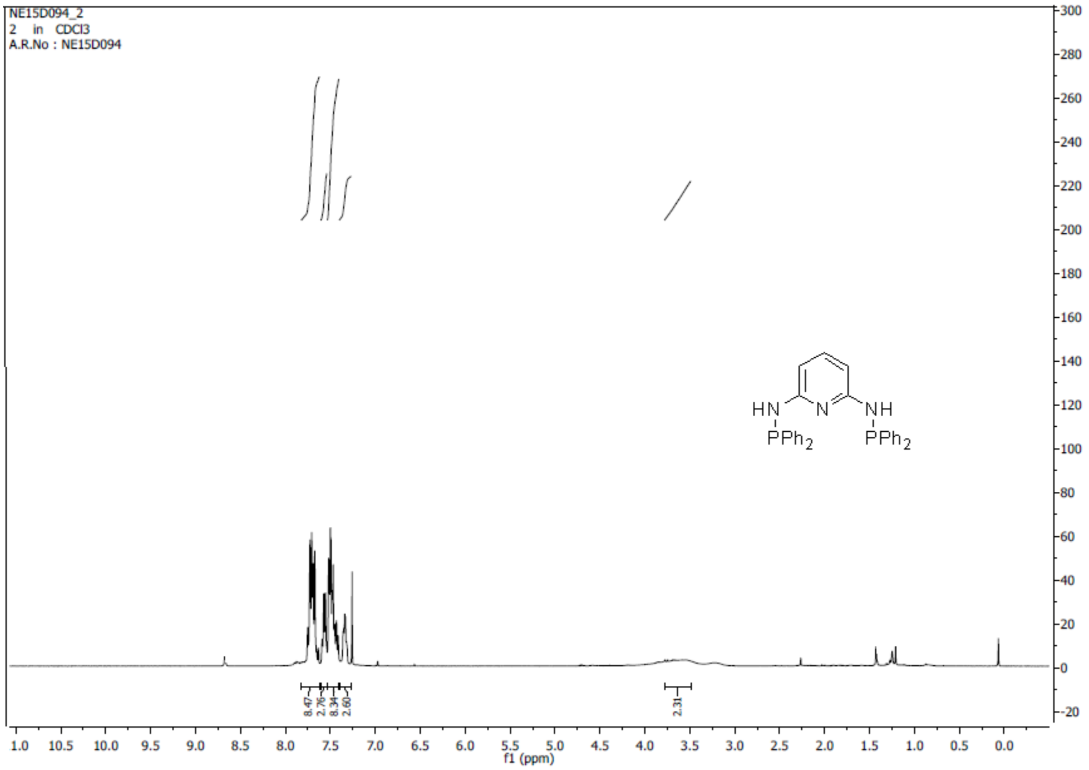


Figure 2.30 ^{1}H NMR spectrum of ligand L-3

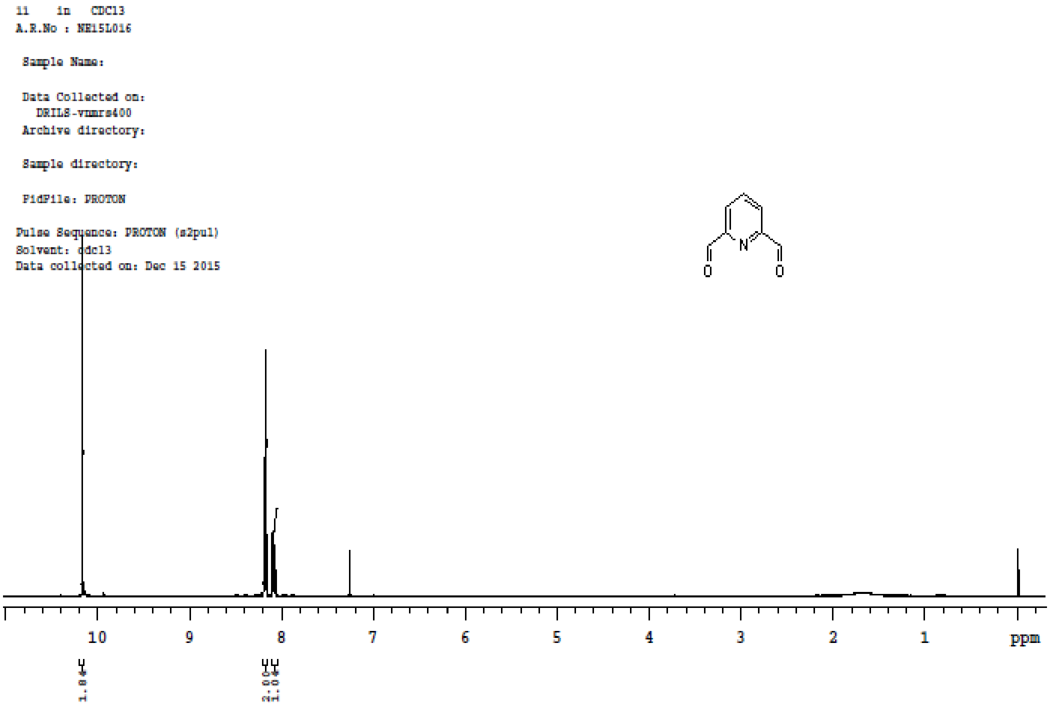


Figure 2.31 ^{1}H NMR spectrum of pyridine-2,6-dialdehyde

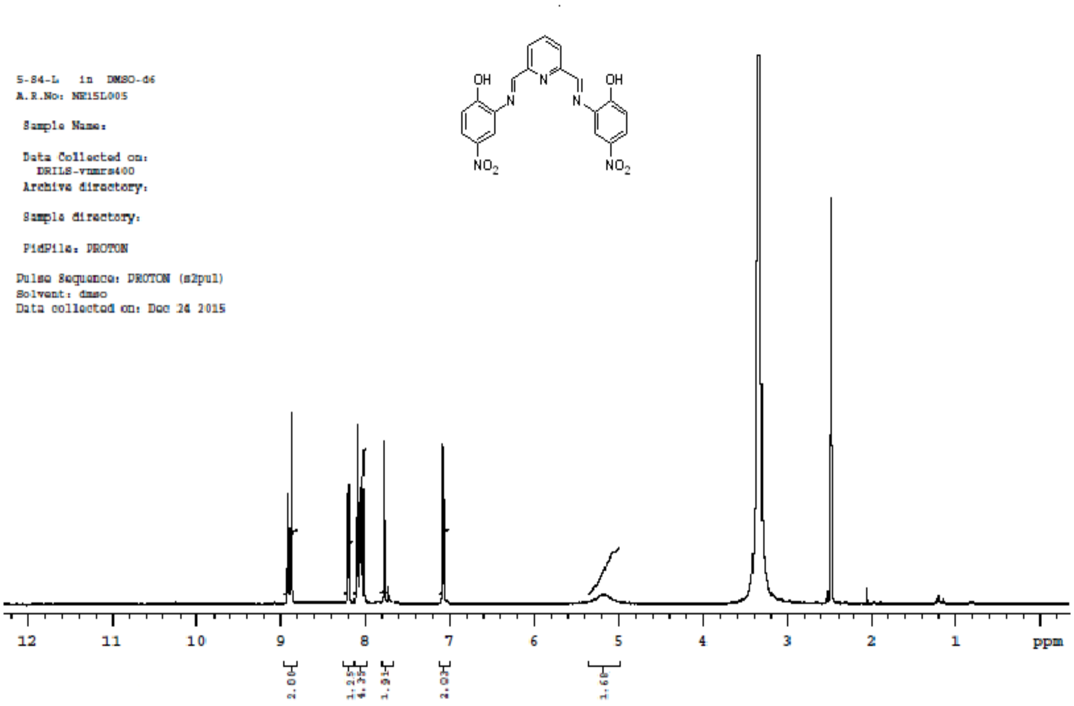
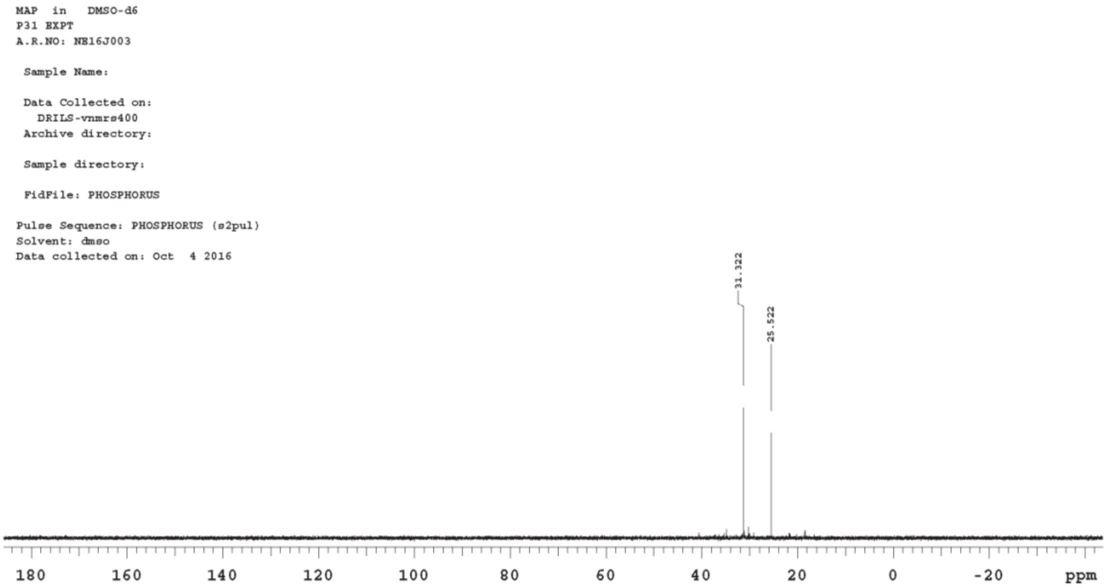


Figure 2.32 ^{1}H NMR spectrum of ligand L-4

A broad singlet was obtained at δ 4.02 for both L-1 and L-2 corresponding to the N-H protons. In L-3, this shift was observed at δ 3.78 – 3.49. The proton NMR of pyridine-2,6-dialdehyde showed the aldehydic singlet at δ 10.16 which disappeared in L-4 on Schiff base formation. A singlet peak corresponding to O-H proton shift was observed at δ 5.18 in L-4. The aromatic protons shift appeared between δ 7.0 and δ 8.0 in all the compounds. The complexes owing to their paramagnetism were NMR inactive and therefore their chemical shifts could not be recorded.

Table 2.6 ^{31}P NMR shifts of ligands

Compound	**Chemical shift (ppm)**
L-1 (Figure 2.33)	δ 25.5 (s, PN), 31.3 (s, PO)
L-2 (Figure 2.34)	δ 25.47 (s, PN)
L-3 (Figure 2.35)	δ 25.46 (s, PN)


MAP in DMSO-d6
P31 EXPT
A.R.NO: NB16J003

Sample Name:

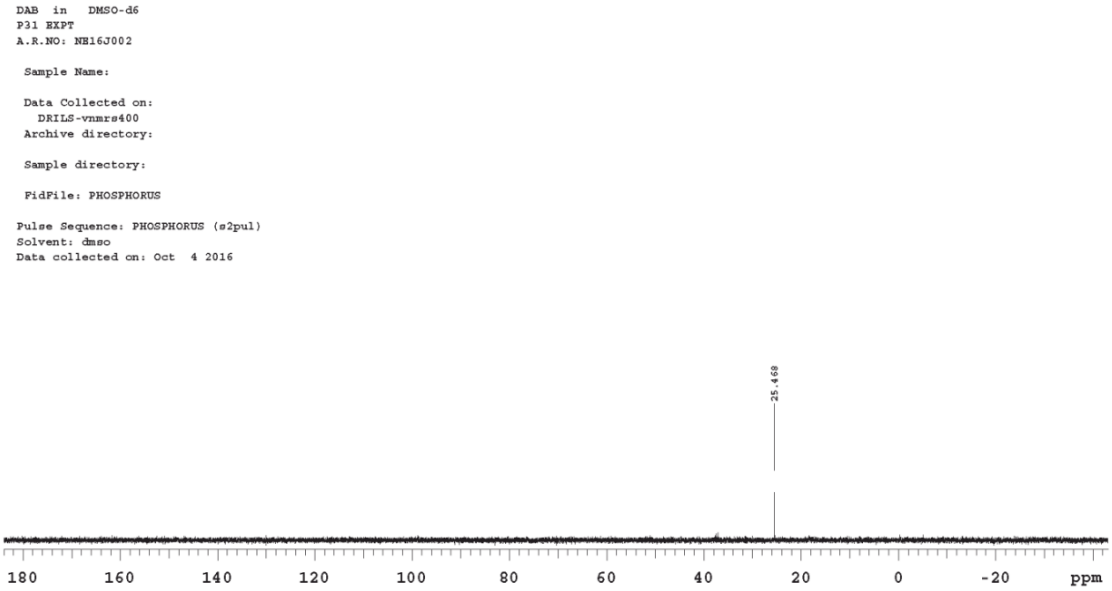
Data Collected on:
DRILS-vnmrs400
Archive directory:

Sample directory:

FidFile: PHOSPHORUS

Pulse Sequence: PHOSPHORUS (s2pul)
Solvent: dmso
Data collected on: Oct 4 2016

Figure 2.33 ^{31}P NMR spectrum of ligand L-1


DAB in DMSO-d6
P31 EXPT
A.R.NO: NB16J002

Sample Name:

Data Collected on:
DRILS-vnmrs400
Archive directory:

Sample directory:

FidFile: PHOSPHORUS

Pulse Sequence: PHOSPHORUS (s2pul)
Solvent: dmso
Data collected on: Oct 4 2016

Figure 2.34 ^{31}P NMR spectrum of ligand L-2

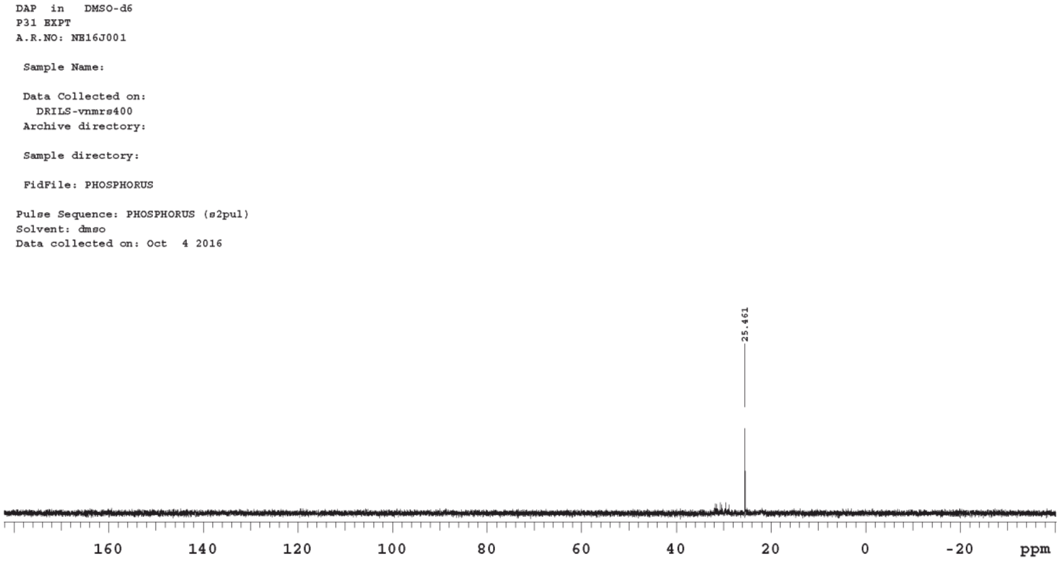


Figure 2.35 ^{31}P NMR spectrum of ligand L-3

L-1, L-2 and L-3 which contains ‘P’ atoms were additionally characterized by ^{31}P NMR. Asymmetrical ligand L-1 shows two distinct peaks, one at δ 25.5 corresponding to P-N and the other at δ 31.3 for P-O. Ligands L-2 and L-3 which are symmetrical show the chemical shift which is a singlet corresponding to P-N at δ 25.47 in L-2 and at δ 25.46 in L-3.

