Electron-Rich Metal Complexes with Multiple NHC Donor Ligands: Synthesis, Characterization and Reactivity

M.Sc. Thesis

By

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DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

June 2018

Electron-Rich Metal Complexes with Multiple NHC Donor Ligands: Synthesis, Characterization and Reactivity

A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
of
Master of Science

by

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June 2018

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Electron-Rich Metal Complexes with Multiple NHC Donor Ligands: Synthesis, Characterization and Reactivity** 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 own work carried out during the time period from July 2017 to June 2018 under the supervision of Dr. Amrendra Kumar Singh, Assistant Professor, IIT Indore.

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.

VISHAL BUDHIJA

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

Dr. AMRENDRA KUMAR SINGH

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Signature of Supervisor | Convener, DPGC

Date: | Date:

Signature of PSPC | Signature of PSPC

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ACKNOWLEDGEMENTS

With deep regards and profound respect, I avail this opportunity to express my deep sense of gratitude and indebtedness to Dr. Amrendra Kumar Singh for introducing the present project topic and for his inspiring guidance, constructive criticism and valuable suggestion throughout the project work. I gratefully acknowledge his constant encouragement and help in different ways to complete this project successfully. I would also like to extend my gratitude to my PSPC committee members Dr. Shaikh M. Mobin and Dr. Ajay Kumar Kushwaha and DPGC convener Dr. Sanjay Kumar Singh for their valuable suggestion and guidance.

I also take this opportunity to express a deep sense of gratitude towards our honorable Director, Prof. Pradeep Mathur for constantly motivating us for research and providing various facilities and a healthy environment, which helped me to focus on the project exclusively. I would also like to acknowledge all the faculty members of Chemistry discipline of IIT Indore for their supportive and humble gesture. Furthermore, I would like to thank SIC IIT Indore for instrumentation facilities.

I extend my regards to my lab mates Dr. Shilpi Misra, Dr, R. Rangasamy, Dr. Abhinav Raghuvanshi, Dr. Sasmita Mishra, Dr. G. Prakash, Dr. Radheshyam Ji, Dr. Kuldeep Gogoi, Ms. Dibya Yadv, Ms. Saniya Sheikh and Mr. Agnideep Das for their help and support and guidelines during the project.

I would like to express my special gratitude to Dr. Suryabhan Singh his help made this work much easier.

I got a lot of guidance from other disciplines also so I would like to extend my thanks to Dr. D.K. Rai and Dr. Sobhan Chatterjee.

I am thankful to Mr. Kinney Pandey, Mr. Ghanshyam Bhavsar, Dr. Archana and Mr. Manish Kushwaha for their technical help and support.

I also need to express my deepest love and gratitude to my lovable parents and friends near and far for their unconditional love and patience during this tenure.

Vishal Budhija

Discipline of Chemistry

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DEDICATED TO.....

MY Family

For their support and belief in my potential!

ABSTRACT

We have synthesized several ruthenium metal complexes with NHC donor ligands and NHC donor based pincer ligands. Interestingly, we have observed a complex containing not so common “abnormal” carbene bonded to the metal. This complex was fully characterized including single crystal x-ray structure. Other complexes having carbene based pincer ligands have also been synthesized and characterized. The catalytic activity of abnormal carbene based Ru(III) complex towards hydrogen transfer reactions for the conversion of ketone to alcohol has been explored. These complexes are potential candidate as a catalyst for several organic transformations.

TABLE OF CONTENTS

LIST OF FIGURES **xi-xii**

LIST OF SCHEMES **xiii**

LIST OF TABLES **xiv**

NOMENCLATURE **xv**

ACRONYMS **xvi**

Chapter One: Introduction **1-5**

1.1. General Introduction 1

1.2. Challenges in CO_2 reduction 1

1.3. Aim of the project 2
1.3.1 N-Heterocyclic Carbene Donors 2
1.3.2 Pincer type ligands 4
1.3.3 Target Complex 4

1.4 Motivation of our work 5

Chapter Two: Experimental Section **6-10**

2.1 Chemicals and Reagents 6

2.2 Instrumentation 6

2.3 Synthesis of Ligands and Complex 7
2.3.1 Synthesis of Ligand L1 7
2.3.2 Synthesis of Ligand L2 7
2.3.3 Synthesis of Ligand L3 8
2.3.4 Synthesis of Ligand L4 9
2.3.5 Synthesis of Ligand L5 9
2.3.6 Synthesis of Complex C1 9
2.3.7 Synthesis of Complex C2 9

2.4 Procedure for Transfer Hydrogenation Catalysis 10

Chapter Three: Results and Discussion 11-34

3.1 Syntheses of Ligands and Characterization 11-23

3.2 Syntheses of Complexes and Characterization 23-33

3.3 Characterization Data for Transfer Hydrogenation 33-34

Chapter 4: Conclusion and Future Prospective 35

4.1 Conclusion 35

4.2 Future Perspective 35

REFERENCES 36-38

LIST OF FIGURES

Figure	Description	Page
Figure 1	Imidazolylidene type NHCs of our interest	3
Figure 2	Abnormal or Pseudo Carbene	3
Figure 3	A Schematic diagram of a pincer-type complex containing pincer ligand and metal M	4
Figure 4	Pincer-type ligand of our interest	4
Figure 5	Proposed Metal Complex	5
Figure 6	Reported complex by Son et al	5
Figure 7	^{1}H NMR Spectrum of L1	12
Figure 8	^{13}C NMR Spectrum of L1	13
Figure 9	LCMS of L1	13
Figure 10	^{1}H NMR Spectrum of L2	14
Figure 11	^{13}C NMR Spectrum of L2	15
Figure 12	LCMS of L2	16
Figure 13	^{1}H NMR Spectrum of L3	17
Figure 14	^{13}C NMR Spectrum of L3	18
Figure 15	LCMS of L3	18
Figure 16	^{1}H NMR Spectrum of L4	19
Figure 17	^{13}C NMR Spectrum of L4	20
Figure 18	LCMS of L4	21
Figure 19	^{1}H NMR Spectrum of L5	22
Figure 20	^{13}C NMR Spectrum of L5	23
Figure 21	LCMS of L5	23
Figure 22	ORTEP view of complex C1 (Hydrogen atoms excluded for a clear view)	26
Figure 23	LCMS of C2	27
Figure 24	ORTEP view of complex C2 (Hydrogen	30

	atoms excluded for a clear view)	
Figure 25	Resonating structures of Normal and Abnormal Carbenes	31
Figure 26	PXRD Pattern for Complex C2	32
Figure 27	The simulated PXRD pattern of Complex C2	33
Figure 28	GCMS data of reaction mixture after 2 hours	33
Figure 29	GCMS data of reaction mixture after 12 hours	34
Figure 30	Future Aspects of Complex C2	35

LIST OF SCHEMES

Scheme	Description	Page
Scheme 1	Synthesis of Ligand L1	11
Scheme 2	Synthesis of Ligand L2	14
Scheme 3	Synthesis of Ligand L3	16
Scheme 4	Synthesis of Ligand L4	19
Scheme 5	Synthesis of Ligand L5	21
Scheme 6	Synthesis of Complex C1	24
Scheme 7	Synthesis of Complex C2	27

LIST OF TABLES

Table	Description	Page
Table 1	Selected standard potentials of CO_2 in aqueous solutions (V vs. SHE) at 1.0 atm and 25 ˚C, calculated according to the standard Gibbs energies of the reactants in reactions	2
Table 2	Selected bond lengths and bond angles for Complex C1	24-25
Table 3	Crystal refinement data for complex C1	25
Table 4	Selected bond lengths and bond angles for Complex C2	28
Table 5	Crystal refinement data for complex C2	28-29

NOMENCLATURE

θ	Theta
λ	Lambda
α	Alpha
β	Beta
γ	Gamma
Å	Angstrom
δ	Delta
ºC	Degree Centigrade
cm	Centimeter
%	Percentage
g	gram
mol	Mole
mmol	Millimole
mL	Milliliter
μL	Microlitre
nm	Nanometre

ACRONYMS

NHC	N-Heterocyclic Carbene
N	Nitrogen
O	Oxygen
C	Carbon
H	Hydrogen
Ru	Ruthenium
PPh_3	Triphenylphosphine
ESI-MS	Electrospray Ionisation Mass Spectrometry
LC-MS	Liquid Chromatography-Mass Spectrometry
TLC	Thin Layer Chromatography
NMR	Nuclear Magnetic Resonance
a.m.u	Atomic mass unit
DMSO	dimethylsulphoxide
ACN	Acetonitrile
UV-vis	Ultraviolet-visible spectroscopy
PXRD	Powder X-Ray Diffraction
$CDCl_3$	Deuterated chloroform
THF	Tetrahydrofuran

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

Carbon dioxide (CO_2) is the most infamous ozone-harming gas, discharged by both characteristic and counterfeit procedures. It is additionally a vital material for the development of every one of earth's plants and for some modern processes *[1–3]*. In a perfect situation, the CO_2 delivered on Earth ought to be adjusted with what is expended so that the level of CO_2 stays steady to keep up natural dependability. Shockingly, with the escalation of human modern exercises, this adjust has step by step been disturbed, driving to more CO_2 generation and making a dangerous atmospheric deviation a squeezing issue. Along these lines, diminishing CO_2 generation and changing over CO_2 into valuable materials is by all accounts essential, surely basic, for natural security, and different governments around the world have flagged their worry by expanding their interest in research to address the CO_2 issue. The distinctive proposed advancements tail one of two important approaches: to catch and topographically sequestrate CO_2, or to change over CO_2 into helpful low-carbon fuels *[4–7]*. In this day and age of high vitality requests, CO_2 change and usage is by all accounts a more appealing and promising arrangement. For CO_2 to be converted into useful materials like methanol, various techniques have been used one of these is molecular catalysis. But there are various challenges that researchers face during CO_2 reduction.

1.2 Challenges in CO_2 reduction

CO_2 is a linear gas having nonpolar nature, both aspects should be kept in mind that are thermodynamic aspects and kinetic challenges. From table 1 we can see that multi-electron transfer is more facile and useful than single electron transfer. So the target complex has to be designed in a way that it should be capable of multi-electron transfer.

