Synthesis and Characterization of Several Cp-Based Organometallic Compounds

A Dissertation
Submitted in partial fulfilment

FOR THE DEGREE OF
Master of Science in Chemistry

Under Academic Autonomy
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Submitted
by
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CERTIFICATE

This is to certify that the dissertation entitled "Synthesis and Characterization of Several Cp-Based Organometallic Compounds" *being submitted by* ***Kausik Sahu*** *to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by them under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.*

Rourkela-769 008

Date:

Dr. Saurav Chatterjee

Supervisor

DECLARATION

I, Kausik Sahu, do hereby declare that the M.Sc. project report entitled "Synthesis and Characterization of Several Cp-Based Organometallic Compounds" being submitted to **National Institute of Technology, Rourkela (Odisha)** for Master of Science (Chemistry) is the result of independent work done by me under the supervision of Dr. Saurav Chatterjee, Dept. of Chemistry, National Institute Of Technology, Rourkela, Odisha. The same has not been submitted elsewhere for any other degree.

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ACKNOWLEDGEMENTS

I take this opportunity to express my deep appreciations and indebtedness to my Guide Dr. Saurav Chatterjee, Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for all of his invaluable guidance, continuous encouragement and sharing of frustrations as well as enjoyment throughout this course of research work. Indeed, the experience of working under him is one of that I will cherish forever.

It is my great pleasure to acknowledge to Prof. B.G. Mishra, Head of the Chemistry Department, National Institute Of Technology, Rourkela for providing me the necessary facilities for this research work.

I am indebted to all faculty and staff members of Department of Chemistry, N.I.T, Rourkela, for their inspiration and help.

I am thankful to Ms Vijayalaxmi Tirkey and Ms Sasmita Mishra for their continuous guidance, support and encouragement for completing this project. My sincere thanks to my labmates Ipsita, Arnab and Sabuj for their support.

Last but not the least; I would like to thank my parents for their unconditional love, support, inspiration and guidance at every step of my life.

ABSTRACT

Monoactylferrocene and diactylferrocene were successfully used to prepare [(η^5-C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4-OH}] **(3)** and C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_5H_4N}] **(4)** and [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4-OH}$_2$] **(5)** and [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_5H_4N}$_2$] **(6)** respectively. These new compounds have been characterized by FTIR, NMR spectroscopic methods.

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CHAPTER 1

INTRODUCTION

1.1 CYCLOPENTADIENYL ORGANOMETALLIC COMPOUNDS

Cyclopentadienyl, abbreviated as Cp^- has been the most important of all the polyenyl ligands as it is firmly bound to the metal and is generally neutral to nucleophilic reagents which signify its flexibility to be used as a stabilising ligand for many complexes. It generally co-ordinates in the η^5-mode and it can adopt rarely the η^1-and η^3-co-oridnation mode (Fig.1). [1]

Fig.1: η^1 and η^5 modes of cyclopentadienyl bonding

In general, three categories of mononuclear cyclopentadienyl complexes of transition metals are known; Cp_2M (metallocenes or sandwich compounds), Cp_2ML_x (bent metallocenes, x=1-3; L= unidentate ligand like H, Cl, CO) and $CpML_y$ (half sandwich or piano stool, y=1-4; unidentate ligand). Some of unique characteristics of Cp have made it an important source of metallocene chemistry in various organometallic synthesis[2].

Since the discovery of ferrocene[3], cyclopentadienyls have been among the most important ligands in organo-transition metal chemistry because they form a wide range of stable complexes whose steric and electronic properties can easily be tailored by varying the ring substituents[4]. A vast number of mono- and dicyclopentadienyl transition metal complexes have been reported in recent years, and over the past few years, Cp based transition metal compounds were being designed to serve the various purposes like molecular sensor, molecular ferromagnet, electrochemical agents, molecular switches, liquid crystal and drugs[5-9]. The η^5- cyclopentadienyl and related early transition metal derivatives have been marked as an important source to serve the purposes of structural, synthetic and catalytic organometallic chemistry. They are useful compounds which have found applications as reagents in organic chemistry[10], as soluble Zieglar-Natta catalysts and as a cancerostatic compounds[11-15]. The Cp based transition metal compounds connect the link between organometallic chemistry to biology, medicine and molecular biotechnology[16]. Recent research has been focussed to explore the chemistry of metal-metal interactions in ferrocenyl complexes as it can act as an important redox active unit undergoing oxidation to the ferrocenium ion[17-24]. This has led to the use of ferrocene as a model for sensors and non-

linear optical films[25,26]. The structure of ferrocene is as much vital as its characteristics (Fig.2).

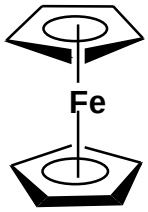


Fig.2: Structure of ferrocene

Ferrocene contains two cyclopenatdiene rings pi-coordinated to Fe(II) atom. The discovery of ferrocene was first reported by Pauson and Kealy in 1951. The reaction was carried out between cyclopentadienyl magnesium bromide and ferric chloride to obtain a product fulvalene. Later the sandwich structure of Cp_2Fe was discovered by G. Wilkinson, R. B. Woodward and E. O. Fischer independently[27]. The structure contains two Cp units in which all five carbon atom of a cyclopentadienyl ligand interacting with the metal centre. Ferrocene has an eclipsed configuration in the gas phase and is nearly eclipsed in the solid state. The barrier to rotation between the two rings is only 4±1 kJ/mol and this allows the rings to have free rotation. All the C-C bonds are of the same length and the iron is equidistant from all the Cp ring carbons. Neutron diffraction has also shown that the hydrogen atoms on the Cp rings are tilted slightly towards the iron centre in ferrocene, presumably because this shift permits a better overlap of the Fe orbitals with the pi-orbitals of the Cp rings. In the recent years, ferrocene is widely applicable for the preparation of functional derivatives used in many areas like catalysis, material science, hydrometallurgy, biology and medicine. Ferrocene is also the safest additive used so far as it does not cause any environmental pollution or health related hazardous[28]. It is claimed that if used as fuel catalyst for rocket propellant, it can improve the combustion speed by 1-4 times, lower the temperature of exhaust pipes, and avoid infrared chase. When used in fuel oils as diesel oil, heavy oil and light oil, it can eliminate smoke, save energy and reduce air pollution.

