SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE SUBSTITUTED ORGANOMETALLIC CHALCONES

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By

Jayanti Betal

ROLL NO - 412CY2005

Under the Guidance of

Dr. Saurav Chatterjee

DEPARTMENT OF CHEMISTRY

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

ORISSA-769008

CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and characterization of phosphine substituted organometallic chalcones"** being submitted by **Jayanti Betal** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bona fide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela   Dr. Saurav Chatterjee

Date   **(Supervisor)**

ACKNOWLEDGEMENT

Rourkela

Date: (Jayanti Betal)

CONTENTS

CHAPTER-1 : INTRODUCTION

CHAPTER-2: SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE SUBSTITUTED ORGANOMETALLIC CHALCONES

Abstract

The current focus in organometallic chalcones is based upon their synthesis, eloectrochemical properties , diverse biological behavior and their facet towards a new field "bioorganometallics'' concerning both organometallic and coordination chemistry . The organometallic chalcones can be used as precursor for the synthesis of various other important biologically active heterocyclic compounds. Ferrocene based derivatives which are one of the most extensively studied among metallocenes has also been reported for their application to materials particularly in designing molecular sensors, molecular ferromagnet, electrochemical agent, molecular switch and non-linear optical material. Recently, phosphine chemistry has gained attention due to their tremendous applications and aspects in the field bioorganometallics. In view of their enormous prospect we carried out the synthesis and characterization of phosphine substituted multimetallic organometallic chalcone.   The electrochemical and biological properties of synthesized organometallic chalcone is under investigation.

CHAPTER 1

INTRODUCTION

1.1. Metal cyclopentadienyl compound

A metal cyclopentadienyl compound is a metal complex where a metal binds with one or more electron rich cyclopentadienyl groups ($C_5H_5^-$, abbreviated as Cp^-). Cp generally co-ordinates in the η^5-mode and it can adopt seldom the η^1-and η^3-co-oridnation mode as shown in Figure 1.[1]

Figure 1: η^1 and η^5 modes of cyclopentadienyl bonding

Based on the type of bonding between the metals and the cyclopentadienyl moieties, metal-cyclopentadienyl complexes are classified into the following three categories:

a) π-complexes: Metals and cyclopentadienyl moieties connected by π-bonds are called π-complexes. π-complexes, especially in the η^5-type coordination mode, are the most typical of the three types of complexes. η^3-type π-complexes are also observed, depending on the electronic configuration of the metal centre. In this mode, three carbon atoms are bonded to the metal as an allyl-anion ligand, and the remaining two carbon of the Cp ring remains like a simple alkene.

b) σ-complexes: σ-complexes have a direct σ-bond between the metal and one of the carbons of the cyclopentadienyl group.

c) Ionic complexes: Ionic complexes primarily involve alkali metal cations and alkali earth metals cations connected to cyclopentadienyl anions. These complexes are not ionic, but the bonding is highly polar and often η^1 bonding is indicated. Ionic type complexes are generally synthesized directly by reaction of cyclopentadiene and the metal in a non-aromatic solvent. These complexes can be good starting materials for several π-type cyclopentadienyl complexes.

1.2. Sandwich compounds

When the two Cp rings are parallel to each other with the metal atom in between, then the complex is known as sandwich compound (Figure 2 and Figure 3). The term sandwich compound was introduced in organometallic nomenclature by J.D. Dunitz, L.E. Orgel and R.A. Rich during 1950.[2]
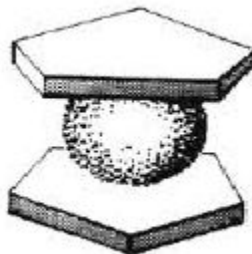

Figure 2: Sandwich compound

Metallocenes are the special class of sandwich compounds with the general formula $(C_5H_5)_2M$ or Cp_2M, where two cyclopentadienyl anions (Cp, which is $C_5H_5^-$) bound to a metal center (M) in the oxidation state II. Metal cyclopentadienyl compounds can be classified into a variety of different compounds on the basis of bonding and structural integrity: sandwich compounds (Cp_2M), half sandwich or piano stool $(CpML_y$, y=1-4; unidentate ligand), bent or tilted $(Cp_2ML_x$, x=1-3; L= unidentate ligand like H, Cl, CO) and multidecker compounds (Cp_xM_y) as shown in Figure 3.

1.3. Ferrocene

Ferrocene was the first metallocene discovered by Keally, Pauson and Miller et. al. in 1951 (Figure 4).[3] Ferrocene is an organometallic metallocene compound with the formula $Fe(C_5H_5)_2$ or Cp_2Fe, systematically named bis(η^5-cyclopentadienyl)iron(II). The d orbitals on Fe^{2+} in ferrocene are coordinated to the π orbitals on the two cyclopentadienyl radicals to form a unique sandwich structure. The sandwich structure of ferrocene was discovered by G. Wilkinson, R. B. Woodward and E. O. Fischer independently in 1951. According to them, ferrocene consists of a "double cone" structure with all five carbon atom of each

Sandwich compounds
(M= Fe, Co, Ni, Ru, Ti, Cr)

