Designing new pincer ligands and their transition metal complexes

M.Sc. Thesis

By

Gaurav Kumar

DISCIPLINE OF CHEMISTRY

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Designing new pincer ligands and their transition metal complexes

A THESIS

Submitted in partial fulfillment of the

requirements for the award of the degree

of

Master of Science

by

Gaurav Kumar

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Designing new pincer ligands and their transition metal complexes,** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my work carried out during the time period from July 2019 of joining the M.Sc. program to March 2020 of M.Sc. Thesis submission under the supervision of Dr. Amrendra Kumar Singh.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Gaurav Kumar

Gaurav Kumar

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

ASingh

Dr. Amrendra Kumar Singh

Gaurav Kumar has successfully given her M.Sc. Oral Examination held on 24-06-19.

ASingh

Signature of Supervisor of M.Sc. thesis
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Convener, DPGC
Date: 31-12-2020

Signature of PSPC Member #1
Date: 27-10-2020

Signature of PSPC Member #2
Date: 28-12-2020

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Gaurav Kumar
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DEDICATED

TO……………………..

MY FATHER

For his unwavering belief in my potential!

ABSTRACT

Synthesis and characterization of pincer ligands containing NHCs and CAACs ligand precursors and metalation of the NHCs ligand precursor with the metal precursor [Ru(CN^{Me})Cl$_3$(OH$_2$)] and formed the metal complex1 [Ru(CNC^{H,Me})(CN^{Me})I]PF$_6$(**1**). The metalation of CAACs ligand precursor has not completed yet. Another metal complex with 4d transition metal, Yttrium, with redox active pincer ligand has been formed with the help of previously reported ligand precursor (NNN) pincer ligand in our research group. This ferrocenyl substituted pyrazole containing (NNN) ligand precursor was treated with the yttrium metal precursor [Y(III)(CH$_3$COO)$_3$·4H$_2$O] to give the metal complex [Y(III)(NNN)(CH$_3$COO)$_2$] (**2**). All the synthesized ligands and metal complexes have been characterized by mass spectrometry and multinuclear NMR spectroscopic techniques.

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NOMENCLATURE

Θ	Angle
α	Alpha
β	Beta
γ	Gamma
˚C	Degree Centigrade
% Nm	Percentage
G	Gram
Mol	Mole
Mmol	Milli Mole
mL	MilliLitre
µL	Micro Litre
K	Kelvin
Δ	Chemical Shift(N.M.R)

ACRONYMS

NHC	*N*-Heterocyclic carbene
CAAC	Cyclic alkyl amino carbene
ESI	Electrospray ionization
LCMS	Liquid chromatography mass spectrometry
HRMS	High resolution mass spectrometry
NMR	Nuclear magnetic resonance
GCMS	Gas chromatography mass spectrometry
DMSO	Dimethylsulfoxide
ORTEP	Oak ridge thermal ellipsoid plot program
MeOH	Methanol
CAN	Acetonitrile
IPA	Isopropanol
Ru	Ruthenium
N	Nitrogen
Ar	Argon
DCM	Dichloromethane
Zn	Zinc
NH_4PF_6	Ammonium hexaflurophosphate
H_2O	Water

Chapter 1 Introduction

1.1. General introduction

The discovery of N-heterocyclic carbenes (NHCs) as a special category of ligands for transition metals is one of the remarkable research in the area of organometallic chemistry [1]. The continuous search for more efficient catalysts, which could hold the key to the development of more atom and energy efficient processes and novel recycling techniques, remains a primary challenge for chemists in a world faced with energy and environmental crises. The reactivity catalyst depends upon the liability for electron transfer. Tuning in electronic and steric properties of ligand may facilitate the formation of new complexes of transition metal, capable of performing numerous catalysis. Therefore, designing of ligands and their complexes has drawn much attention and considered as the most important aspects of synthetic inorganic chemistry.

1.2. Aim of the project

The main aim of our project is to design new ligands for the synthesis of electron rich transition metal complexes with interesting properties and its spectrochemical studies and characterization. The main objective for our project is to form the pincer ligands with their transition metal complexes. There are properity of applications for these kinds of complexes. The best known applications of these transition metal complexes are transfer hydrogenation, CO_2 reduction, ester hydrogenation, small molecule activation etc. It can also be useful for small molecule activation like water oxidation, carbon dioxide reduction and ammonia oxidation Transition.

1.2.1. N-heterocyclic carbene (NHC) donors

Carbene can be defined as a neutral species having a divalent carbon with $6e^-$ in valance shell, due to its incomplete octet and unsaturated coordination environment usually carbene without any support are supposed to be unstable intermediates in many organic reactions. The isolation of thermally stable NHCs by Arduengo in 1991 and their success as ligands in homogeneous catalysis versus the phosphine (PR_3) analogues have attracted considerable interest, one of the most notable examples is the great improvement in the reactivity of Grubbs catalyst by replacement of a phosphine by an NHC. The σ-donating ability of NHC are excellent due to this strong ability they form more stable bond and this bond is not dissociated easily. These carbenes are effective due of its high reactivity, high thermal stability [2]. The majority of applications reported with the NHC incorporated transition metal complexes (Fig.1).

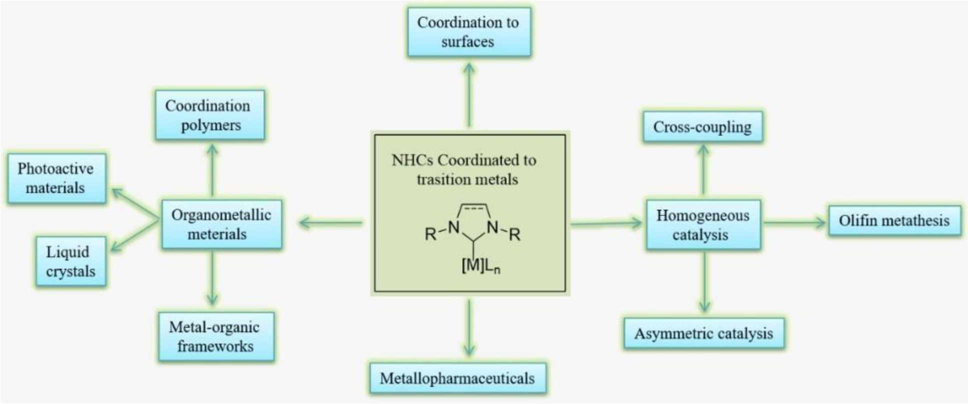


Figure1. Major applications of NHCs coordinated to transition metals[3].

N-heterocyclic carbenes (NHCs) are good ancillary ligand in organometallic chemistry because of their strong electron donating ability and they enhanced the stability of M−NHC bonds in their complexes [4,5]. The NHC ligand provide a good platforms for the designing and synthesis of new catalysts because the binding ability of NHC are excellent due to this region they formed highly stable metal complexes [6,7]. The NHCs demonstrated as a singlet ground-state electronic configuration with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It can be described as a sp^2-hybridized orbital with one lone pair of electron and an unoccupied p-orbital at the C_2 carbon, respectively. The NHCs ligand are stabilized by the “push pull effect” this effect is described as the contiguously present electron-withdrawing and π-electron-donating nitrogen atoms stabilize these structures by lowering the energy of the occupied orbital and donating electron density into the empty p-orbital which leads to the effectiveness of these kind of structures and it is further helpful in different applicational and catalytic studies. The NHCs being cyclic and effectively favour the singlet ground state. The multidentate NHC moieties react by the formation of the chelate complex and reduce ligand dissociation during the catalytic cycles [8-a]. Comparing these complexes with multidentate phosphine ligands, the chemistry of multidentate NHC ligands is still poorly developed and the fundamental knowledge of the mechanistic details is quite limited for the understanding of structure-reactivity relation of NHC based complexes.

1.2.2. Cyclic Alkyl Amino carbene (CAAC) donors

CAAC was discovered in 2005 by Guy Bertrand and co-workers. Cyclic (alkyl) (amino) carbenes (CAACs) are among the most nucleophilic (σ-donating) and also electrophilic (π-accepting) stable carbenes known to date [8-b] (Fig. 2)

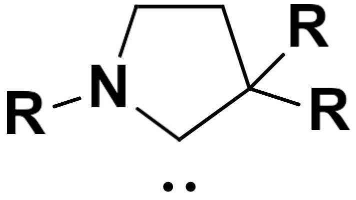


Fig. 2: Structure of CAAC

These are good σ-donar and their catalytic activity is also very interesting. In this type of ligands, one of the electronegative and π-donor amino substituents of diaminocarbenes is replaced by a σ-donating but not π-donating alkyl group, so it might be seen that CAACs are more nucleophilic than diaminocarbenes [9]. The presence of quaternary carbon at the adjacent of carbene carbon may lead to a different extent of efficiency of this ligand and may prove to be better suited in certain applications. CAACs are seen to be helpful in stabilization of paramagnetic complexes but it is poor for organo catalysis as it is poor leaving group because of its basicity. CAACs metal complexes are thermally robust, which allows for their utilization in harsh conditions [10]. CAACs have found interesting applications in the coordination chemistry with the gold (I) and copper (I) [11] metal complexes. It was found that the HOMO of CAACs is slightly higher, and the singlet–triplet gap slightly smaller, than those of NHCs [12] (Fig. 3).

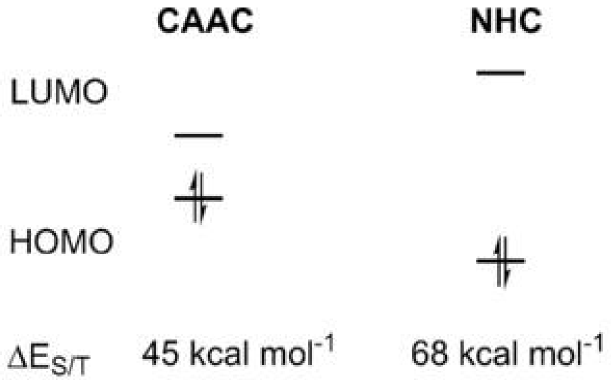


Fig. 3: HOMO-LUMO diagram of NHCs and CAACs

The CAACs containing metal complexes has broad applications in organometllic chemistry i.e., hydrogenation, poymerizarion, olefin metathesis and various organic transformations.