CHAPTER 3

CATALYTIC ACTIVITY OF PINCER COMPLEXES

Chapter 3 describes the Suzuki-Miyaura cross-coupling reaction of phenylboronic acid with aryl halides using the synthesized complexes as homogeneous catalysts. Optimization of the reaction conditions in order to accomplish the coupling conversion are highlighted. The plausible mechanisms were predicted for the present catalytic system.

Suzuki-Miyaura reaction is one of the most popular reactions in modern organic chemistry. Generally, the cross-coupling of an organoboron compound with an organic halide which produces a bis-aryl via direct C-C bond formation are palladium-catalyzed reactions. The reaction has a good amount of applications in organic syntheses, material and medicinal chemistry and it still continues to be an area of intense research. High catalytic activity and selectivity have been achieved in the C-C bond formation using pincer complexes, largely having Pd and to some extent with Ni, Ru as the active metal. High price and relatively less abundance of palladium metal pose a hitch in developing the Pd complexes as potential catalysts for extensive use and scale up. In case of complexes bearing nickel or ruthenium, their relative toxicity compared to other transition metals like Fe, Cu, Co, Mn is not a green and promising aspect. Application of pincer complexes bearing Fe, Cu, Co, Mn to catalyze Suzuki coupling is a very new and challenging field we intend to explore, with an aim of obtaining quite an analogous outcome in terms of yield and efficiency.

The present work intends to make a novel attempt at utilizing pincer complexes with cheaper and benevolent metals like Fe, Cu, Co, Mn in cross-coupling of aromatic halides and phenylboronic acid. The significant conversion of biaryls was determined by Gas Chromatography (GC). The reaction between 4-bromobenzonitrile and phenylboronic acid was chosen as a model reaction to evaluate the catalytic activity of the catalyst precursors. Various factors including solvent, catalyst loading, alkalinity, temperature and time were screened to optimize the reaction conditions.

3.1 EXPERIMENTAL

3.1.1 General procedure for the Suzuki reaction

Aryl halide (1.0 mmol) was added to a mixture of phenylboronic acid (1.3 mmol), pincer complex (0.5 mol%) and base (2.0 mmol) in 5 mL of solvent and heated to 80 °C. The mixture was then cooled to room temperature and the organic phase analyzed by gas chromatography.

3.1.2 Gas chromatography

The product analysis was carried out using Gas Chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% siloxane Restek capillary column (30 m length and 0.25 mm diameter) and flame ionization detector (FID). The initial column temperature was increased from 60 °C to 150 °C at the rate of 10 °C/min and then further raised to 220 °C at the rate of 40 °C/min. N_2 was used as the carrier gas. The temperature of the injection port was kept constant at 150 °C and 250 °C respectively during product analysis. The retention time for different compounds was determined by injecting pure compounds under identical GC conditions.

3.2 RESULTS AND DISCUSSION

3.2.1 Catalytic activity studies of complexes, C-1 to C-12

The reaction conditions were optimized with respect to

- Solvent and reaction temperature
- Base
- Catalyst concentration
- Reaction time

(a) Effect of solvent and temperature

The catalytic activities of C-1 to C-3 were checked in methanol, ethanol, 50% aq. ethanol, 1,4-dioxane, toluene, and acetonitrile media (Figure 3.1A). Amongst the solvents tested, highest catalytic activity was observed with dioxane as the solvent media. Acetonitrile was the second most productive solvent in terms of conversion. Moderate catalytic activities were found in other solvents such as methanol, ethanol, 50% aq. ethanol, and toluene. The catalytic activities of other complexes were checked in ethanol, 1,4-dioxane, toluene and acetonitrile media (Figure 3.1 B-D). As observed for complexes C-1 to C-3, methanol and 50% aq. ethanol did not facilitate the catalytic activity of the complex profoundly, therefore, these solvents were not included in the solvent study for the remaining complexes. Study of the solvent effect on the activity of the catalysts highlights the efficiency of dioxane in terms of percentage conversion between 4-bromobenzonitrile and phenylboronic acid, closely followed by acetonitrile. However, considering the lower reaction temperature with acetonitrile (at 80 °C) and the marginal difference in the GC yield between dioxane and acetonitrile, the latter was optimized as solvent media under reflux temperature for further reactions. The enhanced activity of acetonitrile as a solvent may be attributed to the easy miscibility of reactants and the catalyst in the solvent and the property of acetonitrile to act in itself as a ligand with its exceptional coordinating property (Dyson and Jessop 2016). With acetonitrile chosen as the solvent media, the other parameter considered for optimization is the reaction temperature. The reaction was found to work out best at its reflux temperature.

Also, catalytic runs carried out with the careful exclusion of air and water showed no major difference in the reaction rate, selectivity, and yield as those carried out without any special precautions. This observation indicated that the presence or absence of inert atmosphere had no remarkable effect on the product conversion. All catalytic reactions were then carried out without special effort to remove air and water and with the reflux condenser open to air.

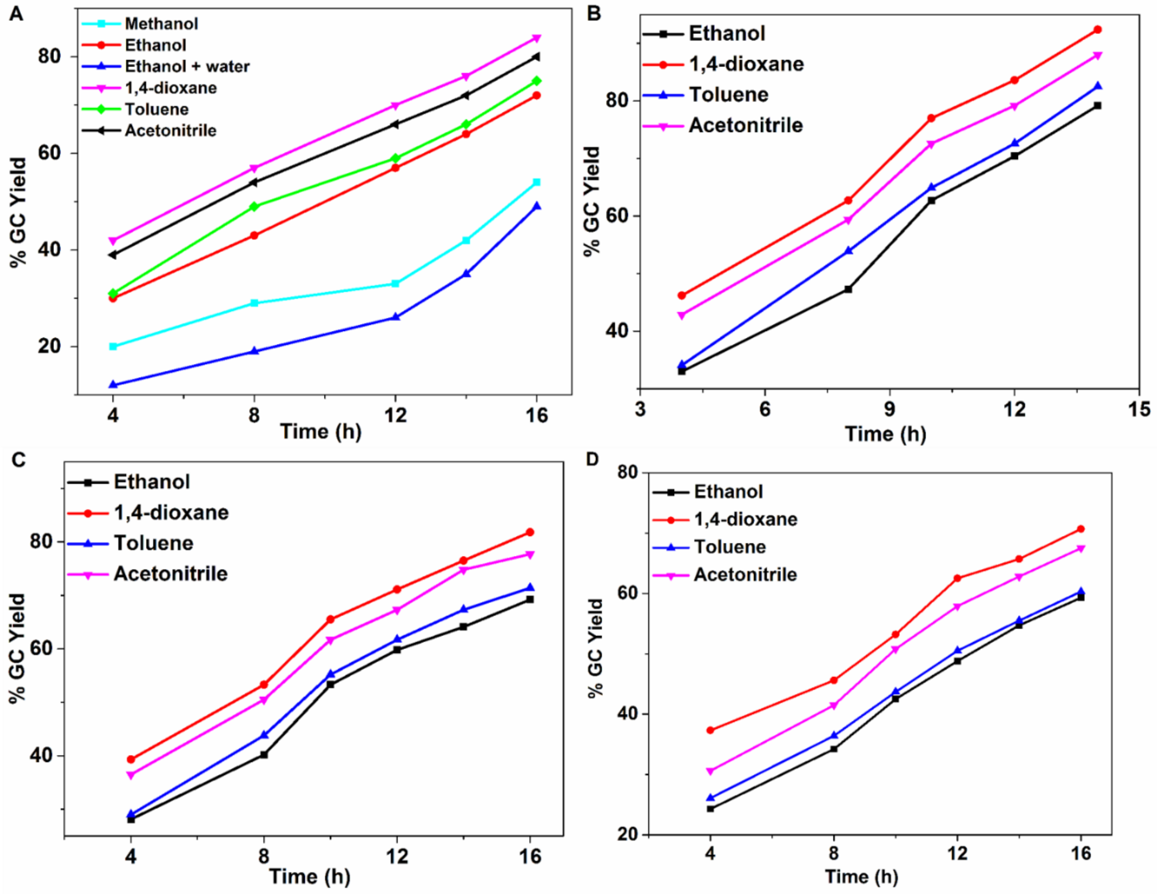


Figure 3.1 Effect of solvent on (A) C-1, (B) C-4, (C) C-7 and (D) C-10

(b) Effect of catalyst concentration and influence of air on the reaction

In order to study the effect of concentration of the catalyst with respect to the substrate, the reaction was studied at the varying substrate to catalyst ratios. The ratio was varied from total catalyst amount 0.1 mol % to 1.0 mol %. From the catalytic activity studies, it was observed that increase in catalyst loading increases the coupling yield, suggesting that catalyst concentration is very much helpful to enhance the product conversion. After reaching the optimum concentration, further increase of catalyst amount did not affect the yield of coupling product significantly and remained almost constant (Figure 3.2), once again substantiating that the product yield is not very sensitive to catalyst loading at higher concentration. 0.5 mol % of C-1 to C-3, 0.4 mol% of C-4 to C-6 and 0.6 mol % of C-7 to C-12 showed optimum efficiency in catalyzing the reaction in acetonitrile media.

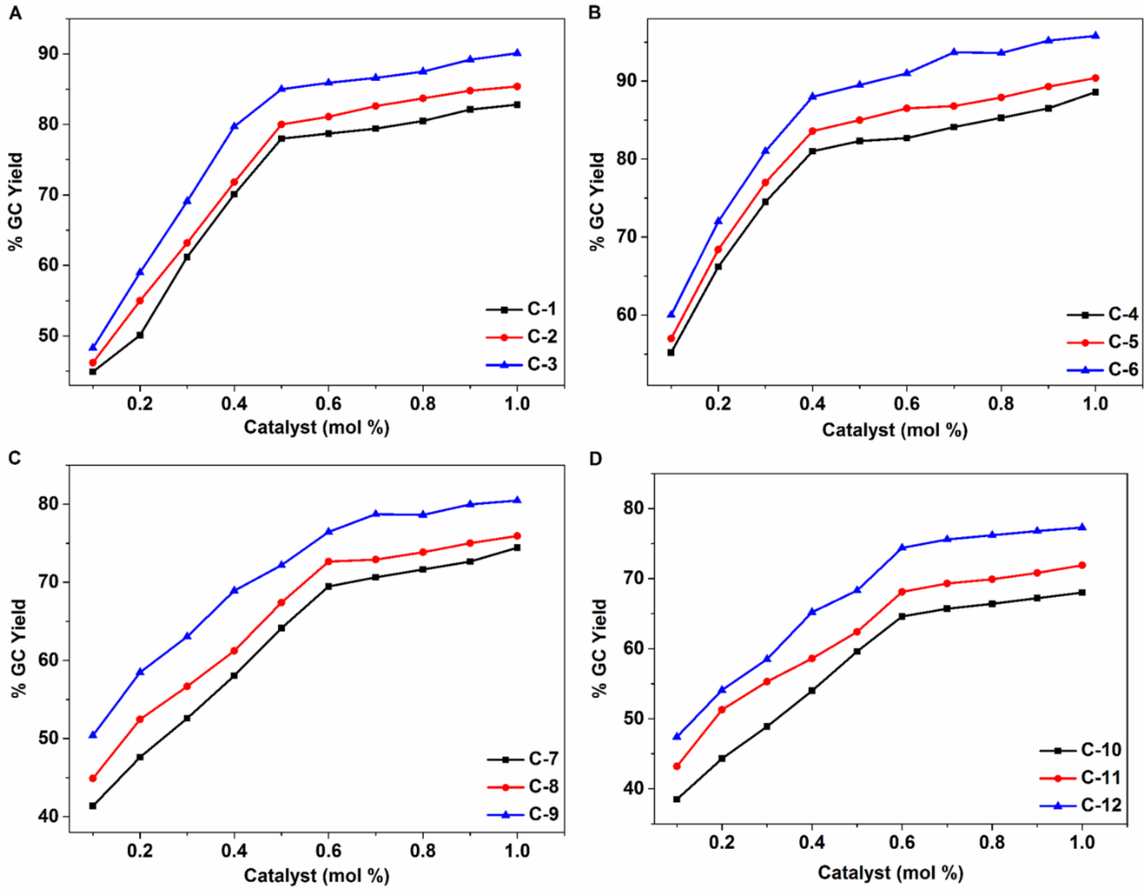


Figure 3.2 Effect of catalyst concentration on the yield of the coupling product

(c) Effect of base

The effect of bases on the product yield was examined for the coupling reaction. Cs_2CO_3 was found to be the most effective base followed by the organic base Et_3N (Figure 3.3). Slightly lower yields were obtained when K_2CO_3, Na_2CO_3, or KO^tBu were used as a base. The unique property of Cs_2CO_3 as a base lie in its well-balanced nature making it a mild base, a feature required for selective deprotonation as well as its suitability for the base-catalyzed reactions. The strongly de-shielded Cs^+ ion makes the base highly reactive and solvating, making the carbonate ion easily available for replacement of the halide ion in the oxidative addition step of the catalytic cycle (Rabie et al. 2017).