$[Ni_2(Cp)_3]^+$
Multidecker complex

Bent/tilted sandwich
compound

Monometallic half sandwich compounds

M = Mo, Cr, W

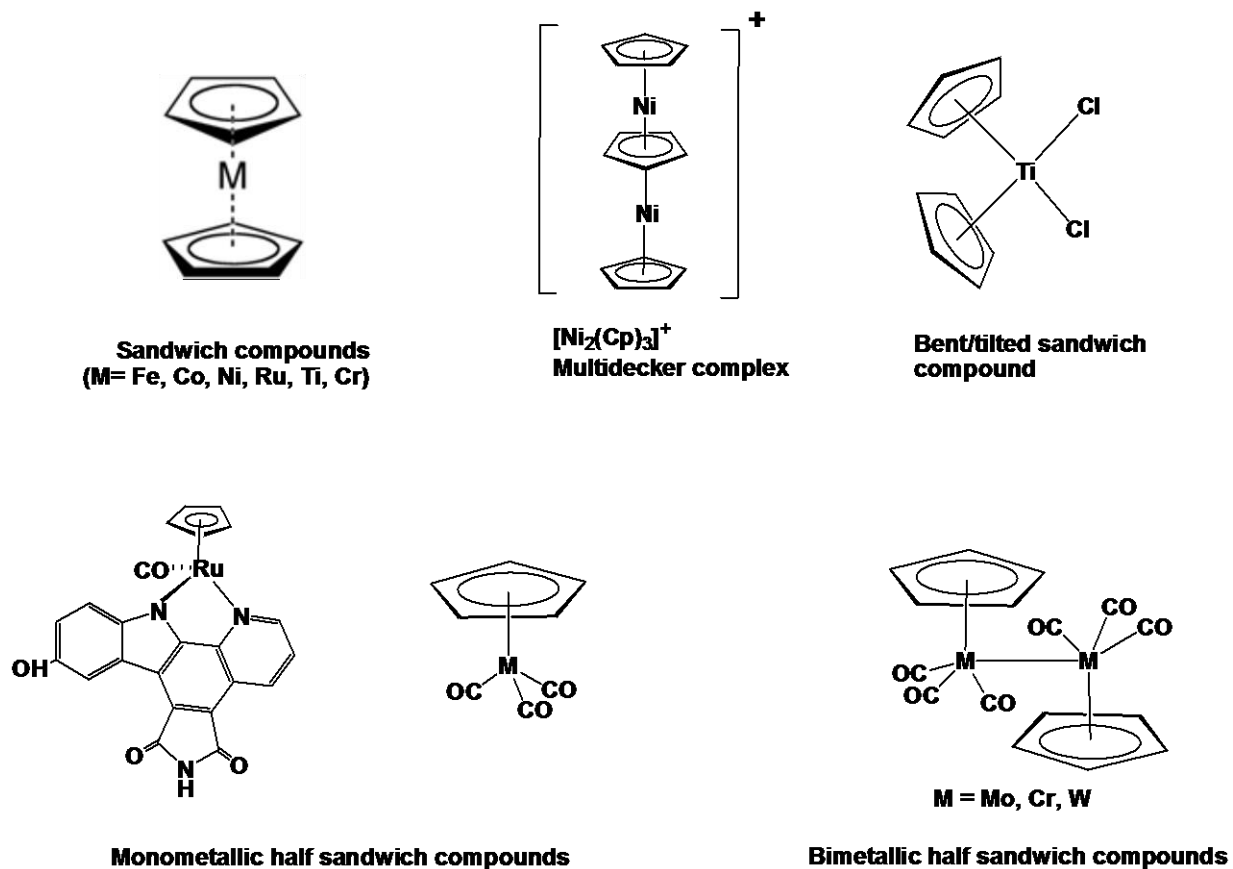**Bimetallic half sandwich compounds**

Figure 3

cyclopentadienyl (Cp) ligands interacting with the Fe metal center. The unique sandwich structure of ferrocene was first predicted by infrared and nuclear magnetic resonance spectroscopy and was later confirmed by single crystal X-ray crystallography in 1954. Wilkinson and Fischer have been honored the Nobel Prize in 1973 for the successive synthesis of ferrocene and its complexes. At room temperature ferrocene is an air stable orange colored solid and it can be oxidized to blue-green ferrocenium cation, $[(C_5H_5)_2Fe]^+$. Ferrocene behaves like an aromatic compound and it is susceptible to direct electrophilic substitution reactions, giving rise to a variety of mono and di-substituted ferrocenyl compounds. It is thermally stable and unaffected by water, strong acids and alkalis. Ferrocene is a fascinating molecule due to its remarkable redox properties and high stability in air and in high temperature.
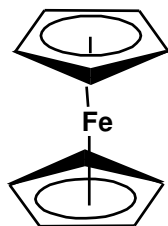
Figure 4 Structure of Ferrocene

1.4. Applications of ferrocenyl compounds

Chemistry of ferrocene led to numerous applications in the field of organic synthesis, homogeneous catalysis, materials science, bio-conjugates, bio-analysis and in bioorganometallic chemistry. Ferrocene behave as a one electron donor by undergoing oxidation to give a stable cationic ferrocenium ion. This led ferrocenyl derivatives to be used as a model for sensors and non-linear optical materials. In contrast to other metallocenes, ferrocenyl compounds is more widely employed in drug design due to its special properties like high stability, redox property, potential as iron source and low toxicity behavior.

1.4.1. Biological properties of ferrocenyl derivative

Research is focused on the insertion of ferrocene into drug molecules to bring significant change in the drug activities. Recent report reveals that ferrocenyl derivatives exhibit a wide range of biological activity due to its high stability and nontoxic behavior. Many ferrocenyl compounds show interesting cytotoxic, anti-microbial, anti-fungal, anti-malarial, anti-cancer and DNA cleaving activities.[4-6]

Edward's research group have synthesized a series of antibiotics containing ferrocene moiety such as ferrocenyl penicillin, ferrocenyl cephalosporine and ferrocenyl hybrid of penicillin and cephalosporine (Figure 5).[7-9]
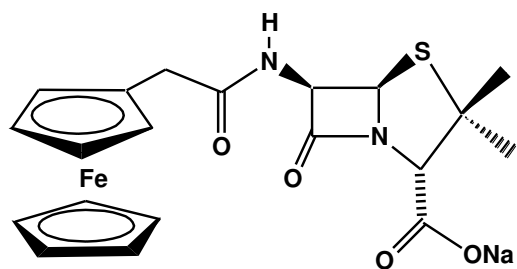
Ferrocenyl penicillin
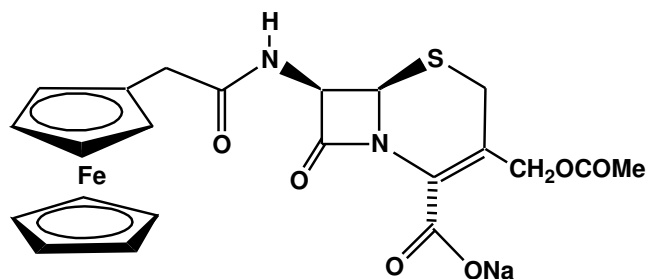
Ferrocenyl cephalosporin
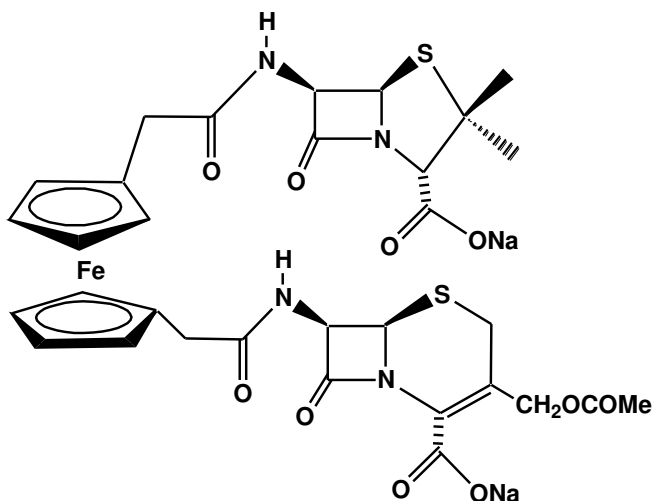
Ferrocenyl hybrid of penicillin and cephalosporin

Figure 5

Incorporation of ferrocenyl fragments into drugs like chloroquine and tamoxifen, results in significant change in activity (Figure 6 and Figure 7). Ferroquine, a ferrocenyl derivative of choloquine is currently the most advanced organometallic drug candidate, which is ready to use in phase III clinical trials as antimalarial drug.[10,11]

Ferroquine

Chloroquine
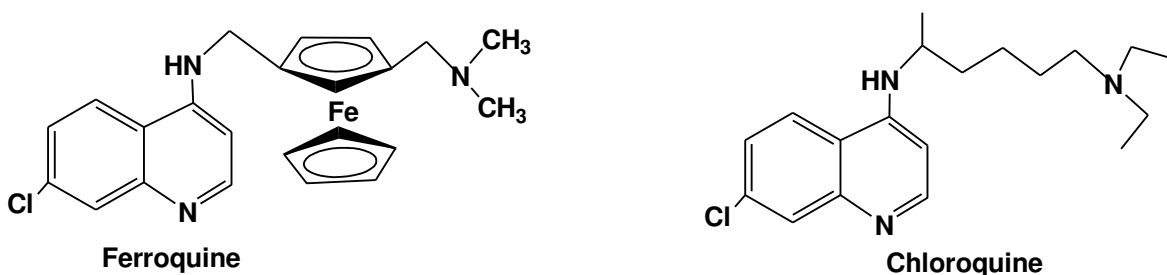
Figure 6

Ferrocifen, derivative of tamoxifen, is known as the first molecules which is active against both hormone dependent and hormone independent breast cancer cells.[12]