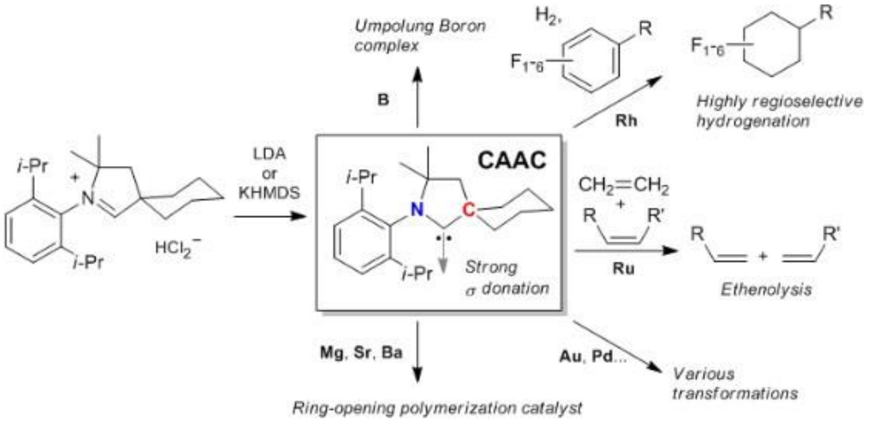


Fig. 4: Potential modification sites in CAACs ligand with different catalytic property.

CAACs containing chelate or pincer ligand platforms are not prepared yet and we have tried to incorporate CAACs into these systems, because the CAACs are good σ-donar and their catalytic activity is also very interesting.

1.2.3. Pincer Type ligands

These type of ligands are special chelating tridentate ligands which binds to metal tightly to three adjacent coplanar sites in a meridional configuration [13-14] (Fig. 5). The Pincer ligand providing a high thermal as well as air-stability, planar and rigid core to metal complex which lead to a very stable complex that can survive very harsh reaction conditions making it suitable for catalytic reactions.

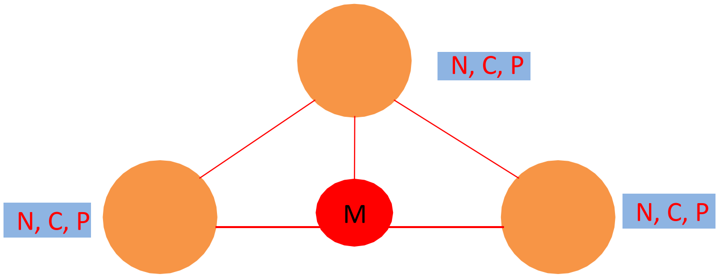


Fig.5: A Schematic diagram of pincer type complex containing pincer ligand and metal M

In our case we have used NHCs based CNC and NNN type pincer ligand. As mentioned earlier NHCs are very strong electron donor so using them in pincer type fashion will surely help in construction of electron rich metal complexes.

1.2.4. Redox Active ligand

The redox active ligands are different than innocent ligands, utilized in Werner complexes where the metal oxidation state was assignable, the non-innocent nature of the redox active ligands were originally defined by Jorgensen in 1966 [15] as on completion with the assignment of charge on metal is enigmatic. The contemporary explanation states that the redox active ligands perform redox processes by settling the electron flow in and out with the metal retaining its original oxidation state. Moreover, these ligands provide the cost effective multi-electron reaction in catalysis which prevents the unwanted side reactions and maintains the nobility of base metals [16].

On the basis of oxidation state of central metal ion, ligands are classified into two categories, innocent and non-innocent ligands. When a redox reaction occurs either on the metal or on the ligand, these ligands are commonly termed as innocent and non-innocent ligands. In general, innocent ligands do not take part in the redox reaction whereas non-innocent ligands do take participate in the redox reaction, therefore, are called as redox active ligands [17].

1.2.5. Target complex

The targeted metal complex having Ru and Y metals, Ruthenium metal complex have six coordinate sites with its three sites occupied by a pincer ligand (CNC) by meridional geometry and two sites occupied by NHC ligand and one site occupied by the halogen and Yttrium metal complex have five coordinate sites with its three sites occupied by a pincer ligand (NNN) by meridional geometry and two sites occupied by acetyl group. As we know, NHC ligands will increase electron density on metal and pincer ligand provides strong chelate effect, preorganized geometry, high tenability, high stability. The vacant site (halogen) will facilitate CO2 coordination and activation with metal. These ligands possess rigid coordination modes for the Ruthenium and Yttrium metal ion which can play a significant role in the efficiency and mechanism of catalysis by the resulting complex.

Chapter 2 Experimental Section

2.1. General Procedure and Meterials:

Generally reaction was performed under a constant supply of inert atmosphere of N_2 in standard Schlenk-line and some reaction was performed inside the glove-box. Solvents were dried and purified over the nitrogen by conventional method. All the chemicals were systematic category and used as received without further purification. These chemicals include 2,6-dibromo pyridine (Alfa Aesar, 98%), potassium carbonate (SRL, 99.5%), Imidazole (SRL, 99%), 1-methylimidazole (Spectrochem, 99%), ruthenium trichloridetrihydrate (SRL), iodomethane (Chem Labs, 99.8%), magnesium sulphate (SRL, 99%), potassium hydroxide (Emplura, 85%), formaldehyde was purchased from Fischer scientific private Ltd, isopropyl bromide (Spectrochem, 99%), cyclohexyl bromide (Spectrochem, 98%), benzyl alcohol (Spectrochem, 99%), tertiary butyl amine (Spectrochem, 99%).

2.2. Instrumentation:

NMR spectra were recorded on an AVANCE III 400 Ascend Bruker BioSpin machine at ambient temperature. Mass spectrometric analyses were done on Bruker-Daltonics, a micro to-Q II mass spectrometer. Single-crystal X- ray structural studies were performed on an Agilent Technology Supernova CCD diffractometer equipped with a low-temperature attachment.

2.3. Synthesis of ligands and its Metal complexes:

2.3.1. Synthesis of Ligand (L). Ligand **(L)** was synthesized as a previously reported synthetic route [18]. Benzimidazole and 2,6-dibromopyridine was commercially bought. Under N_2 atmosphere 2,6-dibromopyridine (2.370 g, 10 mmol) and Benzimidazole (1.416 g, 12 mmol) were taken in 100 mL two neck round bottom flask. After that K_2CO_3 (4 g, 29 mmol), CuI (0.3 g, 2 mmol) were added followed by tetramethylethylene-di-amine (0.7 mL) and dry DMSO (20 mL). After that the reaction mixture was heated under reflux for 24 hrs at 90 ˚C under N_2 atmosphere. The resulting solution was extracted three times by using DCM. The combined extract was concentrated under the vacuum and crude product was isolated by column chromatography. The product was found as a white solid (Yield:1.5 g, 55%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (s,1H),δ 8.00-7.98(d, J=7.99,1H,),δ 7.78-7.76(d, J=7.77, 1H),δ 7.67-7.63(t, J=7.65, 1H),δ 7.45-7.43(d, J=7.44, 1H), δ 7.38-7.34(d, J=7.36, 1H), δ 7.30(d, 1H), δ 7.28(d, 1H) ppm.**^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.76, δ 144.83, δ 141.30,δ 141.07,δ 133.94,δ 125.90,δ 124.78, δ 123.87, δ 120.95, δ 113.03, δ 112.29 ppm. Positive ESI-MS $[M\text{-}Br]^+$ molecular ion peak at m/z=273.6

2.3.2. Synthesis of Ligand [L^1(Br)]

The Ligand was synthesized by using pressure tube (ACE tube). First an oven dried pressure tube charged with Ligand **L** (27 mg, 0.1 mmol). After that added 1-Methly imidazole (82 mg, 0.1 mmol) in pressure tube. After This addition pressure tube was capped using Teflon cap and heated at 150 ˚C of oil bath temperature for 3 hrs stirring. The resulting precipitate was collected through filtration wash with three times by using DCM and diethyl ether. After wash it was dried by using Na_2SO_4 as a drying agent. The resulting evaporated to get white solid as the desired product.^{1}H-NMR data was taken after that which indicate the pure ligand and no further purification was done.The product was found as a white solid (Yield:70 mg, 39.1%)**^{1}H NMR** (400 MHz, DMSO-D_6): δ 10.18 (s, 1H),δ 9.19(s, 1H),δ 8.63(d, 1H),δ 8.45(t, 1H),δ 8.30-8.28(d, J=8.29, 1H), δ 8.18-8.16(d, J=8.17, 1H), δ 8.05-8.03(d, J=8.04, 1H), δ 8.01(d, 1H), δ 7.83-7.81(d, J=7.82, 1H),δ 7.46(d, 1H), δ 7.40(d, 1H), δ 4.04(s, 3H) ppm.**^{13}C NMR** (100 MHz, DMSO-D_6): δ 148.95, δ 148.67, δ 144.55,δ 144.07,δ 142.90,δ 136.17,δ 131.58, δ 125.19, δ 124.79, δ 123.79, δ 120.36δ 119.53, δ 155.26, δ 113.88, δ 111.72 ppm. Positive ESI-MS $[M\text{-}Br]^+$ molecular ion peak at m/z=275.

2.3.3. Synthesis of Ligand L^2: Ligand was synthesized as a previously reported synthetic route [19], 1,3-dibromobenzene and imidazole was commercially bought. Under atmosphere 1,3-dibromobenzene (1957 mg, 0.83mmol) and imidazole (135.61 mg, 1.9mmol) were taken in 100 mL two neck round bottom flask. After that added K_2CO_3 (286.77mg, 2.07 mmol), CuO (26.4 mg, 0.33 mmol) were dissolved in dry DMSO (10 mL). After that the reaction mixture was heated under reflux for 72 hrs at 150 ˚C under atmosphere. The resulting solution was extracted three times by using DCM. The combined extract was concentrated under the vacuum and crude product was isolated by column chromatography. The product was found as a white solid (Yield: 108.18 mg, 62%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (s, 2H), δ 7.54(t, 1H), δ 7.35(d, 2H), δ7.34(s, 1H), δ 7.26(d, 2H), δ 7.17 (d, 2H) ppm. Positive ESI-MS $[M-H]^+$ molecular ion peak at m/z=211.1

2.3.4. Synthesis of Ligand $[L^2(I)]$: The Ligand was synthesized by using pressure tube (ACE tube). First an oven dried pressure tube charged with Ligand **L^2** (420 mg, 2 mmol) and dissolved in THF (5 mL). After that added iodomethane (1.2 mL, 8mmol) in pressure tube. After This addition pressure tube was capped using Teflon cap and heated at 150 ˚C of oil bath temperature for 3 days with continuous stirring. The resulting precipitate was collected through filtration wash with three times by using DCM and dried over Na_2SO4 as a drying agent. Filtered it and evaporated to dryness to get white solid (Yield 325 mg, 33%).**^{1}H NMR** (400 MHz, DMSO-D_6): δ 9.91 (s, 2H), δ 8.39(d, 2H), δ 8.32(t, 1H), δ 8.03(d, 2H), δ 8.00(d, 2H), δ 7.98(s, 1H), δ 4.00(s, 6H) ppm.