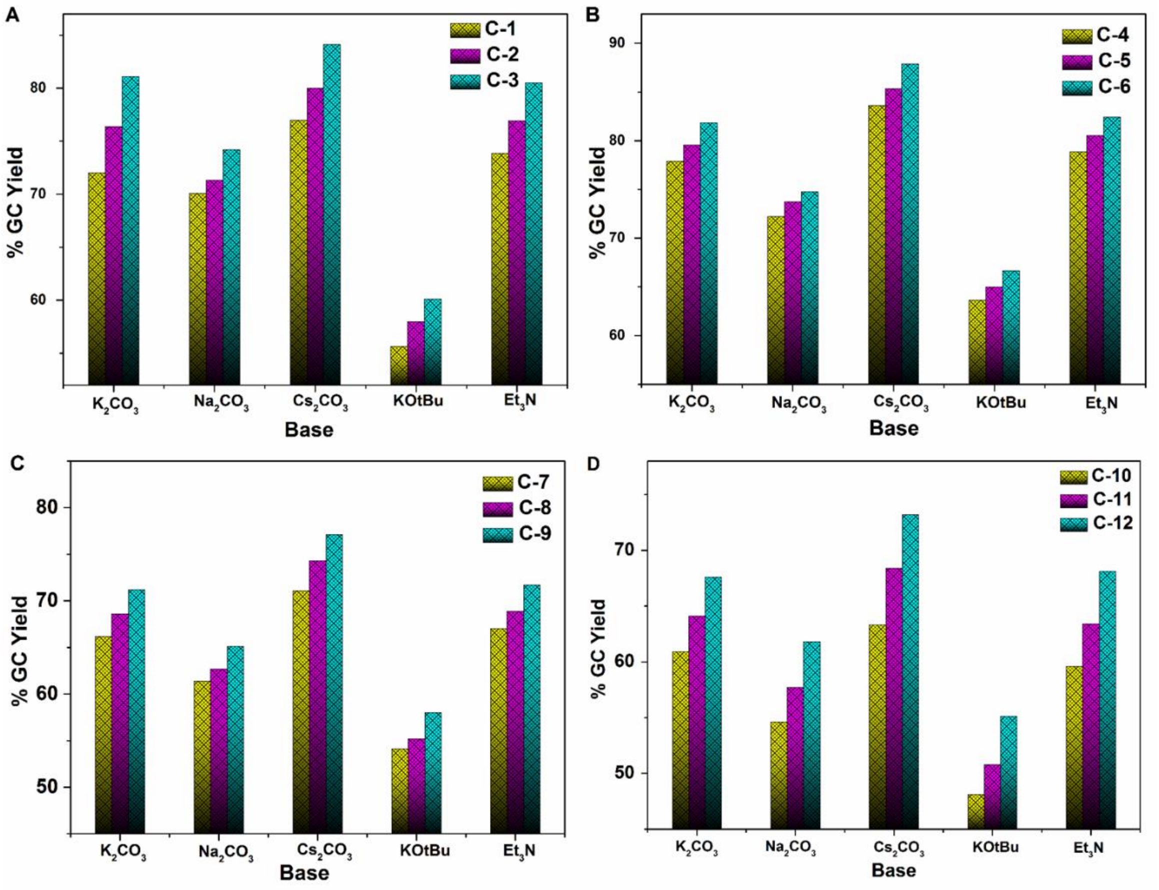


Figure 3.3 Effect of the base on Suzuki coupling of 4-bromobenzonitrile and phenylboronic acid

(d) Effect of reaction time

The dependence of product yield on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time. Most of the 4-bromobenzonitrile was converted by the completion of 14 h. Nevertheless, the dependence of product yield on the reaction time was scrutinized for a period of 20 h (Figure 3.4). Yield variance is apparent to a notable extent up to 16 h of the reaction time for C-1 to C-3 and C-7 to C-12 complexes, further advance in reaction time showed no much effect on the percentage conversion of the product, owing to which the reaction time for the catalytic conversion was optimized for 16 h for these complexes. For C-4 to C-6, which are the iron complexes, the reaction time was optimized at 14 h considering the conversion achieving a steady state at this hour.

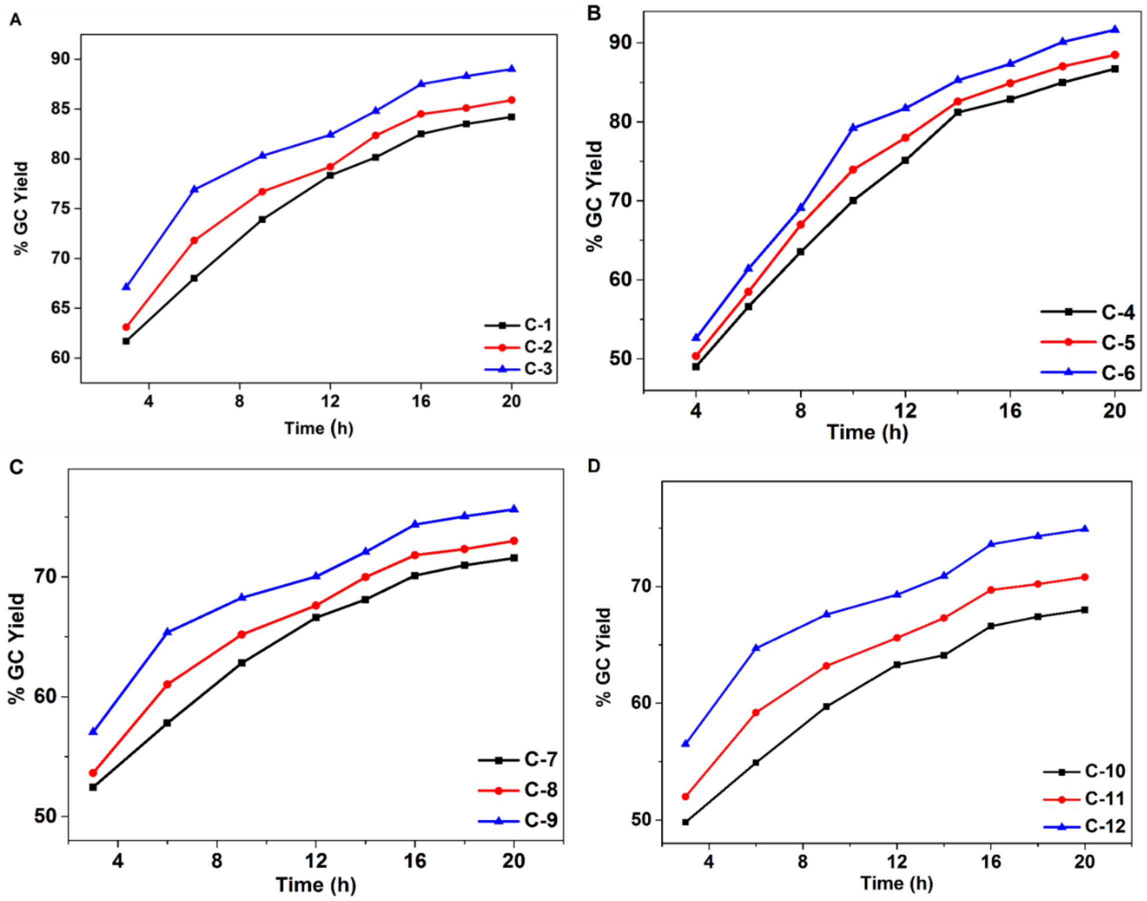
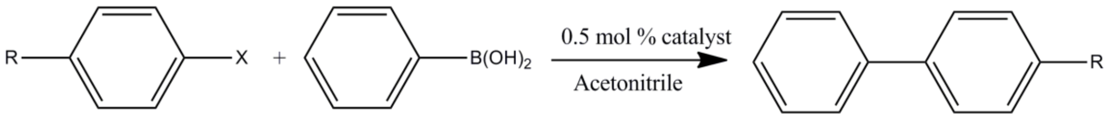


Figure 3.4 Effect of reaction time on C-1 to C-12

Further, the cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized reaction conditions. The results of these reactions are summarized in Table 3.1 for C-1 to C-3, Table 3.2 for C-4 to C-6, Table 3.3 for C-7 to C-9 and Table 3.4 for C-10 to C-12, respectively. The products were isolated using solvent extraction for C-3 and C-6 to have a comparison with the GC yield and this data is included with the % GC yield in parenthesis (Table 3.1 to Table 3.2).

Table 3.1 Catalytic activity study for complexes, C-1 to C-3

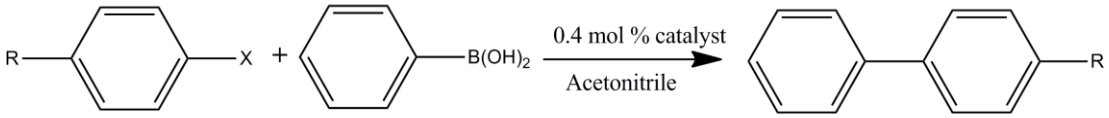


Entry	X	R	Yield (%)[a]		
			C-1	C-2	C-3
1	Br	H	50	54	56 (51.6)
2		CN	81	83	89 (86.4)
3		OCH_3	68	70	76 (72.6)
4		$COCH_3$	77	80	84 (81.3)
5		$NHCOCH_3$	75	81	87 (85.2)
6		F	36	40	41 (36.0)
7		CH_3	53	54	59 (54.7)
8	I	OH	69	71	76 (73.0)
9		CN	87	90	92 (90.2)
10	Cl	CHO	64	68	71 (66.8)

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.3 mmol), Cs_2CO_3 *(2.0 mmol), catalyst (0.5 mol%), solvent (5.0 mL), 16 h.*

[a] *GC yields, an average of 3 trials (Isolated yield).*

Table 3.2 Catalytic activity study for complexes, C-4 to C-6

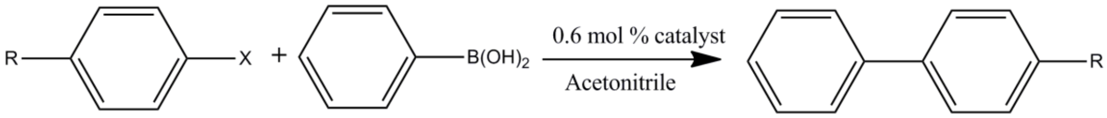


Entry	X	R	Yield (%)[a]		
			C-4	**C-5**	**C-6**
1	Br	H	59	61	64 (56.5)
2		CN	85	89	92 (84.4)
3		OCH_3	74	76	79 (69.3)
4		$COCH_3$	80	87	89 (76.3)
5		$NHCOCH_3$	78	83	87 (80.2)
6		F	40	42	42 (34.0)
7		CH_3	57	60	65 (56.4)
8	I	OH	69	74	78 (70.0)
9		CN	89	94	96 (89.6)
10	Cl	CHO	67	71	74 (66.8)

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.3 mmol), Cs_2CO_3 (2.0 mmol), catalyst (0.4 mol %), solvent (5.0 mL), 14 h.

[a] *GC yields, an average of 3 trials (Isolated yield).*

Table 3.3 Catalytic activity study for complexes, C-7 to C-9

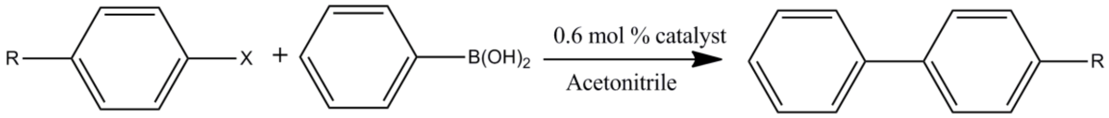


Entry	X	R	Yield (%)[a]		
			C-7	**C-8**	**C-9**
1	Br	H	44	49	51
2		CN	72	75	79
3		OCH_3	60	63	69
4		$COCH_3$	68	72	76
5		$NHCOCH_3$	69	74	77
6		F	32	36	37
7		CH_3	47	49	53
8	I	OH	61	64	69
9		CN	77	81	83
10	Cl	CHO	56	61	64

Reaction conditions: Aryl halide (1.0 mmol), Phenyl boronic acid (1.3 mmol), Cs_2CO_3 *(2.0 mmol), catalyst (0.6 mol %), solvent (5.0 mL), 16 h.*

[a] *GC yields, average of 3 trials.*

Table 3.4 Catalytic activity study for complexes, C-10 to C-12



Entry	**X**	**R**	**Yield (%)**[a]		
			C-10	**C-11**	**C-12**
1	Br	H	42	46	47
2		CN	67	71	75
3		OCH_3	57	59	64
4		$COCH_3$	65	68	71
5		$NHCOCH_3$	63	69	73
6		F	30	34	34
7		CH_3	45	46	49
8	I	OH	58	60	64
9		CN	73	76	77
10	Cl	CHO	53	57	60

Reaction conditions: Aryl halide (1.0 mmol), Phenyl boronic acid (1.3 mmol), Cs_2CO_3 *(2.0 mmol), catalyst (0.6 mol %), solvent (5.0 mL), 16 h.*

[a] *GC yields, average of 3 trials.*

Various substituted aromatic halides underwent Suzuki coupling effectively (Figure 3.5). Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas the presence of electron donating groups brought about lesser conversion. The lowest conversion was observed when aryl halide with a fluorine atom present at the para position was being employed. This may occur due to the destabilization of the aromatic ring due to the competing inductive and resonance effects generally shown by halides attached directly to the aromatic ring. Presence of bulky iodide is preferred as a better leaving group among the halides which is reflected in the results.

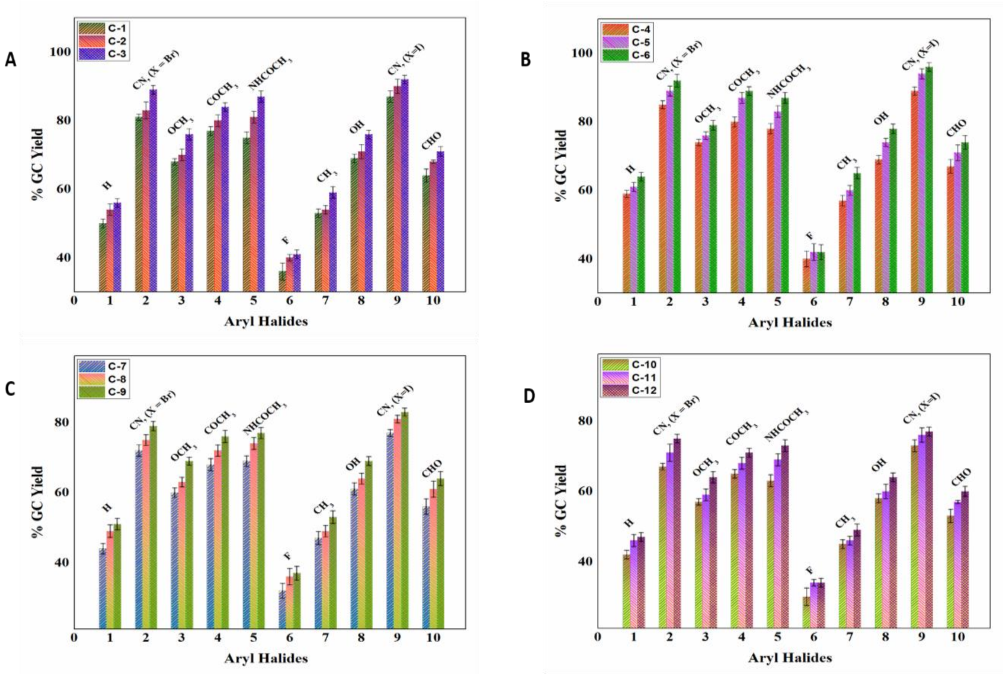


Figure 3.5: Graphical representation of % GC conversion of variously substituted aryl halides

3.2.2 Proposed mechanism of catalysis

Co-complex was used a model complex for describing the mechanism of catalysis. Mechanism of the cobalt(II) catalyzed C–C coupling reaction is quite a complex supposition and requires comprehensive study in understanding the process. The catalytic metal component Co(II) getting reduced to either Co(0) or Co(I) is a possibility, and speculating on the existent active species formed in the catalytic process is quite difficult. We tentatively assume that the catalyst precursor (a) gets reduced to active Co(0) species (b) in the presence of phenylboronic acid and base (Figure 3.6). The coupling process may then start with the oxidative addition of aryl halide to the Co(0) center to form an R^2-Co(II) intermediate (c). Subsequent nucleophilic substitution of the halide group and transmetallation between phenylboronic acid and R^2-Co(L)-CO_3 (d) would result in biaryl R^1-Co(L)-R^2 species (e). In the last step, reductive elimination supposedly takes place yielding the target biaryl (f) and also regenerating Co(0) species (Xi, et al. 2009).