Tamoxifen (X= H)
Hydroxy derivative of tamoxifen (X=OH)

Ferrocifen
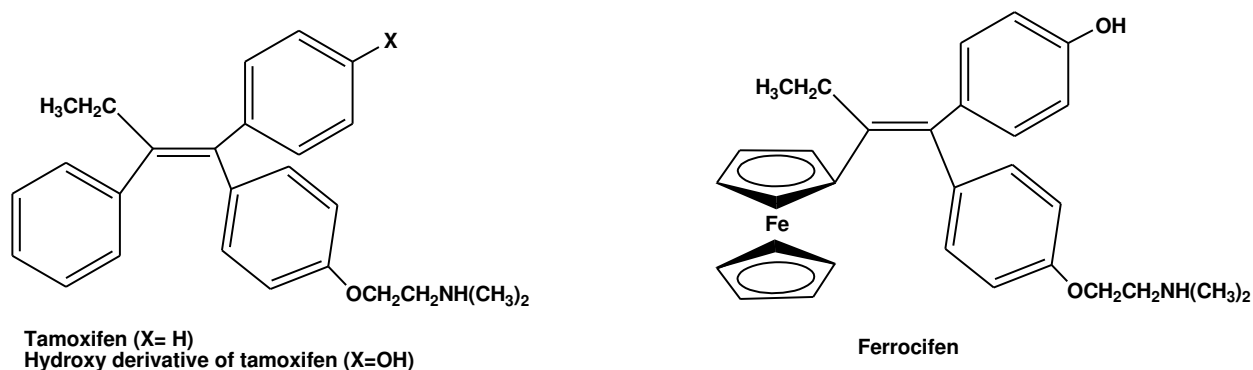
Figure 7

Some ferrocenyl hydrazone compounds are recently investigated which display antiproliferative effects on A2780 ovarian carcinoma cell line comparable to that produced by cisplatin.[13]

Quirante et. al. have synthesized and characterized a series of ferrocene-indole hybrids and their organic analogues as shown in Figure 8 and have revealed their cytotoxic and moderate antimalarial activity. They have reported some of the ferrocenylindole hybrids showing excellent in vitro activities against the A549 human carcinoma cell line, with IC_{50} values of 5 and 7 mM respectively. These ferrocenylindole compounds were up to 25-fold more potent as cytotoxic agents than their purely organic analogues.[14]

X=N, R_1, R_2 = H
X=H, R_1=H, R_2=H / Cl / F
X=H, R_1=OCH$_3$ / NO$_2$ / Cl, R_2=H
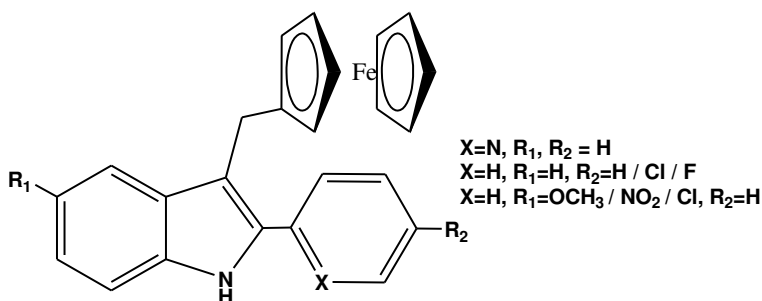
Figure 8

In recent times, some symmetrical and unsymmetrical ferrocenyl hydrazones with their significant antibacterial activity against B. subtilis, E. coli, S. aureus, K. pneumoniae and P. aeruginosa have been explored by our group with moderate to high activity. [15]

Pejovic´ et al. have synthesized ferrocene containing quinolinones and have studied their electrochemical as well as their antimicrobial activity towards pathogenic bacteria and one yeast with MIC values ranging from 0.01-10 µg/ml lower than that of tetracycline (Figure 9).[16]

a) X= H, b) X=Cl, c) X=Br
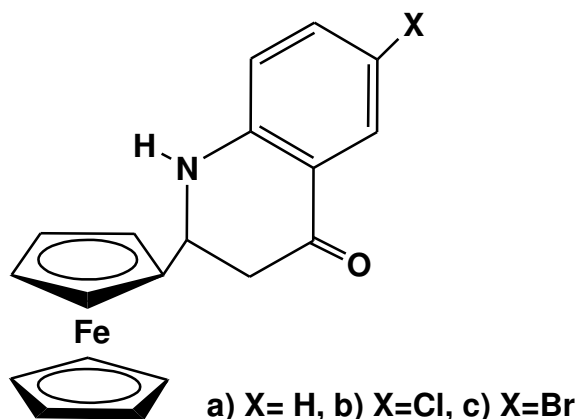
Figure 9

1.4.2. Ferrocenyl derivatives used as catalyst

Ferrocene based ligands have received considerable attention due to their versatile coordination properties and numerous successful applications in catalysis[17,18].

Stepnicka et. al. have synthesized (1,9-diphenylphosphino)-1´-[(diphenylphosphino) methyl] ferrocene (Figure 10) as an unsymmetric dppf congener and have reported the coordination and catalytic study aimed at a comparison of this new donor with the well–studied dppf.[19]
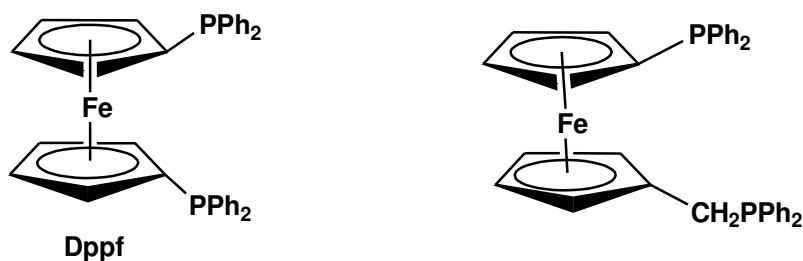
Figure 10

To understand the specific challenges of organocatalysis in terms of kinetic rates and efficiency, Miniere et. al. have synthesized some new ferrocenyl sulfides, exhibiting planar chirality as illustrated in Scheme 1. Incorporation of various heteroatom groups were done and have been evaluated as catalysts for the asymmetric epoxidation of aldehydes *via* sulfonium ylides.[20]
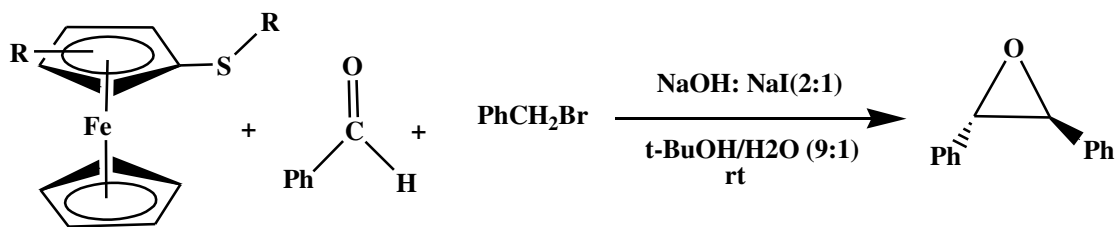
Scheme 1