Metallocenes, including ferrocene, are also known to have a wide range of biological applications. Ferrocene has attracted particular attention due to its aromatic character, stability and low toxicity. It can also be easily derivatized and the central iron atom is also easily oxidised from Fe(II) to Fe(III). The medicinal application of ferrocene is currently an active area of research with many reports showing its activity *in vivo* and *in vitro* and its potential as an anti-tumour, anti-malarial and anti-fungal agent[29]. Therefore, the astounding

diversity of the chemistry demonstrated by this compound is unique in organometallic chemistry.

1.2 FERROCENE AND ITS REDOX PROPERTIES:

Ferrocene, also known as dicyclopentadienyl iron, has the primary chemical formula $C_{10}H_{10}Fe$ with a characteristic orange colour at room temperature. Ferrocene, a crystalline diamagnetic solid is considered as the most stable of all the metallocenes with 18 valence electrons and has a boiling point of 249^{o}C, a melting point of 173-174^{o}C. It sublimes readily and is stable to air or water, which makes purifying the products quite an easy task but can be, oxidized reversibly.

The most important property of ferrocene is its redox property which has popularized this compound. The electron transfer-reactive oxygen species-oxidative stress theory (ET-ROS-OS) has been implicated in the mechanism of action of a wide variety of biologically active compounds, for example nitroaromatics and quinones. Therefore, the development of drugs that enhance Reactive Oxygen Species (ROS) has increased in importance. Also the fact that cancer tissue is known to be in a state of oxidative stress further increases the need for new drugs that can exploit this fact[30]. Increasing the concentration of ROS may overwhelm the cancer cells but leave normal cells unaffected. Elevated levels of ROS are also known to induce apoptosis. Current attention is given on increasing concentration of ROS to lethal levels in cells, interfering with anti-oxidant enzymes and the promotion of catalysts that enhance the toxicity of the ROS.

The loss of an electron from a high energy, non-bonding orbital to yield the ferricenium cation, ($Fc^{+} \longrightarrow Fc$), is an important aspect of the chemistry of ferrocene and is often implicated in its cytotoxicity[30] (Fig.3).

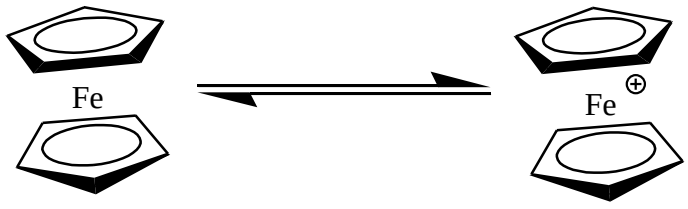


Fig.3: One electron oxidation of ferrocene to ferricenium ion.

In biological systems ferrocene can be oxidised by hydrogen peroxide in the presence of horseradish peroxidise, found in the roots of horseradish, has been extensively studied. The hydroxyl radicals formed from Fc^{+} under physiological conditions are proposed to act as DNA damaging agents for biologically active ferrocene derivatives. The ferricenium cation

has been shown to form charge transfer complexes with donor groups in proteins. The reverse reaction, ($Fc^+ \longrightarrow Fc$), is known to proceed through oxidation of metalloproteins, in the presence of glutathione forming hydroxyl radicals and through oxidation of NADH to NAD^+. The oxidation of NADH to NAD^+ is a good indicator of the ferricenium cations capacity for interfering with biologically important, enzyme controlled electron transfer reactions.

The redox status of a given biological system is vitally important as numerous processes in living cells are mediated by redox reactions. For example, cellular respiration whereby ATP is formed involves a series of reactions including the reduction of NAD^+ and oxygen and the oxidation of sugars. Redox activation of otherwise inactive prodrugs coupled with further chemical modification e.g. hydrolysis, can lead to highly reactive electrophilic compounds. A suitable bio-redox prodrug should have minimal toxicity to healthy cells, stability to metabolism in aerobic cells and suitable bioavailability and pharmacological properties.

1.3 FERROCENYL-SCHIFF BASE ORGANOMETALLIC COMPOUNDS

Over the last few years, several Schiff bases containing ferrocene groups have been prepared and their coordination behaviour studied by means of different physico–chemical measurements such as IR, NMR and electrochemical data and their structure was determined by single crystal X-ray diffractometric investigations. In these studies, Mossbauer spectroscopy was also employed and revealed its important role for a better understanding of the properties of the prepared compounds[31-43] (Fig. 4).

Schiff base compounds are condensation products of arylamines and carbonyl compounds; these compounds are quite stable and represent versatile intermediates for preparation of a numbers of important compounds like arendiazonium nitrates, N-arylarencarboxamides, corresponding amines and cyanoamines, β-lactams etc. Incorporation of ferrocene moiety into Schiff bases imparts the chemical and physiochemical properties which are absent or little manifested in the parent substances. Schiff bases and related analogues bearing ferrocenyl moieties have been widely synthesised and their properties and possible applications investigated[44].