Half-electrochemical thermodynamic reactions	Electrode potentials (V vs. SHE) under standard conditions
$CO_2(g) + 4H^+ + 4e^- = C(s) + 2H_2O(l)$	0.210
$CO_2(g) + 2H_2O(l) + 4e^- = C(s) + 4OH^-$	-0.627
$CO_2(g) + 2H^+ + 2e^- = HCOOH(l)$	-0.250
$CO_2(g) + 2H_2O(l) + 2e^- = HCOO^-(aq) + OH^-$	-1.078
$CO_2(g) + 2H^+ + 2e^- = CO(g) + H_2O(l)$	-0.106
$CO_2(g) + 2H_2O(l) + 2e^- = CO(g) + 2OH^-$	-0.934
$CO_2(g) + 4H^+ + 4e^- = CH_2O(l) + H_2O(l)$	-0.070
$CO_2(g) + 3H_2O(l) + 4e^- = CH_2O(l) + 4OH^-$	-0.898
$CO_2(g) + 6H^+ + 6e^- = CH_3OH(l) + H_2O(l)$	0.016
$CO_2(g) + 5H_2O(l) + 6e^- = CH_3OH(l) + 6OH^-$	-0.812
$CO_2(g) + 8H^+ + 8e^- = CH_4(g) + 2H_2O(l)$	0.169
$CO_2(g) + 6H_2O(l) + 8e^- = CH_4(g) + 8OH^-$	-0.659
$2CO_2(g) + 2H^+ + 2e^- = H_2C_2O_4(aq)$	-0.500
$2CO_2(g) + 2e^- = C_2O_4^{2-}(aq)$	-0.590
$2CO_2(g) + 12H^+ + 12e^- = CH_2CH_2(g) + 4H_2O(l)$	0.064
$CO_2(g) + 8H_2O(l) + 12e^- = CH_2CH_2(g) + 12OH^-$	-0.764
$2CO_2(g) + 12H^+ + 12e^- = CH_3CH_2OH(l) + 3H_2O(l)$	0.084
$2CO_2(g) + 9H_2O(l) + 12e^- = CH_3CH_2OH(l) + 12OH^-$	-0.744

Table 1: Selected standard potentials of CO_2 in aqueous solutions (V vs. SHE) at 1.0 atm and 25 ˚C, calculated according to the standard Gibbs energies of the reactants in reactions *[8]*.

1.3 Aim of the project

Our major aim of this project was to design an electron-rich complex which could be useful for reduction of CO2 into useful compounds like methanol of formate. For this, we have chosen N-Heterocyclic Carbene donor based ligands.

1.3.1 N-Heterocyclic Carbene Donors

Carbenes could be defined as neutral species having a divalent carbon with $6e^-$ in valence shell. Due to incomplete octet and unsaturated

coordination environment usually, carbenes without any support are supposed to be unstable intermediates in many organic reactions.

NHC can be defined as a special class of carbenes containing one carbene carbon and at least one nitrogen atom within ring structure *[9, 10]*. Nitrogen atoms nature of σ- acceptance, and π-donation stabilize the carbene carbon in both ways inductively and mesomerically by donating electrons into empty p-orbital. Cyclic nature of NHC also leads to more stability of singlet state by forcing carbene carbon into a bent, more sp^2 type arrangement. NHC of our interest possesses some extra stability because these are derived from heteroaromatic compounds and have a partial aromatic character such as imidazolium salts.

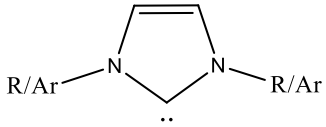


Figure 1: Imidazolylidene type NHCs of our interest

A similar type of species stabilized by just one Nitrogen atom is also known there carbene carbon is formed on the alternate position of C^2 (Figure 2) carbon. These species are termed as "Abnormal" carbene or "Pseudo" carbene *[11,12]*. These species are found to be more electron-donating than their normal analog.

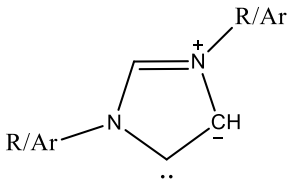


Figure 2: Abnormal or Pseudo Carbene

Other than these type of ligands we have used Pincer type ligands for generation of an electron-rich stable complex.

1.3.2 Pincer type ligands

These type of ligands are special tridentate ligands which bind to metal in a meridional fashion (Figure 3) providing a stable and robust core to the metal complex which leads to a very stable complex that can survive very harsh reaction conditions making it suitable for catalytic reactions.

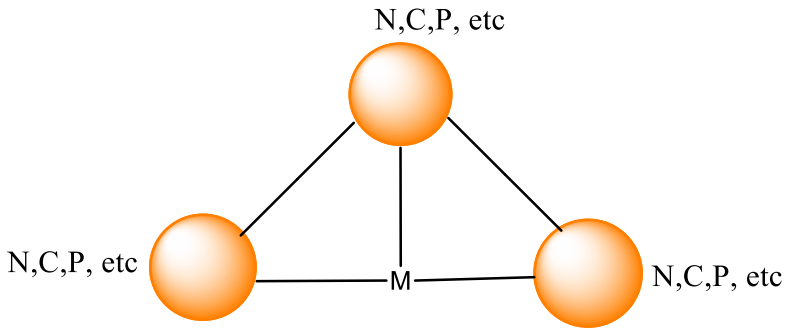


Figure 3: A Schematic diagram of a pincer-type complex containing pincer ligand and metal M

In our case we have used NHC based pincer type ligands as mentioned earlier NHCs are very strong electron donor so using them in pincer type fashion will surely help in the construction of electron rich complex.

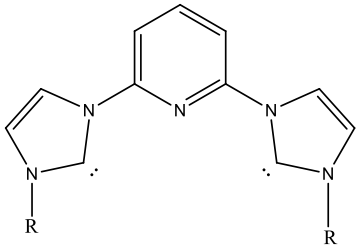


Figure 4: Pincer type ligand of our interest

1.3.3 Target Complex

We have proposed a complex having Ru metal and one NHC ligand occupying 2 coordination sites and one pincer type ligand occupying 3 meridional coordination sites and one site occupied by some halogen

or another group. The NHC and pincer will increase electron density on metal and the vacant site (halogen) will facilitate CO_2 coordination and activation with metal.

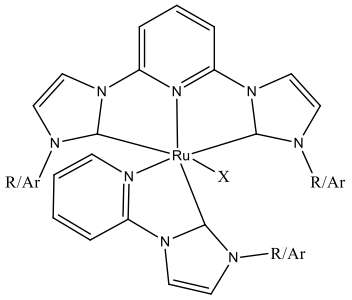
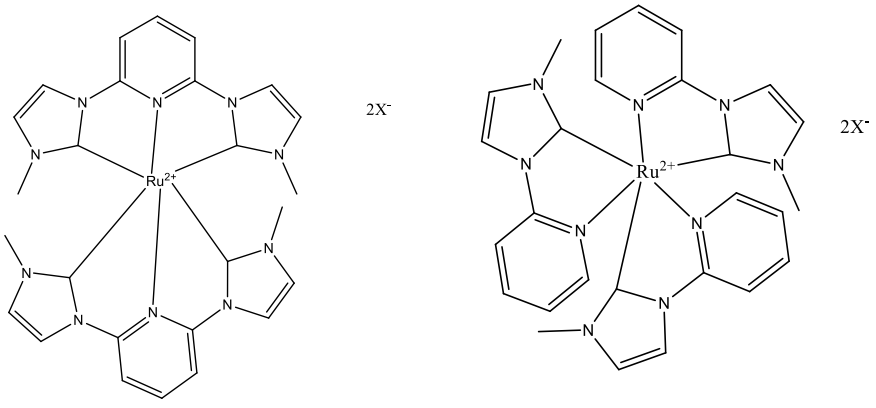


Figure 5: Proposed Metal Complex

1.4 Motivation of our work

Various groups have tried to reduce CO2 by various types of complexes with different metals. Since Ru can shuffle between multiple stable oxidation states so metal chose was Ru. Our main motivation was from Son et al. they reported saturated Ruthenium complexes containing similar type of ligands NHC ligands and Pincer type ligands (Figure 6a,b).



6a 6b

Figure 6: Reported complex by Son et al. *[13]*.

CHAPTER TWO

EXPERIMENTAL SECTION

2.1 Chemicals and Reagents:

All the chemicals were of analytical grade and used as received without further purification. These chemicals included Imidazole (SRL, 99%), 1-methylimidazole (Spectrochem, 99%), 2-bromopyridine (Spectrochem, 99%), 2,6-dibromopyridine (Alfa Aesar, 98%), potassium carbonate (SRL, 99.5%), sodium bicarbonate (SRL, 99.5%), sodium chloride (SRL, 99.9%), ruthenium trichloride trihydrate (SRL), iodomethane (Chem Labs, 99.8%), magnesium sulphate (SRL, 99%), cyclohexanone(Emplura, 99%), potassium hydroxide (Emplura, 85%).

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, microTOF-Q II mass spectrometer. Spectrophotometric measurements were performed on a Varian UV-Vis spectrophotometer (Model: Cary 100) using a quartz cuvette with a path length of 1 cm. Single-crystal X-ray structural studies were performed on an Agilent Technology Supernova CCD diffractometer equipped with a low-temperature attachment. The PXRD pattern for the samples was obtained using a Rigaku SmartLab automated X-ray diffractometer system. The diffraction angle was in the range of 5–40°. GC-MS was performed on GC-MS QP 2010 Ultra mass spectrometer from Shimadzu Analytical India Pvt. Ltd.

2.3 Synthesis of Ligands and Complex:

2.3.1 Synthesis of Ligand L1

L1 was synthesized by a little modification in reported procedure *[14]*. Under N2 atmosphere 2,6-dibromopyridine (2.3690 g, 10 mmol) and 1-methylimidazole (1.6 ml, 20 mmol) were taken in a round bottom flask. The oil bath temperature was set to 145 ˚C and the reaction mixture was set on continuous stirring for 17 h.

Brown solid was treated with DCM and diethyl ether to get the pure product in 80% yield (3.2 g).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 10.25 (s, 2H), 8.73 (s, 2H), 8.60 (t, 1H), 8.19 (d, 2H), 8.05 (s, 2H), 4.01ppm (s, 6H).

^{13}C NMR (DMSO-d6, 100 MHz): δ= 145.88, 145.52, 136.78, 125.72, 120.06, 114.76, 37.21 ppm. LCMS (ESI): calculated [M] $^{2+}$ = 241.1316, $[M/z]^{2+}$; observed $[M/z]^{2+}$ = 120.5779

2.3.2 Synthesis of Ligand L2

L2 was synthesized by combining two literature procedures *[15, 16]*. Under N_2 atmosphere one round bottom flask was charged with 2-bromopyridine (2 mL, 20mmol), K_2CO_3 (5.52 g, 40 mmol) and imidazole (4.08 g, 60 mmol). The reaction mixture was heated at 190 ˚C with continuous stirring for 18 h. The obtained solid was cooled and dissolved in water then extracted with DCM three times organic layers were combined and further washed with a saturated aqueous solution of sodium bicarbonate and one time with brine, the organic layer was dried over magnesium sulfate and the solvent was dried under reduced pressure. This gives pure L4 in 90% yield (2.75 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.64 (s, 1H), 8.52 (s, 1H), 7.98 (t, 1H), 7.81 (s, 1H), 7.52 (d, 1H), 7.4 (t, 1H), 7.36 ppm (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ= 149.19, 139.11, 135.00, 130.64, 122.22, 116.23, 112.41 ppm. LCMS (ESI): [M] calculated = 145.0713 $[M+H]^+$ observed = 146.0786

Now L4 (1 g, 6.53 mmol) and methyl iodide (404 µL, 6.53 mmol) were refluxed in acetonitrile at 80 ˚C under N_2 atmosphere for 8 hours off-white ppt was filtered off and washed with diethyl ether giving pure product in 74% yield (1.426 g)

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 10.04 (s, 1H), 8.65 (s, 1H), 8.50 (s, 1H), 8.22 (t, 1H), 8.02 (d, 2H), 8.05 (s, 1H), 7.97 (s, 1H), 7.64 (s, 1H), 3.98 ppm (s, 3H).