2.3.5. Synthesis of Ligand L^3: Ligand was synthesized by using literature procedure [20-a], Under N2 atmosphere firstly take $DippNH_2$ (3.7 mL, 20 mmol) and $MgSO_4$ (2.407 g, 20 mmol) were taken in 100 mL conical flask. After that added propionaldehyde (8 mL, 30 mmol) were dissolved in dry DCM (10 mL). The reaction mixture was stirred at room temperature for 3 days. After complete the reaction remove the solvent through vacuum. The pale yellow oily compound is obtained and the product was quantitative.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), δ 7.29(d, 2H), δ 7.26 (t, 1H), δ 3.10(m, 2H), δ 2.53(m, 2H), δ 1.35(d, 12H), δ 1.29 (t, 3H) ppm. Positive ESI-MS $[M-H]^+$ molecular ion peak at m/z=218.2

2.3.6. Synthesis of Ligand [L^3(1)]: Ligand was synthesized by using literature procedure [20-b], in presence of glove box. Initially taken $DippN=CHCH_2CH_3$ (3.87 g, 17.83 mmol) in 100 mL conical flask and added dry THF (10 mL) and cooled at -78 ˚C and added n-butyl lithium (10.92 mL, 21.8 4mmol) and then warmed to room temperature and stirred 1hrs and then cooled to -78°C and added the 3-chloro-2-methylpropene (2.14 mL, 21.84 mmol) in three portions and stirred overnight at room temperature. After that removed of the volatiles solvent under high vacuum afforded a mixture of an oil (alkenlyaldimine**L^3(1)**) and a solid (LiCl). The product was quantitative yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), δ 7.29(m, 4H), δ 5.08(t, 3H), δ 3.43(t, 4H), δ 1.42(s, 15H) ppm. Positive ESI-MS $[M-H]^+$ molecular ion peak at m/z=273.6

2.3.7. Synthesis of Ligand [L^3(2)]: The Ligand was synthesized Initially taken crude **L^3(1)** (alkenlyaldimine) (5.0 g, 18.42 mmol) in 100 mL conical flask and added dry THF (15 mL) and then the reaction mixture was cooled at -78 ˚C and then added n-butyl lithium(1.6 M in Hexane) (15 mL, 23.95 mmol) with slowly-slowly then colour change orange to black and then stirred for 1hrs at room temperature and then cooled to -78 °C and then added dibromomethane (0.832 mL, 11.98 mmol) and stirred overnight at room temperature. After that reaction mixture outside the glove box and removed of the volatiles solvent under vacuum.The product was found as a brown colour oily liquid (Yield: 3.8 g, 37%).**^{1}H NMR** (400 MHz,

$CDCl_3$): δ 7.66 (s, 2H,),δ 7.10(t, 6H), δ 4.89 (s, 2H), δ 4.75(s, 2H), δ 4.09(m, 4H), δ 1.61(s, 12H), δ 1.27(s, 24H) ppm.

2.3.8. Synthesis of Ligand [$L^3(BF_4)$] 6: The Ligand was synthesized initially taken crude **L^3(2)** (alkenlyaldimine) (2.12g, 3.73mmol) and added dry diethylether (10 mL) in 100 mL conical flask and then the reaction mixture was cooled at -78 ˚C and then added HCl (7.46 mL, 2 M) precipitation of a colorless powder was immediately observed. The reaction mixture was slowly warmed at room temperature and stirred was continuous for half an hour. The reaction mixture was transfer in pressure tube. After this pressure tube was capped using Teflon cap. The reaction mixture removes outside the glove box after that reaction mixture was heated at 110 ˚C for 24 hrs and then cooled at room temperature. The diethyl ether solution was removed via syringe and the solid was washed with diethyl ether until the solution was colorless. The solid was dried under vacuum to afford a brownish powder, which was the iminium salt with HCl_2^- anion. Taken the iminium salt and added $NaBH_4$ (1.63 g, 14.92 mmol) and added H_2O (14 mL) and stirred for one hour at room temperature. The solid was washed with H_2O (2x8 mL), diethylether (2x8 mL) and hexane(2x8 mL) and then dried under vacuum.The product was obtained as a brownish powder(Yield: 786 mg,37%).**^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.30 (s, 2H),δ 7.52(t, 2H),δ 7.34(d, 4H),δ 2.65(m, 4H), δ 1.34(s, 24H) ppm.

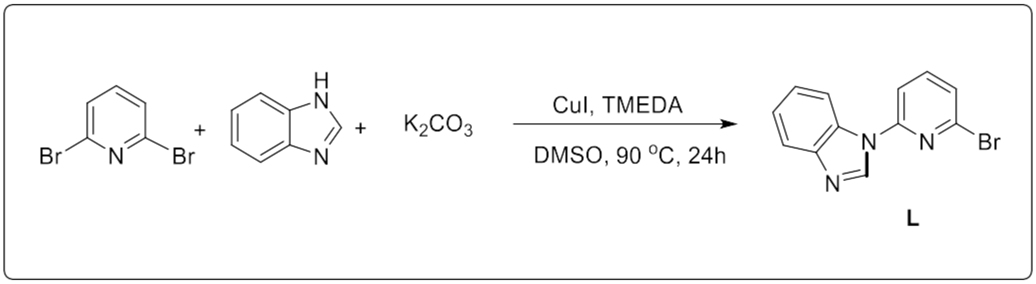
2.3.9. Synthesis of complex 1: The complex was synthesized using Schlenk-tube. First an oven dried Schlenk-tube was charged with L^1(Br) (44 mg,0.123 mmol) and mixture of $[Ru(CN)^{Me}Cl3OH2]$ (47.6 mg, 0.123 mmol) in ethylene glycol (8ml) were refluxed under N2 for 4 h. On completion of the reaction, aq NH4PF6 (163mg, 1 mmol, 10 ml water) was added. The precipitated yellow powder was filtered and triturated it with H2O and then dried it. The resulting yellow solid was then refluxed with Zn (65.7 mg, 1 mmol) in methanol (15 ml) under N2 I have obtained dark yellow compound (Yield:74 mg, 90%). Positive ESI-MS [M-PF_6]$^+$ molecular ion peak at m/z=663.0

2.3.10. Synthesis of complex 2: The complex was synthesized by using Schlenk-tube. Firstly an oven dried Schlenk-tube was charged with previously prepared ligand by our research group L^4 (Pincer Ligand) (58.13 mg, 0.1 mmol) and added the metal precursor [Y(III)(CH_3COO)$_3$·4H20] (33.81 mg, 0.1mmol) and it then added DCM (8 ml) and stirring under N2 for 4 hour after that yellow precipitated appeared filtered it. This was dried into desiccator for overnight to remove any minimal amount of water. (Yield: 37.9 mg, 47%).**^{1}H NMR** (400 MHz, DMSO-D_6): δ 13.20 (s,1H, N-H), δ 8.17(t,1H pyridine),δ 7.92(d, 2H pyridine),δ 7.14(s,2H,pyrazole), δ 4.85-4.79(d,2H and t, 2H J=4.82,Cp ring)δ 4.44-4.34(d, 2H and t, 2H J=4.39,Cp ring), δ 4.13-4.08(d, J=4.105, 10HCp ring), δ 1.80(s, 6H, acetyl) ppm. Positive ESI-MS [M-Na]$^+$ molecular ion peak at m/z=808.0

Chapter 3 Results and discussion

3.1. Synthesis and characterization of Ligands:

Ligand **L** has been synthesized as the reported procedure by reaction of 2,6-dibromopyridine, benzimidazole and tetra methyl ethylene-di-amine in dry DMSO in presence of K_2CO_3 base and CuI as a catalyst shown in Scheme 1 which afforded the white solid of the desired compound. This compound was characterized by ^1H (Fig 3.1) and ^{13}C NMR (Fig 3.2) spectra, and ESI-MS (3.3) spectrogram.



Scheme 1: Synthesis of L

3.1.1 ^1H and ^{13}C NMR spectra and ESI-MS of Ligand L

The ^1H NMR spectrum of L shows that a singlet at 8.46 is for one benzimidazole proton in highly deshielded region and one doublet for one pyridine proton at 8.00-7.98 (J=7.99) and another doublet for one benzimidazole protons at 7.78-7.76 (J=7.77)and one triplet for one pyridine top protons at 7.67-7.63 (J=7.65) and one triplet for one benzimidazole proton at 7.45-7.43 (J=7.44) and another doublet for one pyridine protons at 7.38-7.34 (J=7.36)and one triplet at 7.30 is for one benzimidazole proton and one doublet at 7.28 is for one benzimidazoleproton.

Fig. 3.1: ^{1}H NMR of Ligand **L**

This ^{1}HNMR spectra (Fig: 3.1) matched with the ligand (L). The^{13}C NMR Spectrum of L (Fig. 3.2) shows that there are 11 peaks of carbons instead of 12 carbons and the spectrum is showing 10 different peaks for 10 carbon and one different peaks for 2 carbon. The highly acidic carbon peak could be identified at 149.76 ppm. The mass spectrogram of this compound is $[M\text{-}Br]^+$molecular ion peak at m/z=273.6, the above all the data concluded the formation the ligand(L).