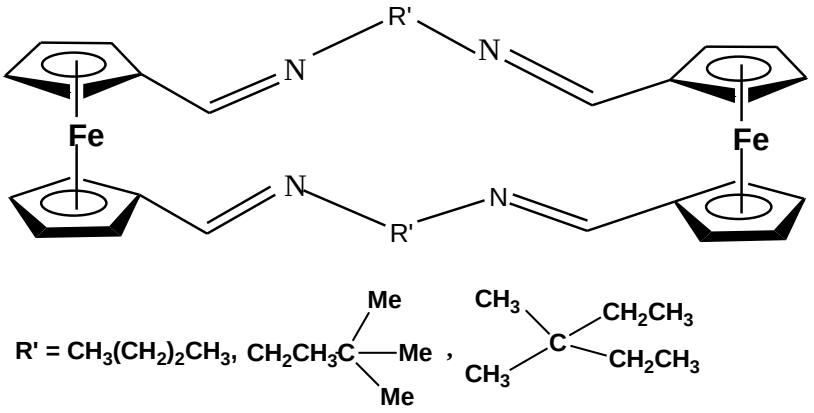


Fig.4- Ferrocenyl Schiff based compound

The most recent research area, bio-organometallic chemistry is gaining a lot of interest in which the use of ferrocenyl-schiff base compounds is highly recommended. Bioorganometallic chemistry is a field devoted to the synthesis and study of organometallic species of biological and medical interest. Keeping in view the reported biological studies, simple schiff bases, schiff bases, with ferrocene addition and their reactants were investigated for their biological activities towards antitumor, antioxidant and DNA protecting effects. In a recent study crown gall tumor inhibition assay is used for verification of anticancerous activity of some of the ferrocenyl schiff bases. The purpose of DPPH scavenging assay was to evaluate the antioxidative potential of test samples. While in vitro OH radical induced DNA damage system served to evaluate DNA protection in oxidative stress. 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[45].

A series of ferrocenyl carboxylic acid has been prepared and condensed, via their acid chlorides or in the presence of N,N'-dicyclohexylcarbodimide, with both 6-aminopenicillanic acid and 7-aminocephalosporanic acid. Almost all of the Ferrocenyl-penicillin (Fig.5) and cephalosporins (Fig.6) exhibited anti-biotic activity, some being highly active, with others proved to be potent β-lactamase inhibitors.

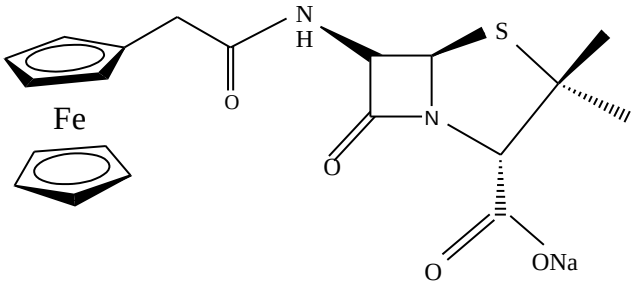


Fig.5: Ferrocenyl-penicillin

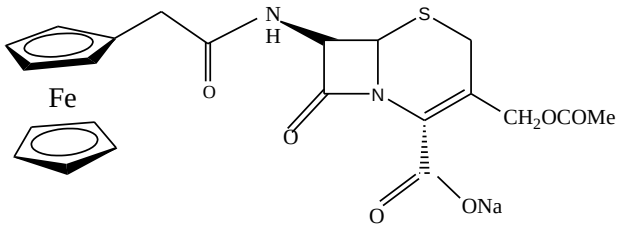


Fig.6: Ferrocenyl-cephalosporins

1.4 FERROCENYL PEPTIDE CONJUGATES AS ANTI-CANCER AGENTS

Standard peptide coupling procedures were used by Kelly *et al* to prepare a series of *N*-(ferrocenylmethyl)fluorobenzene-carboxamide derivatives as shown in Fig.7. The inclusion of fluorine is a recognized strategy in the development of various drug types[46]. This series was screened against ER(+) MDA-MB-435-S-F breast cancer cells. This particular compound was found to be the most active with an IC50 value of between 11 and 14 μM. As the concentration of compound was increased, cytotoxicity increased, indicating a dose dependent relationship.

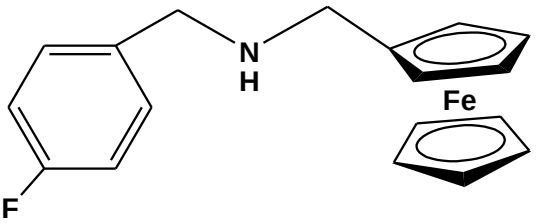


Fig.7: Structure of *N*-(ferrocenylmethyl)fluorobenzene-carboxamide

N-(ferrocenyl) benzoyl dipeptide esters have also been shown to be highly active *in vitro*[47-49]. *N*{ortho-(ferrocenyl)-benzoyl}-glycine ethyl ester was initially tested for its *in vitro* anti-proliferative activity towards lung cancer cells (H1299 and H1299 carboplatin resistant variant) which was found to be cytotoxic whereas the starting material, ortho-ferrocenyl ethyl

benzoate, was completely inactive. Therefore other derivatives were evaluated for their anticancer activity against lung cancer cells. This compound was found to be cytotoxic and had an IC50 value of 48μM, whereas the starting material, ortho-ferrocenyl ethyl benzoate, was completely inactive against this cell line. The dipeptide derivative *N*-{*ortho*-(ferrocenyl)-benzoyl}-glycine-glycine ethyl ester was shown to have an IC50 value of approximately 20 μM, while *N*-{*ortho*-(ferrocenyl)-benzoyl}-glycine-L-alanine ethyl ester (Fig.8) had an IC50 value of 5.3 μM. The activity of these compounds is possibly due to their low redox potentials and their ability to form reactive oxygenated species (ROS) under physiological conditions. The activity of compound *N*-{*ortho*-(ferrocenyl)-benzoyl}-glycine-L-alanine ethyl ester is not solely due to ferrocene so it is plausible that the peptide chain is involved in a secondary mode of action. The lipophilic ferrocene group may anchor to the cell membrane and the peptide chain may block the opening of channels in the cell membrane leading to cell death[50].