^{13}C NMR (DMSO-d6, 100 MHz): δ= 149.64, 146.74, 141.02, 135.93, 125.56, 125.18, 119.36, 114.51, 36.81 ppm. LCMS (ESI): $[M]^+$ observed = 160.0869; $[M]^+$ calculated = 160.0997.

2.3.3 Synthesis of Ligand L3

L3 was synthesized by literature procedure *[17]*. Under N_2 atmosphere one round bottom flask was charged with 2,6-dibromopyridine (1 g, 3.78mmol), K_2CO_3 (2.089 g, 15.12 mmol) and imidazole (1.546 g, 22.73 mmol). The reaction mixture was heated at 190 ˚C with continuous stirring for 18 h. The obtained solid was cooled and dissolved in water then extracted with DCM three times organic layers were combined and further washed with a saturated aqueous solution of sodium bicarbonate and one time with brine, the organic layer was dried over magnesium sulfate and the solvent was dried under reduced pressure. This gives pure L3 in 87 % yield (735 mg).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.53 (s, 1H), 8.52 (s, 2H), 8.12 (t, 1H), 7.82 (s, 2H), 7.44 (d, 2H), 7.38 ppm (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ= 148.83, 142.56, 135.43, 131.57, 116.55, 110.08 ppm. LCMS (ESI): [M] calculated = 211.0750; $[M+Na]^+$ observed = 234.0938.

2.3.4 Synthesis of Ligand L4

Earlier described in the synthesis of L2.

2.3.5 Synthesis of Ligand L5

L5 was synthesized by a little modification in reported procedure *[14]*. Under N2 atmosphere 2-bromopyridine (670 µL, 6.72 mmol) and 1-t-butylimidazole (1 mL, 8.06 mmol) were taken in a round bottom flask. The oil bath temperature was set to 145 ˚C and the reaction mixture was set on continuous stirring for 17 h.

Brown solid was treated with DCM and diethyl ether to get the pure product in 83% yield (1.58 g).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 10.04 (s, 1H), 8.65 (s, 1H), 8.50 (s, 1H), 8.22 (t, 1H), 8.02 (d, 2H), 8.05 (s, 1H), 7.97 (s, 1H), 7.64 (s, 1H), 3.98 ppm (s, 3H).

^{13}C NMR (DMSO-d6, 100 MHz): δ= 149.64, 146.74, 141.02, 135.93, 125.56, 125.18, 119.36, 114.51, 36.81 ppm. LCMS (ESI): $[M]^+$ calculated= 202.1339; $[M]^+$ observed =202.1426.

2.3.6 Synthesis of Complex C1

This complex was formed during synthesis of our final complex (Figure 5) L1 and L2 both were taken 1:1 equivalent and were refluxed with rutheniumtrichloride trihydrate in ethylene glycol for 14 hours solution turned yellow and methanol solution of ammonium hexafluorophosphate nothing was precipitated out and the mixture was left for 5-6 days undisturbed yellow colour crystals were obtained later on X-Ray analysis that complex was the same as reported by Son et. al. but these crystals were not reported.

2.3.7 Synthesis of Complex C2

This material was prepared by a literature procedure *[20]*. To 1.0 g (3.8 mmol) of rutheniumtrichloride trihydrate were added 1.12 g (3.8

mmol) of L2 and 5.0 mL (5.0 mmol) of 1.0 N HCl. The mixture was stirred for 30 min and then allowed to stand in a stoppered flask for 15 days. The reaction was filtered, washed with water and ether, and allowed to dry in air to yield 1.4 g (93%) of brown solid crystals. LCMS (ESI): $[M]^+$ calculated = 348.9313; $[M]^+$ observed = 348.9333.

2.4 Procedure for Transfer Hydrogenation Catalysis

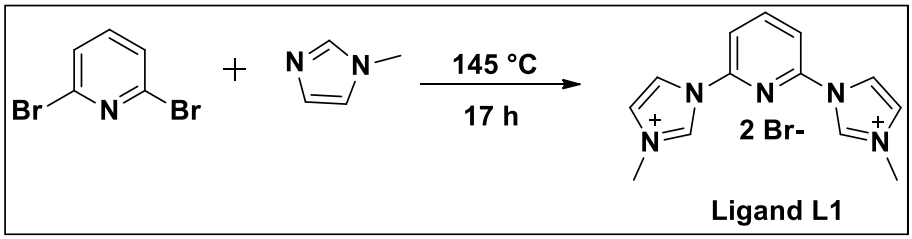
Cyclohexanone (0.2 ml) was refluxed with KOH in isopropanol with 0.2 mg of complex C2 at 80 °C for 12 hours and GC was taken after 2 hours and after completion of conversion.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Syntheses of Ligands and Characterization

Ligand L1 was synthesized by heating 2,6-dibromopyridine with methylimidazole as shown in Scheme 1. The final product was obtained with 80% yield. Obtained solid was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



Scheme 1: Synthesis of Ligand L1.

Figure 7 showing the ^{1}H NMR spectrum of L1 from there we can see that a singlet at 10.25 is for two imidazolium protons and 1 triplet for 1 hydrogen is there that is for pyridines top carbon. 3 doublet of 2 protons each are there in aromatic region (8.75-8.05) 1 from pyridine and the other 2 doublets that contains 2 hydrogens 1-1 each from methylimidazoles from each imidazole, a singlet at 4.01 with 6 protons 3 from each methyl present in molecule this signifies that our idea about the doublets was completely justified and the molecule is symmetric and both methylimidazoles are identical.

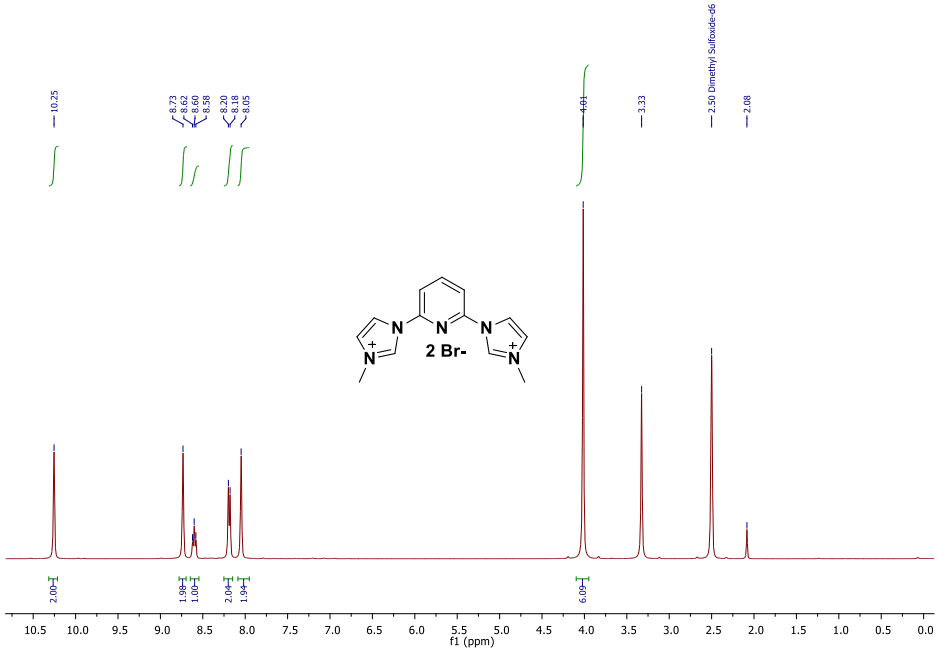


Figure 7: ^{1}H NMR Spectrum of L1

Since the molecule is symmetric its ^{13}C NMR spectrum clear the picture more in Figure 8 we can see that there are 8 peaks of carbons instead of 13 carbons because one plane of symmetry is passing from pyridine containing nitrogen and one carbon dividing the whole molecule into two identical halves each containing one methylimidazole so 3 carbons from imidazole ring and one of methyl and two of half pyridine appears on the same ppm values as other half and one peak corresponds to the carbon from which plane of symmetry is passing.

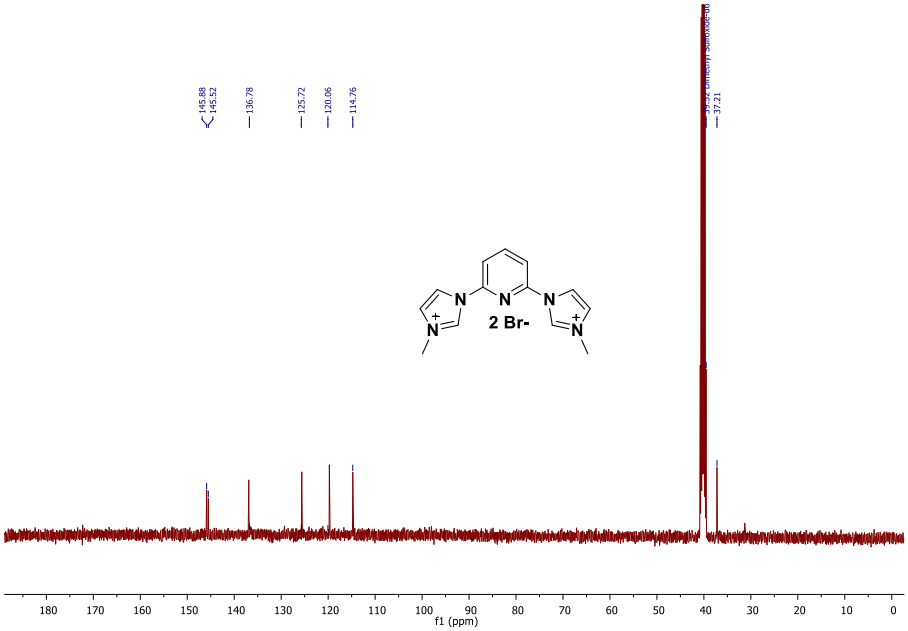


Figure 8: ^{13}C NMR Spectrum of L1

For final confirmation LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 9. Calculated [M] $^{2+}$ = 241.1316, [M/z]$^{2+}$= 120.5658; observed [M/z] $^{2+}$ = 120.5779

