

Synthesis and characterization of organometallic Schiff base compounds

A Dissertation

Submitted in partial fulfillment

FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

By

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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis and characterization of organometallic Schiff base compounds**” being submitted by BASANTI EKKA to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by her under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

N.I.T. Rourkela.

Date:

Dr. Saurav Chatterjee

(Supervisor)

Abstract:

Ferrocenyl monochalcone was prepared by reacting monoacetyl ferrocene with benzaldehyde and characterized by FTIR and NMR spectroscopy. Ferrocenyl monochalcone was reacted with hydrazine hydrate to form three products. The major orange product has been spectroscopically characterized as ferrocenyl pyrazoline derivative. Cyclopentadienyl manganese tricarbonyl compound was acetylated and reacted with salicylal hydrazide to obtain schiff base compound of acetylcymantrene. The compound was characterized by FTIR, ¹NMR and CHN analysis.

ACKNOWLEDGEMENTS

With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to Dr.Saurav Chatterjee , Department of Chemistry, National Institute of Technology, Rourkela, for introducing the present project topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I most gratefully acknowledge his constant encouragement and help in different ways to complete this project successfully. I acknowledge my sincere regards to all staff's member, Department of Chemistry, NIT Rourkela for their enthusiasm in promoting the research in chemistry and for their kindness and

I am thankful to my lab mates Vijaylakshmi, Sagarika,Subhashree,Sucheta,Nishi,pushpanjali and Ayan who helped me since last one year and to my classmates also. Last but not the least, I remember with gratitude my family members who were always a source of strength, support and inspiration.

Rourkela

Date:

(Basanti Ekka)

1.1 Cyclopentadienyl transition metal compounds

In recent years, cyclopentadiene transition metal compounds based molecular sensor ^[1], molecular ferromagnet ^[2], electrochemical agents ^[3], molecular switches ^[4], liquid crystal ^[5], drugs were designed and explored. The new field of bio-organometallic chemistry is also gaining lot of research interest where cyclopentadiene ligated transition metal compounds forms a link between organometallic chemistry to biology, medicine and molecular biotechnology ^[6]. Prime interest has been focused on ferrocene based compounds due to its unique redox properties and highly resonance stabilized behavior. Ferrocene contains two cyclopentadiene ring pi-coordinated to Fe(II) atom. Ferrocene is one of the most important metallocene ^[7]. It has attracted the interest of many scientists and research groups worldwide because of its applications in material science^[8], and asymmetric synthesis^[9], and ferrocenyl derivatives have found numerous uses in various fields of science from biology to materials chemistry^[10]. The sandwich structure of Cp₂Fe was discovered in 1951 by G. Wilkinson, R. B. Woodward and E. O. Fischer independently^[11]. They suggested a “double cone” structure with all five carbon atom of a cyclopentadienyl ligand interacting with the metal center. Wilkinson and Fischer were awarded the Nobel Prize for the subsequent synthesis of ferrocene and further complexes in 1973. Compounds containing ferrocene can also be used as non-linear optical materials ^[12-16] as it can act as electron donor and undergoes oxidation to the ferrocenium ion. The spectrochemical and electrochemical properties are favorable for various biological applications and for conjugation with biomolecules. In these bioconjugates ferrocene serve as the molecular sensor, redox and catalytic site. Ferrocene has been found to be covalently bonded to the biomolecules like amino acids, peptides, proteins, DNA, RNA, PNA, carbohydrates and hormones forming the bioconjugates^[17].

The growth of Material Sciences and Bio-organometallic Chemistry is gathering much interest in the multinuclear metal complexes owing to the redox and photo-reactive metal centers coupling electronically through an unsaturated bridging ligand. The investigators in the area of schiff base ligands are concentrating on their biological activity like potent inhibitors and variable bonding ^[18-23]. The thermal stability and the strong bonding of the ligand to the d- block and f-block elements have made the complexes more interesting. The pharmaceutical companies are targeting on the synthesis of the schiff base ligands and their heterometallic and heterobimetallic complexes due to their improved potency and wide specificity like antitumor and anticancerous properties. The Ferrocenyl based schiff base compounds are found to undergo unique changes in solution which

makes them an interesting material for further research on their complexation and other other behaviors. Some ferrocene based schiff –base ligands are prepared by addition – elimination reaction and find applications in asymmetric catalysis, stoichiometric reactions ^[24-31] and in isotactic polymerization of propylene ^[32-33].