Fig. 3.2: ^{13}C NMR of Ligand **L.**

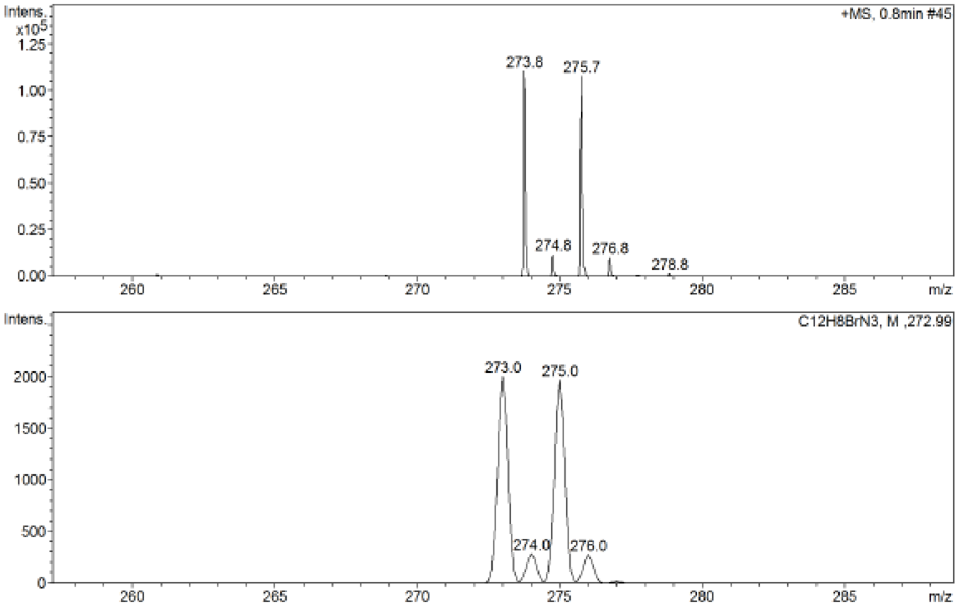
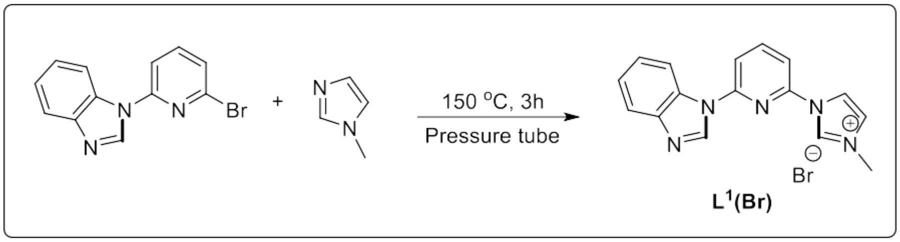


Fig 3.3: ESI-MS of ligand **L** in MeOH.

After the formation of ligand **L**, we move forward to our project title to synthesize the NHC type ligands by doing functionalization in the two different aromatic ring. This ligand will further give better metalation scope.

Ligand **L^1(Br)** has been synthesized by using pressure tube. The ligand (**L)** taken in pressure tube followed by addition of 1-Methly imidazole as shown in scheme. It result white solid compound. This compound was then characterized by ^{1}H NMR (Fig 3.4), ^{13}C NMR (Fig 3.5) spectra, and ESI-MS (Fig 3.6).



Scheme 2: Synthesis of L^1(Br)

3.1.2 ^{1}H and ^{13}C NMR spectra and ESI-MS of Ligand L^1(Br)

The ^{1}H NMR (Fig 3.4) spectrum of ligand L^1(Br) shows that a singlet at 10.18is for 1-methylimidazolium proton and another singlet for one benzimidazole protons at 9.19 both the proton are in deshielded region and one doublet for benzimidazole proton at 8.63 and triplet for one pyridine top proton at 8.45 and one doublet for one proton of imidazolium 8.30-8.28 (J=8.29) and another one doublet for one proton of imidazolium at 8.18-8.16 (J=8.17) and another one doublet for one proton of pyridine at 8.05-8.03 (J=8.04) and another one doublet for one proton of pyridine at 8.01 and one triplet for one proton of benzimidazole at 7.83-7.81 (J=7.82) and another one doublet for one proton of Benzimidazole at 7.46 and another one triplet for one proton of Benzimidazole at 7.40 are observed in aromatic region. The methyl peak of methylimidazole is comes in shielded region at 4.04 ppm for 3 protons.

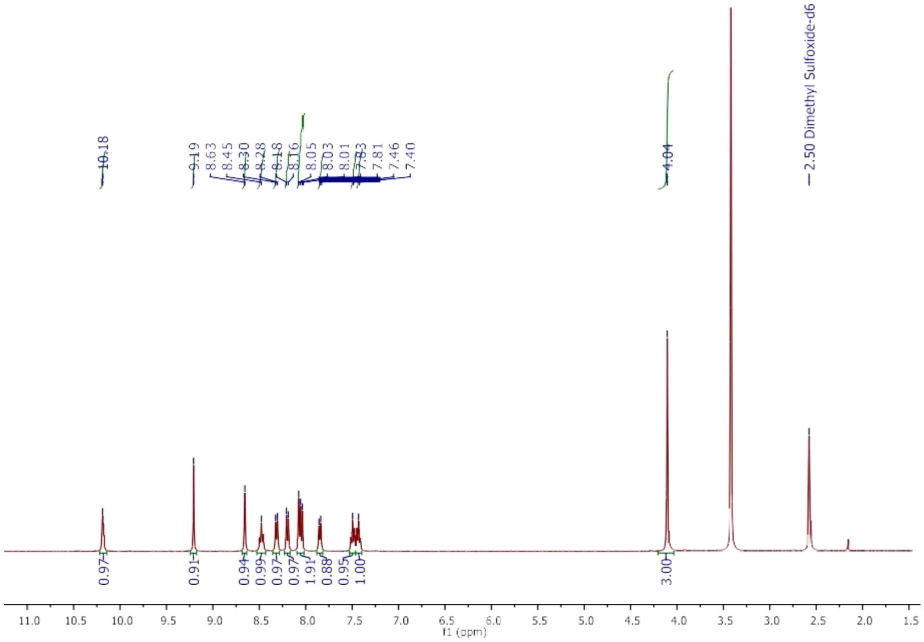


Fig. 3.4: ^{1}H NMR of Ligand **L^1(Br)**.

From ^{13}C NMR Spectrum of L^1(Br**)** Fig. 3.5 we can see that there are 15 peaks of carbons instead of 16 carbons and spectrum is showing 14 different peaks for 14 carbons and one different peaks for 2 carbon. The highly acidic carbon peak could be identified at 148.95 ppm and the methyl of methylimidazole carbon identified at 111.38 ppm. This NMR spectra (Fig: 3.5) also give the supporting data for the formation of the ligand L^1(Br). The mass spectrogram was also concluded the formation of ligand [M-Br]$^+$ molecular ion peak at m/z=275.9

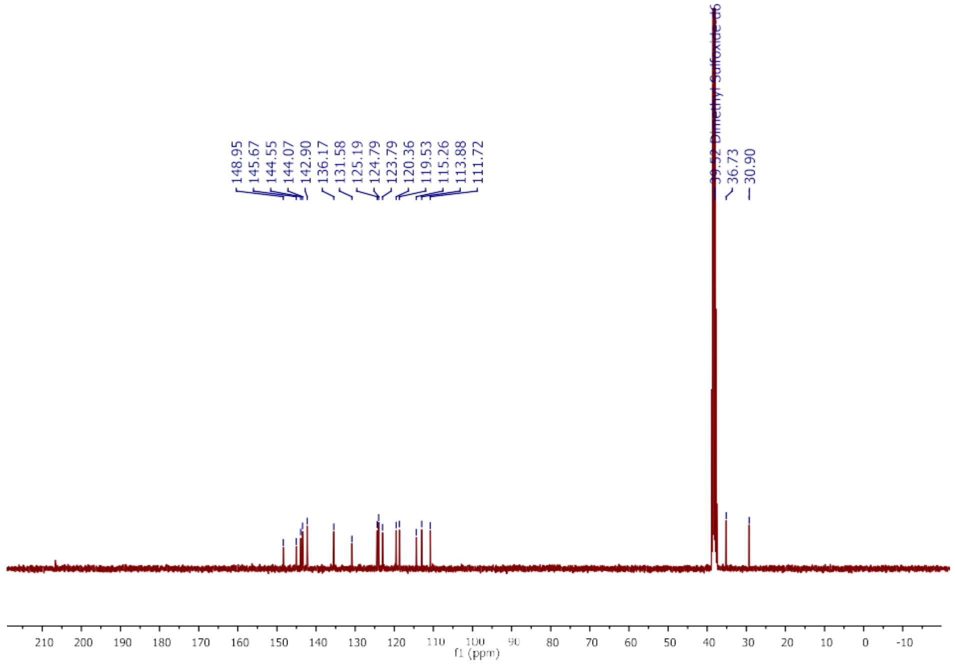


Fig 3.5: ^{13}C NMR of Ligand **L^1(Br)**

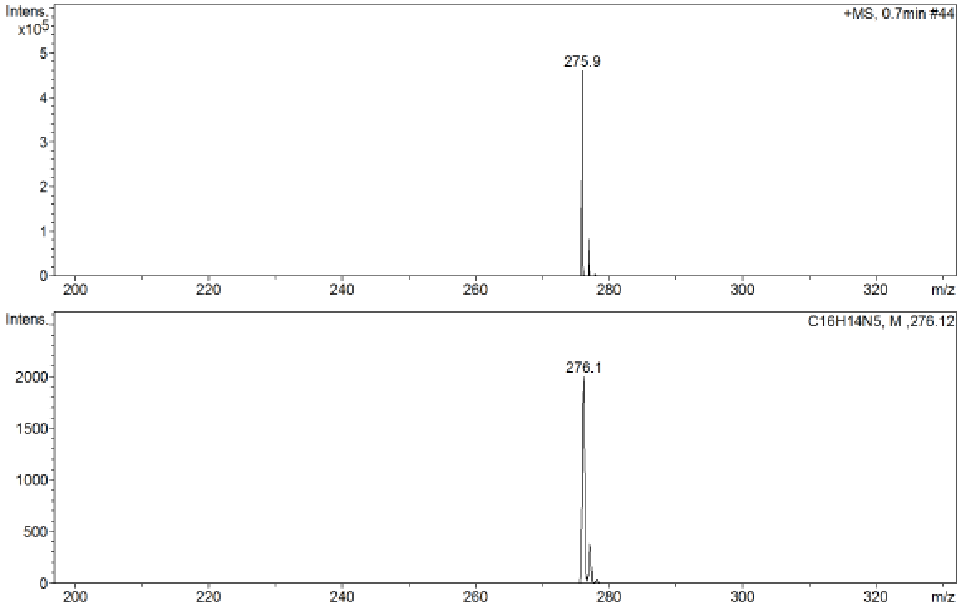
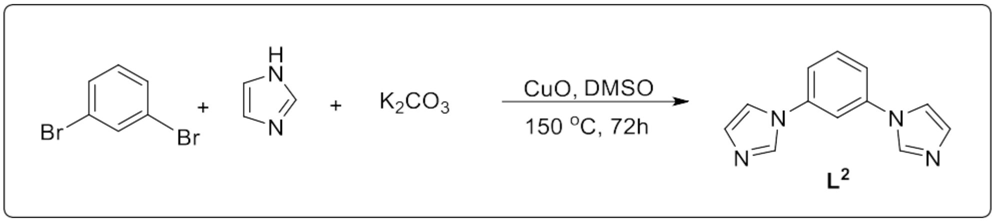


Fig 3.6: ESI-MS of ligand **L^1(Br)** in MeOH

Ligand **L**^{2} has been synthesized reported procedure by reaction of 1,3 dibromobenzene, and imidazole in dry DMSO in presence of K_2CO_3 and CuO as a catalyst shown in Scheme 3, which give white solid compound. This compound was characterized by ^{1}H NMR (Fig 3.7) spectra, and ESI-MS (Fig 3.8).