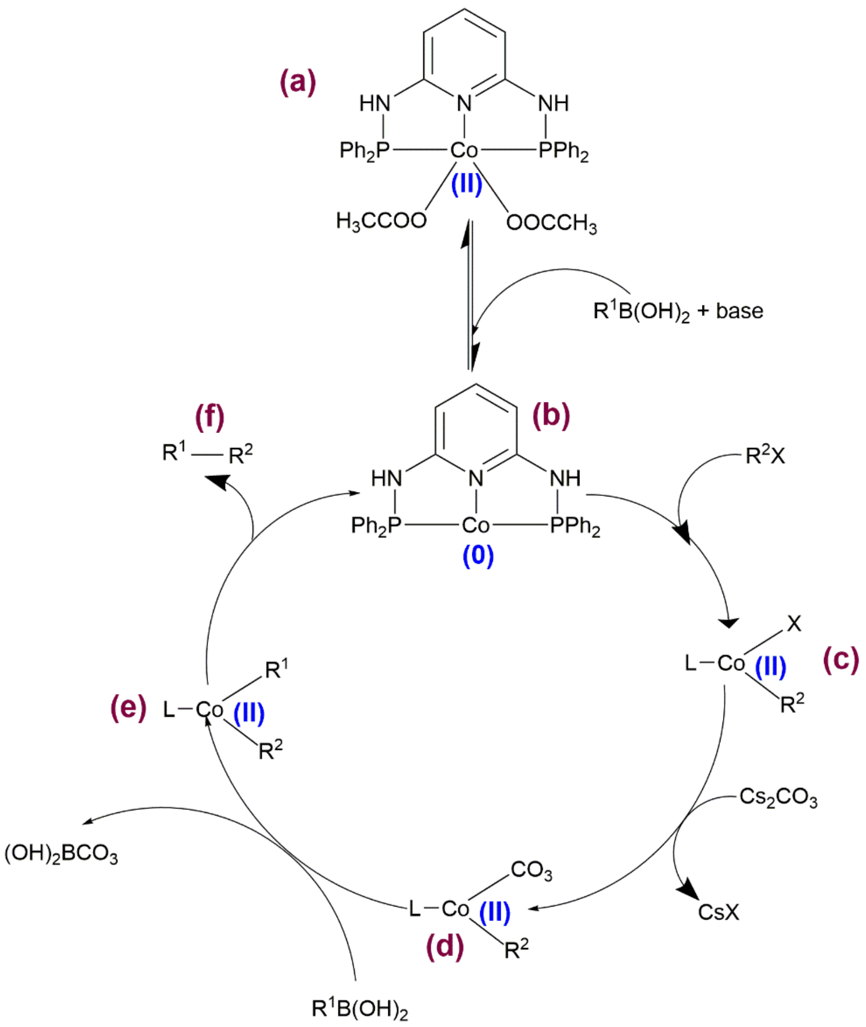


Figure 3.6 Plausible mechanism for C-C coupling by C-3

3.2.3 Catalytic activity studies of C-13 to C-16

The reaction conditions have been optimized with respect to

- Solvent and reaction temperature
- Base
- Catalyst concentration
- Reaction time

(a) Effect of solvent and temperature

The catalytic activities of C-13 to C-16 were checked in methanol, ethanol, ethanol: water, 1,4-dioxane, toluene and acetonitrile media (Figure 3.7).

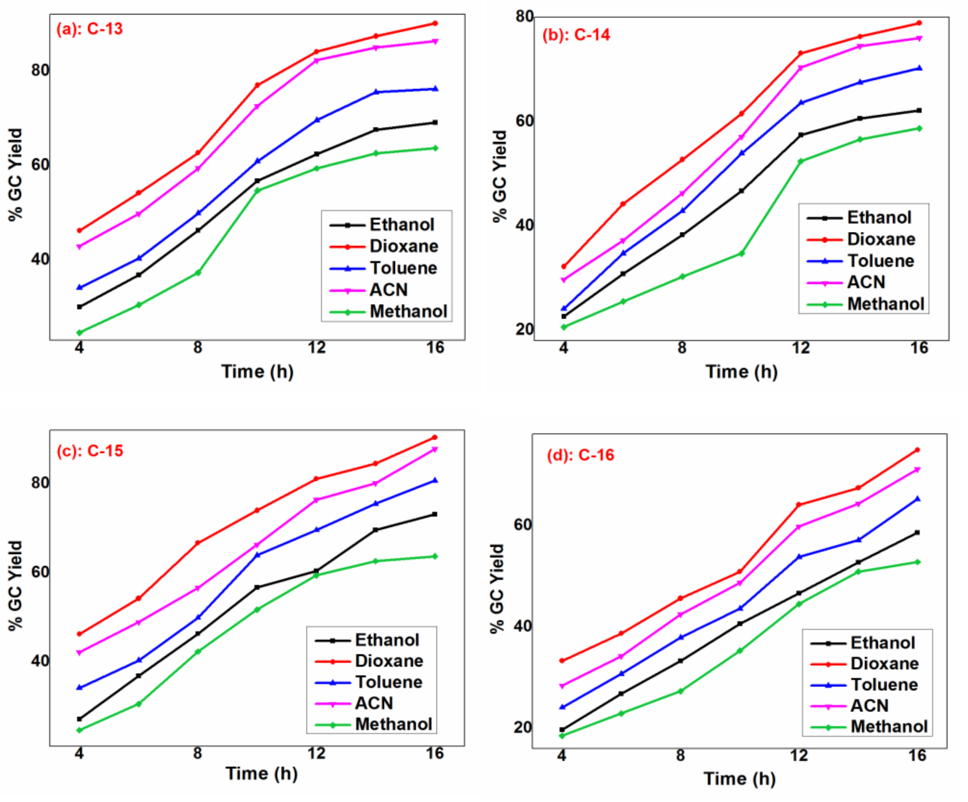


Figure 3.7 Effect of solvent on: (a) C-13, (b) C-14, (c) C-15, (d) C-16

The reactions were all optimized at the reflux temperature of the specific solvents. Amongst the solvents tested, highest catalytic activity was observed with dioxane as the solvent media. Acetonitrile was the second most productive solvent in terms of conversion. Moderate catalyst activities were found in other solvents such as methanol, ethanol, and toluene. Ethanol: aqueous mixture, however, did not aid in carrying out the reaction and therefore not considered further for reaction optimization. Acetonitrile was chosen as the optimum solvent for carrying out the reactions considering the lower reaction temperature of acetonitrile (at 80 °C) and since the difference in yield between dioxane and acetonitrile is quite marginal. The enhanced activity of acetonitrile as a solvent may be attributed to the property of acetonitrile to act in itself as a ligand with its exceptional coordinating property (Dyson and Jessop 2016).

(b) Effect of base

The reaction was also optimized for efficient use of the base in the reaction. In this context, we investigated the Suzuki coupling reaction using different bases like Cs_2CO_3,

Et_3N, K_2CO_3 and Na_2CO_3 in ACN solvent. The different bases produce different yields as represented in Figure 3.8. From the results, it is observed that Cs_2CO_3 provide better yield than other selected bases which can be attributed to the ability of the base to easily donate its carbonate ion for replacement of the halide ion in the oxidative addition step of the catalytic cycle due to its high solvation and reactivity as a balanced base (Rabie et al. 2017). Hence among the different bases employed in the proposed Suzuki reaction, Cs_2CO_3 was considered as an optimized base to achieve enhanced catalytic efficiency and greater yield.

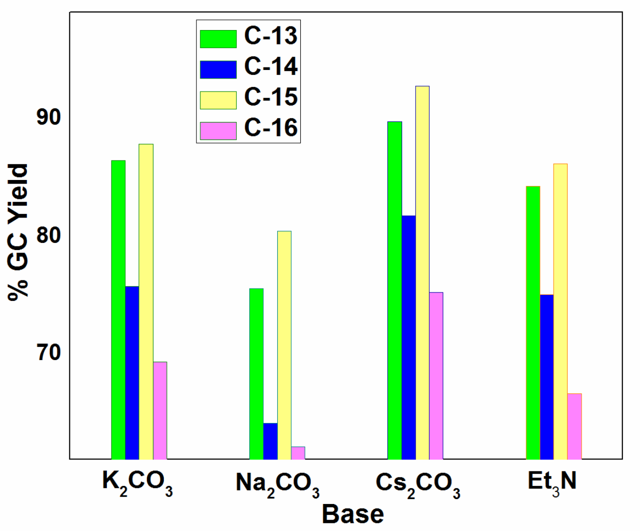


Figure 3.8 Effect of the base on the catalytic reaction

(c) Effect of catalyst concentration on the reaction

Catalyst loading for the reaction was another optimized parameter. In order to study the effect of concentration of the catalyst, the reaction was studied under optimized conditions of ACN as solvent and Cs_2CO_3 as a base, in the presence of different amount of catalyst. Figure 3.9 shows the yield percentage vs. catalyst load with the catalyst load varied from 0.1 mol % to 1.0 mol %. From the figure, it is observed that the increase in catalyst loading linearly increases the coupling yield, suggesting that amount of catalyst plays a crucial role in yield of the reaction. When the catalyst load reaches 0.3 mol% for C-13, C-15, 0.4 mol% for C-14 and 0.5 mol% for C-16 respectively, the maximum conversion was observed. However, with a further rise in catalyst load, there was no significant contribution to the product yield. Thus, from the obtained results, we considered 0.3 mol% of the catalyst C-13 and C-15, 0.4 mol% of C-14 and 0.5 mol% of C-16 as optimized catalyst load.

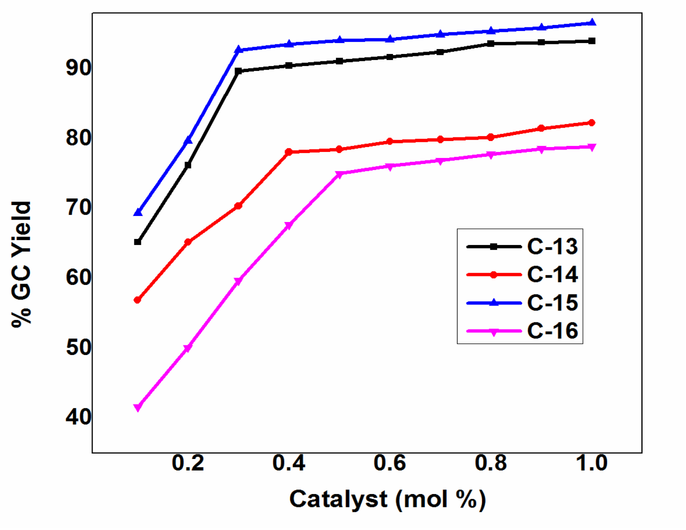


Figure 3.9 Effect of catalyst concentration

(d) Effect of reaction time

Effect of reaction time on the catalytic activity was studied by analyzing the reaction aliquots at regular intervals of time. Figure 3.10 shows GC yield vs. time taken to complete the reaction in the presence of C-13 - C-16 catalyst. From the figure, it is observed that with optimized conditions like catalyst concentration, alkalinity, and solvent, the catalysts show a notable rise in yield up to 12 h of the reaction time. However, a further rise in reaction time does not contribute much to increase in product yield and the graph shows almost steady-state yield. Thus, 12 h is considered to be the optimized reaction time for C-13 to C-16 catalysts.

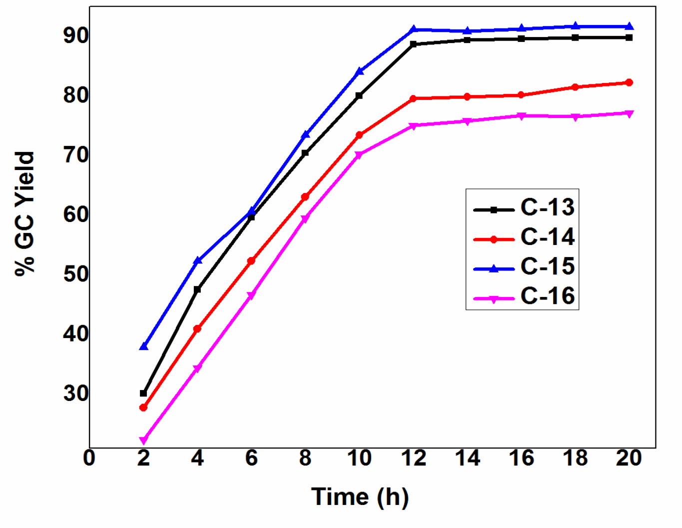
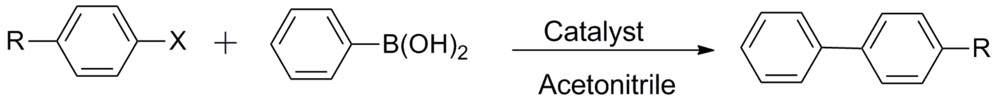


Figure 3.10 Effect of reaction time on C-13 to C-16

Further, the cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized reaction conditions. The results of these reactions are summarized in Table 3.5. Product isolated with solvent extraction method have been mentioned with the GC yield in parenthesis.

Table 3.5 Catalytic activity study for complexes



Entry	X	R	Yield (%)[a]			
			C-13	C-14	C-15	C-16
1	Br	H	59	54	61	50
2		CN	91 (85.8)	81	93 (89.4)	77
3		OCH_3	88 (82.1)	76	84	67
4		$COCH_3$	90 (85.3)	76	89 (83.8)	72
5		$NHCOCH_3$	92 (85.7)	78	93 (88.3)	76
6		F	46	38	51	32
7		CH_3	59	52	62	49
8	I	OH	75	72	79	66
9		CN	96 (90.5)	85	98 (93.9)	79
10	Cl	CHO	74	68	79	60

Reaction conditions: Aryl halide (1.0 mmol), Phenyl boronic acid (1.3 mmol), Cs_2CO_3 (2.0 mmol), catalyst: C-13 & C-15 (0.3 mol%), C-14 (0.4 mol%), C-16 (0.5 mol%), solvent (5.0 mL), 12 h.

[a] *GC yields, average of 3 trials (Isolated yield).*

Various substituted aromatic halides underwent Suzuki coupling effectively (Figure 3.11). Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas the presence of electron donating groups brought about lesser conversion. The lowest conversion was observed when aryl halide with a fluorine atom in the para position was being employed which perhaps occurs due to the destabilization of the aromatic ring due to the competing inductive and resonance effects generally shown by halides attached directly on the aromatic ring. Presence of iodide is preferred as a better leaving group among the halides which is reflected in the results.

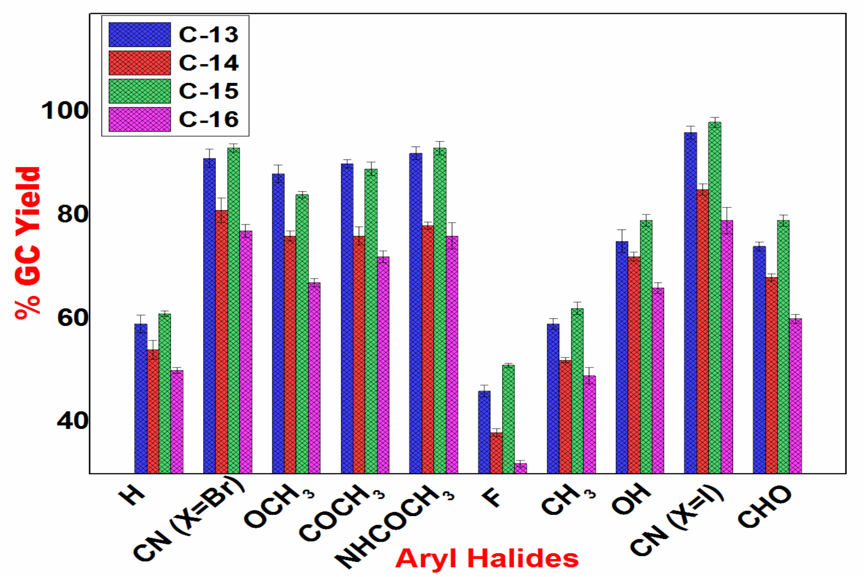


Figure 3.11: Graphical representation of % GC conversion of the substituted aryl halides

3.2.4 Proposed Mechanism of catalysis

Mechanism of the pincer complex catalyzed Suzuki coupling reaction proceeds quite like the typical Pd catalyzed coupling reaction. The catalytic metal component M(II) which is the catalyst precursor (a) here possibly gets reduced to M(0) species (b) in the presence of phenylboronic acid and base (Figure 3.12). The coupling process may then start with the oxidative addition of aryl halide to the M(0) center to form an R^2-M(II) intermediate(c). Subsequent nucleophilic substitution of the halide group and transmetallation between phenylboronic acid and R^2-M(L)-CO_3 (d) would result in biaryl R^1-M(L)-R^2 species (e). In the last step, reductive elimination supposedly takes place yielding the target biaryl (f) and also regenerating the active metal species for further catalytic action (Xi et al. 2009).