1.2 OTHER METALLOCENES:

Metallocenes are organometallic compounds which consist of a metal between two planar polyhapto rings ^[34]. They are informally called “sandwich compounds”. One of the ligands encountered in metallocenes is cyclopentadienyl. The cyclopentadienyl ligand (C₅H₅) has played a major role in the development of organometallic chemistry and a huge number of metal cyclopentadienyl compounds are known today. These compounds belong to the most commonly organometallic derivatives and utilized in various areas of chemistry and technology ^[35]. Oligomeric metallocene based compounds displaying multielectron redox chemistry have attracted much attention with respect to their electrochemical, electronic, and magnetic properties.^[36] Although there are many studies on bridged biferrocenyl systems, in which the well-defined redox chemistry of ferrocene serves as a powerful electrochemical probe to investigate ground-state electronic coupling through space or through bonds,^[37] biruthenocenyl compounds have been much less studied, presumably partly due to the irreversible redox chemistry of ruthenocene itself.^[38] Biheterometallocene complexes containing two different types of metal are generally less straightforward to prepare than symmetrical species. This appears to be the reason why they have been studied only in a few cases,^[39] and even fewer studies of systems incorporating a conjugated ferrocene-ruthenocene framework have been described.^[40] Experimental and theoretical studies on higher nuclearity polymetallocene assemblies are relatively scarce, despite the potential of these studies to provide one of the most powerful and sensitive probes to elucidate aspects of intercomponent intramolecular electron-transfer. Only very few electrochemical studies have been published on linear bridged ferrocene triads,^[41] whereas the chemistry of trimetallocene triads bearing at least a ruthenocene moiety remains unexplored. The elucidation of multisite effects on electron-transfer phenomena in trimetallocene complexes provides the link between the understanding of such processes in bimetallocene species and in extended arrays and metallosupramolecular systems.

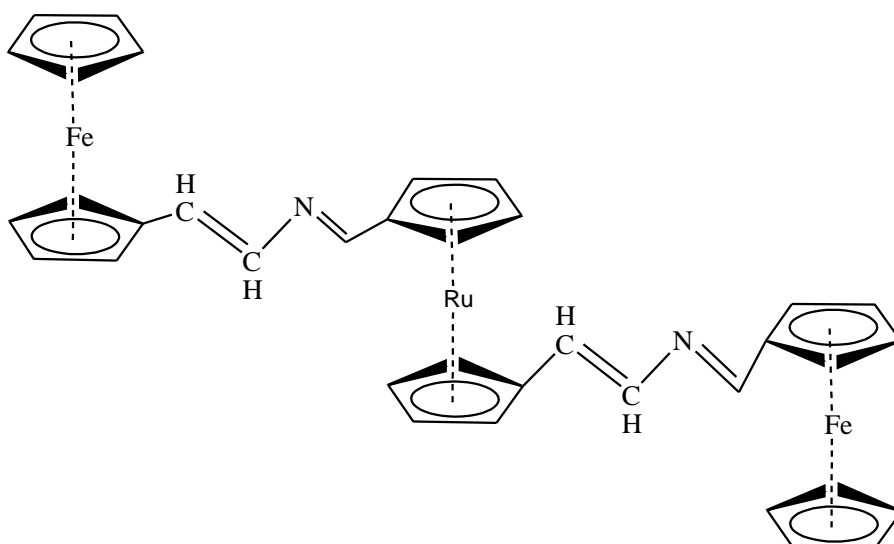


Figure: 1.1

Interestingly spectroelectrochemical^[42] studies of compound bearing two peripheral ferrocene units and one central ruthenocene moiety revealed the presence of low energy bands in the near-infrared region, which indicates a rather unusual intramolecular charge transfer between the ferrocene and ruthenocene units. These triads show selective cation sensing properties.

1.3 Ferrocene based ligands and their metal complexes

Ferrocene, an orange crystalline and diamagnetic solid, has high stability and reversible redox characteristics so it has been extensively used as starting materials in the synthesis of versatile ferrocenyl derivatives^[43]. Ferrocene, with 18 valence electrons, is the most stable member in the metallocene series. It sublimes readily and is stable to air or water, but can be oxidized reversibly^[44]. It has been found that ferrocene behaves in many respects like an aromatic electron-rich organic compound, which is activated towards electrophilic reactions almost like phenyl. As a consequence, the organometallic moiety is treated like a simple phenyl group^[45]. It undergoes Friedel-Crafts acylation and alkylation, Vilsmeier formylation and mercuration^[46]. Ferrocene derivatives containing asymmetric substituents are used as ligands for asymmetric hydrogenation catalysts^[47].

Ferrocenyl-schiff base ligands and their metal complexes have attracted the attention of researchers only since recent years. Different Ferrocenyl-schiff bases are under clinical trials to investigate their potential to exhibit a wide range of Biological activity such as anti-tumour, anti-bacterial and anti-viral. Lanthanide ion complexes with ferrocenyl schiff base ligands have proven to be very important in the area of photobiology and ligand to metal energy transfer studies^[48].

Ferrocene containing metal-chelate complexes can be regarded as multinuclear molecules possessing both the features of organometallics and of co-ordination chemistry. Mutual interaction between the ligated metal in different coordination environments and variable oxidation states with the ferrocenyl systems may lead to interesting electron transfer processes (Figure: 1.2a, 1.2b). Such interactions may also introduce a new type of reactivity towards different substrates.