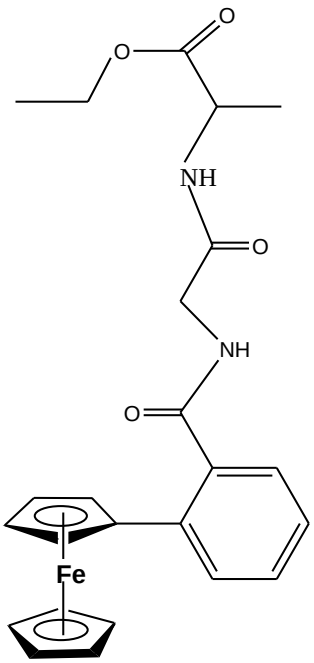


Fig.8: Structure of *N*-{*ortho*-(ferrocenyl)-benzoyl}-glycine-L-alanine ethyl ester

1.5 FERROCENYL BASED COMPOUNDS AS ANTIMALARIAL AGENTS

Malaria is a mosquito-borne disease of humans and other animals caused by eukaryotic protists of the genus Plasmodium, of which Plasmodium falciform is the most dangerous and accounts 90% of all deaths from malaria. Malaria is a tropical disease and It is estimated that the number of deaths ranges from 1.5 to 2.7 million per annum[51], the majority

of these deaths occur in Africa and South East Asia. Quinine, prepared from cinchona bark, was the first antimalarial drug developed and the synthetic anti-malarials like choloroquine, primaquine, proguanil, pyrimethamine and mefloquine were developed later. Chloroquine (CQ) (Fig.9), introduced for chemotherapy of malaria in 1943, is the most widely used drug.

Inspired by the work of Jaouen in cancer chemotherapy, an attempt has been made to use a bio-organometallic strategy to generate an antimalarial class of compounds having ferrocene. Ferroquine[52] (Fig.10), a ferrocene analogue of chloroquine, has recently entered initial clinical trials and is found to be more active than chloroquine against Plasmodium Falciparum which is resistant to chloroquine. Ferroquine (FQ) satisfies the 'Lipinski's rule of 5'which orally active drugs must follow to be efficient.

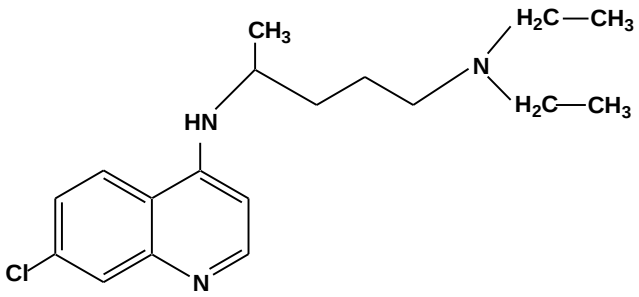


Fig.9: Structure of Chloroquine

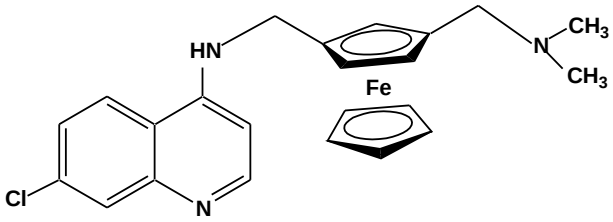


Fig.10: Structure of Ferroquine

The mechanism of action of ferroquine was found to be similar to that of chloroquine[53]. In red blood cells the drug becomes protonated, subsequently it binds to heme to form a drug-heme complex that is highly toxic to the cell. Ferroquine activity against chloroquine resistant parasites is attributed to an increase in lipophilicity and differences in electronic and geometric structure. The continuing biological success of FQ means that this avenue of research will remain open for a long time[54].

1.6 FERROCENE AS A LUMINESCENCE QUENCHER

The photochemical behaviour of ferrocene and its derivative has also been investigated[55]. Although they often are photochemically inert, ferrocene and ferrocenyl derivatives may undergo chemical modifications in the presence of light, or may be used as excited state quenchers or photosensitizers, that is as catalysts of photochemical reactions. It has been seen that some properties of ferrocenyl compounds, which are profitably used in photochemistry, also are of major interest for photophysics. Ferrocene has been widely used as a luminescence quencher in intermolecular processes taking place in solution. From a fundamental viewpoint, these quenching studies mainly allowed the nature of the excited states to be characterized. Luminescence quenching led to numerous applications in the areas of analytical chemistry, molecular organized systems and biology. Recently, new compounds have appeared, in which the ferrocenyl derivative is covalently linked to a luminescent molecule. Interaction is, therefore, of the intramolecular type. The phosphorescence spectrum of ferrocene, which should correspond to the radiative deactivation of the excited triplet state, has been studied in details. As early as 1961, Scott and Becker reported that ferrocene was phosphorescent when excited to the singlet excited states[56]. The spectrum displayed a wide band centered at 20 000 cm−1. After this many research groups reported different reports on phosphorescence spectrum of ferrocene. Finally, Müller-Goldegg and Voigtländer attributed these phosphorescence reports from the early literature to photolysis products of ferrocene[57]. It is now generally accepted that, unlike other metallocenes, ferrocene is not phosphorescent at all.

The ferrocenyl derivative and the fluorescent molecule were brought together in solution. Quenching was, therefore, of the intermolecular type. Recently, some new compounds have appeared in which the ferrocenyl derivative is covalently linked to a luminescent moiety as shown in fig.10. Luminescence quenching, if any, is then achieved intramolecularly. Applications range from artificial photosynthesis aiming at light energy storage, to the design of photodiodes, potentially useful for molecular electronics.