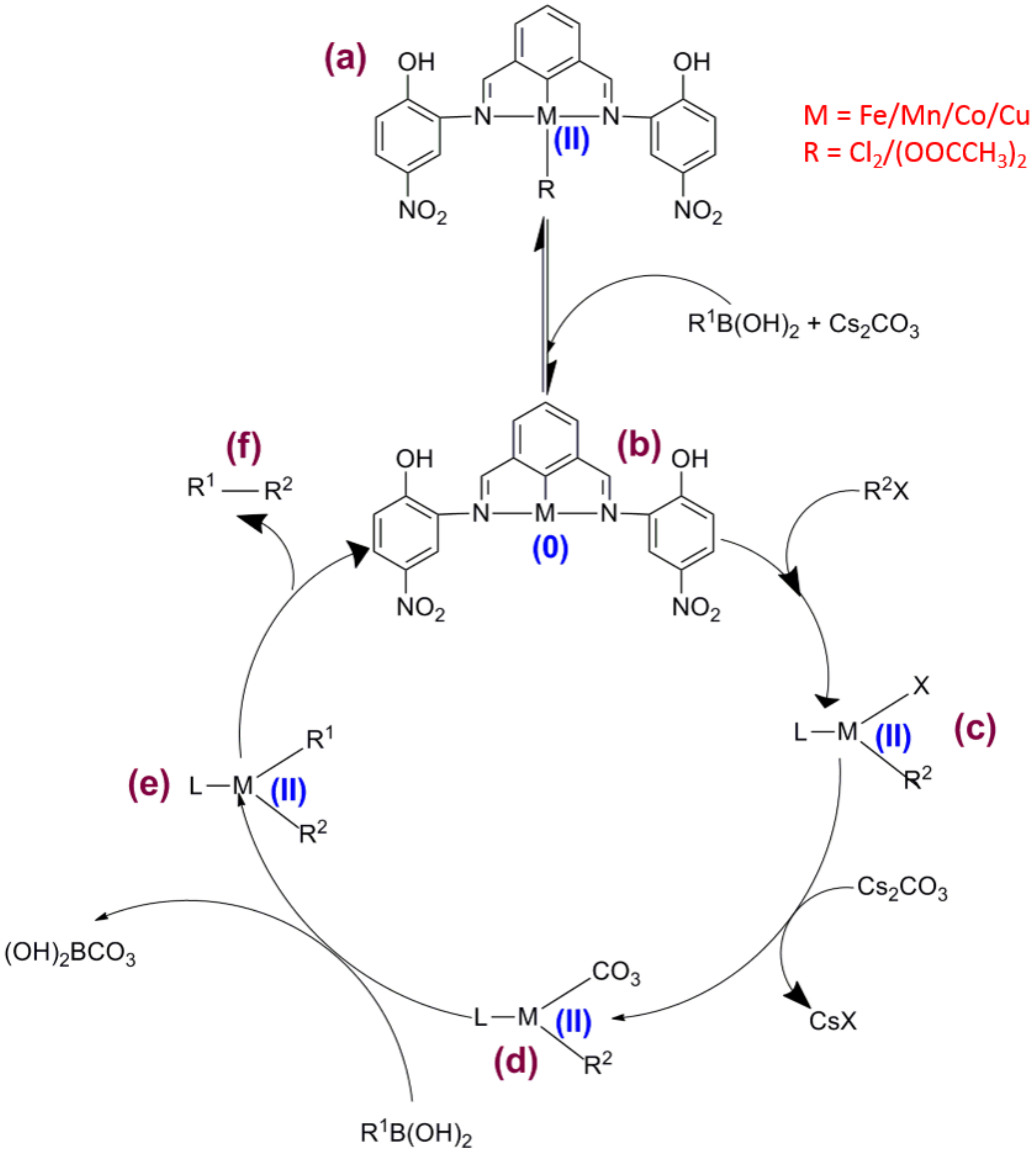


Figure 3.12 Possible mechanism for C-C coupling by C-13 to C-16

3.3 SUMMARY

The method proposes the use of low cost, abundant and environmentally benign metals in the synthesis of complexes and thereafter their efficient catalytic use in cross-coupling reaction. Three series of complexes of cobalt, iron, copper, and manganese with tridentate pincer ligands were synthesized to study their catalytic activity in Suzuki-Miyaura coupling reactions. Asymmetrical PCP (POCNP) pincer ligand [C_6H_4-1-($NHPPh_2$)-3-($OPPh_2$)] (**L-1**) and symmetrical PCP (PNCNP), PNP (PNNNP) pincer ligands C_6H_4-2,6-$(NHPPh_2)_2$ **(L-2)** and C_5H_3N-2,6-$(NHPPh_2)_2$ (**L-3**) were synthesized by the reaction of diphenylchlorophosphine with m-aminophenol, m-phenylenediamine and 2,6-diaminopyridine respectively in a 2:1 ratio in the presence of triethylamine as a base and tetrahydrofuran as solvent media. The synthesized complexes were examined for their C-C coupling efficiency in cross-coupling between phenylboronic acid and para-substituted halobenzenes. Effect of variation of the ligand on the catalytic activity of the pincer complexes was explored based on the coupling yields. The present study has led to the consideration of the role of ligands and their electron donating ability in enhancing the catalytic activity of a complex. It is observed that as the number of ‘N’ atoms increases in the side arm of the ligand; the donating ability of the ligand increases which leads to the increased catalytic activity of the complex. The complexes with symmetrical PNP (PNNNP) pincer complex were found to be more effective as a catalyst among the complexes synthesized and reported in the present study.

Since it was observed that the catalytic activity of the complex enhanced with the increase in the number of ‘N’ atoms in the sidearm, in the next series, the ‘P’ donor in the side arm of the complexes is replaced with the ‘N’ donors in the pincer skeleton and pincer-like complexes of cobalt, iron, copper, and manganese with NNN ligand were synthesized to study their catalytic activity in Suzuki-Miyaura coupling reactions. NNN pincer ligand (**L-4**) was synthesized by the reaction of pyridine-2,6-dicarboxaldehyde with 2-amino-4-nitrophenol and the ligand was refluxed with metal salts, cobalt (II) acetate, copper (II) acetate, iron (II) chloride and manganese (II) chloride respectively in 1:1 ratio in THF. The synthesized complexes were examined for their C-C coupling efficiency in cross-coupling between phenylboronic acid and para-substituted bromobenzenes. Complexes, C-13 to C-16 have effectively catalyzed the Suzuki coupling reactions, with the iron complex, C-15 displaying the best coupling activity (Figure 3.13).

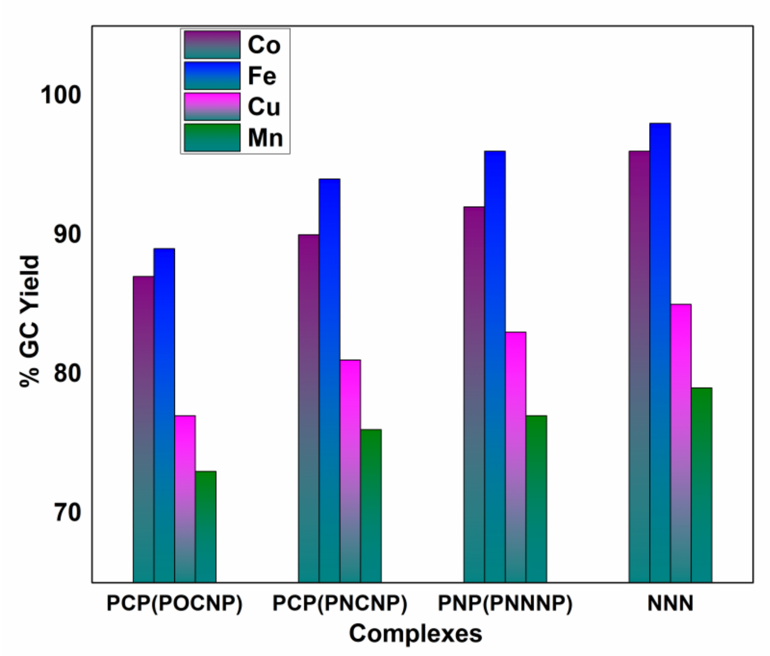


Figure 3.13 Comparison of yield in homogeneous 4-cyanobiphenyl conversion

CHAPTER 4

IMMOBILIZATION OF PINCER COMPLEXES

Chapter 4 focusses on the heterogeneous aspect of the synthesized complexes and is achieved by immobilizing the complexes on the graphene oxide substrate. The analytical and physical methods used for the characterization of the immobilized complexes are also addressed.

Transition metal complexes are conventional catalysts which are considerably used in the homogeneous organic reactions with a high efficacy. But the major drawback with these catalysts would be their recovery from the reaction mixture which can hamper the application of these catalysts majorly prompting a contamination threat in the reaction system. Immobilizing the homogeneous catalysts on some insoluble supports can be quite an assurance in tackling the recovery problem. Graphene and its derivatives have raised expectations in the heterogeneous catalysis field as a solid substrate to the acting catalysts. One of the catalytic applications in which graphene support may provide some significant advantages is in the area of C–C cross-coupling chemistry. The oxygenic functional groups present in graphene oxide could immobilize various catalytic materials as active sites.

In this chapter, we report the synthesis of graphene oxide from graphene and its functionalization by silane support. The functionalized GO was used to immobilize PNP pincer complexes of cobalt, copper, and iron (C-3, C-6, and C-9) and NNN pincer complexes of cobalt, copper and iron (C-13, C-14 and C-15).

4.1 EXPERIMENTAL

4.1.1 Materials

All the chemicals used were of analytical grade. Graphite powder (320 mesh, 99.5%), potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4), concentrated hydrochloric acid, concentrated nitric acid, phosphoric acid, hydrogen peroxide (H_2O_2 30%), 3-aminopropyltriethoxysilane (3-APTES) were purchased from Merck and used without further treatment.

4.1.2 Experimental techniques

A variety of physicochemical methods were employed to characterize the immobilized complexes. A brief account of these methods is given below.

(a) X-ray diffraction (XRD)

The X-ray diffractograms of the purified complexes were obtained using Bruker AXS Diffractometer D8 powder XRD. The diffraction patterns were recorded at room temperature with a Cu Kα radiation ($\lambda = 1.5418$ Å) at a scan rate of 2 °/min. This technique was used to determine the grafting of the metal complexes on GO substrate.

(b) Scanning electron microscopy (SEM)

The morphology of purified samples was analyzed using a Joel JSM-6380LA Scanning Electron Microscope. The samples were coated with gold using a sputter coating unit, to avoid charging during the recording. The nanostructure and morphology of the grafted particles were observed.

(c) Infrared spectra

Fourier transform infrared (FTIR) spectra were recorded on a Bruker-Alpha ECO-ATR FTIR spectrometer within the range of 4000−400 cm^{-1}.

(d) X-ray photoelectron spectroscopy (XPS)

XPS was recorded on Oxford Instruments-Omicron Nanotechnology XPS system (ESCA+) with a monochromatic Al-Kα radiation source of 1486.7 eV and 124 mm hemispherical electron analyzer.

4.1.3 Synthesis

4.1.3.1 Synthesis of graphene oxide (GO)

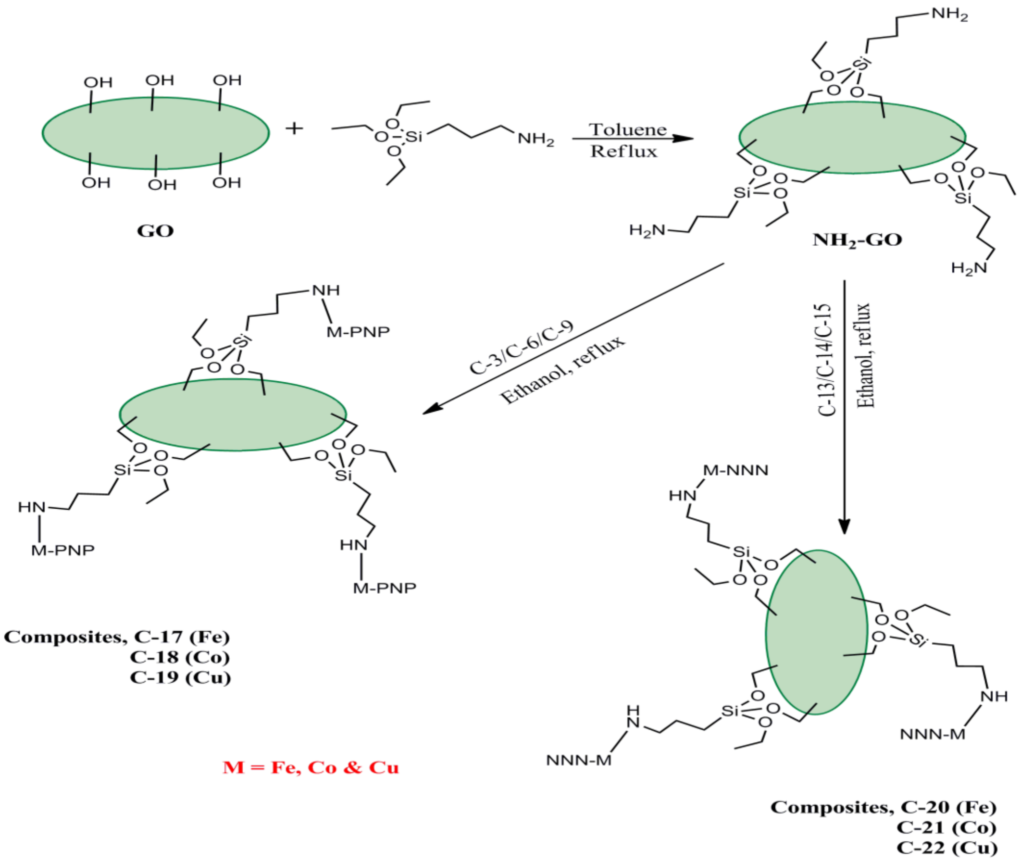
Graphene oxide was prepared and purified using improved Hummers’ method (Marcano et al. 2010).

4.1.3.2 Synthesis of amino-functionalized graphene oxide (NH_2–GO)

Graphene oxide substrate was functionalized with 3-aminopropyltriethoxysilane (3-APTES) as per the reported procedure (Su et al. 2014). The resulting coated graphene oxide was dried in a vacuum oven at 40 °C for 24 h and labeled as NH_2–GO.