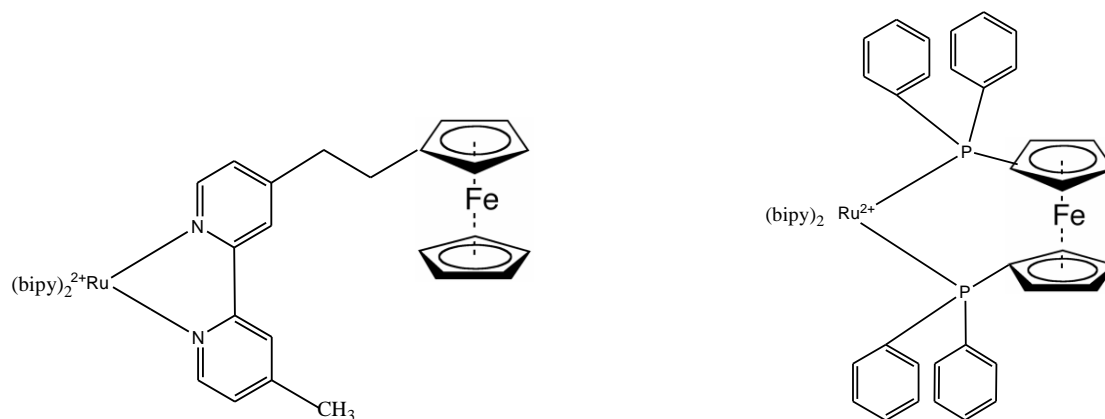


Figure: 1.2a

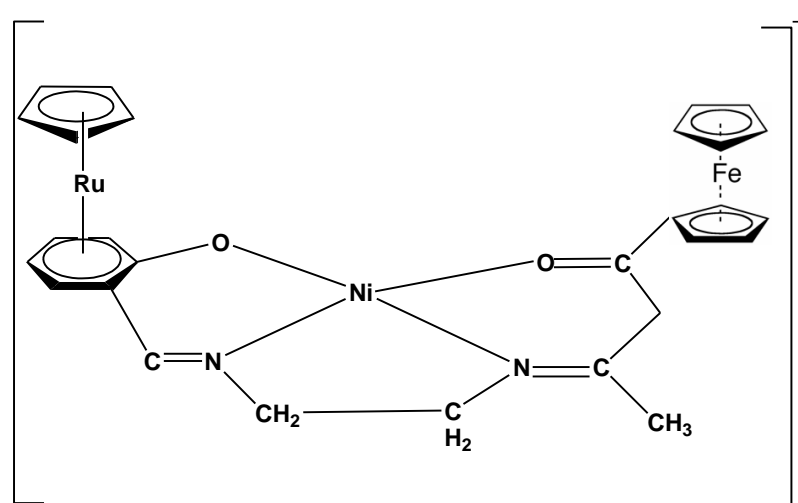


Figure 1.2b: Complexes of Ferrocenyl based ligands

1.4 Medicinal chemistry of ferrocenyl compounds

The growth of bio-organometallic chemistry concerning ferrocene is gathering much interest in the multinuclear metal complexes owing to the redox and photo-reactive metal centers coupling electronically through unsaturated bridging ligand. Ferrocenium compounds play an important role in the inhibition of the tumor cell growth. Ferrocene is not water soluble compound

and it does not show any biological activity even if it is solubilized in water. There are some methods in the literature to overcome this problem. One of them is to create a salt form on the organic residue of ferrocene moiety and other method is to form salt through oxidation of central iron atom. It has been reported that ferrocenium salts (Figure 3) are exhibiting antitumor activity against number of tumors ^[49]. Although they have high solubility in water their tumor inhibitory effect is not related to the water solubility. Their antitumor activity is shown to be related to the oxidation state of the central iron atom of the ferrocene moiety. It has been reported that only the ferrocenium salts **in** which the central iron atoms have the oxidation state of +3 exhibit antitumor activity.

Tamoxifen is the drug used against breast cancer cells that are mediated by ER_α estrogen receptors ^[50] (Figure 1.3). There are two types of breast cancer cells: one of them is breast cancer cells that are mediated by ER_α estrogen receptors and the other is breast cancer cells that are mediated by ER_β estrogen receptors. Tamoxifen is not effective on breast cancer cells that are mediated by ER_β estrogen receptors. In 2002, Jaouen and co-workers have investigated the tamoxifen analogs that contain an organometallic moiety by replacing the phenyl group with ferrocenyl group. The resulting compound called ferrocifen showed a strong effect against breast cancer cells that are mediated by both ER_α and ER_β estrogen receptors ^[51].