1.4.3 Electrochemical, optical and sensing properties of ferrocenyl derivatives

Recently, Thakur and coworkers[21] have reported the electrochemical, optical, and cation-sensing properties of two synthesized triazole-tethered ferrocenyl benzylacetate derivatives (Figure 11). The binding properties of both the receptors can be inferred either from a redox shift (A: $\Delta E_{1/2}$ = 106 mV for Hg^{2+} and $\Delta E_{1/2}$ = 187 mV for Ni^{2+}; B: $\Delta E_{1/2}$ = 167 mV for Hg^{2+} and $\Delta E_{1/2}$ = 136 mV for Ni^{2+}) or a highly visual output response (colorimetric) for Hg^{2+}, Ni^{+2}, and Cu^{2+} cations. The redox and colorimetric responses toward Hg^{2+} are preserved in the presence of water, which can be used for the selective colorimetric detection of Hg^{2+} in an aqueous environment over Ni^{+2} and Cu^{2+} cations. The changes in the absorption spectra are accompanied

by the appearance of a new low-energy peak at 625 nm for both compounds A and B due to a change in color from yellow to purple for Hg^{2+} cations in CH_3CN/H_2O. The ferrocene-based triazole ligand is the rare example of a dual electrochemical−optical Ni^{2+} ion sensor in which the Fc/Fc$^+$ redox couple is significantly shifted ($\Delta E_{1/2} = 187$ mV) on complexation, with a concurrent change in color from yellow to blue which permits its potential use for "naked eye" detection.
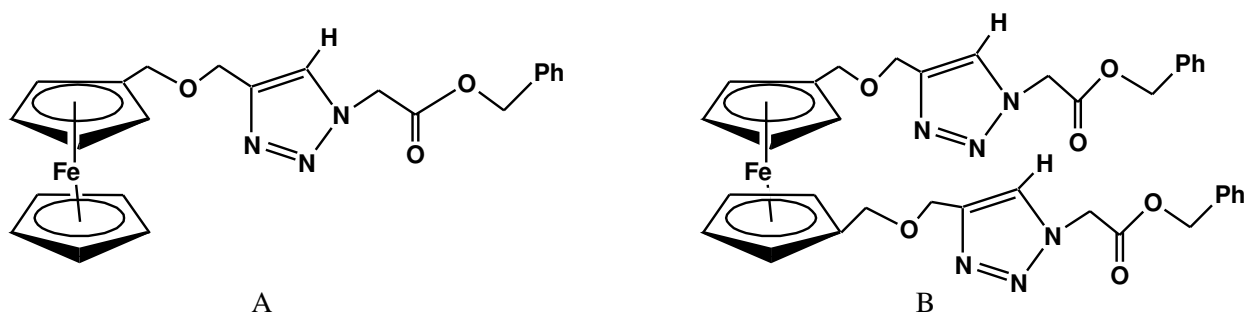

Figure 11

In 2013, Romero et al have synthesized a number of mono and di substituted ferrocene based triazoles by copper catalyzed click reactions and have studied their optoelectronic properties. Some of the compounds are optically active molecular sensors for anions such as F$^-$, AcO$^-$, $H_2PO_4^-$, $HP_2O_7^-$ and some of the compounds behave as dual redox and optically sensors for cations such as Hg^{+2}, Pb^{+2}, Ni^{+2}.[22]

Two ferrocenylchalcones containing the fluorescent anthracenyl group, Ferrocene-COCH=CH-Anthracene and Anthracene-COCH=CH-Ferrocene, prepared by solvent free aldol condensation have been reported by Noh et al.[23] The cyclic and differential pulse voltammetry analysis showed one reversible cycle corresponding to the Fc/Fc$^+$ and one irreversible peak corresponding to the oxidation of anthracenyl group. The authors also have studied the UV-Visible spectra of the ferrocenyl chalcones in some solvents of different polarity and have concluded that $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the enone linkage were not influenced by the solvent polarity, but the d→d transition for both Ferrocene-COCH=CH-Anthracene and Anthracene-COCH=CH-Ferrocene were shifted by 16nm and 14nm respectively. So, Ferrocene-COCH=CH-Anthracene could be used as a non-linear optical (NLO) material due to its strong solvatochromic shift.

Recently, Trivedi *et. al.* reported a simple one-pot synthesis, characterization, optoelectronic and cation sensing properties of 1-(2-pyridyl)-3-ferrocenylpyrazolines (scheme 2). They have described that these ferrocene compounds behave as selective multichannel chemosensors in the presence of Co^{2+}, Cu^{2+}, and Zn^{2+} ions. A maximum cathodic shift in the redox potential of the ferrocenium couple was observed towards the Co^{2+} ion, while a minimum shift was observed with the Zn^{2+} ion on complexation with this receptor.[24]

1. 20% KOH, r.t.

2. 2-PyNHNH2

Ar= 1-napthyl, 9-anthryl, 1-pyrenyl
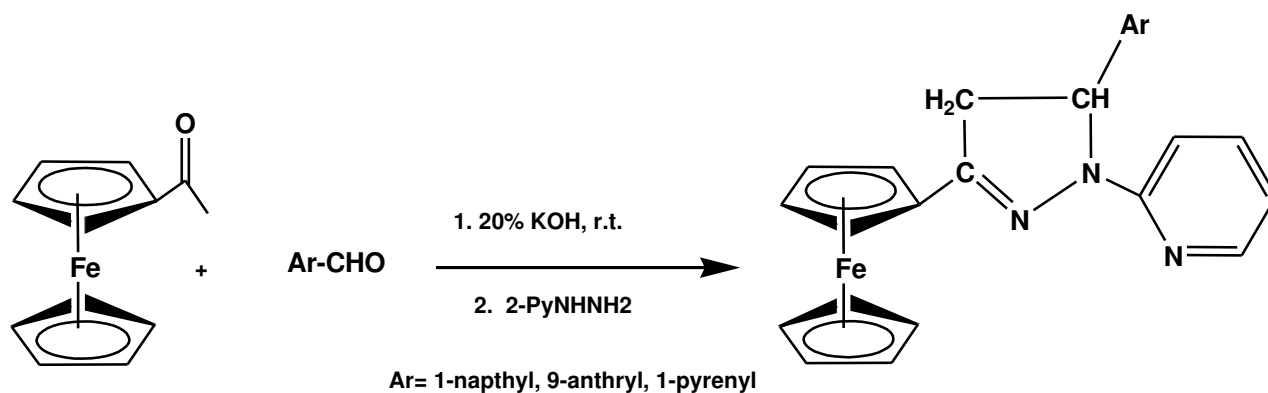
Scheme 2

1.4.4. Ferrocenyl derivatives as a ligand scaffold

Chiral ferrocenyl phosphines are used as ligands for transition-metal catalyzed reactions. Some of them have found industrial applications in the synthesis of pharmaceuticals and agrochemicals. For example, the diphosphine 1,1'-bis(diphenylphosphino)ferrocene (dppf), organophosphorus compound commonly used as a ligand in homogeneous catalysis is a valuable ligand for palladium-coupling reactions.

1.5. Metal Carbonyl chemistry

Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands. They occur as neutral complexes, as positively charged metal carbonyl cations or as negatively charged metal carbonylates. The carbon monoxide ligand may be bound terminally to a single metal atom or bridging to two or more metal atoms.