4.1.3.3 Immobilization of PNP and NNN pincer complexes on amino-functionalized graphene oxide

1 g of NH_2–GO was dispersed in 30 mL ethanol and then 100 mg of Fe-PNP complex (C-6) was added. The mixture was refluxed at 70 °C for 3 h. After cooling to room temperature, the mixture was filtrated and washed with ethanol to remove the undigested material, followed by drying. The resulting solid powder was labeled as C-17. Other composites, C-18 to C-22 were synthesized using C-3, C-9, C-13, C-14 and C-15 under similar synthetic conditions (Scheme 4.1).



Scheme 4.1: Synthetic outline of C-17 to C-22 from GO

4.2 RESULTS AND DISCUSSION

The immobilized complexes were characterized by FTIR, XRD, SEM and XPS analysis. All the results were in full agreement with the proposed structure.

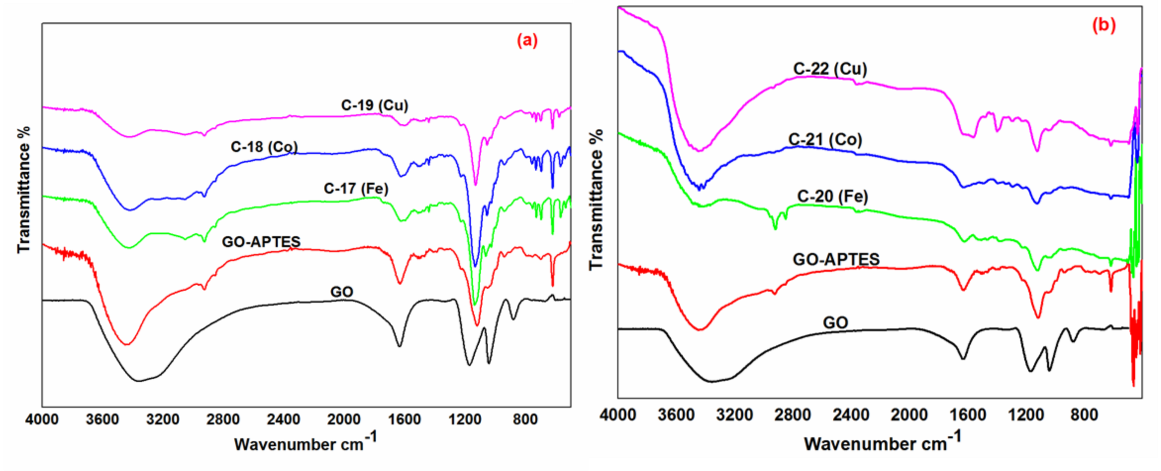


Figure 4.1 FTIR spectra of GO, amino-functionalized GO and immobilized complexes (a) C-17 to C-19 (b) C-20 to C-22

Figure 4.1 depicts the transition from GO to GO-metal composites. In the FTIR spectrum of GO (Figure 4.1 a & b), peaks at 3370 cm^{-1}, 1630 cm^{-1} corresponds to the presence of O-H stretching and -C=O stretching. Also, C-OH stretching and C-O-C asymmetric stretching is reflected at 1170 cm^{-1} which cause broadening of the peak and the C-O-C symmetric stretching peak is observed at 1050 cm^{-1} respectively. In GO-APTES spectrum, peaks corresponding to GO are present with a noticeable change in the peak at 3450 cm^{-1} due to the presence of N-H stretching indicating successful binding of APTES over GO and another peak at 620 cm^{-1} attributed to O-Si stretching. In FTIR spectra of the composites C-17 to C-22 the peaks corresponding to GO-APTES are present in addition to the corresponding metal's fingerprint pattern. This suggests the formation of immobilized metal pincer ligand complex onto APTES grafted GO.

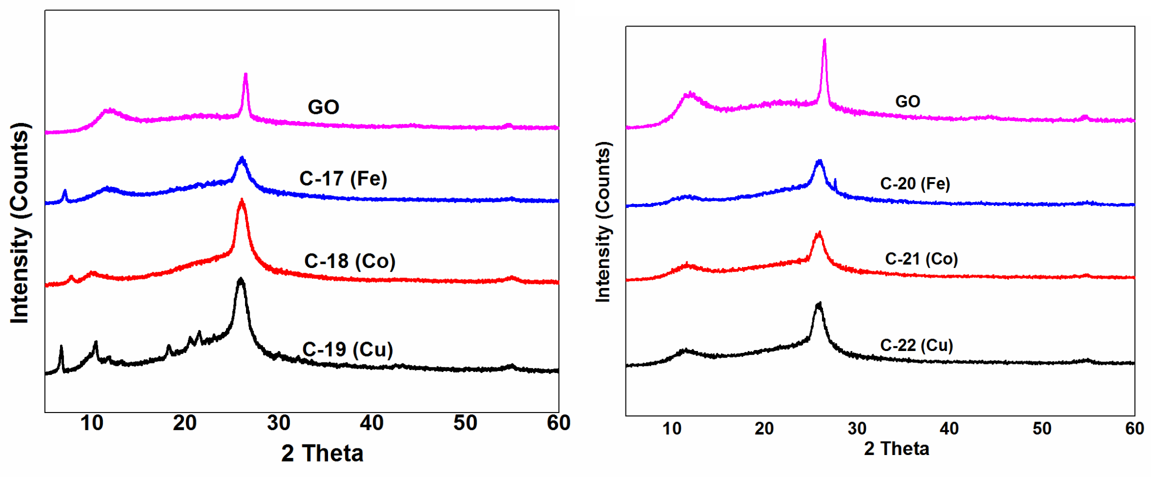


Figure 4.2 XRD spectra of immobilized complexes C-17 to C-22 in comparison with GO

Figure 4.2 (a) provides XRD pattern of complex C-17, C-18, and C-19 in comparison to graphene oxide. The peak at 2θ equal to 11° corresponds to 001 plane of graphene oxide whereas at 26° is indicative of residual graphite in the sample. The C-17 has an additional peak at 6° due to the low degree of order from immobilized Fe. Similarly, in C-18, the peak at 7° is due to the low degree of order from immobilized Co. C-19, however, shows multiple peaks for copper at 6.8°, 10.43, 18.2, 20.5, 21.5, 30 and 32° which indicates a higher amount of Cu present in C-19 as compared to Fe and Co in C-17 and C-18, respectively. This is the result of better surface coverage of copper pincer complex on GO. Similarly, Figure 4.2 (b) compares the XRD pattern of GO with complex C-20, C-21, and C-22. Again, as observed, the GO peaks have been suppressed in presence of these complex which is indicative of its better interaction between GO and complexes. Additionally, there are no noticeable elemental peaks corresponding to the central metal which is due to the amorphous nature of complex and even distribution over the surface of GO. The surface coverage was later examined in SEM analysis.

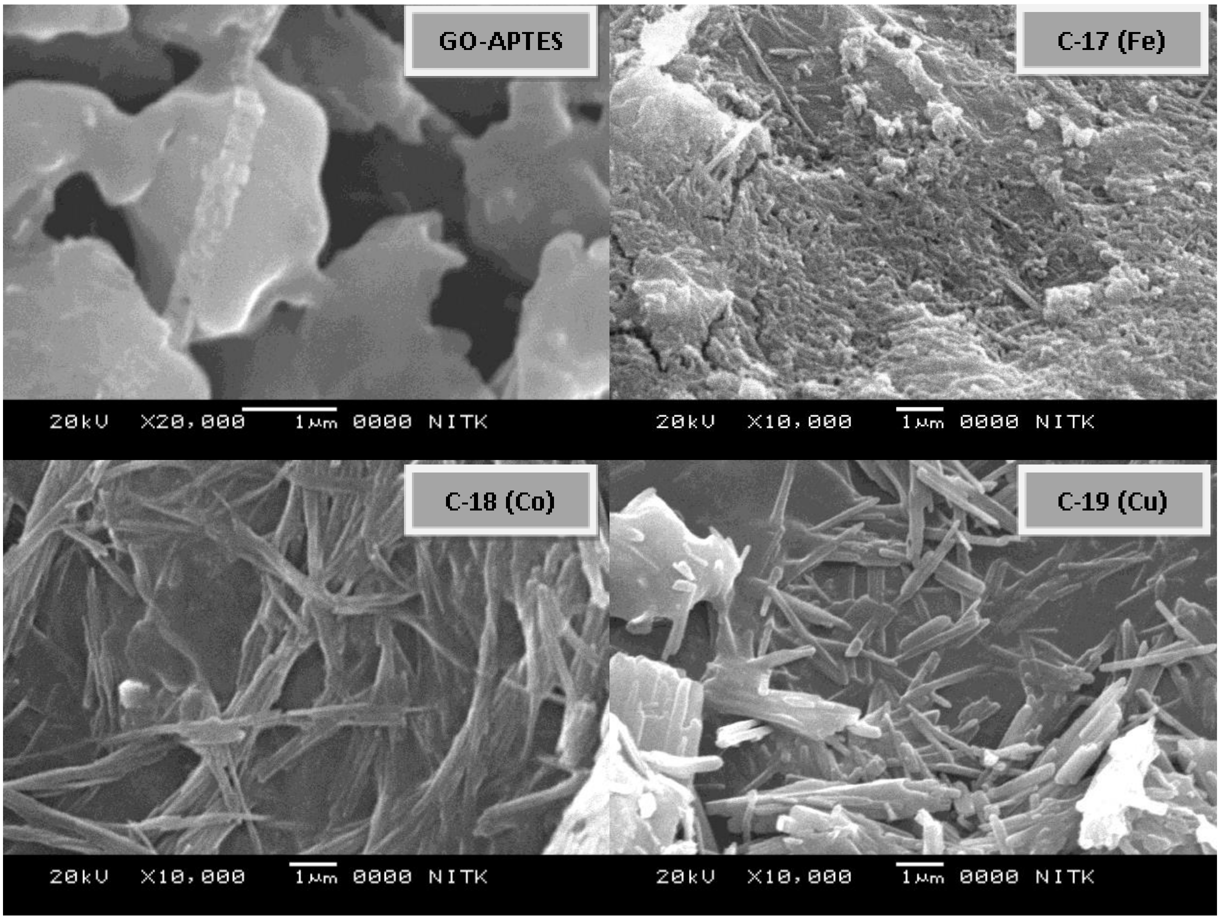


Figure 4.3 SEM images of amino-functionalized GO and immobilized complexes C-17 to C-19

Figure 4.3 shows light on the surface morphology of prepared immobilized complexes on GO. APTES grafting over GO had very good surface coverage as evident for SEM of GO-APTES. SEM of C-17 complex shows good coverage of Fe-Pincer ligand but, there is lack of well-defined shape of the covering, thereby rendering a more amorphous coating which was even evident from the XRD of C-17 complex in Figure 4.2 (a). C-18 complex showed more elongated rod-like covering over GO whereas C-19 have a regular rod-like structure covering the surface of GO. This covering also supports the XRD pattern obtained for the catalyst where C-19 showed more crystalline nature which is due to the presence of regular rod-like structure over the surface of GO. Whereas for C-17 (Fe) and C-18 (Co), lack of such regular structure leads to more amorphous character and hence only a single broad peak was observed in XRD.

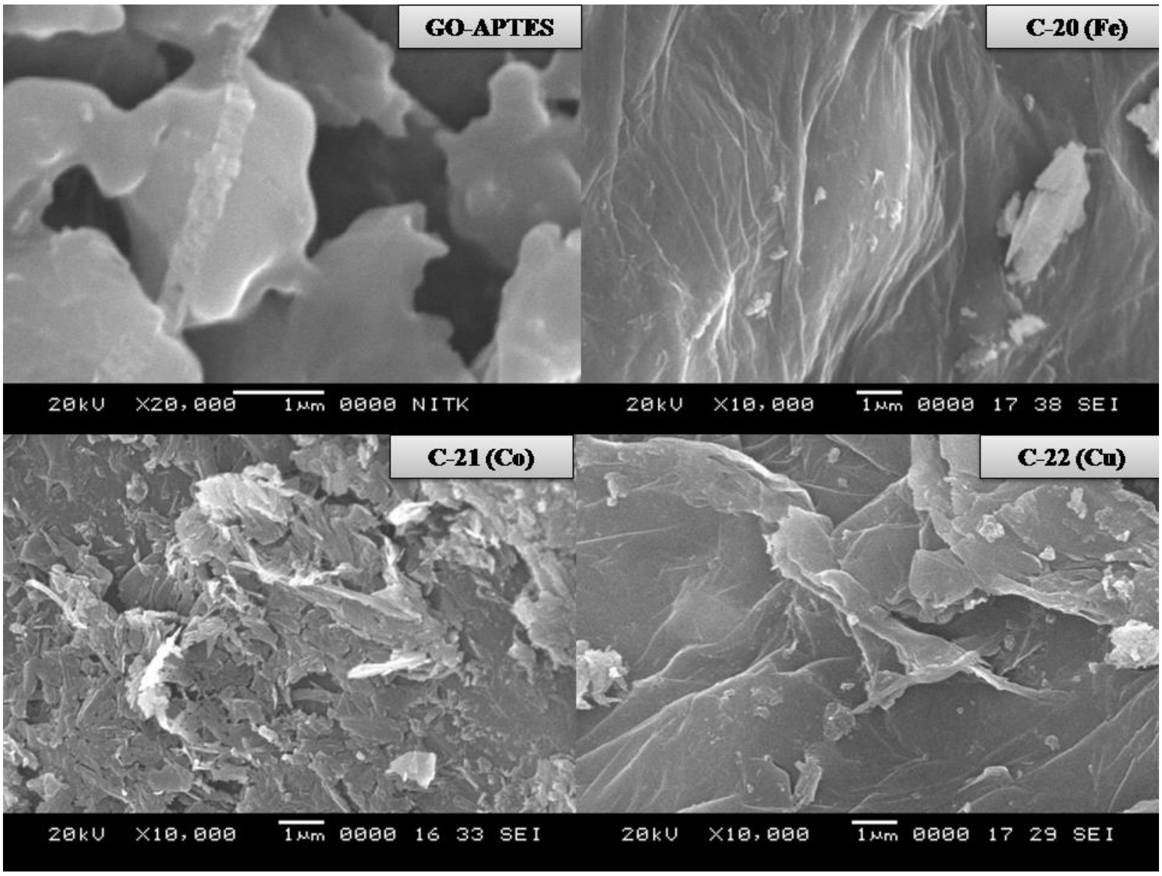


Figure 4.4 SEM images of amino-functionalized GO and immobilized complexes C-20 to C-22

Figure 4.4 compares the surface morphology of amino functionalized GO with GO immobilized with complexes C-20 to C-22. The surface converge was observed to be even for all the complex. However, in case of Co, agglomeration was more evident. The similarity in the surface coverage among all the complexes agrees with the XRD results presented in Fig. 4.2 (b) where all these complexes show identical suppression of GO peaks. Better surface coverage leads to high catalytic efficiency for these complexes, which will be discussed later.