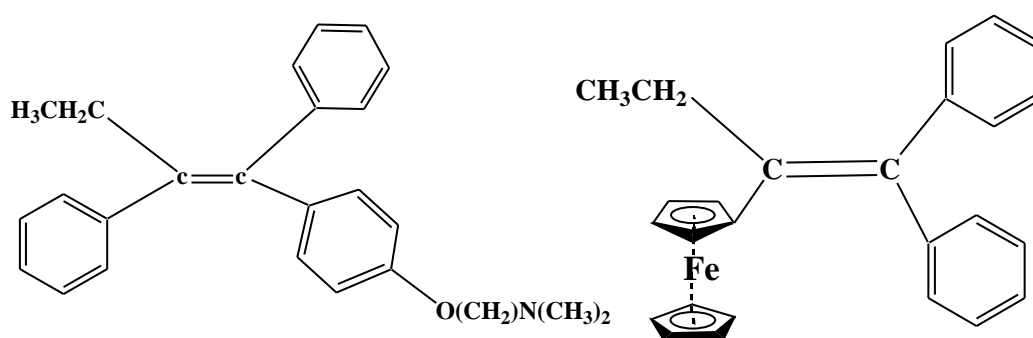


Figure 1.3: Biologically active compounds as antitumor agent

Ferrocene has also shown anti-tumor effect in mice bearing established lung metastases of B-16 melanoma. It has been postulated that the anti-tumor activity of ferrocene is mediated by immune stimulation. Maximal anti-tumor effect has been attained at doses of 0.05– 0.2 mg/kg and it has been found that lower or higher doses are not effective. Ferrocene is a stable, small molecule that exhibits immune stimulatory and anti-tumor properties by a distinct mechanism and is effective at low doses upon i.p. (administration) and oral administration. It has been reported that it may offer therapeutic advantages over some immune stimulatory agents ^[52].

Another biologically active ferrocenyl compound is ferroquine, a hybrid compound of chloroquine (Figure 4). Several drugs, such as chloroquine, are used against malaria parasite. Unfortunately resistance to these drugs is increasing ^[53]. Brocard and co-workers inserted a ferrocenyl group into the side chain of the chloroquine and it has been reported that the resulting compound ferroquine is much more safe and effective in mice, as well as non-mutagenic.

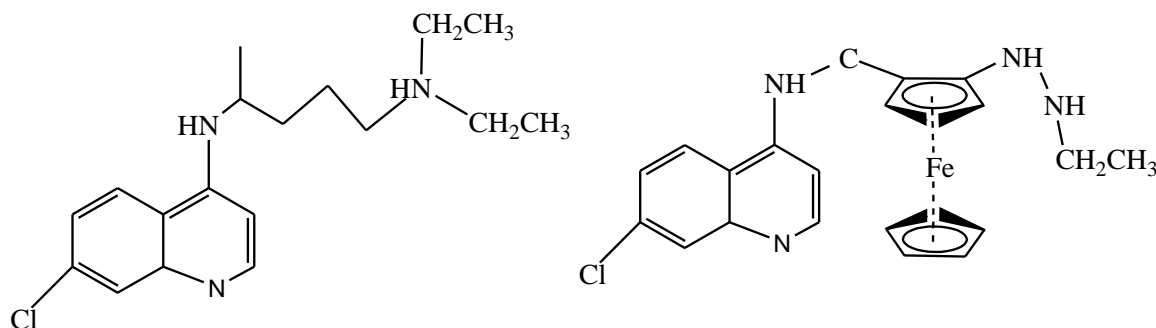


Figure 1.4: Biologically active compounds as malaria parasite drugs

Cyanoacrylates have been the subject of intense interest for the past decades as one kind of herbicides by disrupting photosynthetic electron transport. Among these cyanoacrylates, (*Z*)-ethoxyethyl-2-cyano-3-(4-chlorophenyl) methylamino-3-isopropylacrylate has been a representative compound because of its excellent herbicidal activity (Figure 1.5). Qingmin and co-workers tried to synthesize a new compound by replacing phenyl group with ferrocenyl moiety and they observed that ferrocenyl cyanoacrylates still retained excellent herbicidal activities ^[54].

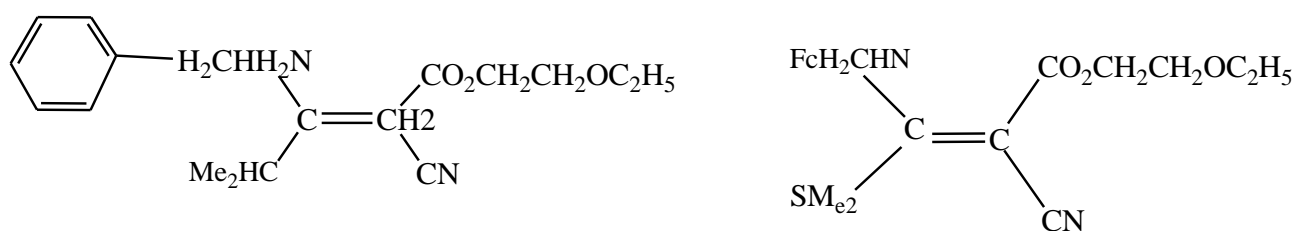


Figure 1.5: Herbicidally active compounds (Fc = Ferrocene)