Scheme 3: Synthesis of L^2

3.1.3 ^{1}HNMR spectra and ESI-MS of Ligand L^2

The ^{1}H NMR spectrum of L^2 shows that a singlet at 7.84 for two imidazole proton in more deshielded region and one triplet for one benzene top proton at 7.54 and one doublet for 2 benzene protons at 7.35 and one singlet at 7.34 is for one benzene bottom proton and one doublet at 7.26 is for two imidazolium protons and another one doublet at 7.17 for two imidazolium protons. All protons are observed in aromatic region 7.84-7.17 ppm. The mass spectrogram (Fig 3.8) of this ligand concluded that the compound was formed $[M-H]^+$ molecular ion peak at m/z=211.1

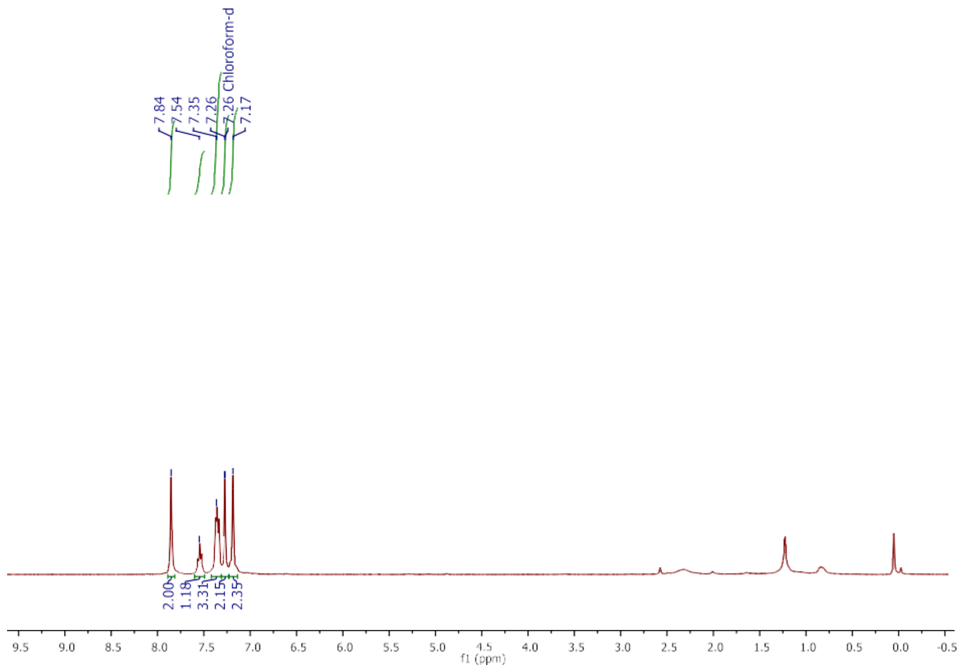


Fig 3.7: ^{1}H NMR of Ligand $\mathbf{L^2}$

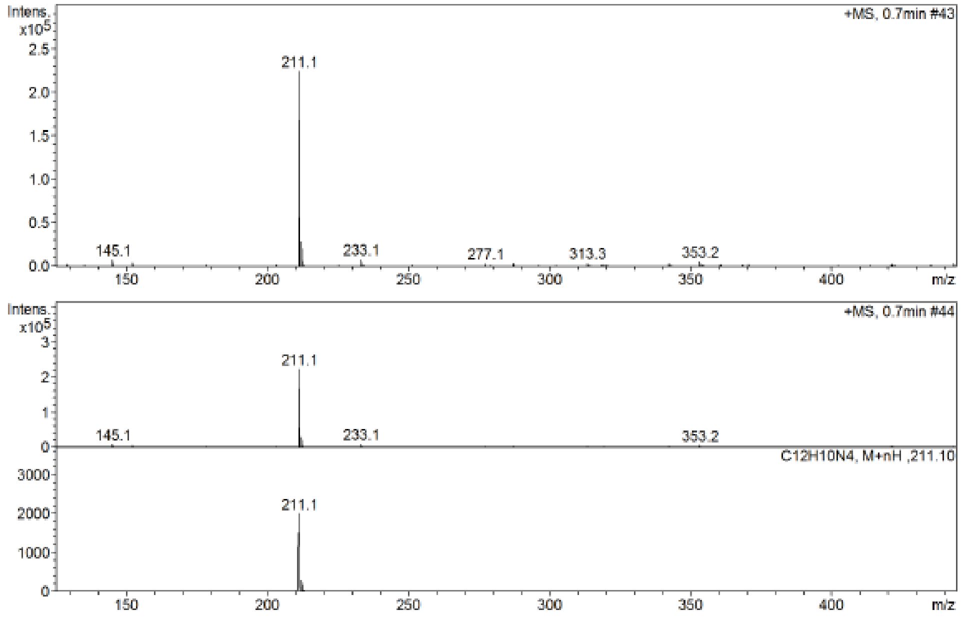
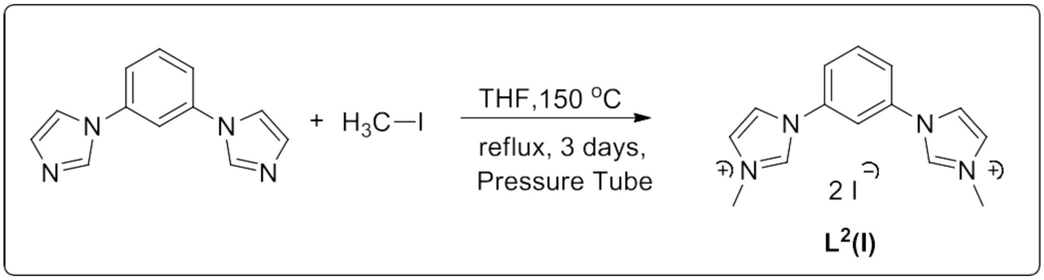


Fig 3.8: ESI-MS of ligand $\mathbf{L^2}$ in MeOH

Ligand $\mathbf{L^2}$**(I)** has been synthesized by dissolving the ligand L^2 in THF in pressure tube followed by addition of 4 equivalent of iodomethane into it and heated at 150 ˚C for 3 days as a shown scheme 4. It results in a white solid compound. This compound was then characterized by ^{1}H NMR spectroscopy (Fig 3.9).



Scheme 4: Synthesis of L^2(I)

3.1.4 ^{1}HNMR spectra of Ligand L^2(I)

The ^{1}H NMR spectrum (Fig 3.9) of L^2(I) shows that a singlet at 9.91 ppm for two imidazolium protons in more deshielded region and one doublet for two benzene protons at 8.39 and one triplet for one benzene top proton at 8.32 and one doublet at 8.03 is for two imidazolium protons and another one doublet at 8.00 is for two imidazolium protons one singlet at 7.98is for one benzene bottom proton and another one singlet for methyl group of methylimidazole protons at 4.00 for 6 protons. The spectra concluded that the molecule is symmetric and both methyl imidazoles are identical in nature.

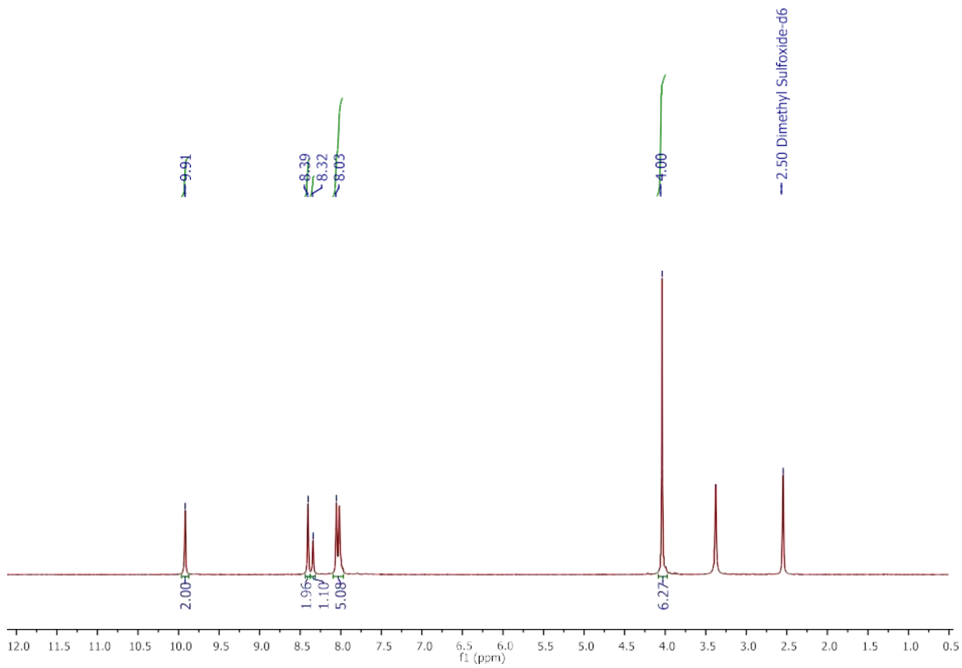
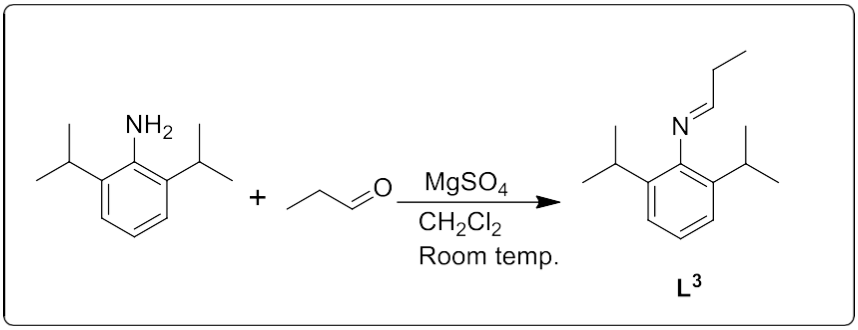


Fig 3.9: ^{1}H NMR of Ligand **L^2(I)**

Ligand **L^3** has been synthesized as the reported procedure by the reaction of DippNH$_2$ and propionaldehyde in dry DCM in presence of MgSO$_4$ as shown in Scheme 5, which gave pale yellow oily liquid compound. This compound was characterized by ^{1}H NMR spectra (Fig 3.10), and ESI-MS (Fig 3.11).