1.5.1. Structure and bonding of metal carbonyls

Carbon monoxide bonds to transition metals using "synergistic π back-bonding." The bonding has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of nonbonding sp-hybridized electron pair on carbon with d-, s-, and p-orbitals on the metal. A pair of π bonds arises from overlap of filled d-orbitals on the metal with a pair of π-antibonding orbitals projecting from the carbon of the CO. For the second kind of binding, the metal should have d-electrons and have relatively low oxidation state which makes the back donation process favorable. As electrons from the metal fill the π-antibonding orbital of CO, they weaken the carbon-oxygen bond compared with free carbon monoxide, while the metal-carbon bond is strengthened. The distance between the metal and carbon is relatively short due to the multiple bond character of the M-CO linkage. There are three common types of metal carbonyl bonding modes: terminal CO, bridging CO (μ_2) and triply bridging CO (μ_3) (Figure 12).
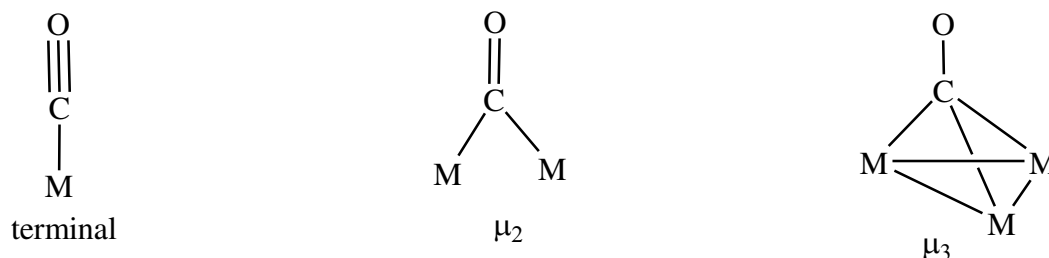
Figure 12

Infrared spectroscopy is a sensitive probe for detection of bridging carbonyl ligands and can be used for the determination of the type of metal carbonyl bonding in several such compounds. Metal carbonyls are important precursors for the synthesis of other organometallic complexes and can be used as metal probes and therapeutic agent in medicine. The half sandwich cyclopentadienyltricarbonylmanganese commonly known as cymantrene is an important metal carbonyl compound in organometallic chemistry. Recent research is focused on the properties of cymantrenyl derivatives including electrochemical properties and biological activity.[15,25-27]

1.5.2. CO substitution

The substitution of CO ligands can be induced thermally or photochemically by donor ligands. Some of the substituting ligands are cyclopentadiene, phosphines, cyanide (CN^-), olefins, nitrogen donors, and ethers. Substitution of 18-electron complexes generally follows a dissociative mechanism, involving 16-electron intermediates.

Substitution proceeds via a dissociative mechanism:
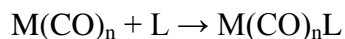
$$M(CO)_n \rightarrow M(CO)_{n-1} + CO$$
$$M(CO)_{n-1} + L \rightarrow M(CO)_{n-1}L$$
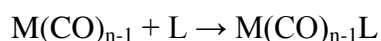
Substitution in 17-electron complexes, which are rare, proceeds via associative mechanisms with a 19-electron intermediate.

$$M(CO)_n + L \rightarrow M(CO)_nL$$
$$M(CO)_nL \rightarrow M(CO)_{n-1}L + CO$$

Sometime the rate of substitution in 18-electron complexes is sometimes catalyzed by catalytic amounts of oxidants, via electron-transfer.

1.6. Chalcones

Chalcones [(Ar–COCH=CH–Ar')] are the α,β- unsaturated ketones which forms the central core for a variety of important biological compounds. These are colored in nature due to the existence of the chromophoric group (-CO-CH=CH-) and depends on the presence of other auxochromes. Chalcones are present in edible plants and constitute one of the major classes of natural products with wide range distribution in fruits, vegetables, tea and soy based food stuff. Chalcones are present in nature as precursors of flavionoids and as precursors of isoflavionoids. Chalcones can be synthesized in the laboratory by various synthetic methods. The most common method used is the condensation of ketone with aromatic aldehyde following Claisen–Schmidt reaction as given below in Scheme 3.
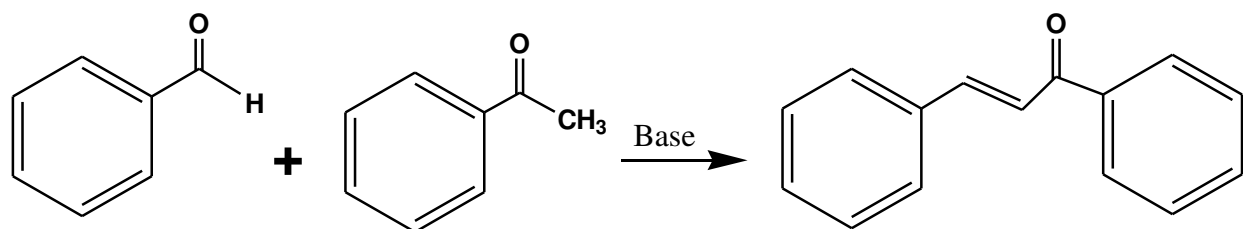
Scheme 3

The main functions of some chalcone derivatives in biological system are purifying blood, strengthening immune system, monitors cholesterol level, regulates blood pressure, prevents thrombus, suppress acid secretion, prevent cancer and promotes metabolism. Both natural chalcones as well as synthetic chalcones have gain the attention of researchers due to their pharmacological as well as biological activities such as anti-inflammatory, antifungal, antimicrobial , antioxidant, antitumor, cytotoxic, and anticancer activities.[29-35]

A plant polyphenol, butein (3, 4, 2', 4'-tetrahydroxychalcone), has been traditionally used in some countries for treatment of pain, stomach cancer, thrombotic disease gastritis, parasitic infections, as well as a food additive .[36,37]

In 2010, Chopde and co-workers have synthesized some bioactive chalcones having 8-hydroxy -quinoline moiety and have shown their moderate activity towards antibacterial study as compared to standard drug (Scheme 4).[38]

Scheme 4

13
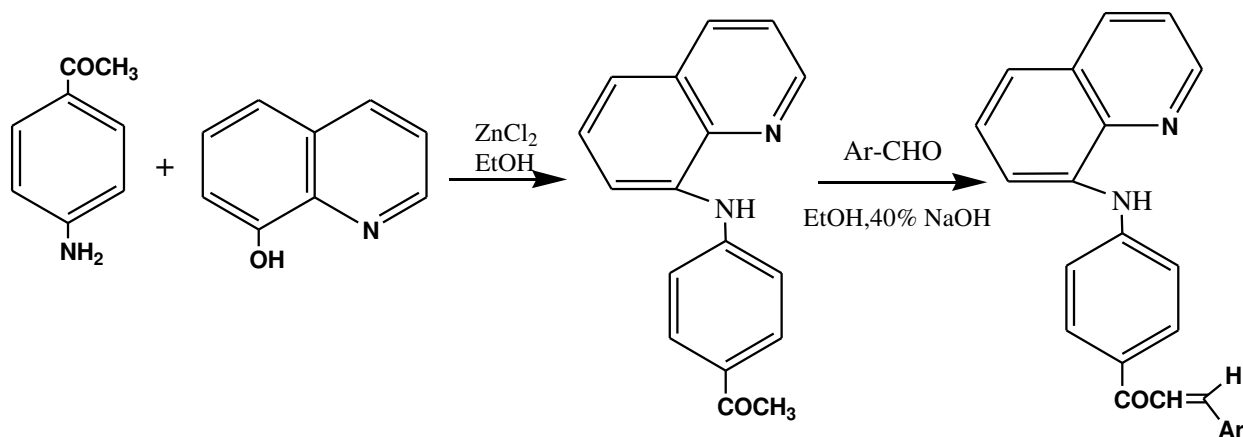
1.7. Chalcone containing organometallic tag