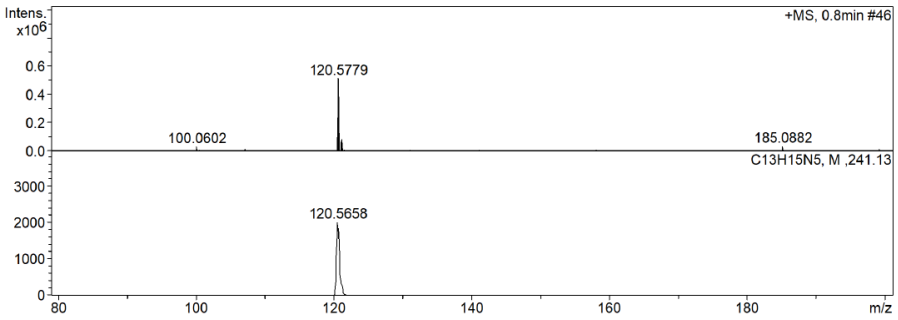
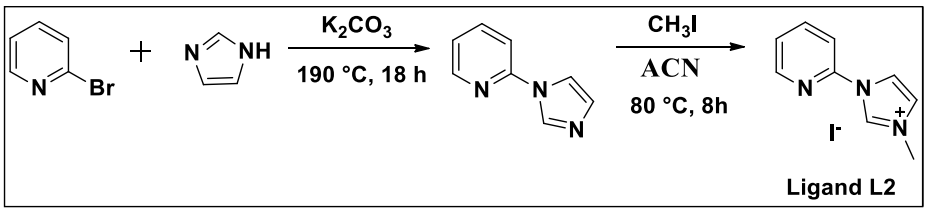


Figure 9: LCMS of L1

Ligand L2 was synthesized by heating 2-bromopyridine in neat condition with potassium carbonate and imidazole as shown in scheme

2 and with obtained product next step reaction was set up with methyl iodide in acetonitrile. The final compound was obtained with 74% yield. Obtained solid was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



Scheme 2: Synthesis of Ligand L4 and Ligand 2.

Figure 10 showing the ^{1}H NMR spectrum of L2 from there we can see that a singlet at 10.04 is for imidazolium proton and 1 triplet for 1 hydrogen is there that is for pyridines top carbon. 6 peaks in aromatic region (8.65-7.64) 4 from pyiridine and the other 2 hydrogens from methylimidazole, a singlet at 3.98 with 3 protons from methyl present in molecule.

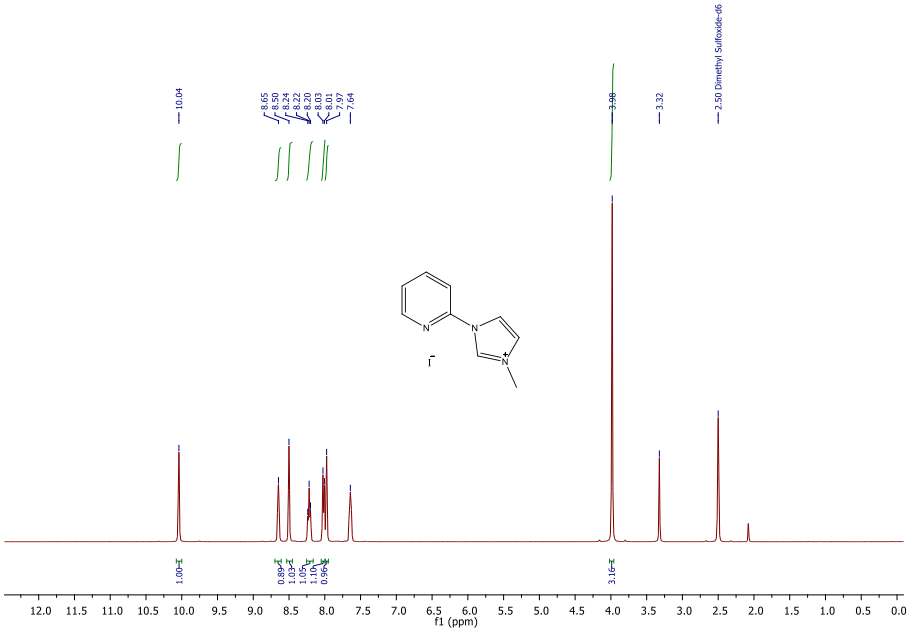


Figure 10: ^{1}H NMR spectrum of L2

From ^{13}C NMR Spectrum of L2 Figure 11, we can say that each carbon is different and the spectrum is showing 9 different peaks for 9 carbons. The methyl carbon peak could be identified at 36.81 ppm.

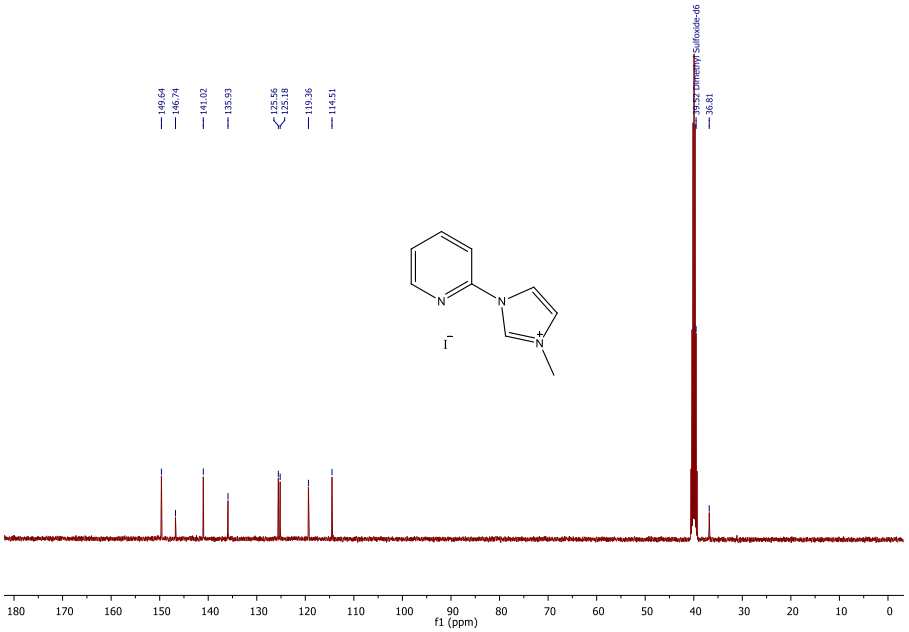


Figure 11: ^{13}C NMR Spectrum of L2

For final confirmation LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 12. $[M]^+$ observed = 160.0869; $[M]^+$ calculated = 160.0997.

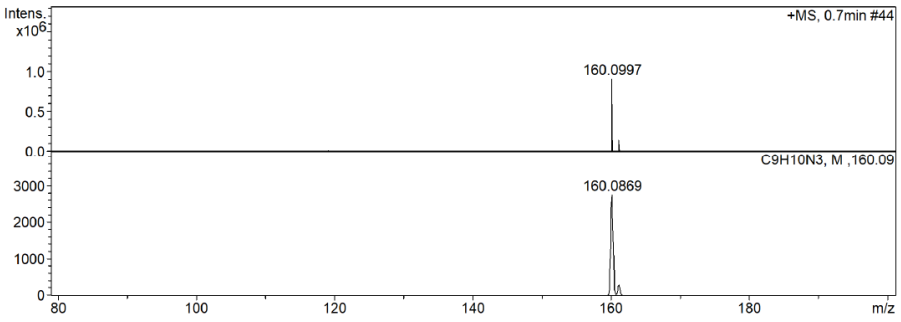
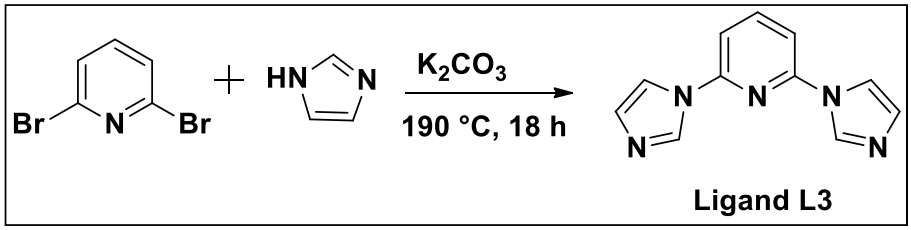


Figure 12: LCMS of L2

Ligand L3 was synthesized by heating 2,6-dibromopyridine with potassium carbonate and imidazole as shown in scheme 3. The final product was obtained with 87% yield. Obtained solid was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



Scheme 3: Synthesis of Ligand L3

Figure 12 showing the ^{1}H NMR spectrum of L3 from there we can see that a singlet at 8.53 is for two imidazole protons at C1 and 1 triplet for 1 hydrogen is there that is for pyridines top carbon. 3 doublet of 2 protons each are there in aromatic region (8.14-7.38) 1 from pyridine and the other 2 doublets that contains 2 hydrogens 1-1 each from imidazoles from each imidazole, this signifies that our idea about the doublets was completely justified and the molecule is symmetric and both imidazoles are identical.

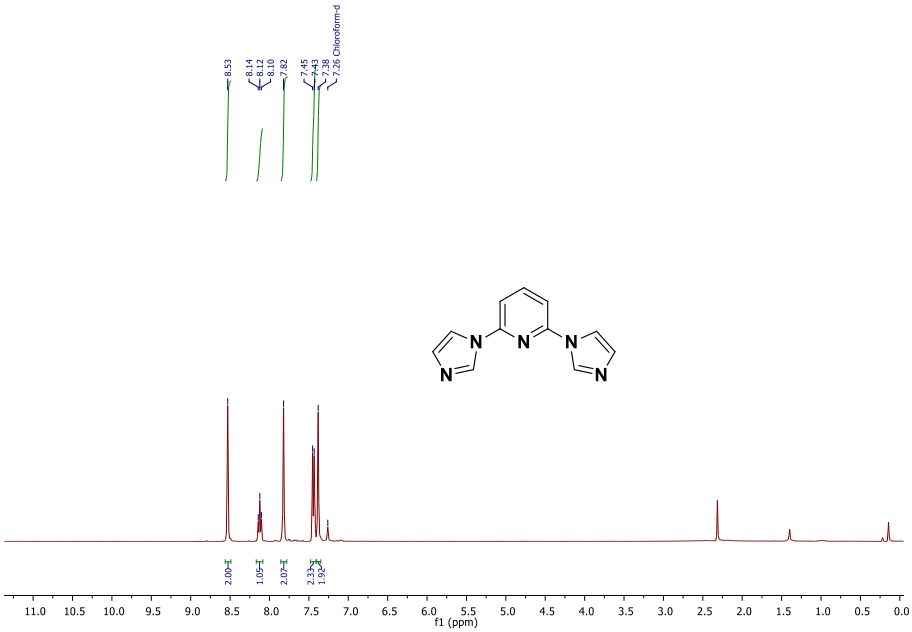


Figure 13: ^{1}H NMR Spectrum of L3

Since the molecule is symmetric its ^{13}C NMR spectrum clear the picture more in Figure 14 we can see that there are 6 peaks of carbons instead of 11 carbons because one plane of symmetry is passing from pyridine containing nitrogen and one carbon dividing the whole molecule into two identical halves each containing one imidazole so 3 carbons from imidazole ring and two of half pyridine appears on the same ppm values as other half and one peak corresponds to the carbon from which plane of symmetry is passing.