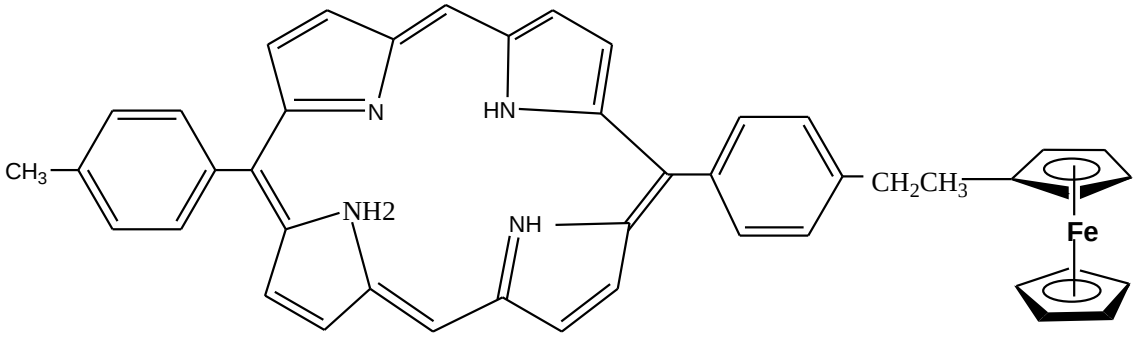


Fig.10: Ferrocene linked to the luminescent moeity

1.7 CONCLUSION

The use of organometallic compounds for targeted medical purposes is a flourishing area of research. Biologically active ferrocene derivatives can be classified into two groups, namely novel ferrocene compounds that exert a biological effect and ferrocene analogues of known drugs that have been prepared in order to overcome the problem of resistance.

Numerous other applications can also be expected to emerge at the frontiers of biology and photophysics. For example, ferrocene can be incorporated into amino acids and these could be used as building blocks in modified peptides, which can also bear photosensitizing chromophores and electron acceptors. Such peptides could be potentially useful for photo harvesting. Finally, since ferrocene can be introduced in a molecule without destroying the fluorescence properties, the door is now open on a new generation of compounds, both photo- and electrochemically active.

The well established redox properties of ferrocene have been utilized in preparing various electrochemical sensors, and this redox activity has been strongly associated with the biological activity of ferrocenyl complexes.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF FERROCENYL AND CYMANTRENYL SCHIFF BASE COMPOUNDS

2.1 η^5-C_5H_5 based Schiff base compounds

Recently the research field of bioorganometallic chemistry is increasingly drawing much interest due to their distinctive properties and features concerning both organometallic and coordination chemistry [58]. The use of ferrocenyl derivatives as bioactive molecule has been growing very rapidly, and several reports shows that a large number of ferrocenyl compounds display interesting cytotoxic, anti tumor, anti malarial, anti-fungal and DNA cleaving activities [59-62]. A large part of the research is concentrated on the synthesis of conjugates of peptides and peptide nucleic acids with organometallic fragments. However, investigation of bioactivity in organometallic compounds has been most extensively concentrated on ferrocene containing derivatives. In recent years some Cp based half sandwich compounds have been studied to some extent for their interesting biological and labeling properties. Several metallo carbonyl N-hydroxysuccinimide esters, for example rhenium based N-hydroxysuccinimide ester (Fig.11) were synthesized and characterized by classical spectroscopic methods and labelling of several proteins was achieved with these complexes [63].

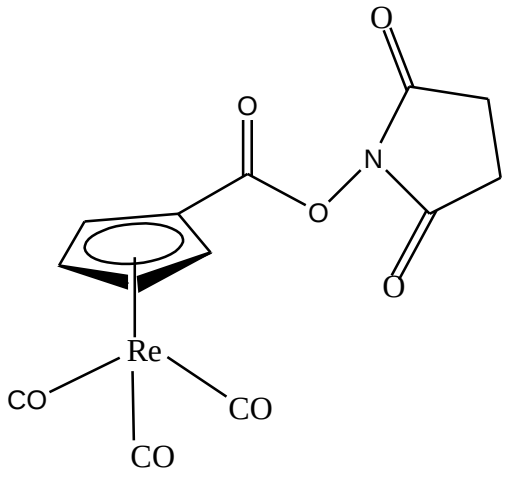


Fig.11: Rhenium based N-hydroxysuccinimide ester

Substantially less study has been carried out with cymantrene based compounds and on their biological properties, in spite of their stability and easy attachment to bioactive molecules. Very recently, cymantrene based carboxylic acid derivatives were introduced to peptides for IR labeling studies [64] (Fig.12).

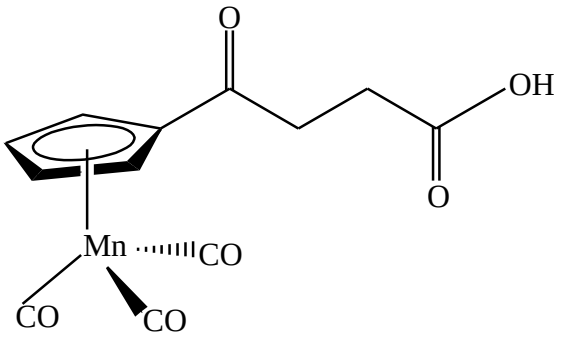
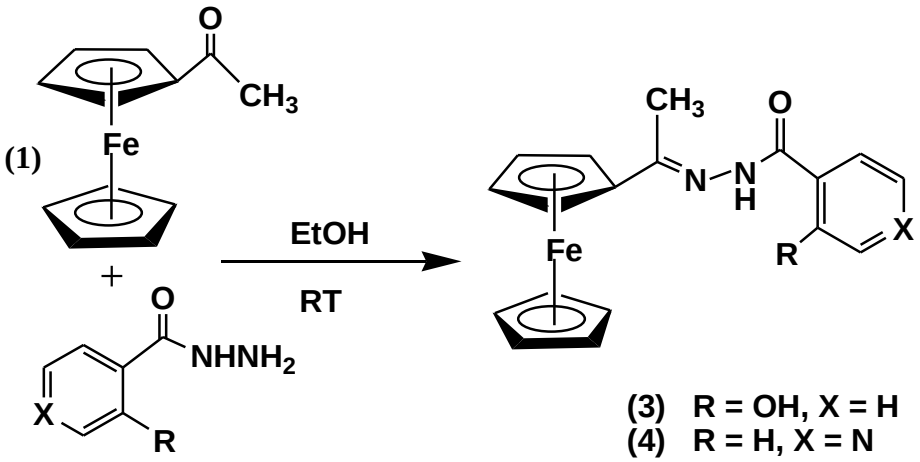