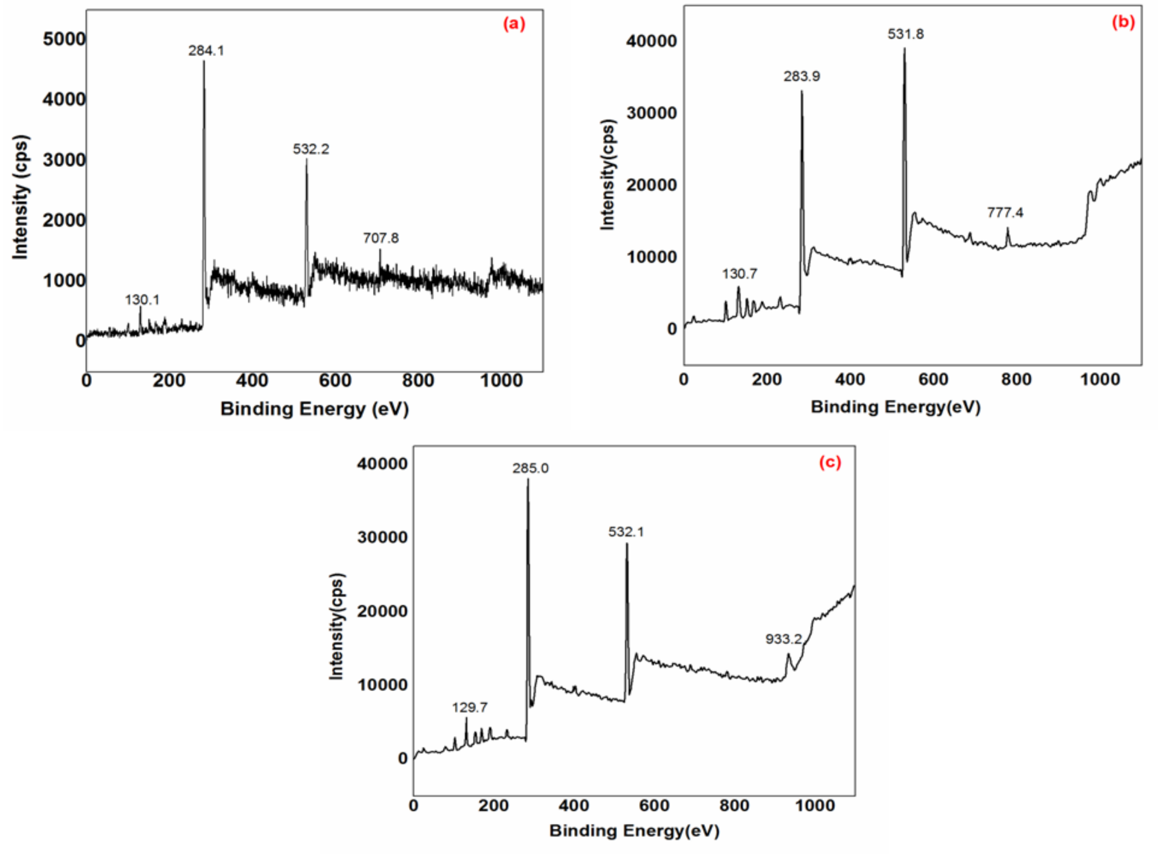


Figure 4.5 XPS of (a) C-17, (b) C-18, (c) C-19

Figure 4.5 presents XPS of the composites formed. As we grafted graphene oxide with APTES and subsequently bonded the dangling grafts with the pincer ligand complexes, the presence of C, Si-O, P and respective metals were expected on the surface. On analyzing the surface using XPS, the peaks at 130.1, 284.1, 532.2 in C-17, 130.7, 283.9, 531.8 in C-18 and 129.7, 285, 532.1 in C-19 were observed corresponding to the P, C, and Si-O respectively. Presence of the metals was seen at 707.8 for Fe, 777.4 for Co and 933.2 for Cu respectively in the spectra of C-17 to C-19. This again supports successful immobilization of the pincer complexes on the graphene oxide substrate.

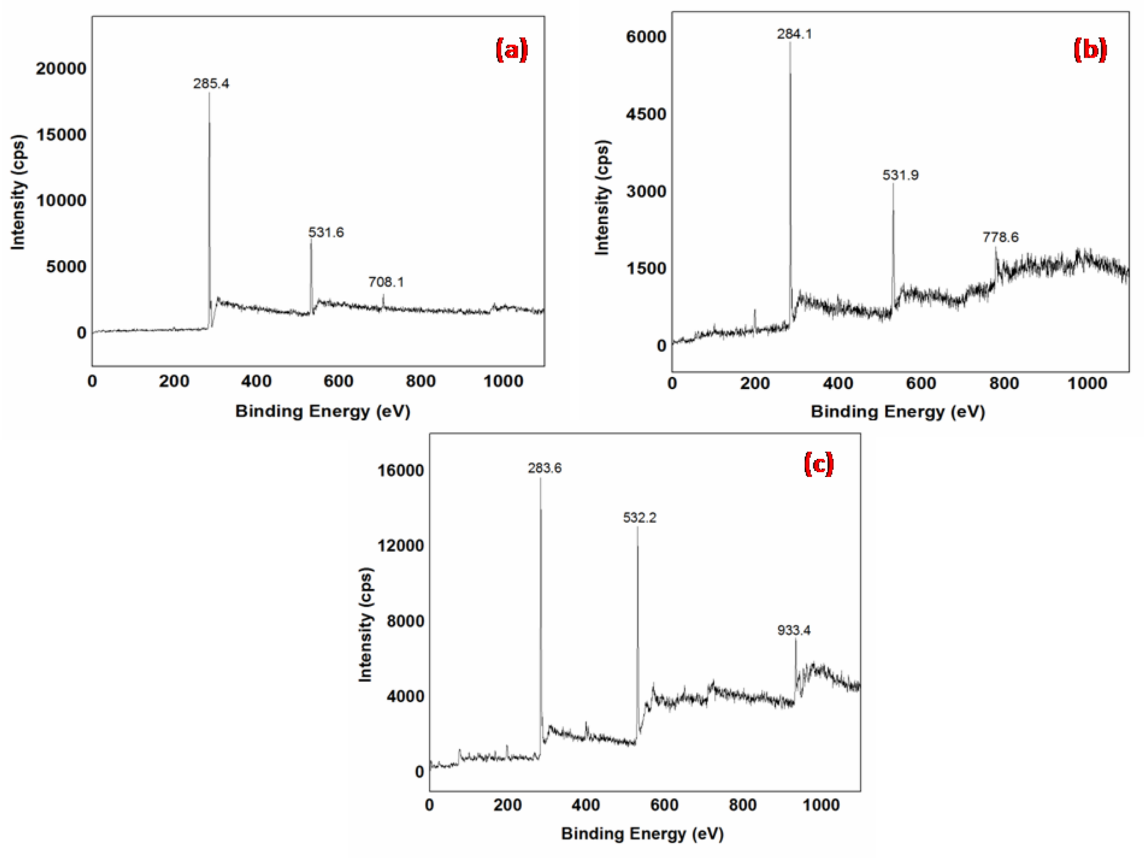


Figure 4.6 XPS of (a) C-20, (b) C-21, (c) C-22

XPS of composites C-20 to C-22 are given in Figure 4.6. Surface analysis of the composites produce peaks corresponding to C, Si-O, and the respective metal centers which indicates the successful immobilization of the complexes on the graphene oxide substrate. In C-20, carbon peak is observed at 285.4, a Si-O peak at 531.6, and at 708.1 corresponding to Fe. The peaks observed at 284.1, 531.9 and 778.6 in C-21 corresponds to C, Si-O, and Co metal respectively. In C-22, carbon peak is seen at 283.6 and the Si-O peak at 532.2. The peak at 933.4 corresponds to the Cu metal present in the composite C-22.

4.3 SUMMARY

Six heterogeneous complexes, C-17 to C-22 were synthesized by immobilization of the PNP and NNN pincer complexes of Fe, Co & Cu on GO substrate further to its functionalization with 3-APTES. Formation of the composites has been successfully explained with the FTIR, XRD and SEM and XPS characterization data.

CHAPTER 5

CATALYTIC ACTIVITY OF IMMOBILIZED GRAPHENE OXIDE COMPOSITES

Chapter 5 describes the Suzuki-Miyaura cross coupling reaction of phenylboronic acid with aryl halides using the immobilized complexes. Effect of catalyst concentration with respect to percentage composition on the GC conversion is being optimized for attaining maximum catalytic conversion.

Palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates namely the Suzuki reaction is a general and efficient method for the formation of carbon-carbon bonds. Mild reaction conditions, easy availability of the reactants and the relatively nontoxic byproducts makes this reaction to be popularly applied in the C-C bond formation in various disciplines of chemistry. Homogeneous catalysis of Suzuki-Miyaura reaction entails an intricate and impracticable catalysis recovery process which can be surmounted by the process of immobilizing the homogeneous catalysts on some insoluble supports like graphene oxide. An attempt at the recovery of the catalysts synthesized leads us towards its immobilization on to the graphene oxide substrate and comparing their catalytic activity in Suzuki-Miyaura reaction with their homogeneous counterparts.

The present work intends to carry out cross-coupling of aromatic halides and phenylboronic acid using immobilized metal complexes on graphene oxide with an aim to improvise the yield, product isolation, and quality and mostly the catalyst recovery. Graphene oxide composites with Fe, Co and Cu complexes of PNP and NNN ligand have been chosen to catalyze the Suzuki coupling heterogeneously. The significant conversion of biaryls was determined by Gas Chromatography (GC). The reaction between 4-bromobenzonitrile and phenylboronic acid was chosen as a model reaction to evaluate the catalytic activity of the composites. The reaction was optimized for only the % composition of the composite. Other parameters like reaction solvent, the alkalinity of reaction media, temperature and the time were considered as in the catalyzed reactions using the metal complexes used for composite preparation.

5.1 EXPERIMENTAL

5.1.1 General procedure for the Suzuki reaction

Aryl halide (1.0 mmol) was added to a mixture of phenylboronic acid (1.3 mmol), GO composite (0.1 mmol) and base (2.0 mmol) in 5 mL of solvent and heated to 80 °C. The mixture was then cooled to room temperature and the organic phase analyzed by gas chromatography.

5.1.2 Gas chromatography

The reaction product analysis was carried out using Gas Chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector (FID). The initial column temperature was increased from 60 °C to 150 °C at the rate of 10 °C/ min and then to 220 °C at the rate of 40 °C/min. N_2 was used as the carrier gas. The temperature of the injection port was kept constant at 150 °C and 250 °C respectively during product analysis. The retention time for different compounds was determined by injecting pure compounds under identical GC conditions.

5.2 RESULTS AND DISCUSSION

5.2.1 Catalytic activity studies of C-17 to C-19 composites

(a) Effect of catalyst concentration (% composition)

Percentage composition of the GO composites was considered for the reaction optimization studies. The loading of the metal complexes onto the GO surface was varied from 5% to 25% and the model reaction was carried out with each of the composites using acetonitrile media and Cs_2CO_3 as the base for a period of 16 h. Their GC conversions are represented in Figure 5.1 and it is observed from the graph that the product conversion appears to remain constant from 15% composition of C-17. In case of C-18 and C-19, a constant conversion is observed from 10% compositions of the metal complexes on GO. Therefore, 15% composite of C-17 and 10% composites of C-18 and C-19 were considered to be the optimum concentration of the catalysts for the coupling reaction.

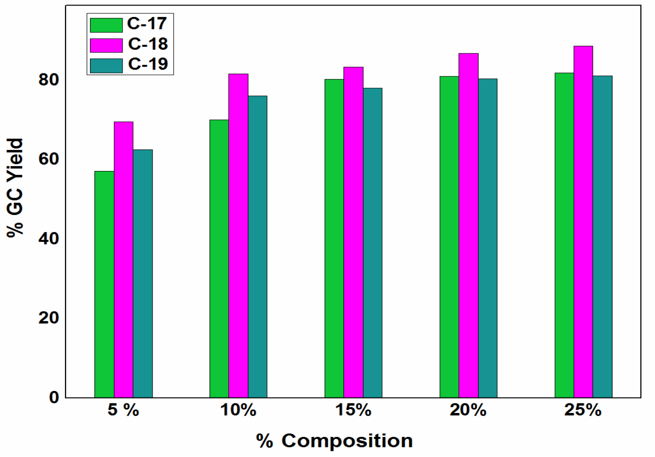


Figure 5.1: Effect of catalyst concentration (C-17 to C-19)

Further, the cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized catalyst loading. The results of these reactions are summarized in Table 5.1.

Table 5.1 Catalytic activity study for GO composites, C-17 to C-19

Entry	X	R	Yield (%)[a]		
			C-17	**C-18**	**C-19**
1	Br	CN	80	81	71
2		OCH_3	70	68	62
3		$COCH_3$	81	75	69
4		$NHCOCH_3$	77	81	71
5	I	OH	67	67	59
6		CN	90	87	75
7	Cl	CHO	59	63	56

Reaction conditions: Aryl halide (1.0 mmol), Phenyl boronic acid (1.3 mmol), Cs_2CO_3 *(2.0 mmol), catalyst (0.1 mmol), solvent (5.0 mL), 16 h.*

[a] *GC yields, average of 3 trials.*

Various substituted aromatic halides underwent Suzuki coupling effectively (Figure 5.2). Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas the presence of electron donating groups brought about lesser conversion. Presence of iodide is preferred as a better leaving group among the halides which is reflected in the results.

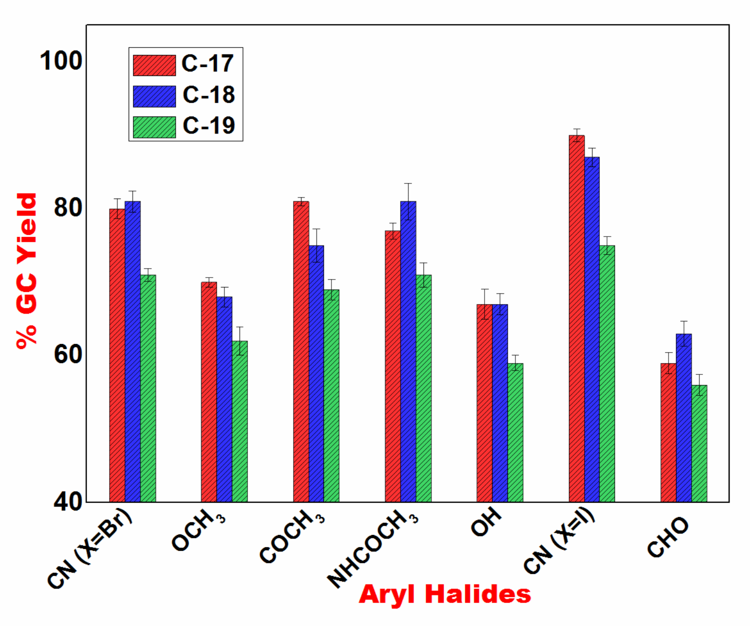


Figure 5.2: Graphical representation of % GC conversion of variously substituted aryl halides

(b) Catalyst reusability

The reusability of catalyst was investigated in the reaction of 4-iodobenzonitrile with phenylboronic acid for 5 successive trials. The used catalyst was separated from the reaction mixture by simple extraction with filtration followed by wash with ethanol. The coupling reaction was carried out 5 times under identical reaction conditions. A slight decrease in the GC yield of product is seen on the consecutive trials showing that the deactivation of the catalyst is possible after successive trials (Figure 5.3). However, this marginal decrease observed does not substantially affect the reusability aspect of the catalyst for 5 successive trials.