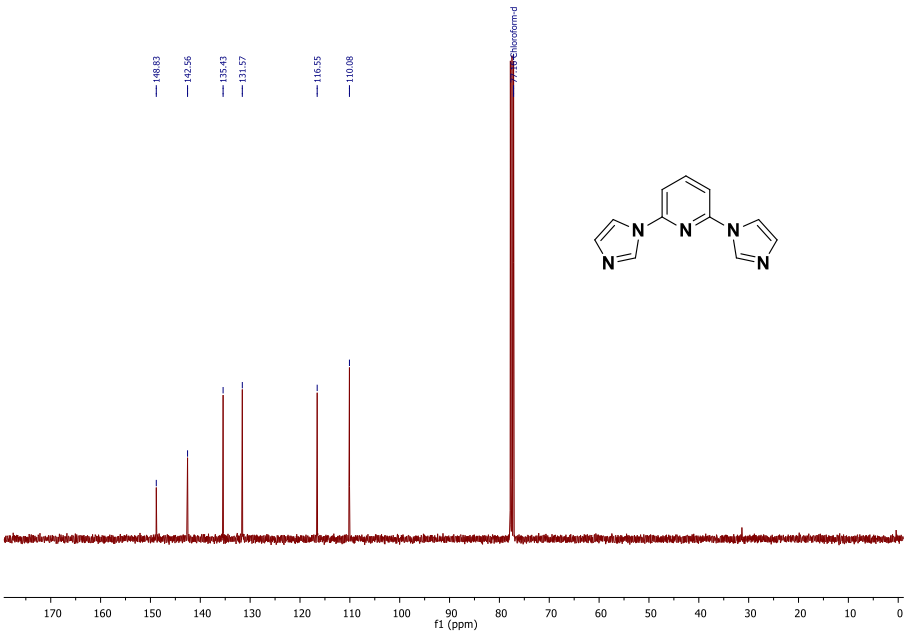


Figure 14: ^{13}C NMR Spectrum of L3

For final confirmation LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 15. [M] calculated = 211.0750; $[M+Na]^+$ observed = 234.0938.

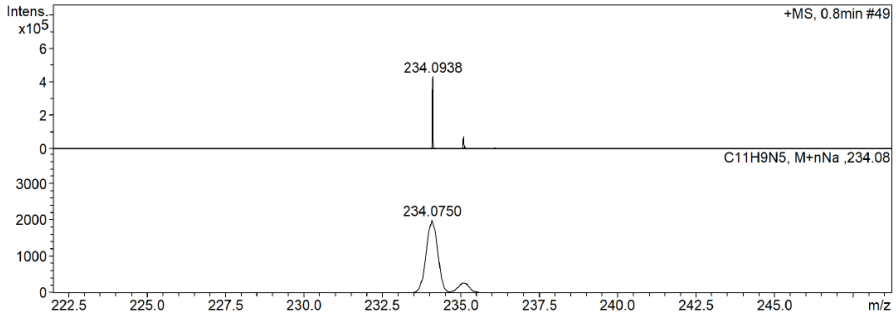
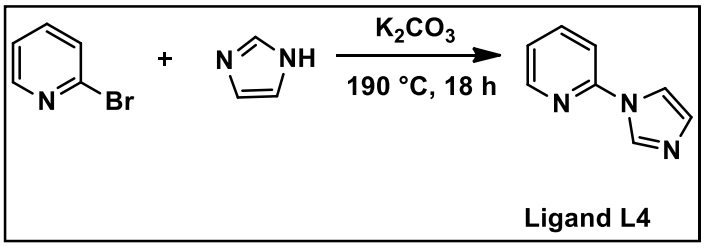


Figure 15: LCMS of L3

Ligand L2 was synthesized by heating 2-bromopyridine in neat condition with potassium carbonate and imidazole as shown in scheme 4. The final product was obtained with 90% of yield. Obtained solid was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



Scheme 4: Synthesis of Ligand L4

Figure 16 showing the ^{1}H NMR spectrum of L2 from there we can see that a singlet at 8.04 is for imidazole C1 proton and 1 triplet for 1 hydrogen is there that is for pyridines top carbon. 6 peaks in aromatic region (8.52-7.35) 4 from pyridine and the other 2 hydrogens from imidazole.

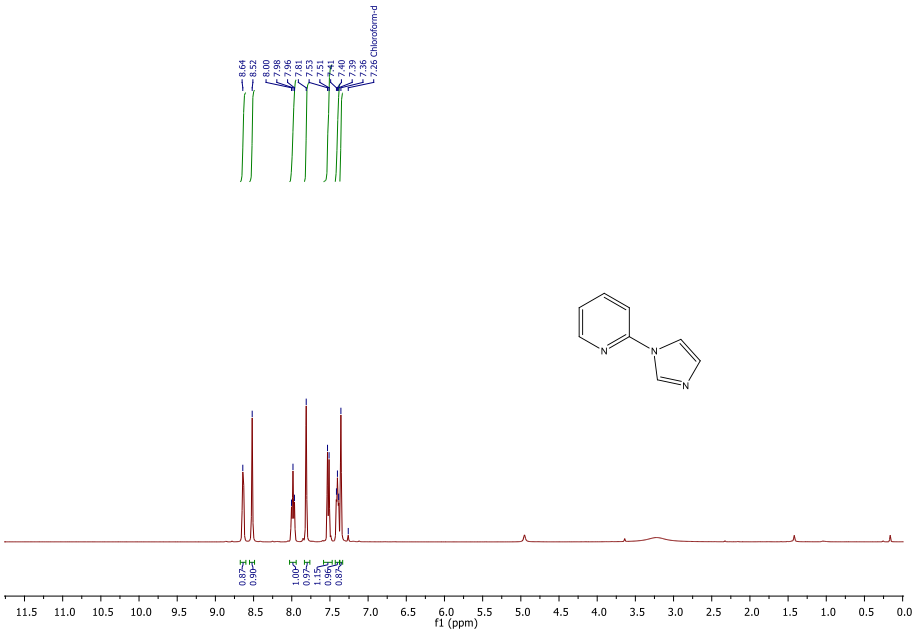


Figure 16: ^{1}H NMR Spectrum of L4

From ^{13}C NMR Spectrum of L2 Figure 17, we can say that each carbon is different and the spectrum is showing 8 different peaks for 8 carbons.

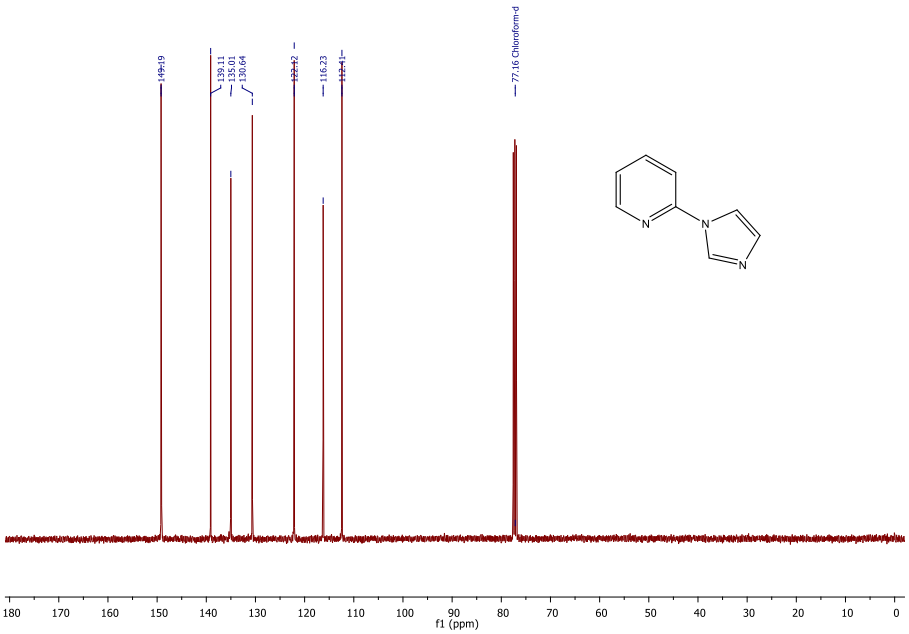


Figure 17: ^{13}C NMR Spectrum of L4

For final confirmation LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 18. [M] calculated = 145.0713; $[M+H]^+$ observed =146.0786.

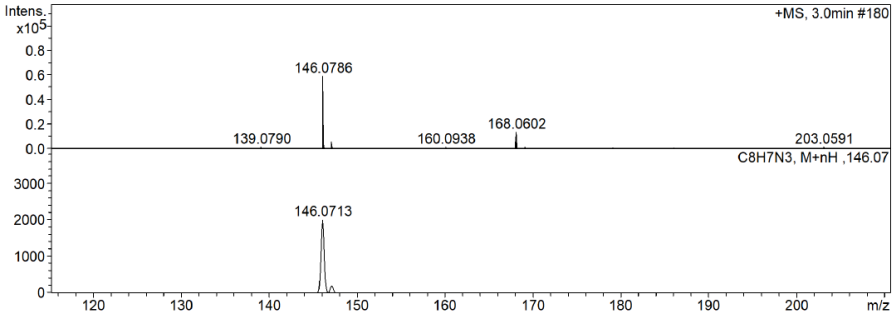
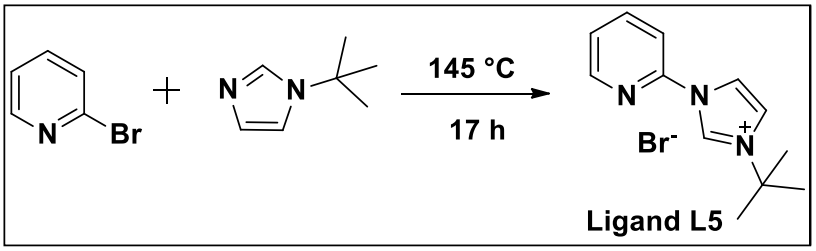


Figure 18: LCMS of L4

Ligand L1 was synthesized by heating 2-bromopyridine with t-butyllimidazole as shown in Scheme 5. The final product was obtained with 83% yield. Obtained solid was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.



Scheme 5: Synthesis of Ligand L5

Figure 19 showing the ^{1}H NMR spectrum of L2 from there we can see that a singlet at 9.98 is for imidazolium proton and 1 triplet for 1 hydrogen is there that is for pyridines top carbon. 6 peaks in aromatic region (8.66-7.64) 4 from pyridine and the other 2 hydrogens from methylimidazole, a singlet at 1.68 with 9 protons from t-butyl group present in the molecule.