1.5 NLO Active Ferrocene system

Crystal engineering based on understanding of physical phenomena such as charge transfer, electrostatic interaction, hydrogen bonding, van der Waals interaction and pi-pi stacking is a powerful technique for the production of functionalized solid materials with optimized properties. It has been applied to various organometallic compounds. Flexible pi bonds between metals and

ligands produce variable organometallic structures and packing modes depending on the solid state intra and inter-molecular non-bonding interactions. Because of this significant electron donating strength of the ferrocenyl group it is regarded as a good donor part of a donor – π acceptor system for chromophores with high Non-Linear optical (NLO) responses ^[55]. Thus far, most efforts to synthesize non-linear optical materials have concentrated on mono-acceptor conjugated ferrocenyl compounds. The bis substituted ferrocenyl molecule with readily available aromatic alcohols such as 1, 3- dihydroxy benzene has the NLO active molecular conformation ^[56]. Ferrocene adopt various conformations, depending on the magnitude of the rotational barrier and are considered in a sense as non-rigid molecules that have variable structure.

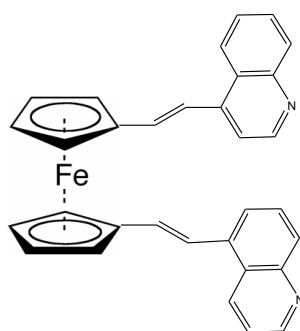


Figure 1.6: Ferrocenyl based NLO active molecules.

1.6 Application of ferrocene based ligands in Catalysis:

Recently there has been a growing interest in amino phosphine ligands for asymmetric synthesis. A growing area of application of amino phosphine ligands in asymmetric synthesis is in ruthenium catalyzed hydrogenation. Chen et al have described the use of ferrocenyl aminophosphines in ruthenium catalyzed asymmetric hydrogenation of acetophenone (Figure 1.7, 1.8). Using precatalyst $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ and the ferrocenyl based aminophosphines ligand; they found that the hydrogenation proceeded efficiently with reasonable enantioselectivity.

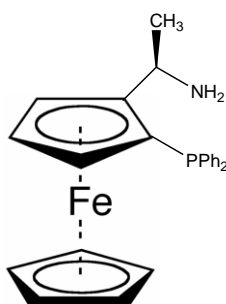


Figure 1.7: Ferrocenyl based amino phosphine ligands

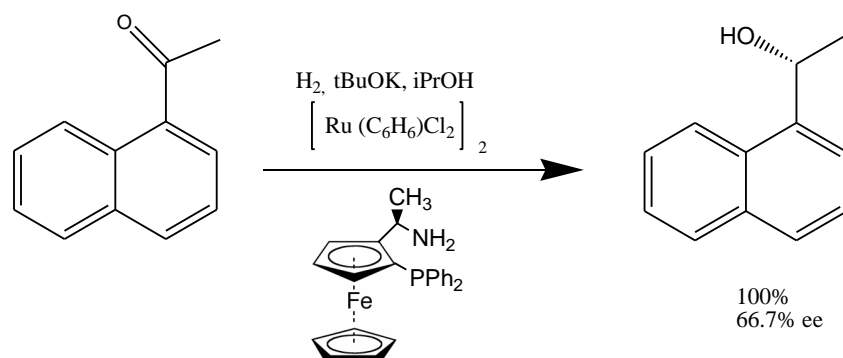


Figure 1.8: The reaction catalyzed by ferrocenyl aminophosphines ligands

An attractive feature of all such ferrocenyl aminophosphines is their remarkable stability towards air oxidation, as samples containing these compounds exposed to air up to 3 years shows no less enantioselectivity or activity in rhodium catalyzed hydrogenation. Another example of such ligand is amidoaryl ferrocenyl diphenylphosphine ligands in the Cu catalyzed addition of diethyl zinc to enones^[57] shown in Figure 1.9.

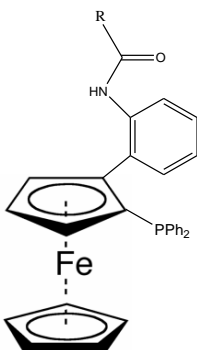


Figure 1.9: Amidoaryl ferrocenyl diphenylphosphine ligand

2.1 Introduction:

A variety of metal complexes have been used as drugs and are well known to increase their activity^[58-60]. Moreover, several drugs have been administered as metal complexes and show higher activity towards specific targets. Carbohydrazones are a special class of azomethine compound^[61] which are found to contain ionic and neutral moieties (Figure 2.1). The β nitrogen present in these compounds coordinated to the metal atom has an interesting stereochemistry whereas nitrogen remains uncoordinated. On the other hand the remaining oxygen atom can form a covalent bond with the metal atom. Some metal complexes of thiosemicarbazone/semi carbazone have also been reported to show potential antitumor^[62], antibacterial^[63], antiviral^[64], anti-fungal^[65], and anti-malarial activities^[66].