Scheme 5: Synthesis of L^3

3.1.5^{1}H NMR spectra and ESI-MS of Ligand L^3

The ^{1}H NMR spectrum (Fig 3.10) of L^{3}shows that a singlet at 7.78 is for one imine more acidic protons and one doublet for 2 benzene meta-protons at 7.29 and one triplet for one benzene para proton at 7.26 and one multiplet at 3.10is for two alkylene protons and another one multiplet at 2.53 is for two isopropyl protons and one doublet at 1.35 for 12 proton of methyl and one triplet at 1.29 is for 3 protons of methyl. The NMR spectra (Fig: 3.10) concluded the formation of the ligand. The mass spectrogram (Fig 3.11) was also concluded the formation of the compound [M-H]$^+$molecular ion peak at m/z=218.2

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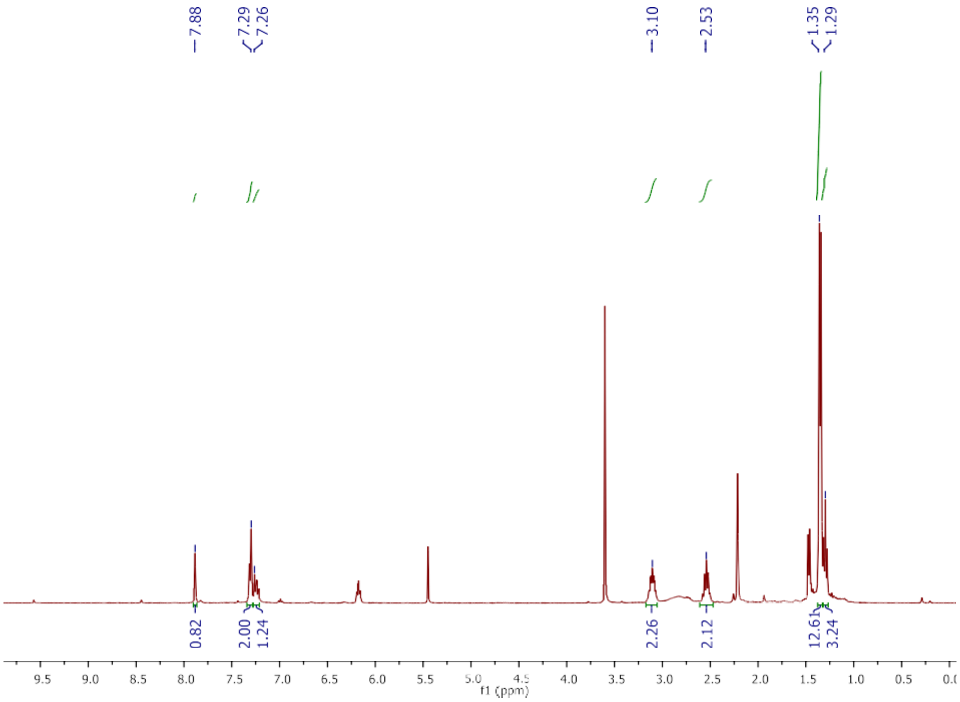


Fig 3.10: ^{1}H NMR of Ligand **L^3**

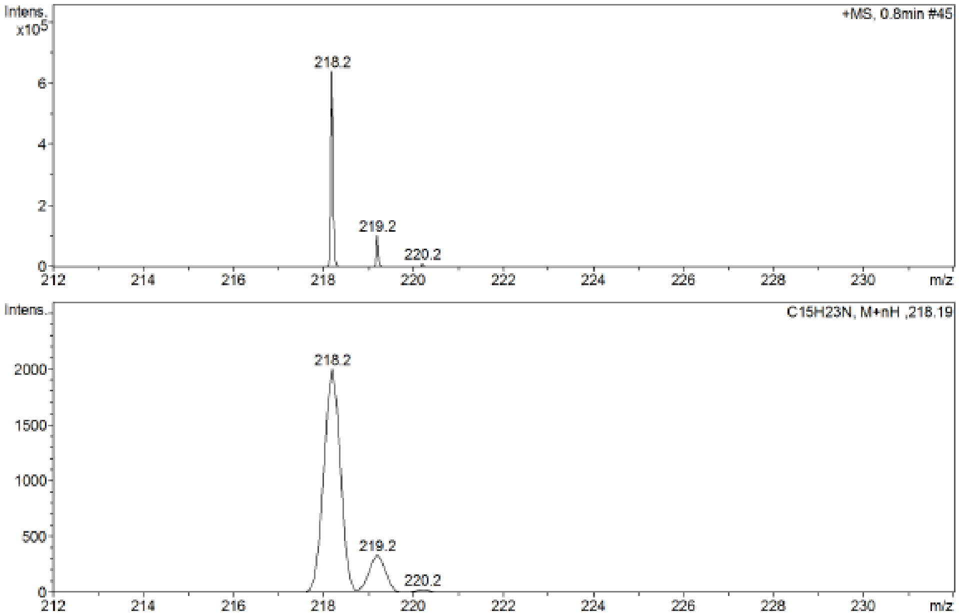
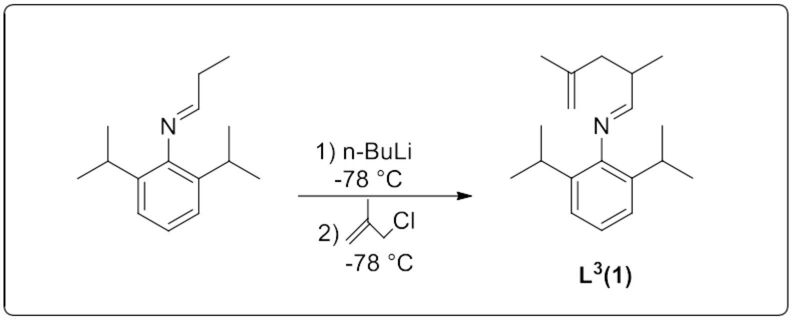


Fig 3.11: ESI-MS of ligand **L**$^{\mathbf{3}}$in MeOH

After the formation of ligand **L**$^{\mathbf{3}}$, we move to next step, Ligand **L**$^{\mathbf{3}}$**(1)** has been synthesized by dissolving the ligand L^{3} in THF in conical flask followed by addition DippN=CHCH$_2$CH$_3$ and cooled at -78 ˚C and added n-butyl lithium and added the 3-chloro-2-methylpropene. It results in orange oily liquid compound. This compound was then characterized by ^{1}H NMR spectroscopy (Fig 3.12), and ESI-MS (3.13).



Scheme 6: Synthesis of L^{3}(1)

3.1.6 ^{1}H NMR spectra and ESI-MS of Ligand L^3(1)

The ^{1}H NMR spectrum (Fig 3.12) of L^3(1)shows that a singlet at 7.84is for one imine more acidic protons and one doublet for 2 benzene meta protons at 7.29 and one triplet for one benzene para proton at 7.26 and one doublet at 5.08 for alkene protons and one doublet at 3.43 for two protons and one multiplet at 3.10 for two alkylene protons and another one multiplet at 2.53 is for two isopropyl protons and one doublet at 1.35 is for 12 proton of methyl and one triplet at 1.29 is for 3 protons of methyl. This NMR spectra (Fig: 3.12) matches with the reported data but some impurity but in indication the formation of the ligand. The mass spectrogram (Fig 3.13) [M-H]$^+$molecular ion peak at m/z=272.2, both the spectra concluded that the ligand was formed with some impurities.