Recently chalcones containing organometallic fragment are of great interest due to their immense applications in the area of biology and medicine. Ferrocenyl chalcones are chalcones in which one or both the aromatic group in the chalcone is replaced by the ferrocenyl group. The chemistry of ferrocenyl chalcone has generated intensive scientific studies throughout the world due to their vast applications towards optoelectronic activity, electrochemistry, biology and medicine.[39-44]

1.8. Applications of organometallic chalcones

1.8.1. Biological activity of organometallic chalcone:-

Major part of the study on ferrocenyl chalcones are based upon their significant biological properties. Ferrocenyl chalcones displays a variety of biological properties such as anticancer, anti-inflammatory, antimalarial, anti microbial activities.[45-47]   A series of novel chalcone derivatives have been designed and synthesized, and their biological activities were also evaluated as potential inhibitors of tubulin. These compounds were assayed for in vitro growth-inhibitory activity against MCF-7 and A549 cell lines. One of the compounds showed the most potent antiproliferative activity against MCF-7 and A549 cell lines with IC50 values of 0.03 and 0.95 µg /mL and exhibited the most potent tubulin inhibitory activity with IC50 of 1.42 µg /mL and can be used as a potential anticancer agent.[48]

The facile and efficient synthesis of quinoline-appended ferrocenyl chalcones via the condensation of acetylferrocene (or substituted 2-methyl-3-acetylquinoline) with 2-chloro-3-formylquinoline (or ferrocenecarboxaldehyde) in ethanol under basic conditions by the ultrasonic method is reported by Prasath et. al. (Figure 13).[49] Redox chemistry of the new chalcones was investigated by cyclic voltammetry which showed quasi-reversible one-electron redox processes with potentials correlated with electron-withdrawing substituents. The compounds showed promising antimicrobial properties.
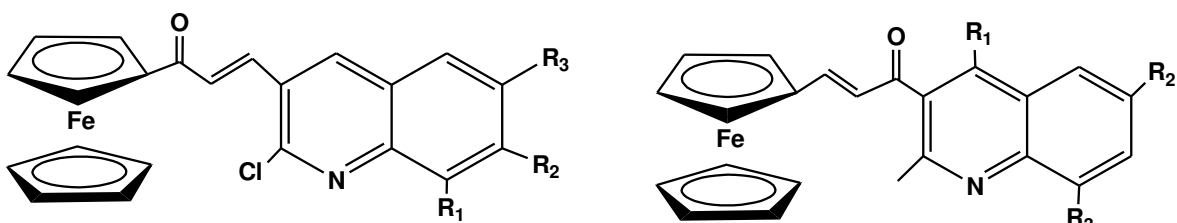
Figure 13

1.8.2. Electrochemical properties of organometallic chalcones

Ferrocenyl chalcones can be tuned for different significant properties for the redox behaviour of ferrocene group present in it. Based upon this research has also been focused on the study of electrochemistry of ferrocenyl chalcone derivatives.

E. Erasmus[50] has synthesized some chalcones containing diphenyl group, chalcones containing one organometallic moiety such as ferrocene or ruthenocene and chalcones having two organometallic moieties or both as shown in Scheme 5. It was observed from UV/Vis spectra of the chalcones, that the compounds having a ferrocenyl moiety exhibited two absorption bands, where as the compounds having a ruthenocenyl moiety showed one absorption band. Cyclic voltammetry of the compounds revealed a chemically and electrochemically reversible Fc/Fc^+ couple and an irreversible Rc/Rc^{2+} couple as it showed no reduction peak. It has been found out that the position of the metallocene closer to the carbonyl or the double bond influences the reduction potential of the electroactive metallocenyl moiety in chalcones. It was reported that chalcones with the carbonyl group adjacent to the metallocene are more difficult to oxidize than the metallocene adjacent to the double bond.
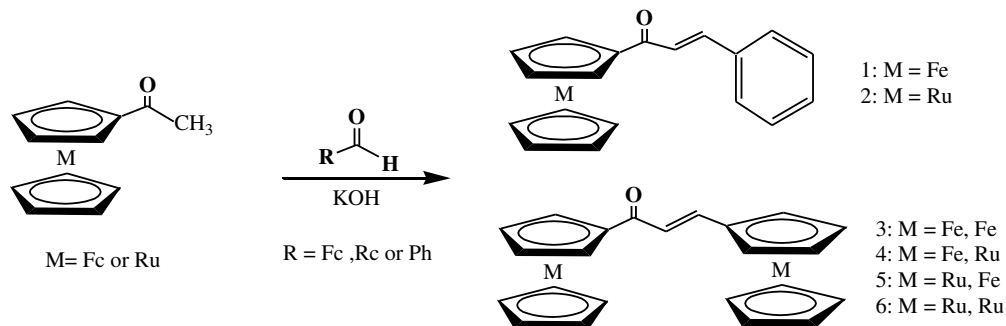
Scheme 5

15

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE SUBSTITUTED ORGANOMETALLIC CHALCONES

2.1. Introduction

The current focus in organometallic chalcones is based upon their synthesis, eloectrochemical properties and diverse biological behavior. The organometallic chalcones can be used as precursor for the synthesis of various other important biologically active heterocyclic compounds. Recently, phosphine chemistry has gained attention due to their tremendous applications and aspects in organometallic and coordination chemistry. [51-55]

A new series of hybrid organometallic-organic and dinuclear organometallic chalcones containing the cyrhetrenyl fragment were synthesised and characterized by Arancibia et al. Evaluation of the compounds for antimalarial activity in vitro against the chloroquine-susceptible strain 3D7 and the chloroquine-resistant strain W2 of Plasmodium falciparum, indicated that these cyrhetrene conjugates are more active compared to their ferrocenic analogues. [56]

Novel chiral monodentate phosphite ligands holding cymantrene fragment (Figure 14) have been prepared by Lyubimov et al. The phosphate substituted cymantrene compound provided higher enantioselectivity than its unsubstituted analogue and was a better asymmetric catalyst in hydrogenation of (Z)-methyl-2-acetamido-3-phenylacrylate. [57]
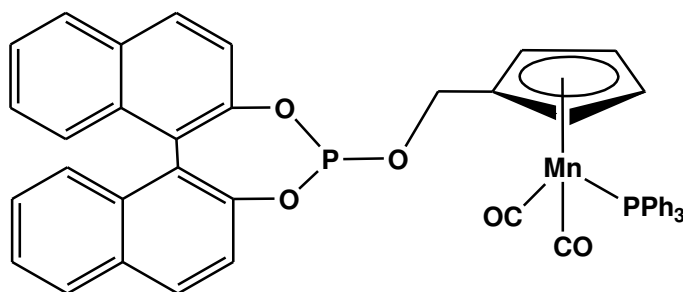
Figure 14