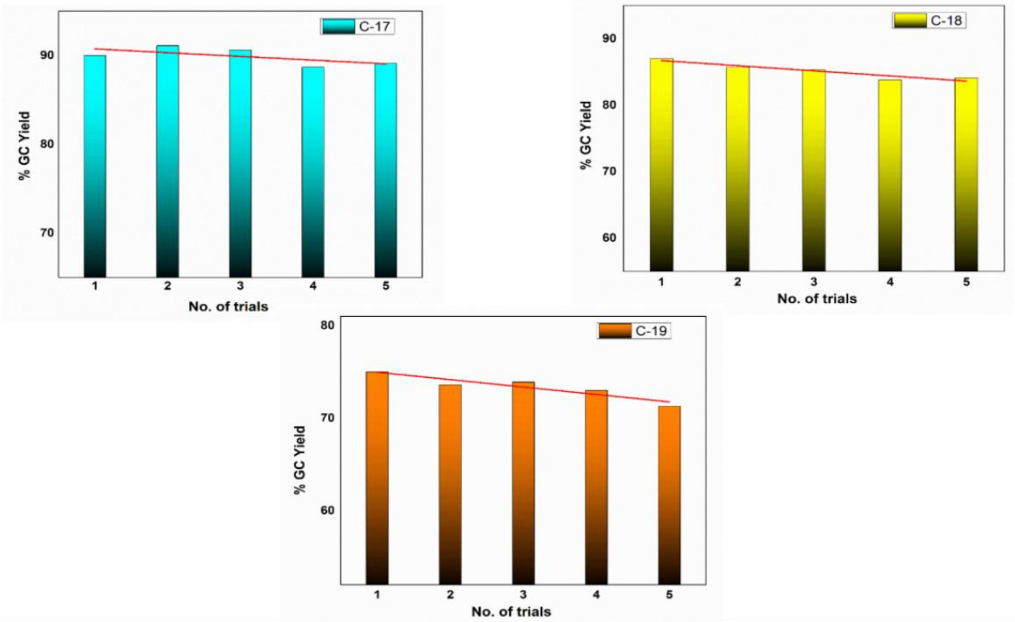


Figure 5.3: Reusability study of composites C-17 to C-19

5.2.2 Catalytic activity studies of C-20 to C-22

(a) Effect of catalyst concentration (% composition)

Percentage composition of the GO composites was considered for the reaction optimization studies. The loading of the metal complexes onto the GO surface was varied from 5 % to 25 % and the model reaction was carried out with each of the composites using acetonitrile media and Cs_2CO_3 as the base for a period of 12 h. Their GC conversions are represented in Figure 5.4 and it is observed from the graph that C-20 exhibits constant catalytic activity after 20% composition. A constant conversion is observed from 15% compositions of the metal complexes on GO in case of C-21 and C-22. Therefore, 20% composite of C-20 and 15% composites of C-21 and C-22 were considered to be the optimum concentration of the catalysts for the coupling reaction.

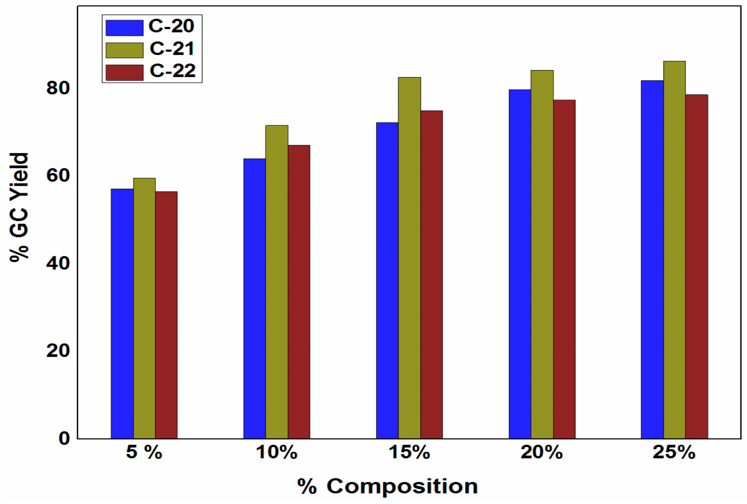


Figure 5.4: Effect of catalyst concentration (C-20 to C-22)

Further, the cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized reaction conditions. The results of these reactions are summarized in Table 5.2.

Table 5.2 Catalytic activity study for GO composites, C-20 to C-22

Entry	**X**	**R**	**Yield (%)[a]**		
			C-20	**C-21**	**C-22**
1	Br	CN	80	84	76
2		OCH_3	73	80	71
3		$COCH_3$	76	81	72
4		$NHCOCH_3$	82	85	72
5	I	OH	69	68	65
6		CN	85	82	78
7	Cl	CHO	67	65	60

Reaction conditions: Aryl halide (1.0 mmol), Phenyl boronic acid (1.3 mmol), Cs_2CO_3 *(2.0 mmol), catalyst (0.1 mmol), solvent (5.0 mL), 12 h.*

[a] *GC yields, average of 3 trials.*

Various substituted aromatic halides underwent Suzuki coupling effectively (Figure 5.5). Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas the presence of electron donating groups brought about lesser conversion. Presence of iodide is preferred as a better leaving group among the halides which is reflected in the results.

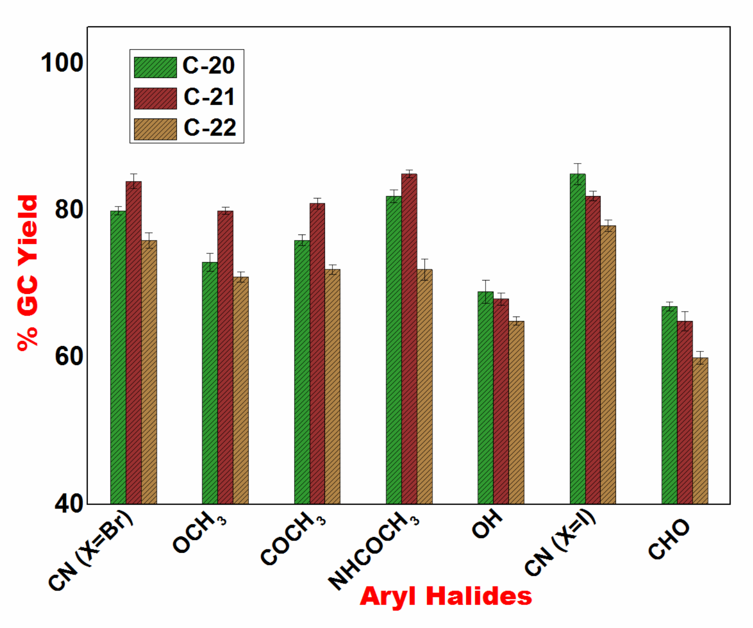


Figure 5.5: Graphical representation of % GC conversion of variously substituted aryl halides

(b) Catalyst reusability

The reusability of catalyst was investigated in the reaction of 4-iodobenzonitrile with phenylboronic acid for 5 successive trials. The used catalyst was separated from the reaction mixture by simple extraction with filtration followed by wash with ethanol. The coupling reaction was carried out 5 times under identical reaction conditions. A similar trend of decrease in the product yield was observed on the consecutive trials carried (Figure 5.6).

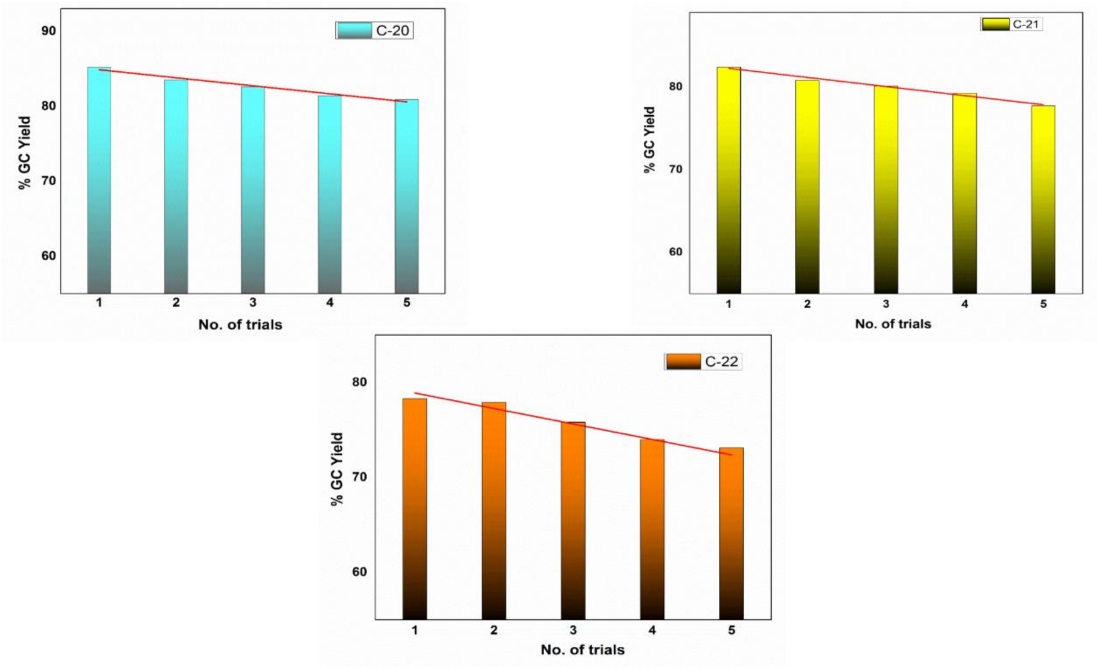


Figure 5.6: Reusability study of composites C-20 to C-22

5.3 SUMMARY:

The immobilization of pincer complexes over amino functionalized graphene oxide have reflected the advantage of the heterogenous catalysts over its homogenous counterpart. The catalyzed Suzuki Miyaura coupling reaction showed an efficient conversion to biaryls, thus concluding that the immobilized amino graphene oxide composites are suitable catalysts for C-C coupling reaction. This study also shows that the catalyst can be easily recovered and reused as there is no significant decrease in the yield of catalyzed reaction even after using the catalyst successively 5 times.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Chapter 6 outlines the summary of the research work presented in the thesis with a note on the conclusions drawn from the catalytic study. Scope for future work has also been covered.

6.1 SUMMARY:

PCP and PNP pincer complexes (C-1 to C-12) were synthesized using the low cost, abundant and environmentally benign cobalt, iron, copper and manganese metals. The complexes showed moderate to good catalytic activity in the cross coupling of phenylboronic acid with aryl halides thereby ascertaining themselves as a competitive and a worthy replacement to the otherwise expensive Pd catalyzed cross coupling reactions. It was also an observation that as the number of 'N' atoms increased in the side arm of the ligand, the donating ability of the ligand increased which led to the increased catalytic activity of the complexes with PNP donor ligand (3 'N' atoms including the center donor nitrogen). This theory steered the synthesis of the next series of complexes (C-13 to C-16) with NNN tridentate pincer ligand with an anticipation of better performance in their catalytic activity. A fair escalation in the percentage conversion of the coupled products were observed which supported the choice of more 'N' donor atoms in the pincer skeleton. However, the homogeneous role of the catalysts posed a setback in the product recovery as well as the catalyst recovery. This impediment was tackled by attempting to heterogenize the complexes by the immobilization method. The PNP and NNN pincer complexes of Co, Cu and Fe metals were immobilized on the aminofunctionalized graphene oxide substrate to now act as heterogeneous catalysts for Suzuki coupling. Increase in product conversion in terms of GC yield was not marked, however the catalyst recovery was possible and their reusability was shown for successive 5 trials with no significant decrease in the yield of catalyzed reaction. Also, iron as a catalytically active metal center was found to yield highest product conversion in homogeneous condition whereas in case of the GO composites, its activity was found to reduce in comparison to Co and Cu composites. This parameter can be used to analyze the extent of immobilization of the metal complexes on the GO substrate. The product conversion indicates that the Co and Cu composites have covered the surface of the substrate better in comparison to the Fe composites

6.2 CONCLUSIONS:

Following conclusions were drawn based on the present research study

- Presence of iron as the active metal center in the pincer skeleton caused highest catalytic activity among the homogeneous complexes synthesized.
- PNP (PNNNP) complexes C-3, C-6, and C-9 and C-12 showing high coupling efficiency can be attributed to the presence of highest electron-rich nitrogen donor atoms in the pincer skeleton. Replacement of ‘P’ donor with ‘N’ donor in the complexes with NNN ligand, L-4 has shown further improvement in the catalytic efficiency.
- Presence of electron withdrawing substituents on the aryl halides favor the coupling process while the electron donating substituents slightly slows down the biaryl conversion.
- Bulkiness of iodide group makes it preferable as a better leaving group among the halides, causing high coupling efficiency for aryl iodides.
- Immobilization on GO substrate has controlled leaching of the composite into the reaction media thereby contributing to the catalyst recovery and reusability.
- Morphological studies of composites suggest better composite formation of C-19 and C-22 with Cu as metal which is reflected in their better catalytic performance in comparison to other metal composites.

6.3 SCOPE FOR FUTURE WORK:

The work carried out in the present thesis could be extended to the following areas:

- A comparative study with substituted derivatives of aryl halides or the substituted phenylboronic acid functionality could focus on the versatility of the catalysts synthesized.
- The catalytic activity study can also be extended to other noteworthy cross coupling reactions like the Heck, Sonogoshira coupling and so on.
- An attempt to apply the complexes and the composites catalytically to carry out other organic reactions is also desirable.

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LIST OF PUBLICATIONS

(A) Research papers in International Journals

1. Lolakshi M.K and B. Ramachandra Bhat (2017) “Cobalt pincer complex catalyzed Suzuki-Miyaura cross coupling – a green approach” *J. Organomet. Chem.*, 827, 41–48.
2. Lolakshi M.K, Rasheeda M. Ansari and B. Ramachandra Bhat (2018) “Catalytic activity of Fe(II) and Cu(II) PNP pincer complexes for Suzuki coupling reaction” *Appl. Organomet. Chem,* 32 (2), e4054.
3. Lolakshi M.K, Praveen Mishra and B. Ramachandra Bhat (2018) “Iron pincer complex and its graphene oxide composite as catalysts for Suzuki coupling reaction” *Journal of Saudi Chemical Society,* (doi:10.1016/j.jscs.2018.08.005).
4. Lolakshi M.K and B. Ramachandra Bhat (2018) “Iron pincer complexes as catalysts in cross-coupling of aryl halides and phenylboronic acid” *International Journal of Engineering & Technology,* 7 (4.5) 428-430.
5. Lolakshi M.K, Praveen Mishra and B. Ramachandra Bhat. “Fe-PNP pincer complex immobilized on graphene oxide as catalyst for Suzuki-Miyaura coupling reactions” Communicated to Catalysis Letters.
6. Lolakshi M.K, Praveen Mishra and B. Ramachandra Bhat. “NNN pincer complexes of 3d- transition metals for cross-coupling of aryl halides and phenylboronic acid” Manuscript under preparation.
7. Lolakshi M.K, Praveen Mishra and B. Ramachandra Bhat. “Graphene oxide immobilized Co pincer complex as catalyst for Suzuki coupling reaction” Manuscript under preparation.

(B) Research papers presented in International Conferences

1. Lolakshi M. K and B. Ramachandra Bhat (2014). "Application of cobalt pincer complex in Suzuki-Miyaura cross-coupling reaction." 13th Eurasia Conference on Chemical Sciences. 14-18th December, 2014. Indian Institute of Science, Bangalore, India.

2. Lolakshi M. K and B. Ramachandra Bhat (2015). "Copper pincer complex as a catalyst precursor for Suzuki Miyaura cross coupling." International Conference on Advances in Chemical Engineering. 20-22nd December, 2015. National Institute of Technology, Karnataka, India.
3. Lolakshi M. K and B. Ramachandra Bhat (2016). “Five coordinate cobalt pincer complex as a catalyst precursor for Suzuki Miyaura cross coupling.” National conference on recent trends in chemical science (NCRTCS 2016), 11-12th January, 2016. Manipal University, Manipal, Karnataka, India.
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