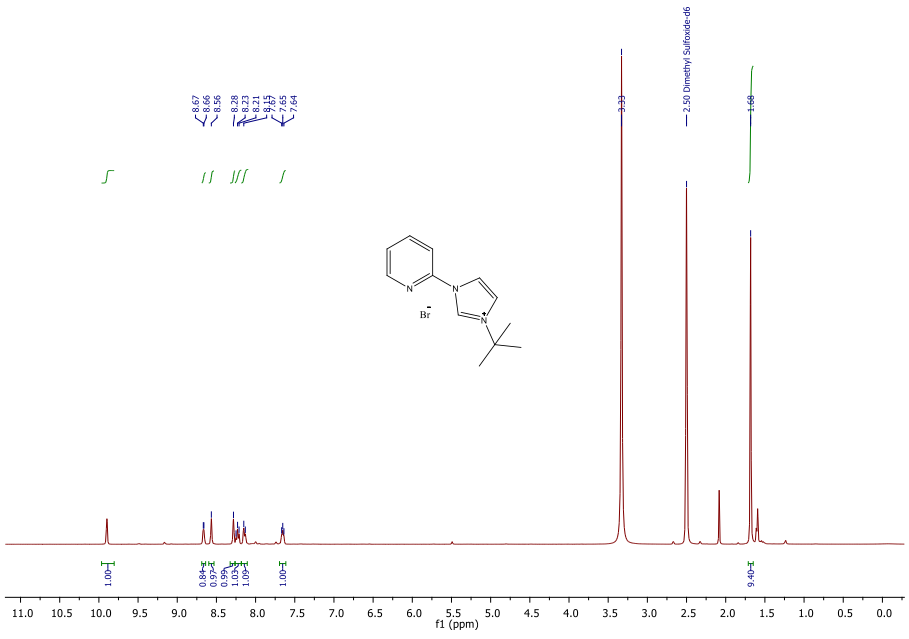


Figure 19: ^{1}H NMR Spectrum of L5

From ^{13}C NMR Spectrum of L5 Figure 20, we can say that each carbon is different and the spectrum is showing 9 different peaks for 9 carbons. The methyl carbons of t-butyl are all identical and their peak could be identified at 20.24 ppm.

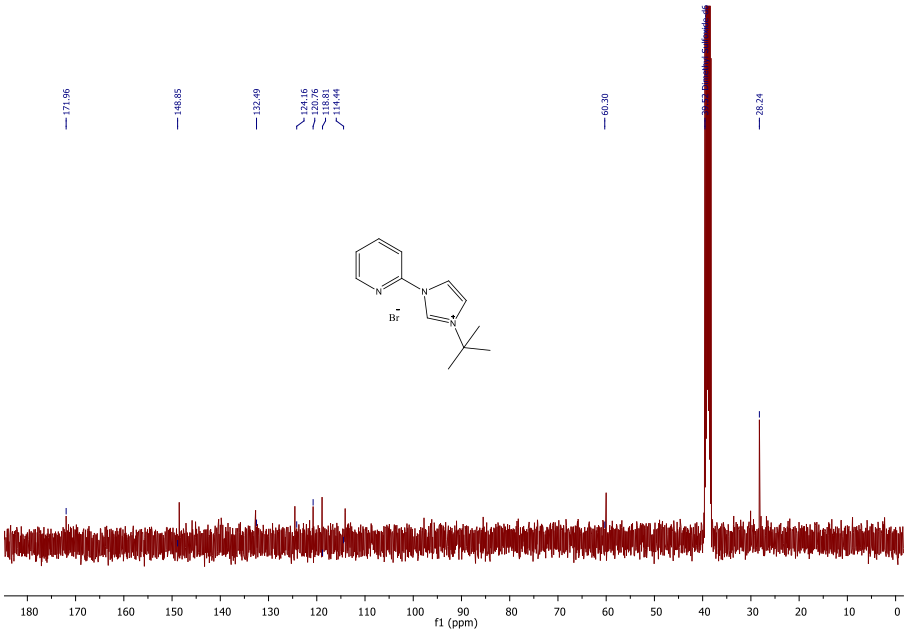


Figure 20: ^{13}C NMR Spectrum of L5

For final confirmation LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 21. $[M]^+$ calculated= 202.1339; $[M]^+$ observed =202.1426.

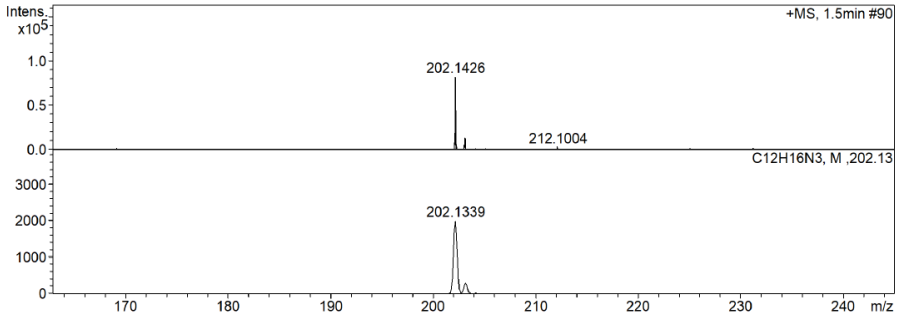
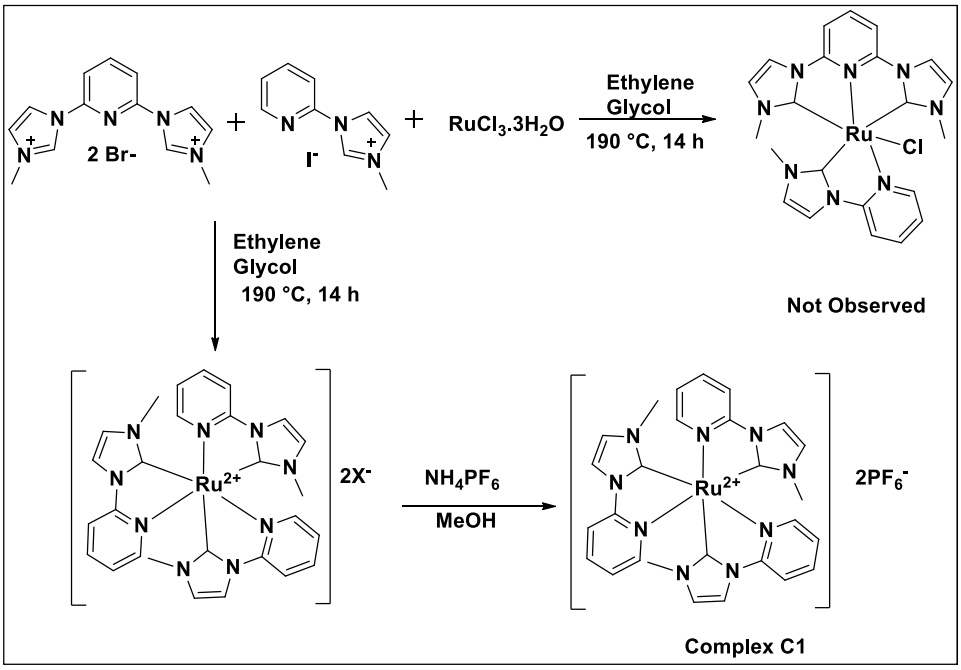


Figure 21: LCMS of L5.

3.2 Syntheses of Complexes and Characterization

Complex C1 was synthesized by refluxing L1 and L2 with rutheniumtrichloride trihydrate in ethylene glycol as shown in scheme 6. This complex was characterized by Single Crystal X-Ray Diffraction.



Scheme 6: Synthesis of Complex C1.

For complex C1 selected bond lengths and bond angles are given in Table 2 and the details of data collection conditions and parameters of refinement process are given in Table 3.

Complex C1	
Ru(1)- C(1)	2.080(8)
Ru(1)- N(1)	2.052(5)
C(1)-Ru(1)-C(1)^2	97.1(4)
N(1)-Ru(1)- N(1)^2	95.7(3)
N(1)-Ru(1)-C(1)	78.6(3)

N(1)-Ru(1)-C(1)^2	173.0(3)
C(1)-Ru(1)- N(1)^2	88.9(3)

Table 2: Selected bond lengths and bond angles for Complex C1

Complex C1	
Empirical Formula	C7.71 H7.71 F3.43 N2.57 P0.57 Ru0.29
Formula weight	248.17
Crystal system	Trigonal
Space group	P 3 c 1
a (Å)	10.4762(5)
b (Å)	10.4762(5)
c (Å)	17.0593(10)
α (°)	90
β (°)	90
γ(°)	120
V (Å^3)	1621.43(18)
ρ_{calcd} (mg m^{-3})	1.779
Z	7
μ (mm^{-1})	0.688
θ ranges (°)	3.278 to 28.968
Reflections collected/ unique	12684 / 2606
R(int)	0.0615
Goodness-of-fit (GOF) on F^2	1.052
Final R indices [I > 2σ(I)]	R1 = 0.0566, wR2 = 0.1358
R indices (all data)	R1 = 0.0927, wR2 = 0.1710

Table 3: Crystal refinement data for complex C1

Crystal Structure of Complex C1

Complex one has a mononuclear trigonal structure having Ruthenium metal in the centre with octahedral geometry. Out of six coordination sites three are occupied with Nitrogen and other three are occupied by carbene carbons. This is a highly symmetric structure with all the three ligands being identical and same bond lengths from central atom justify the observation. Ruthenium is having +2 charge which is neutralized by counterion hexafluorophosphate. Figure 23 showing the ORTEP view of Complex 1 with 30% probability. Hydrogen atoms were excluded for more clarity and understanding. From its structure, we can see that complex is having complete symmetry so only one of the three ligands atoms is labeled as N1, C1 etc. While all others are considered to be identical to these atoms.