Nabavizadeh et al. have synthesized a series of cyclometalated diplatinum(II) complexes each containing a 1,1'-bis(diphenylphosphino)ferrocene (dppf) spacer ligand using a general synthetic approach involving the ligand replacement from the corresponding precursor having a labile ligand SMe_2. The kinetic and mechanistic investigation on the related replacement reactions have been carried out by using UV-visible and NMR spectroscopies. The absorption and electroluminescence spectroscopic studies of the complex showed interesting photophysical properties (Figure 15). [58]

Figure 15

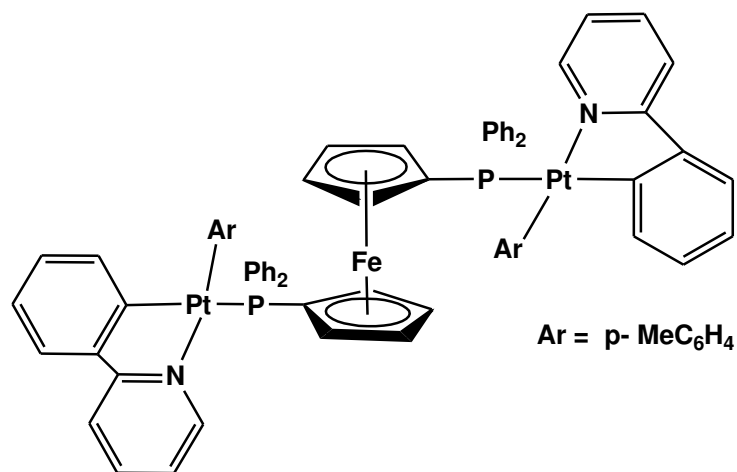Some of these interesting features related to organometallic chalcones and phopshine moieties have prompted us to investigate in detail the chemistry of organometallic chalcones towards phosphine substitution and their influence in navigating interesting properties like electrochemical and biological behavior.

2.2. EXPERIMENTAL SECTION

2.2.1. General Procedures

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified nitrogen using standard schlenk line techniques. Solvents were purified, dried and distilled under nitrogen atmosphere prior to use. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I spectrometer as dichloromethane solutions in 0.1 mm path lengths KBr cell and NMR spectra on a 400 MHz Bruker spectrometer in $CDCl_3$. HPLC grade dichloro methane is used for all spectroscopic analysis. TLC plates (20x20 cm, Silica gel 60 F254) were purchased from Merck. The compound $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4) CH=CHCO(\eta^5\text{-}C_5H_4)Mn(CO)_3]$ (**1**) was synthesized and characterized according to the procedure established by our research group.

2.2.2. Synthesis of [(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$) CH=CH CO(η^5-C$_5$H$_4$)Mn(CO)$_2$PPh$_3$] (2)

In a two necked round bottom flask compound (**1**) (0.01gm, 0.025mmol) was taken with THF and was stirred in room temperature under nitrogen atmosphere. To this reaction mixture, PPh$_3$ (0.013gm, 0.05mmol) was added and was irradiated with ultraviolet light under nitrogen atmosphere in room temperature for 10 minutes under ice cooled condition. The reaction mixture was then stirred for 17 hours in room temperature under nitrogen atmosphere. The reaction was monitored by TLC. On completion of the reaction, the solution was dried under vacuum and the residue was dissolved in dichloromethane solvent and subjected to chromatographic work- up using preparative TLC. Elution with hexane/dichloromethane (40:60) solvent mixture separated the following compounds in order of elution : colorless triphenyl phosphine, unreacted [(η^5-C$_5$H$_5$) Fe(η^5-C$_5$H$_4$) CH=CH CO(η^5-C$_5$H$_4$)Mn(CO)$_3$](**1**) and an orange colored compound [(η^5-C$_5$H$_5$) Fe(η^5-C$_5$H$_4$) CH=CH CO(η^5-C$_5$H$_4$)Mn(CO)$_2$PPh$_3$] (**2**).

2 : IR (ν$_{CO}$, cm^{-1}, CH$_2$Cl$_2$) 1935 (s), 1876(s), 1645(vs). ^{1}H NMR (δ, CDCl$_3$): 4.18 (t, η^5-C$_5$H$_5$ (Fc), 5H), 4.47 (t, η^5-C$_5$H$_4$ (Fc), 2H), 4.59 (t, η^5-C$_5$H$_4$ (Fc), 2H), 5.24 (t, η^5-C$_5$H$_4$ (Mn), 2H), 5.32 (t, η^5-C$_5$H$_4$ (Mn), 2H), 6.61 (d, CH=, 2H), 7.38-7.5 (m, Ph, 15H) 7.74 (d, =CH, 2H). ^{31}P NMR (δ, CDCl$_3$): 90.1

.

2.3. Results and discussion

UV irradiation of Compound **1** with PPh$_3$ in THF solvent and subsequent stirring at room temperature gave an orange colored compound **2**, which was isolated and purified by Thin Layer Chromatography using pet -ether and dichloromethane solvent mixture in 40:60 ratio (Scheme 6). Spectroscopic characterizations have been carried out with the pure isolated compound. Infrared spectrum of **2** shows peaks corresponding to terminal metal carbonyls in the region 1934-1874 cm^{-1} and ketonic CO at 1645 cm^{-1}. The peak pattern for metal carbonyls is exactly similar to phosphine mono substituted cymantrene derivative. ^{1}H NMR spectra reveals the presence of unsubstituted and substituted ferrocenyl Cp protons at δ 4.18 (s) and δ 4.47 (t),

δ 4.59 (t) respectively. Peaks corresponding to cymantrenyl Cp protons have been obtained in the region δ 5.25 (t) and δ 4.16 (t). The two olefinic CH protons have been obtained as a doublet at δ 6.61 and δ 7.74 region. The more downfield doublet may be assigned for the CH close to C=O unit. Multiplet in the region δ 7.35-7.5 for 15 protons reveals the presence of phenyl rings attached to phosphorus. ^{31}P NMR spectrum shows the presence of peak at 90.1 corresponding to the only phosphorous atom in the compound.
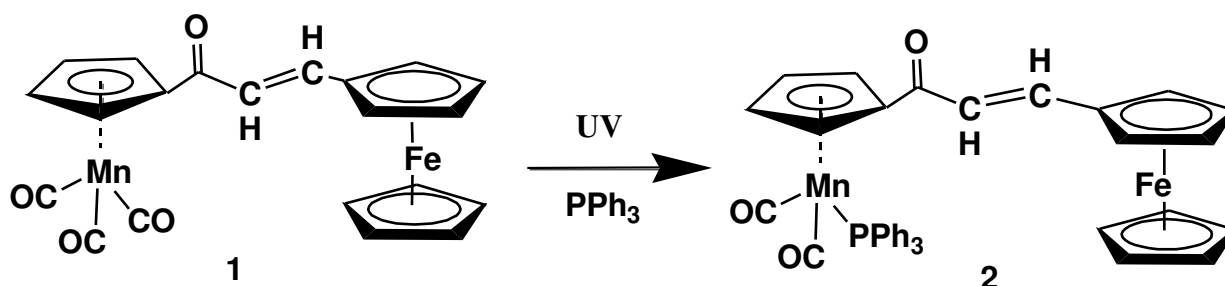
Scheme 6

3. CONCLUSION

Some novel phosphine and ferrocenyl diphosphine substituted organometallic chalcones containing both ferrocenyl and cymantrenyl moieties have been prepared and are characterized by FTIR, ^{1}H NMR and ^{31}P NMR spectroscopy. Reaction with monodentate triphenylphosphine gave only one phosphine substituted compound, while the reaction with diphosphine (dppf) results in the formation of two different phosphine substituted chalcones.