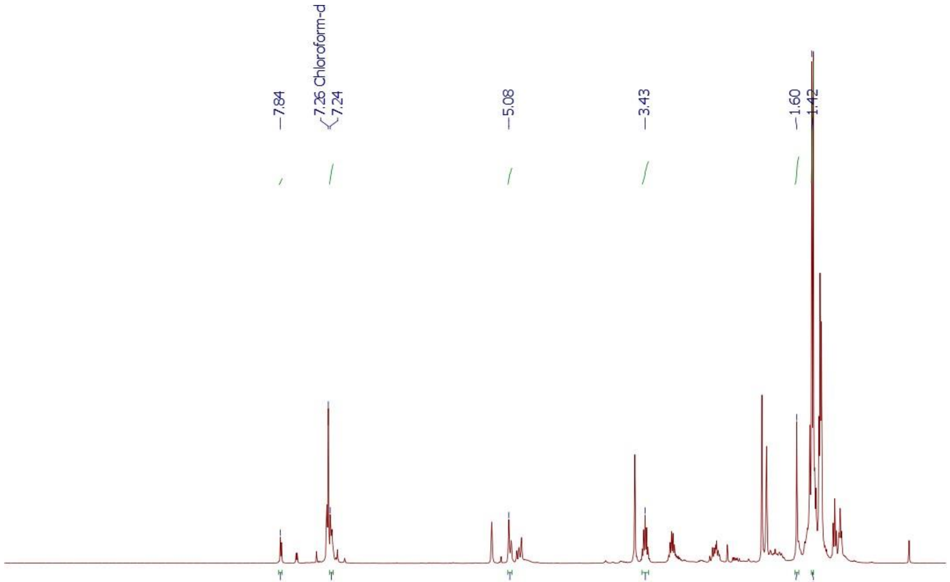


Fig 3.12: ^{1}H NMR of Ligand **L^3(1)**

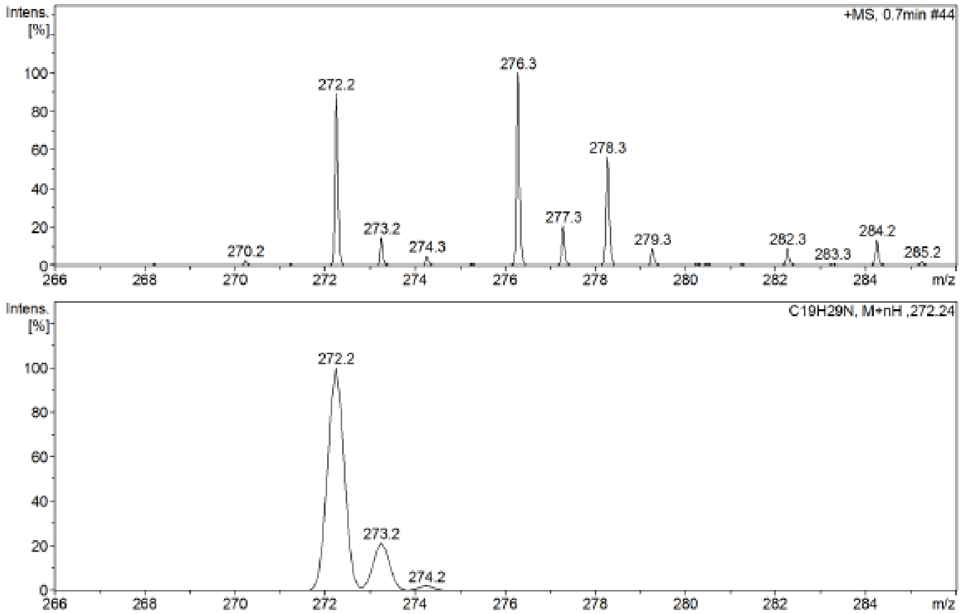
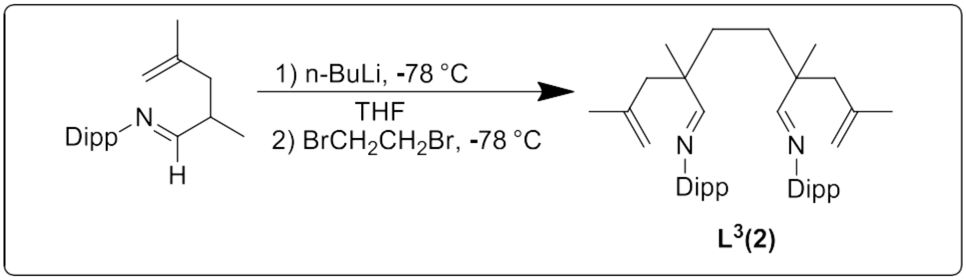


Fig 3.13: ESI-MS of ligand **L^3(1)** in MeOH

After the formation of Ligand **L^3(1)**, we move to next step, Ligand **L^3(2)** has been synthesized by dissolving the ligand**L^3(1)** in THF in conical flask followed by the addition of n-butyl lithium and then added dibromomethane. It result brown oily liquid compound. This compound was then characterized by ^{1}H NMR spectroscopy (Fig 3.14).



Scheme 7: Synthesis of L^3(2)

3.1.7^{1}H NMR spectra of Ligand L^3(2)

The ^{1}H NMR spectrum of L^3(2) shows that a singlet at 7.66 for two imine more acidic protons and one peak at 7.10 for six aromatic benzene protons and one peak for two alkene protons at 4.89 and one peak for two alkene protons at 4.75 and one peak at 4.09 for-CH_2- linker protons and another one multiplet at 1.81 for four isopropyl protons and one singlet for 12 alkyl protons at 1.61 and another one peak for 24 alkyl protons at 1.27 ppm. This NMR spectra (Fig: 3.14) concluded the formation of ligand with some impurities.

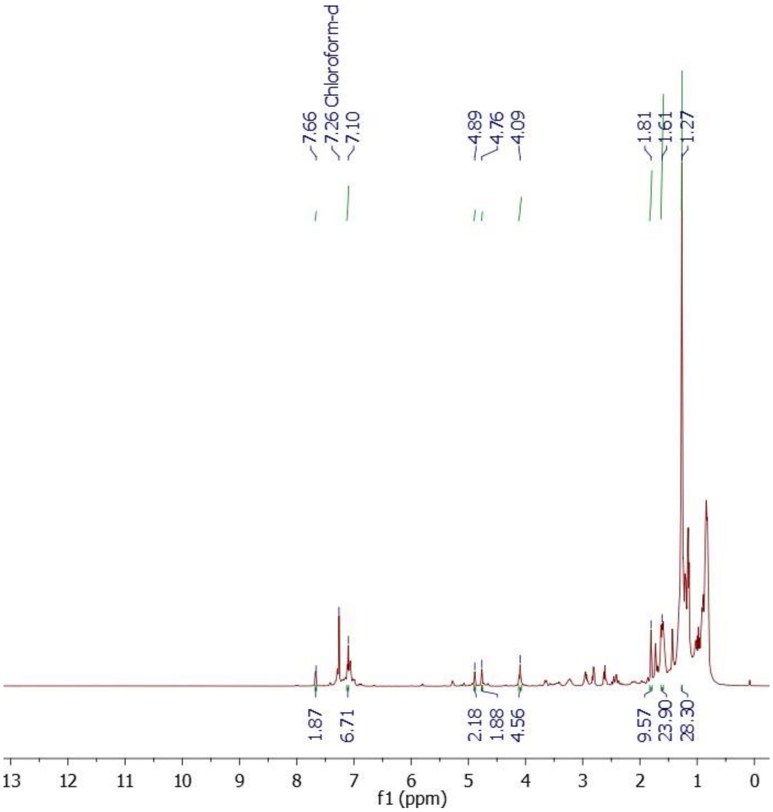
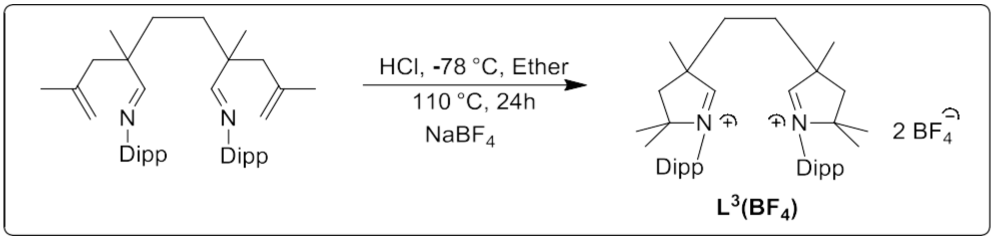


Fig 3.14: ^{1}H NMR of Ligand **L^3(2)**

After the formation of Ligand **L^3(2)**, we move to next step, Ligand **$L^3(BF_4)$** has been synthesized by dissolving the ligand **L^3(2)** in dry diethyl ether in conical flask followed by addition of HCl after then reaction mixture was heated at 110 ˚C for 24 hrs as a shown scheme 8. It results in a brown solid compound. This compound was then characterized by ^{1}H NMR spectroscopy (Fig 3.15).



Scheme 8: Synthesis of L^3(BF$_4$)

3.1.8 ^{1}H NMR spectra of Ligand L^3(BF$_4$)

The ^{1}H NMR spectrum(Fig 3.15) of L^3(BF$_4$)shows that a singlet at 9.30for two iminum protons more deshielded region and one triplet for 2 benzene protons at 7.52 and one doublet for 4 benzene protons at 7.34 and one multiplet at 2.65 is for 4 isopropyl protons and one singlet for 24 alkyl protons at 1.34 ppm. In this spectra the alkene protons comes in the region 4 to 5 ppm has disappeared, it was concluded that the cyclization takes place and the desired compound was formed.

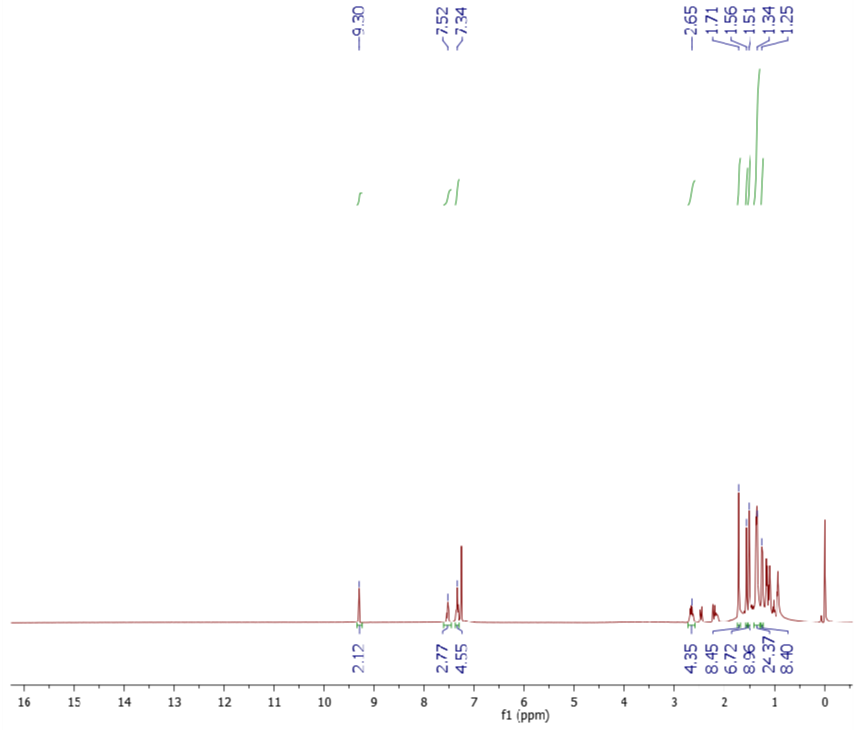
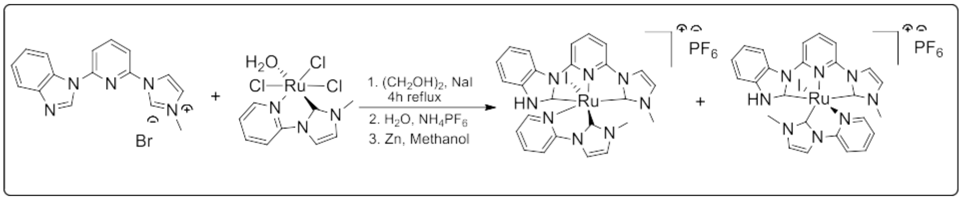


Fig 3.15: ^{1}H NMR of Ligand **L^3(BF$_4$)**

3.2. Synthesis and characterization of complexs:

After the formation of ligand precursor stried the metalation of these ligands with 4d transition metals. Complex **1** and **2**were synthesized by using the reaction condition which is shown in the scheme **9** and **10**.These metal complexes are [Ru(CN)^{Me}Cl3OH2] and [Y(III)($CH_3COO)_3\cdot 4H_2O$]. These complexes were prepared by the tridentate ligand precursors refluxed with the metal precursors refluxed in ethyleneglycol and DCM respectively in the Schlenk tube.