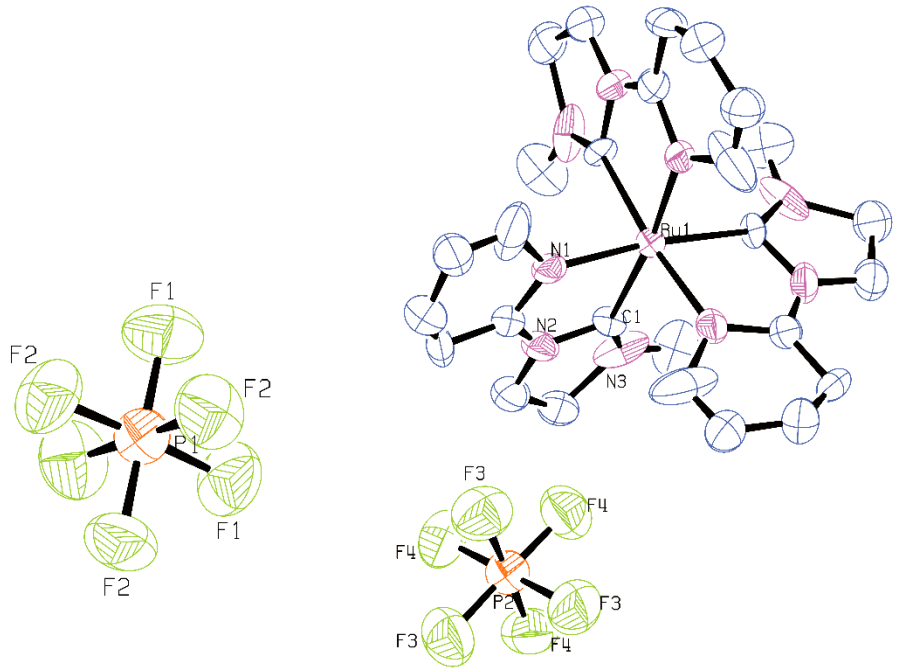
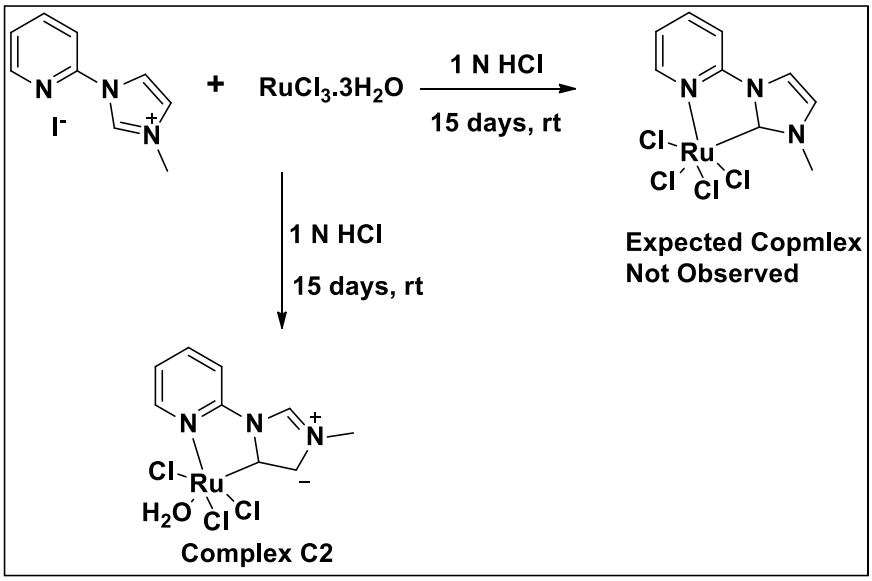


Figure 22: ORTEP view of complex C1 (Hydrogen atoms excluded for a clear view)

Complex C2 was synthesized by adding L1 and rutheniumtrichloride trihydrate to HCl and kept for 15 days as shown in scheme 7 and the final product was obtained with 93% yield. Complex C2 was then characterized by mass spectrometry, Single, and Powder X-Ray Diffraction.



Scheme 7: Synthesis of Complex C2.

LCMS in positive mode was performed for the compound in methanol and was compared with the simulated pattern for this compound from Bruker mass analysis software and that was matching with the spectrogram obtained for our compound that could be seen from Figure 23.

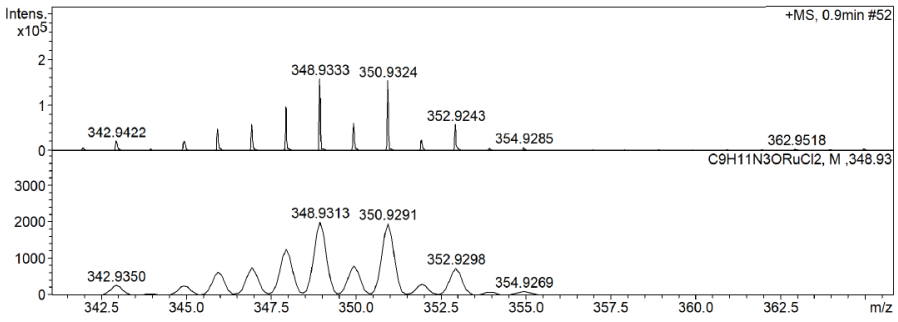


Figure 23: LCMS of C2

For complex C2 selected bond lengths and bond, angles are given in Table 4 and the details of data collection conditions and parameters of refinement process are given in Table 5.

Complex C2	
Ru(1)-C(1)	1.969(5)
Ru(1)-N(4)	2.076(4)
Ru(1)-O(w1)	2.233(3)
Ru(1)-Cl(1)	2.3651(13)
Ru(1)-Cl(3)	2.3740(13)
Ru(1)-Cl(2)	2.3845(13)
C(1)-Ru(1)-N(4)	79.50(18)
C(1)-Ru(1)-O(w1)	175.47(17)
N(4)-Ru(1)-O(w1)	97.09(15)
C(1)-Ru(1)-Cl(1)	91.73(14)
N(4)-Ru(1)-Cl(1)	88.59(12)
O(w1)-Ru(1)-Cl(1)	85.18(10)
C(1)-Ru(1)-Cl(3)	94.49(14)
N(4)-Ru(1)-Cl(3)	86.84(12)
O(w1)-Ru(1)-Cl(3)	88.27(10)
Cl(1)-Ru(1)-Cl(3)	171.49(5)
C(1)-Ru(1)-Cl(2)	95.11(14)
N(4)-Ru(1)-Cl(2)	174.50(11)
O(w1)-Ru(1)-Cl(2)	88.35(10)
Cl(1)-Ru(1)-Cl(2)	92.70(5)
Cl(3)-Ru(1)-Cl(2)	92.53(5)

Table 4: Selected bond lengths and bond angles for Complex C2

Complex C2	
Empirical Formula	C9 H11 Cl3 N3 O1.50 Ru
Formula weight	392.63
Crystal system	Monoclinic
Space group	I 2/a

a (Å)	16.1655(5)
b (Å)	8.2118(3)
c (Å)	21.0093(7)
α (°)	90
β (°)	102.546(3)
γ(°)	90
V (Å^3)	2722.34(16)
ρ_{calcd} (mg m^{-3})	2722.34(16)
Z	8
μ (mm^{-1})	1.731
θ ranges (°)	3.563 to 28.843
Reflections collected/ unique	6396 / 3111
R(int)	0.0454
Goodness-of-fit (GOF) on F^2	1.060
Final R indices [I > 2σ(I)]	R1 = 0.0449, wR2 = 0.0987
R indices (all data)	R1 = 0.0649, wR2 = 0.1138

Table 5: Crystal refinement data for complex C2

Crystal Structure of Complex C2

Complex C2 is a mononuclear monoclinic complex having Ruthenium as a central atom with octahedral geometry. Out of six coordination sites two are occupied by our NHC but here our expectation was that metal will bind to the C1 carbon of imidazole that is the carbene carbon but instead metal is bound to one nitrogen from pyridine and C5 of imidazole means “abnormal” carbene generation has taken place. Although the reason of this is not clear this might be justified as a

special case and normal carbene complex could be a kinetically stable product but complex 2 seems to be thermodynamically stable product because crystal growing takes 15 days. The other three sites are occupied by chlorine and remaining one is occupied by water. Ruthenium is in +3 oxidation state which is neutralized by three attached chlorides. Figure 24 showing the ORTEP view of Complex C1 with 30% probability. Hydrogen atoms were excluded for more clarity and understanding.

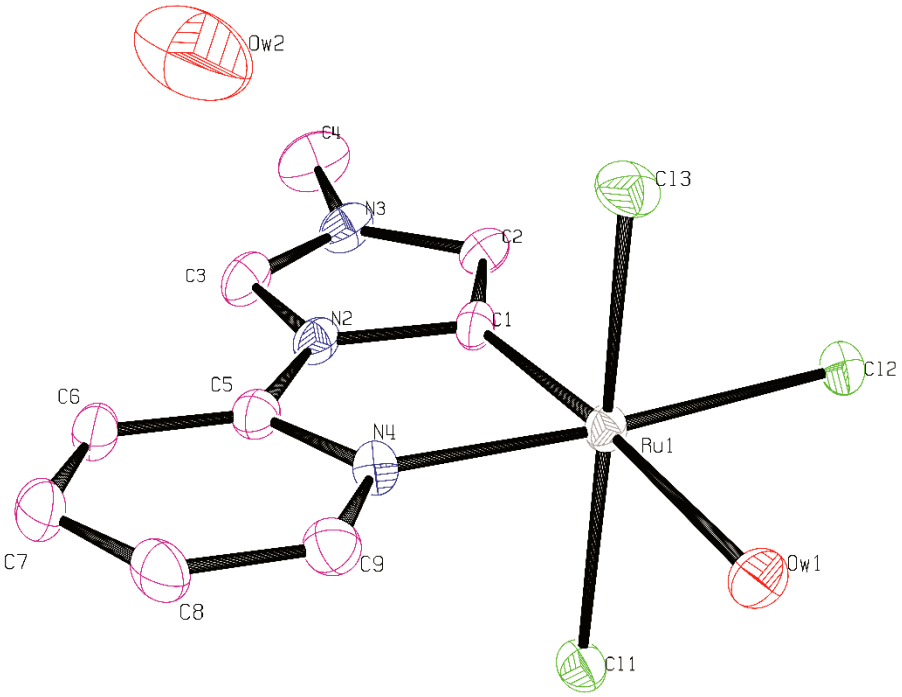


Figure 24: ORTEP view of complex C1 (Hydrogen atoms excluded for a clear view)

Formation of abnormal carbene can be explained by two possible reasons.

1. Steric Factor: in case of normal carbene the alkyl substituent on Nitrogen is in close vicinity of metal so to avoid that steric effect rotation around single bond can take place and instead of normal carbene binding *[18,19]*.
2. Electronic Factor: Abnormal carbenes are stronger electron donors than Normal carbenes when metal is in higher oxidation state it prefers to bind with abnormal carbene to overcome its electron deficiency.

In our case, the 2nd reason is more prominent because substituent is methyl group that is not very bulky so steric factor could be neglected and metal is in +3 oxidation state that could force the metal to bind with abnormal carbene donor.