Fig.12: Example of a cymantrene based carboxylic acid derivatives

To explore the variety of biologically active organometallic compounds the synthesis and characterization of some ferrocenyl and cymantrenyl organometallic compounds have been carried out and their redox and biological properties were investigated.

2.2 Results and Discussion:

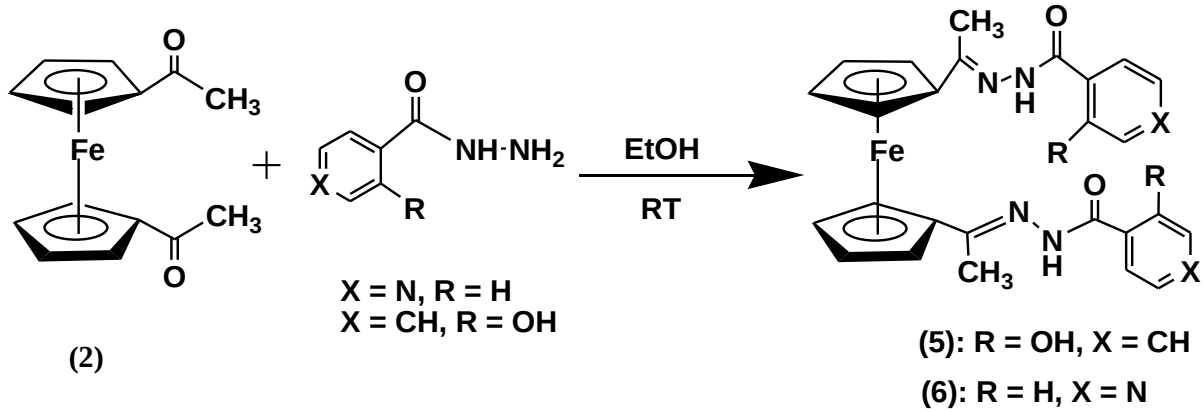
Room temperature reaction of an ethanol solution of salicyloyl hydrazide or isonicotino-hydrazide with monoacetyl ferrocene **(1)** for 3 hours gave an orange colored compounds $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)C(CH_3)=N\text{-}N(H)C(O)\text{-}C_6H_4\text{-}OH\}]$ (**3**) and $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)C(CH_3)=N\text{-}N(H)C(O)\text{-}C_5H_4N\}]$ (**4**) respectively (scheme-1).



Scheme-1

Pure compounds were isotaled by preparative TLC for spectroscopic characterization. Similar reaction of 1,1'-diacetyl ferrocene **(2)** with two equivalents of salicyloyl hydrazide and isonicotino-hydrazide led to the isolation of orange compounds $[Fe\{(\eta^5\text{-}$

$C_5H_4)C(CH_3)$=N-N(H)C(O)-C_6H_4-OH$\}_2$] (**5**) and [Fe$\{(\eta^5$-$C_5H_4)C(CH_3)$=N-N(H)C(O)-$C_5H_4N\}_2$] (**6**) respectively (scheme-2).



Scheme-2

Infrared spectra for compound **3** and **5** as KBr pellet shows peaks at 1627cm^{-1},1607 cm^{-1},1635 cm^{-1},1607 cm^{-1} corresponding to C=N and C=O groups respectively. Presence of ferrocenyl Cp protons has been confirmed by ^{1}H NMR spectral data at δ 4.1-δ 4.3 along with NH, OH and methyl protons at δ 11.14- δ 11.84 and δ 2.23 respectively. Although, the synthesis of compound **3** and **5** have been reported earlier in thermal reaction condition, we have been able to synthesise both the compounds by reaction at room temperature condition. Similarly Infrared spectra for compound **4** as KBr pellet shows peaks at 1578 cm^{-1} and 1600 cm^{-1} corresponding to C=N and C=O groups respectively. Presence of ferrocenyl Cp protons has been confirmed by ^{1}H NMR spectral data at δ 4.1-δ 4.3 along with NH and methyl protons at δ 10.93 and δ 2.30 respectively. The IR and NMR spectral characterization reveals the presence of two hydrazone unit attached to each of the ferrocenyl Cp units.

2.3. Experimental Sections

2.3.1 General Procedures

All reactions and manipulations were carried out under an inert atmosphere of dry, pre-purified argon using standard schlenk line techniques. Solvents were purified, dried and distilled under argon atmosphere prior to use. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I spectrometer as KBr pellet and NMR spectra on a 400 MHz Bruker spectrometer in $CDCl_3$. Elemental analyses were performed on a Vario El Cube analyser. TLC plates (20x20 cm, Silica gel 60 F254) were purchased from Merck. [(η^5-C_5H_5)Fe(η^5-

$C_5H_4COCH_3$)], [Fe(η^5-$C_5H_4COCH_3$)$_2$], [(CO)$_3$Mn(η^5-$C_5H_4COCH_3$)], [H_2NN(H)C(O)-R], (R = -C_6H_4-OH, C_6H_4N) were prepared by following reported procedures.