The synthesis of complex 1 (Scheme 9), takes place by dissolving the ligand **L^1(Br)** in ethylene glycol and [Ru(CN)^{Me}Cl3OH2] and refluxed under N2 for 4 hrs followed by Zn/methanol reduction to afford the complex. This compound was characterized by the ESI-MS data [M-PF$_6$]$^+$ molecular ion peak at m/z=663.0. It was concluded that the complex was formed and the mass spectrogram was matched with the isotopic pattern of the ruthenium with this metal complex.



Scheme 9: Synthesis of complex **1**

3.2.9ESI-MS of Complex 1

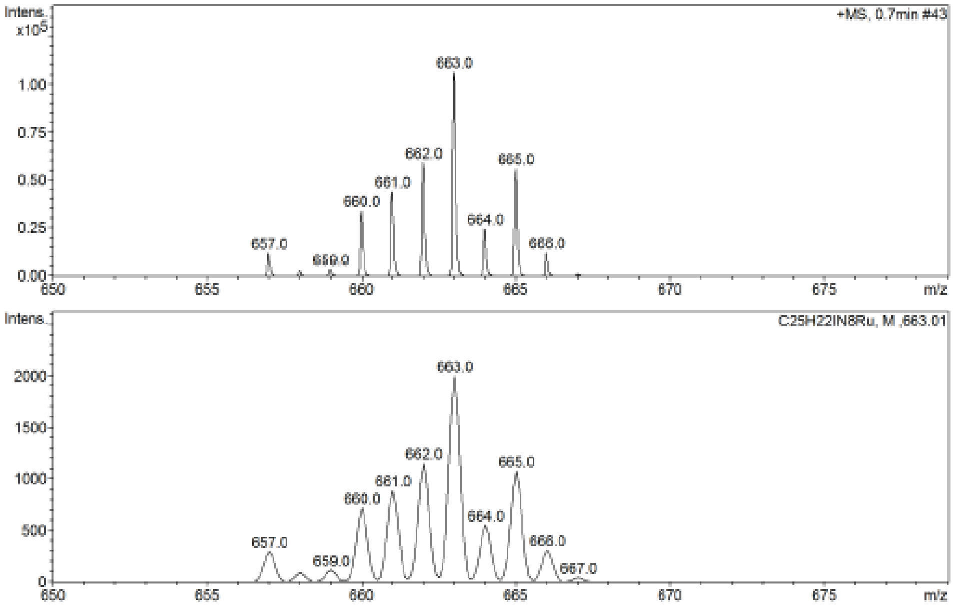
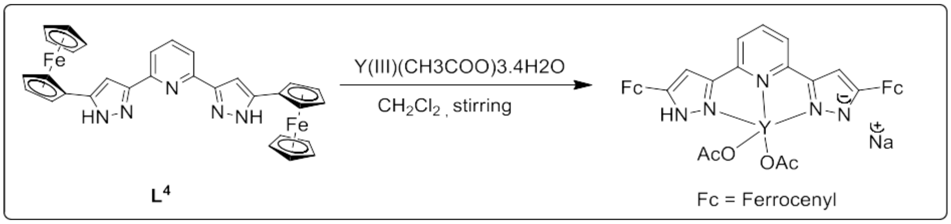


Fig 3.16: ESI-MS of Complex **1** in MeOH

The synthesis of complex 2 (Scheme 10), takes place by dissolving the ligand **L^4** and metal precursor $[Y(III)(CH_3COO)_3{\cdot}4H20]$ in DCM under N2 atmosphere for 12 hrs to afford the complex.This compound was characterized by ESI-MS and ^{1}H NMR spectroscopy.



Scheme 10: Synthesis of Complex 2

3.2.10 ^{1}H NMR spectra and ESI-MS of Complex 2

The ^{1}H NMR spectrum of complex 2 (Fig. 3.17) shows that a singlet at 13.20 is for one N-H peak in very highly deshielded region and one triplet for one pyridine proton at 8.17 and doublet for two pyridine protons at 7.92 and one singlet for two pyrazole protons at 7.14 and one doublet and one triplet for two Cp (cyclopentadienyl) ring proton at 4.85-4.79 (J=4.82) and one doublet and one triplet for two Cp ring proton at 4.44-4.34 (J=4.39) and doublet for 10 proton for other two Cp ring at 4.13-4.048 (J=4.105)and one singlet at 1.80 is for 6 acetyl proton. This compound was characterized by the ESI-MS data (Fig 3.18) the molecular ion peak at m/z=808.0. It was concluded that the complex was formed and the mass spectrogram was matched with the isotopic pattern of the yttrium with this metal complex.

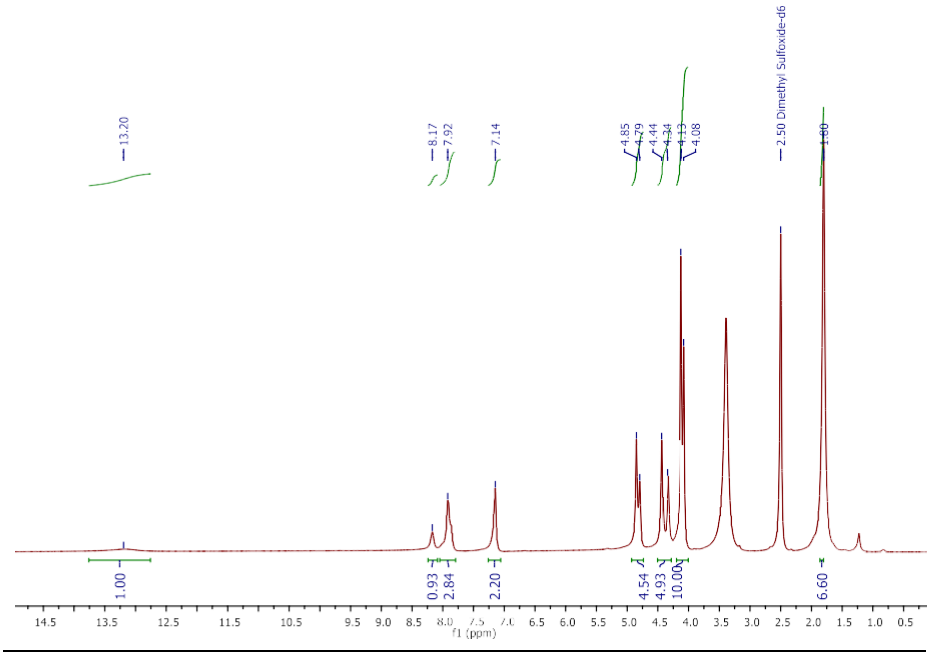


Fig 3.17: ^{1}H NMR of Complex **2**

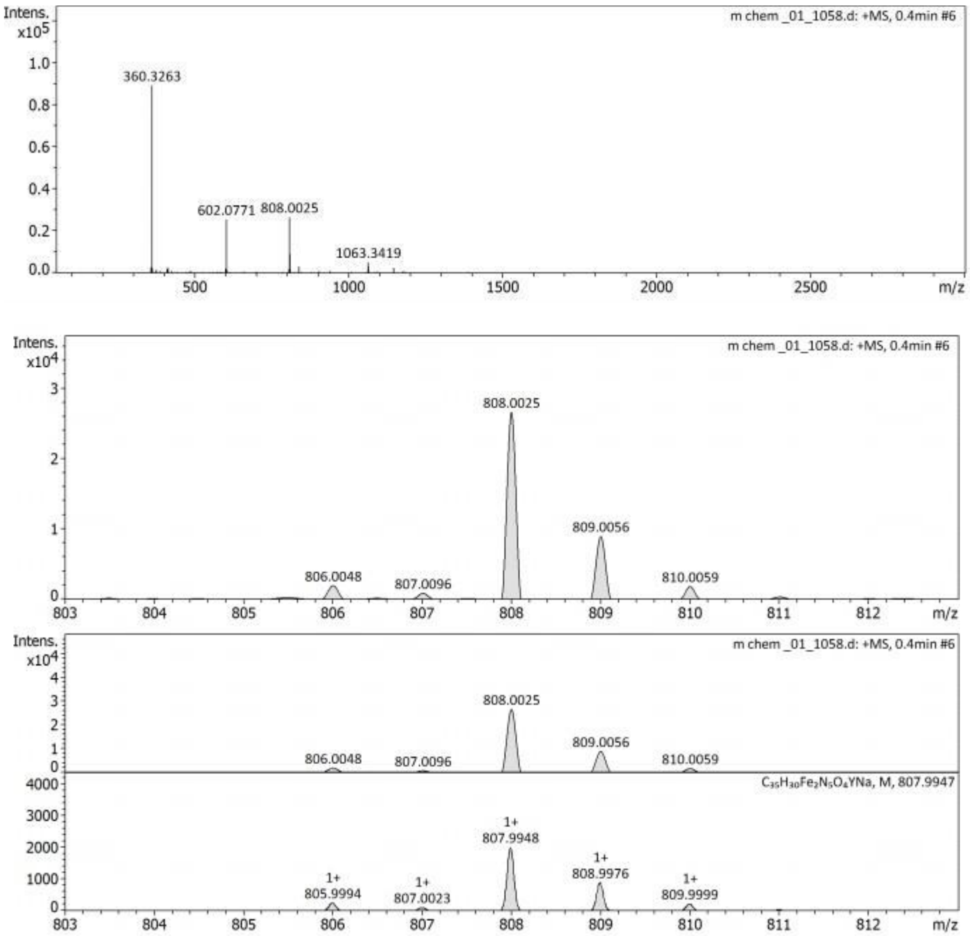


Fig 3.18: ESI-MS of Complex **2**in MeOH

Chapter four Conclusion and Future Prospective

4.1 Conclusion

We have reported two newly synthesized complex **1** and **2**with the pincer ligand platforms. Our literature survey also suggest metalation into the pincer cavity. Ruthenium (II) octahedral complexes having protic as well as classical carbenes with the help of earlier reported bi-dentate NHCs metal precursor and Yttrium complex reported with the NNN based pyrazole pincer ligand platforms. All the synthesized ligands and metal complexes have been characterized by different spectroscopic techniques.

4.2 Future prospective

In future properties and different catalytic activity of these metal complexes may be explored. The Ruthenium metal complex may show interesting activities towards transfer hydrogenation, small molecule activation like CO_2 and N_2 reduction. The newly synthesized Yttrium complex can be explored for its redox activity of the ligand.

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