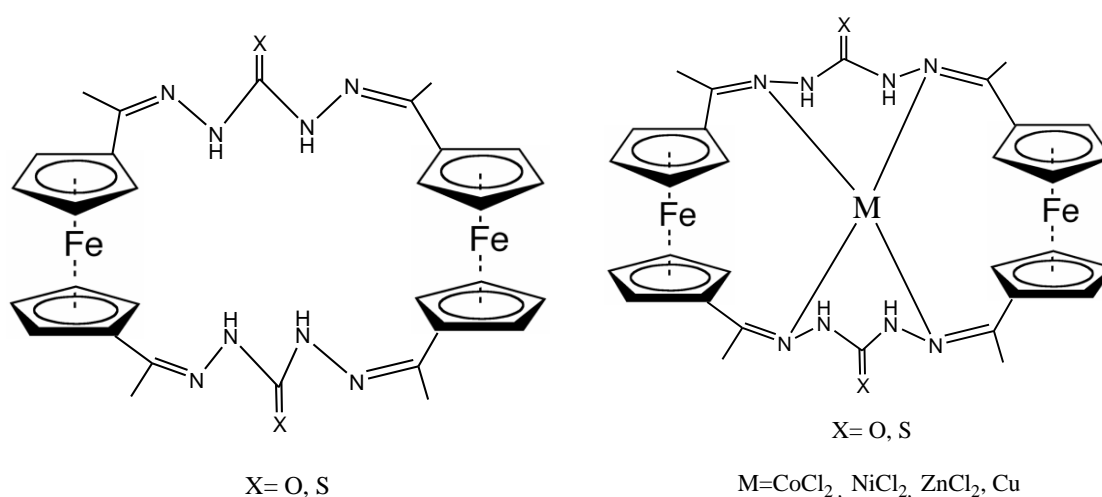
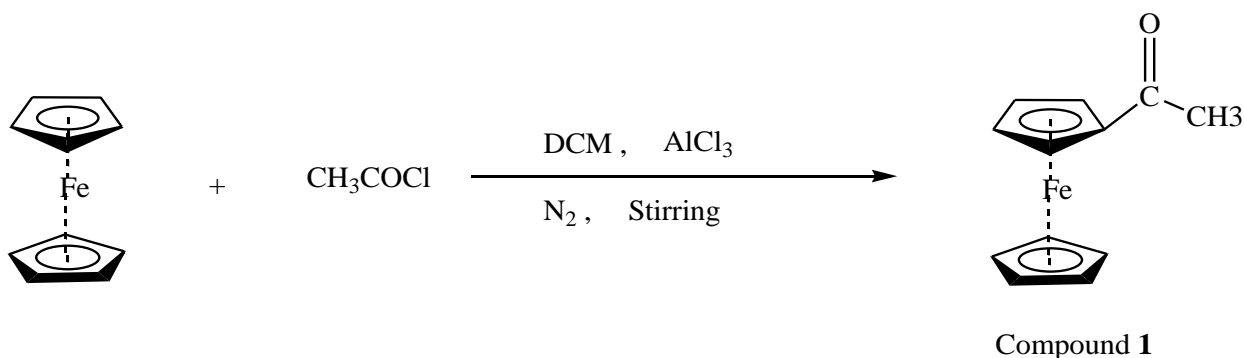


Figure 2.1: Bis 1, 1' disubstituted ferrocenyl carbohydrazone ligands and its metal complexes

The use of ferrocenyl derivatives as bioactive molecule has been growing rapidly, and several promising applications have been developed since ferrocene is a stable, nontoxic compound and has interesting redox properties. Many ferrocenyl compounds display interesting cytotoxic, anti tumor, anti malarial, anti-fungal and DNA cleaving activities. Some of these ferrocenyl compounds have been used as ligands which can form different types of metal complexes. The interest in the research of metal complexes of ferrocenyl ligands is based on expectation that the cyclopentadienyl metal moiety in ferrocene may cause electronic effects on the coordination behavior of the donor centers of these ligands that may influence the *in vitro* antibacterial, antifungal properties of such organometallic based compounds. In the present work, a synthetic strategy has been developed to prepare various schiff base compounds containing organometallic species like ferrocene and cymantrene and characterize them by spectroscopic techniques.