2.3.2 Synthesis of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-R}] {R = C_6H_4-OH (3); C_5H_4N (4)}

In a typical reaction, salicyloyl hydrazide or isonicotino hydrazide was taken in a two necked round bottomed flask and 10 ml of ethanol solvent was added. To the reaction mixture 0.1 mmol of monoacetyl ferrocene and 1 drop of HCl or acetic acid was added at room temperature under stirring and inert atmosphere condition. The reaction was continued for 3hrs or 12 hrs under nitrogen atmosphere. After the reaction, the solution was filtered and the orange precipitate was washed with cold ethanol and vacuum dried. The product was further purified by preparative TLC in 5% ethanol:pet ether solvent mixture.

3: IR(ν_{CO}, cm^{-1},CH_2Cl_2): 1607 (s), 1627 (s), 2922 (vs), 3446(br), 798(m). ^{1}H NMR (δ, $CDCl_3$): 2.23 (s, 3H, CH_3) 4.23 (s, 5H, η^5-C_5H_5), 4.42 (t, 2H, η^5-C_5H_4), 4.69 (t, 2H, η^5-C_5H_4), 6.96-7.01 (m, 2H, C_6H_4), 7.39-7.42 (t, 1H, C_6H_4), 7.95-7.97 (d, 1H, C_6H_4), 11.16 (s,1H, O*H*), 11.84 (br, 1H, N*H*).

4: IR(ν_{CO}, cm^{-1},CH_2Cl_2):. 1600 (vs), 1578(vs), 3412 (br). ^{1}H NMR (δ, DMSO): 10.93 (s, 1H) 8.82 (d, 2H, J=5.4 Hz) 7.86 (d, 2H, J=5.4 Hz), 4.78 (m, 2H), 4.49 (m, 2H) 4.29 (s, 5H), 2.30 (s, 3H).

2.3.3 Synthesis of [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-R}$_2$] {R = C_6H_4-OH (5); C_5H_4N (6)}

In a two necked flask, salicyloyl hydrazide or isonicotino hydrazide was taken and ethanol solvent was added. The mixture was heated under nitrogen atmosphere to obtain a clear solution. To the reaction mixture 0.1 mmol of diacetyl ferrocene and 1 drop of HCl was added at room temperature and stirring was continued for 3hrs. After the reaction, the solution was filtered and the orange precipitate was washed with cold ethanol and vacuum dried. The product was further purified by preparative TLC in 5% ethanol:pet ether solvent mixture.

5: IR(ν_{CO}, cm^{-1},CH_2Cl_2): 1607 (s), 1635 (s), 2930 (vs), 3277(br). ^{1}H NMR (δ, $CDCl_3$): 2.23 (s, 3H, CH_3) 4.59 (s, 4H, η^5-C_5H_5), 4.77 (s, 4H, η^5-C_5H_5), 6.77-6.89 (m, 4H, C_6H_4), 7.25-7.29 (t, 2H, C_6H_4), 7.90-7.92 (d, 2H, C_6H_4), 11.14 (s, 2H, O*H*), 11.59 (br, 2H, N*H*).

2.4. CONCLUSION

Monoactylferrocene and diactylferrocene has been synthesized and characterized by FTIR and NMR spectroscopy. Monoactylferrocene was successfully used to prepare [(η^5-C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4-OH}] and C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_5H_4N}] compounds. Similarly diactylferrocene was used to prepare [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4-OH}$_2$] and [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_5H_4N}$_2$] compounds. The compound,[(η^5-C_5H_4)$COCH_3Mn(CO)_3$] was reacted with isonicotino hydrazide to obtain [$(CO)_3$Mn{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4N}] . These compounds have been characterized by FTIR, NMR and the biological and electrochemical studies are under investigation.