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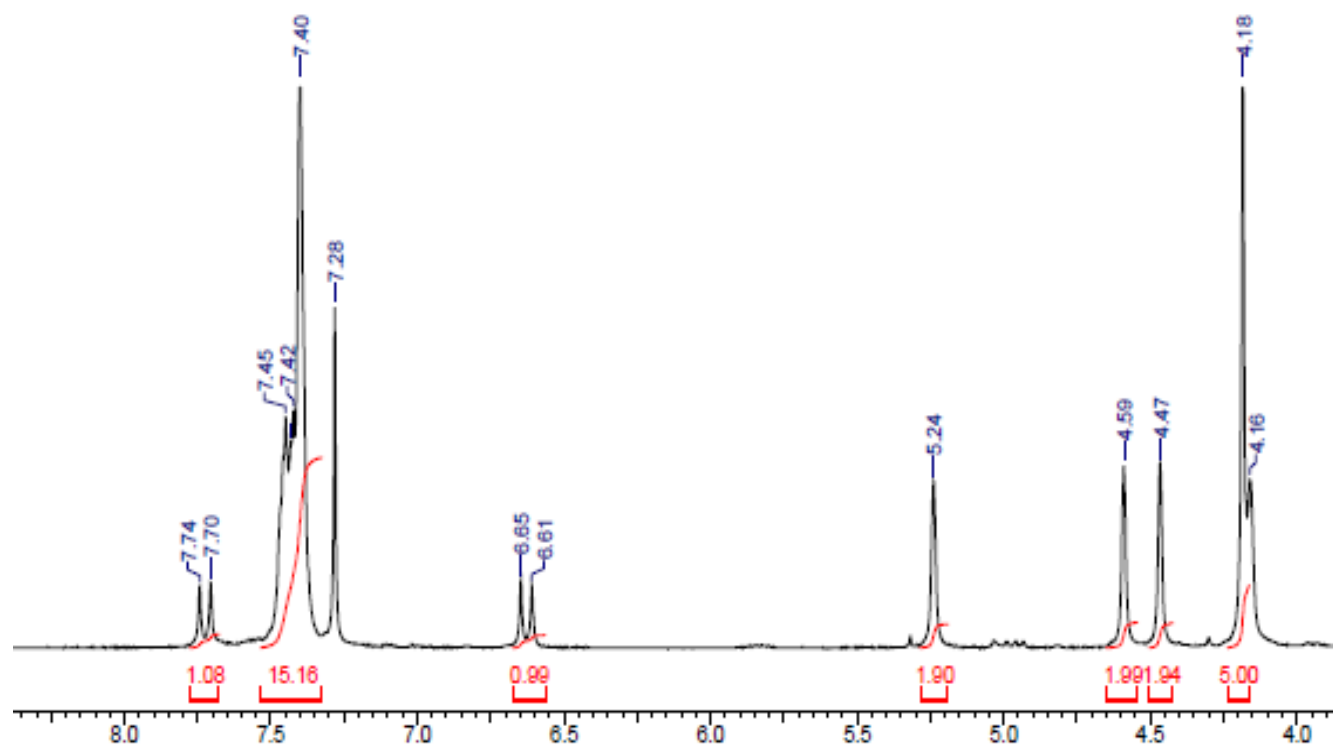43. G. Nabi, Z. Q. Liu, Bioorg. & Med. Chem., 2011, 21, 944.

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5. Annexure

IR spectroscopy of compound 2
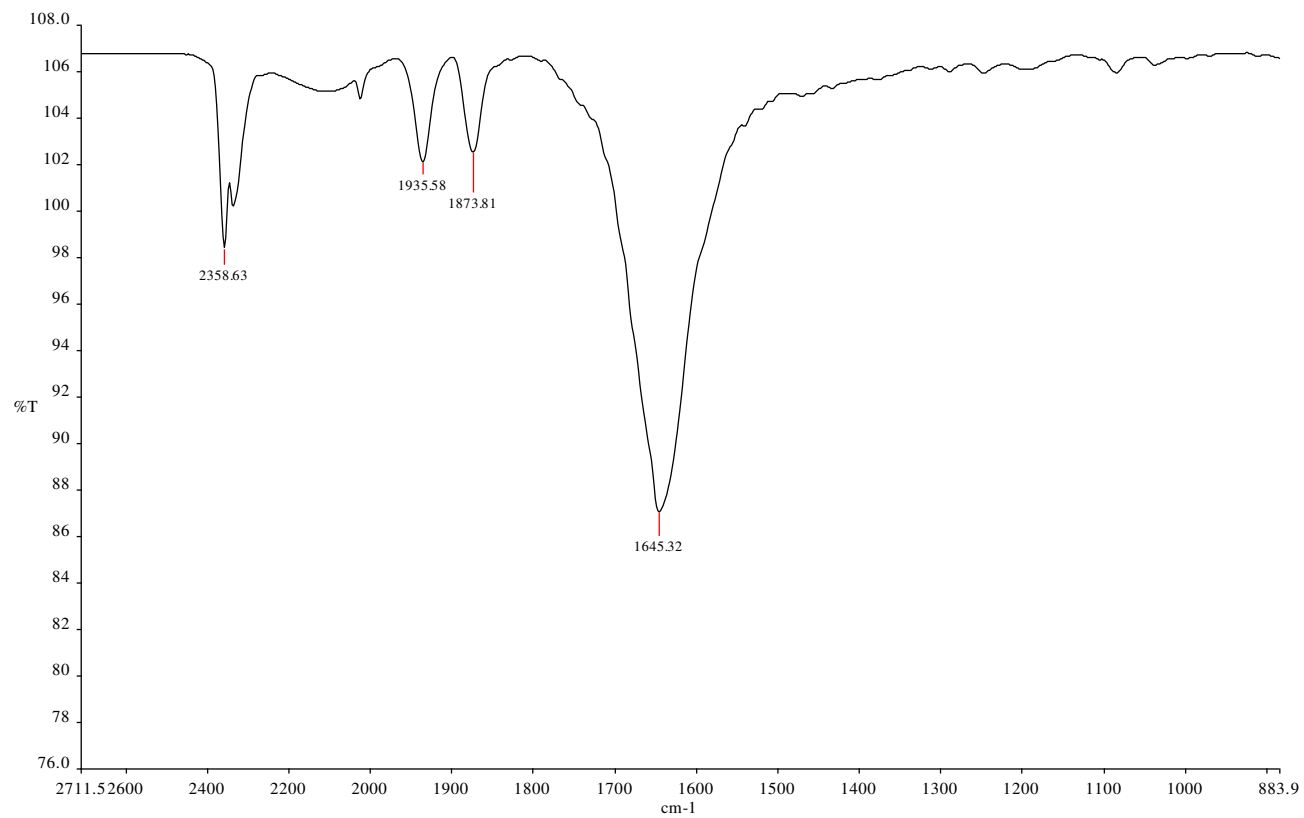
¹H NMR of compound 2

³¹P NMR of compound 2

89.77

100   95   90   85   80