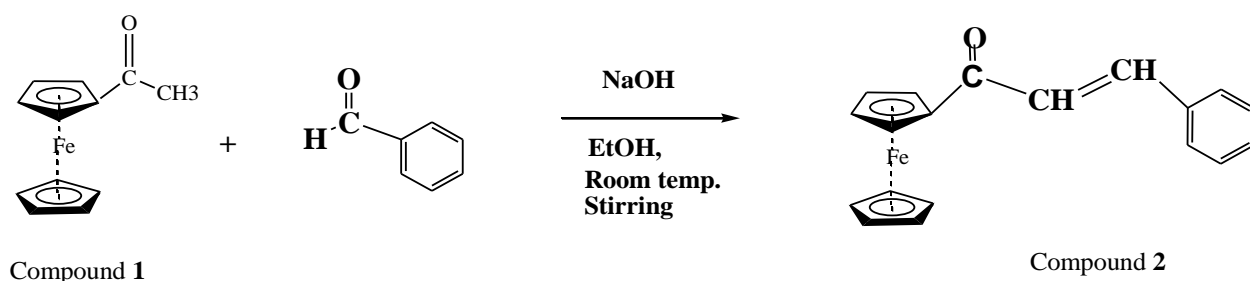
2.2. Results and Discussions:

Monoacetyl ferrocene compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{COCH}_3]$ (**1**) was prepared by reacting ferrocene and acetyl chloride in presence of anhydrous AlCl_3 in dichloromethane solvent. The reaction was carried out in N_2 atmosphere and stirred for 3-4 hours. The IR spectrum of compound **1** shows peak at 1662 cm^{-1} and is indicative of its carbonyl group due to $\nu_{\text{C=O}}$ stretching vibration.



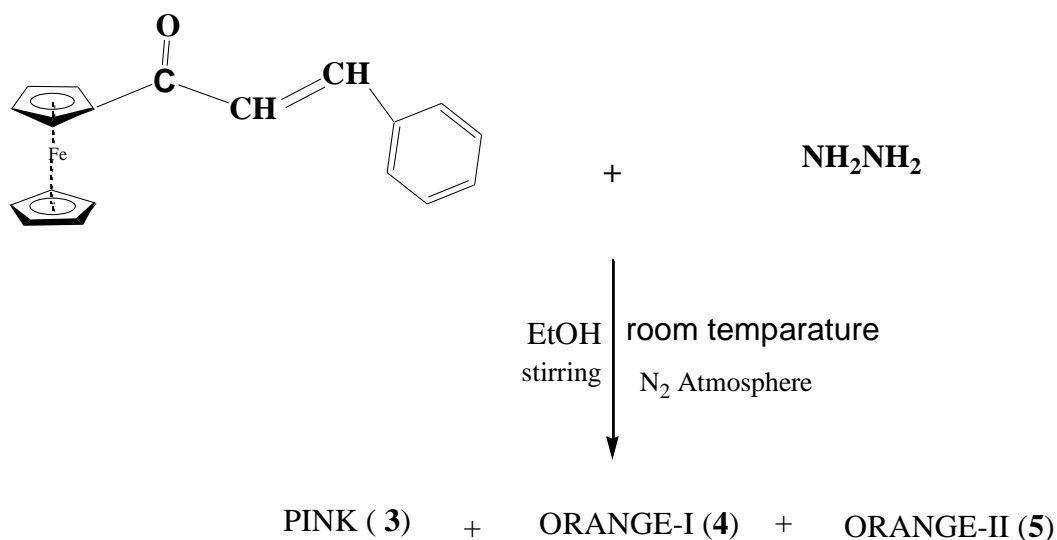
Scheme-2.1

Compound **1** was reacted with benzaldehyde in presence of sodium hydroxide in ethanol medium to form ferrocenyl-monochalcone (**2**) as shown in scheme-2. Compound **2** was characterized by FTIR and NMR spectroscopic techniques. The IR of compound **2** shows peaks at 1649 cm^{-1} which reveals the presence of carbonyl group due to $\nu_{\text{C=O}}$ stretching vibration and peaks at 1595 cm^{-1} is due to ($\nu_{\text{C=C}}$) stretching vibration (Figure 2.3). The ^1H NMR spectrum of the compound **2** exhibits a multiplet at δ 7.3-7.7 region for phenyl protons, doublet for substituted Cp ring at $\delta=4.924$ and 4.78 and a singlet for unsubstituted Cp ring at $\delta=4.226$. Peaks at 7.788 (doublet) and 7.12 (doublet) reveals the presence of olefin protons (Figure 2.4).



Scheme-2.2

Room temperature reaction of compound **2** with hydrazine hydrate results in the formation of three compounds: one pink and two orange compounds (**3-5**) as shown in the scheme-2.3.



Scheme-2.3

A tentative structure of the compound 3-5 has been proposed from the preliminary spectroscopic characterization data as shown in figure-2.2.

Figure-2.2

Cymantrene was added with acetyl chloride in presence of AlCl₃ in dichloromethane solvent at about 1:1 ratio and subjected to 5hrs stirring at 50⁰C in nitrogen atmosphere. After completing of the reaction, yellow colour compound (6) was formed. The IR of compound 4 shows peaks at 1648 cm⁻¹ indicative of its carbonyl group due to ν_{C=O} stretching vibration and peaks at 2025 cm⁻¹ and 1932 cm⁻¹ due to terminal metal carbonyl group(Figure2.5).