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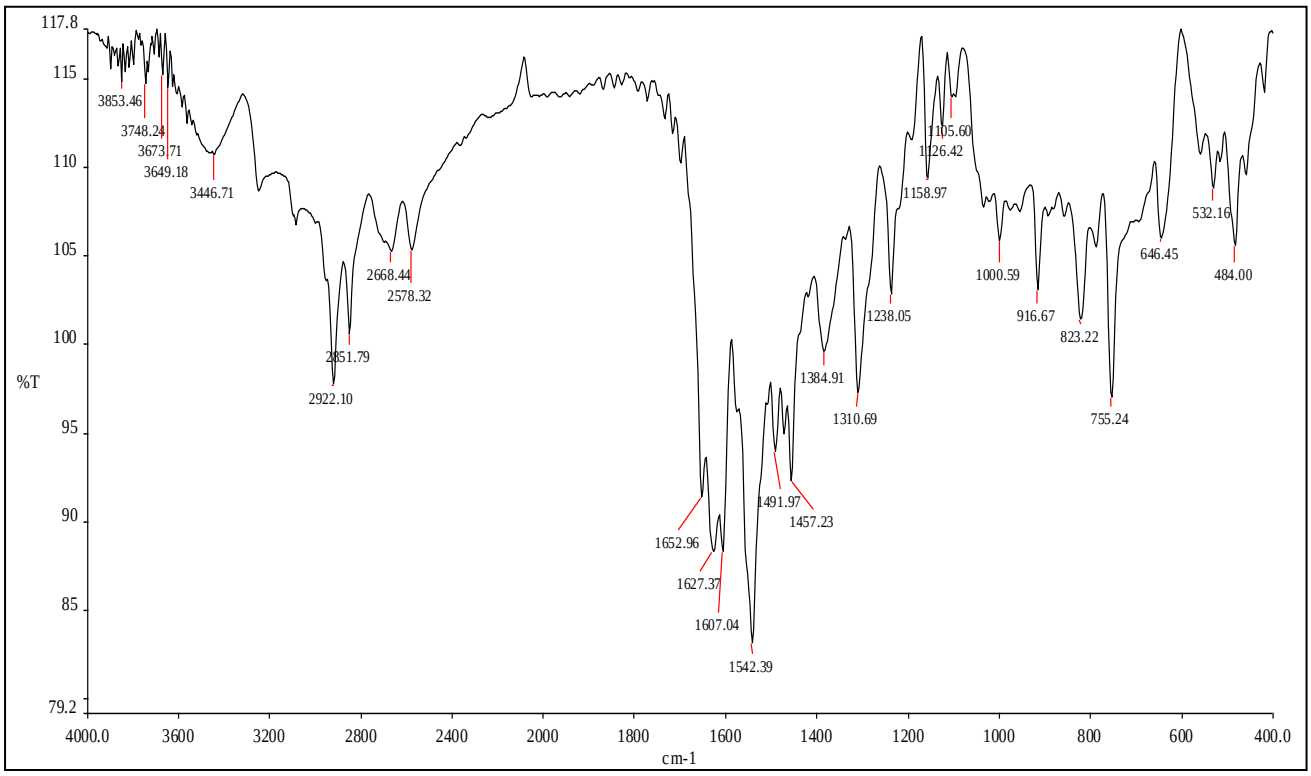
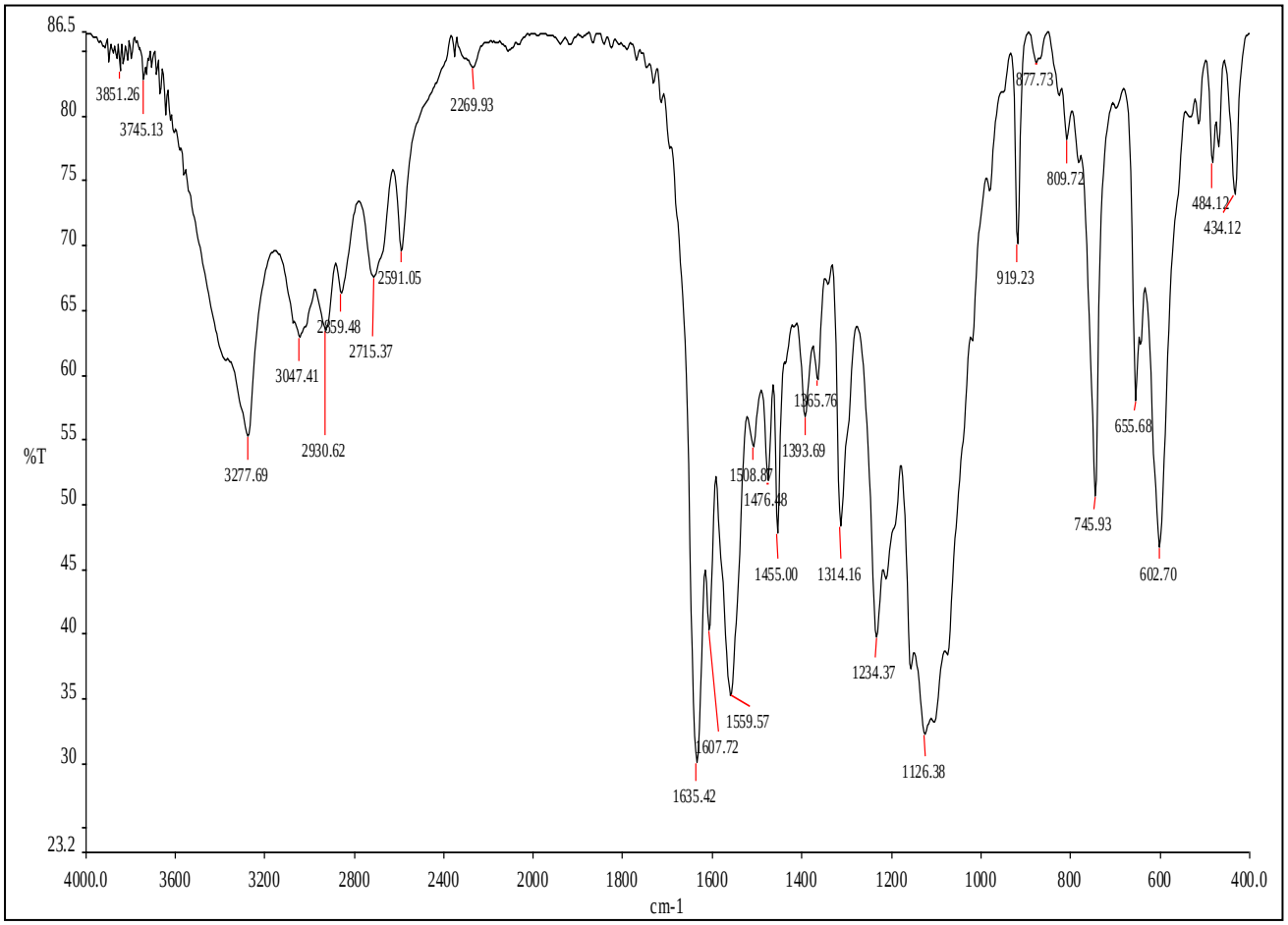
ANNEXURE

IR Spectra of $[(\eta^5\text{-}C_5H_5)Fe\{(\eta^5\text{-}C_5H_4)C(CH_3)=N\text{-}N(H)C(O)\text{-}C_6H_4\text{-}OH\}]$ (3)



IR Spectra of [Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_6H_4-OH}$_2$] (5)



IR Spectra of [(η^5-C_5H_5)Fe{(η^5-C_5H_4)C(CH_3)=N-N(H)C(O)-C_5H_4N}] (4)