2.3 Experimental Section:

2.3.1 General Procedures

All reactions were performed under nitrogen atmosphere using standard schlenk line techniques. Solvents were purified and distilled prior to use. FT-IR spectra as KBr pellets of the samples were recorded on a Perkin elmer VX-II spectrometer. HPLC grade dichloromethane and ethanol were used for spectroscopic studies. ¹H NMR spectrum was recorded on a 400 MHz Bruker instrument. Ferrocene was procured from Spectrochem and used without purification. Salicyloyl hydrazide and anthraniloyl hydrazide were prepared by literature method.⁶².

2.3.2 Preparation of monoacetyl ferrocene (1)

To a 100 ml round bottomed flask 2 g (0.01 moles) of ferrocene was taken and dissolved in 25 ml of CH₂Cl₂. To the stirring solution of ferrocene, 1.5 ml (0.019 moles) of acetyl chloride was added drop wise with a syringe and the stirred reaction mixture was cooled in the ice bath and then 2.5 g (0.019 moles) of anhydrous AlCl₃ was added in small portions. After the addition of AlCl₃ the ice bath was removed and the reaction mixture was stirred for additional 30 minutes at room temperature. The formation of the monoacetyl derivative of ferrocene was monitored by Thin Layer Chromatography (using CH₂Cl₂ / hexane in 1:1 ratio). The reaction mixture was then poured on 50 g of crashed ice in 50 ml of water in a beaker. The organic layer was separated which contain monoacetyl ferrocene, [(η⁵-C₅H₅)Fe(η⁵-C₅H₄)COCH₃] (**1**). Purification of compound **1** was done by column chromatography using Pet-ether/ethyl acetate as solvent mixture.

1: IR (KBr, cm⁻¹): 1662 (vs)

2.3.3 Reaction of Monoacetyl ferrocene (**1**) with Benzaldehyde:

A 100 ml two necked flask equipped with glass stoppers, magnetic stirring bar was connected with a nitrogen cylinder. To this flask 0.1140 gm (0.5mmol) of monoacetyl ferrocene, 0.0530 gm (0.5mmol) of benzaldehyde and 6 ml of ethanol was added and the solution was stirred for 15 minutes. After 15 minutes 0.0200 gm (0.5mmol) of sodium hydroxide and 2 ml of ethanol was added. The reaction mixture was then stirred at room temperature for another 2 hours to obtain a red precipitate of [(η⁵-C₅H₄)Fe(η⁵-C₅H₅)COCH₃CH=CH-C₆H₅] (**2**).

2: IR (cm⁻¹):1649(ν_{C=O}), 1595(ν_{C=C}). ¹H NMR (CDCl₃): δ 7.788(1H ,d, =CH), δ 7.120(1H, d,=CH), δ 7.159-7.668(5H, m, Ph-), δ 4.924 (2H, d, C₅H₄), δ 4.78(2H,d, C₅H₄), δ 4.226 (5H,s, C₅H₅).

2.3.4 Reaction of Ferrocenyl-monochalcone (**2**) with hydrazine hydrate:

A 100 ml two necked flask equipped with glass stoppers, magnetic stirring bar was connected with a nitrogen cylinder. In 5 ml ethanol 1mmole of ferrocenyle monochalcone (**2**) was added and stirred for 15 minutes. Then 0.1mmole of hydrazine hydrate was added and stirred for 1 hour. The reddish pink colour changed to dark orange. Three products (**3,4,5**) were separated by thin layer chromatography using pet ether /ethanol solvent mixture.

2.3.5 Synthesis of Acetylcymantrene (6):

To the 100 ml flask 2 g (0.01mmoles) of cymantrene was added and then to it 25 ml of CH₂Cl₂ was poured. To the stirring solution of cymantrene 1.5 ml (0.019m moles) of acetyl chloride was added drop wise with a syringe. Then 2.5 g (0.019 mmoles) of anhydrous AlCl₃ was added in small portions. The colour of the reaction mixture transformed to reddish brown. The reaction mixture was then poured on 50 g of crashed ice in 50 ml of water in a beaker. The flask was then rinsed with small amount of CH₂Cl₂ and the combined layers were transferred into a separator funnel. The organic layer contained the desired product of acetylcymantrene 3 and was extracted with CH₂Cl₂. Purification of the compound **6** was done by column chromatography using Pet-ether/dichloro methane as solvent mixture.

6: IR (KBr, cm⁻¹):1684(vs), 2025(s), 1932 (s, br)

3. Conclusions:

Monoactylferrocene and ferrocenyl-monochalcone has been synthesized and characterized by FTIR and NMR spectroscopy. Monoactylferrocene was successfully used to prepare ferrocenyl monochalcone. Ferrocenemonochalcone was reacted with hydrazine hydrate to obtain pyrazoline derivatives, isolation and preliminary characterization was performed. Acetylcymantrene Schiff base was synthesised and has been characterized by FTIR, NMR and CHN analysis. Biological and electrochemical studies are under investigation.

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