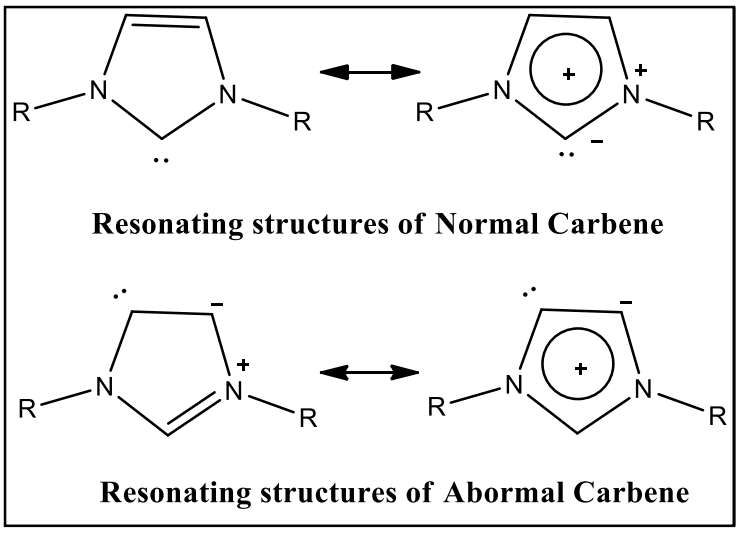


Figure 25: Resonating structures of Normal and Abnormal carbenes.

Powder X-Ray Diffraction Pattern

Although structure of Complex C2 was confirmed by Single Crystal XRD but to check the uniformity of the product that complete product is same or just some part is crystallized as C2 we performed PXRD

and compare PXRD pattern of our complex (Figure 25) with that of simulated via mercury software for single crystal (Figure 26). And that pattern was in accordance to the simulated pattern so we can say that a uniform product was formed during this reaction and that is complex C2.

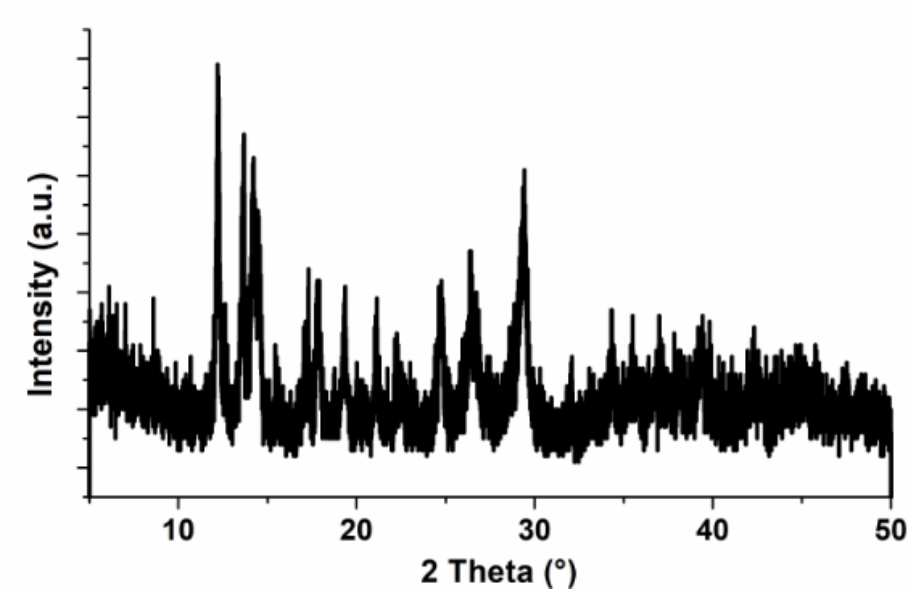


Figure 26: PXRD Pattern for Complex C2

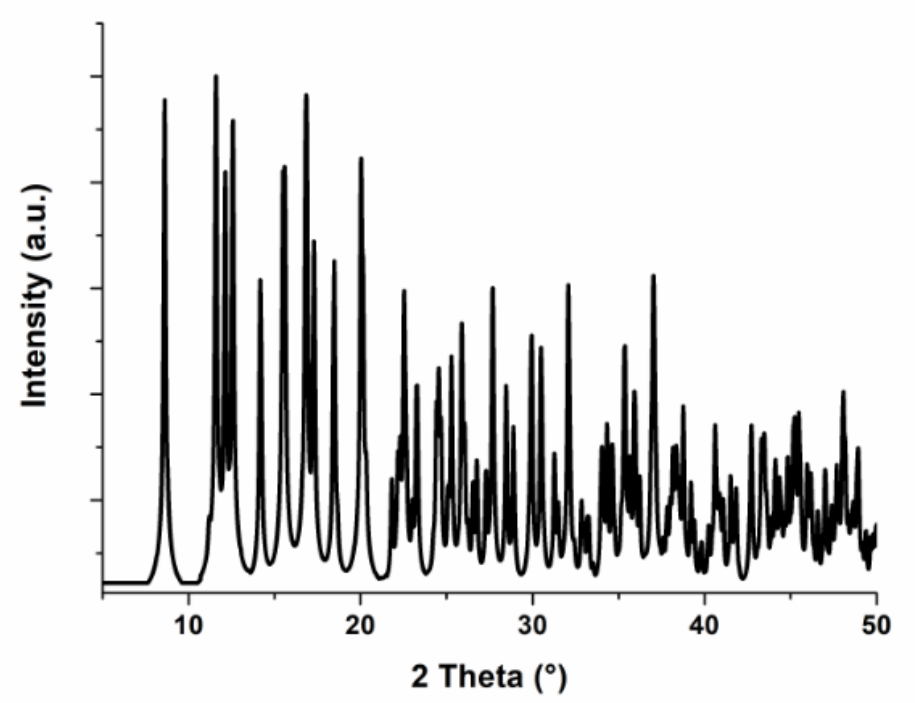
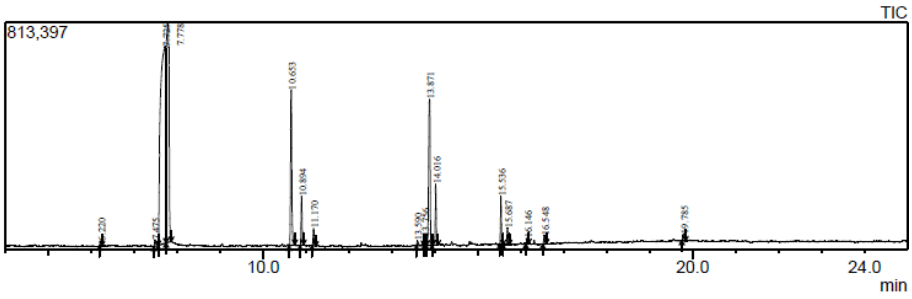


Figure 27: Simulated PXRD pattern of Complex C2

Apart from intensity peak positions are matching with the simulated pattern.

3.3 Characterization Data for Transfer Hydrogenation

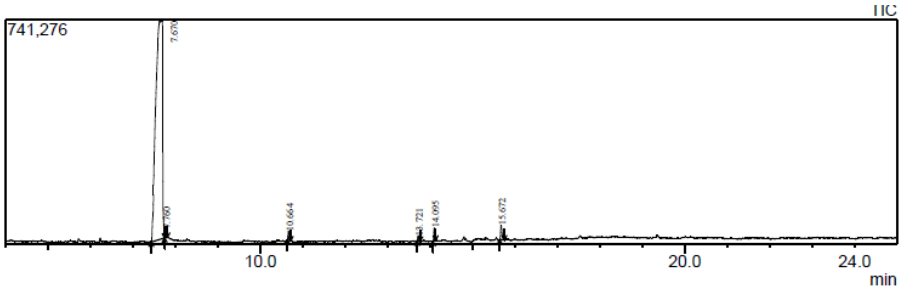
Gas Chromatography:



Peak Report TIC

ak#	R.Time	Area	Area%	Height	eight%	A/H	Name
1	6.220	32234	0.24	17527	0.51	1.84	Cyclotrisiloxane, hexamethyl-
2	7.475	74987	0.56	21518	0.63	3.48	Cyclohexanol
3	7.725	6176690	45.74	704683	20.53	8.77	Cyclohexanone
4	7.778	3330268	24.66	788791	22.98	4.22	Cyclohexanol
5	10.653	1195348	8.85	558853	16.28	2.14	2-Butanone, 4-cyclopentylidene-
6	10.894	267640	1.98	177164	5.16	1.51	4-Acetyl-1-methylcyclohexene
7	11.170	102967	0.76	62404	1.82	1.65	Cyclohexanone, 2-(1-methylethylidene)-
8	13.590	72493	0.54	17735	0.52	4.09	cis-syn-trans-Tricyclo[7.3.0.0(2,6)]dodec-7-ene
9	13.756	55838	0.41	33044	0.96	1.69	(7R)-trans-syn-cis-Tricyclo[7.3.0.0(2,6)]-dodecan-7-ol
10	13.871	1260966	9.34	523019	15.24	2.41	2-(1-Cyclohexenyl)cyclohexanone
11	14.016	389018	2.88	218758	6.37	1.78	Cyclohexanone, 2-cyclohexylidene-
12	15.536	286113	2.12	172718	5.03	1.66	Bicyclo[2.2.1]heptane, 2-(1-buten-3-yl)-
13	15.687	103116	0.76	58327	1.70	1.77	1-(1-Ethyl-2,3-dimethyl-cyclopent-2-enyl)-ethanone
14	16.146	33490	0.25	20072	0.58	1.67	(3aR,4R,7R)-1,4,9,9-Tetramethyl-3,4,5,6,7,8-hexahydro-2H
15	16.548	63343	0.47	32322	0.94	1.96	Tricyclo[3.3.0.0(2,8)]octan-3-one, 4-(m-anisyl-2-ethyl)-
16	19.785	60660	0.45	25317	0.74	2.40	
		3505171	100.00	3432252	100.00		

Figure 28: GCMS data of reaction mixture after 2 hours.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	A/H	Name
1	7.670	8043419	96.34	725190	81.31	11.09	Cyclohexanol
2	7.760	52726	0.63	28185	3.16	1.87	Cyclohexanone
3	10.664	49777	0.60	29972	3.36	1.66	Cyclohexene, 3-methyl-
4	13.721	32054	0.38	17693	1.98	1.81	1(2H)-Naphthalenone, 3,4-dihyd
5	14.095	66978	0.80	42433	4.76	1.58	6-Hydroxy-3-methyl-9-oxabicycl
6	15.672	104454	1.25	48420	5.43	2.16	1-Triazene, 1-(4-methylphenyl)-
		8349408	100.00	891893	100.00		

Figure 29: GCMS data of reaction mixture after 12 hours.

According to previous reports we tried our complex C2's activity towards transfer hydrogenation and for monitoring the reaction technique used was GCMS after 2 hours of reaction setup data could be seen from Figure 27 showing only 25% of area is occupied by cyclohexanol with lot of by-products, but when we have taken the GCMS data after 12 hours (Figure 28) then 96% of area is covered by cyclohexanol with almost negligible amount of cyclohexanone left.

CHAPTER FOUR

CONCLUSION AND FUTURE PROSPECTIVE

4.1 Conclusion

We have successfully synthesized a new Ruthenium (III) octahedral complex with abnormal carbene with the help of earlier reported NHC donor Ligand. This complex is showing some catalytic activity in Transfer Hydrogenation and other activities are yet to be explored.

4.2 Future Perspective

Ruthenium Complexes have shown a vast range of applications in past and our synthesized complex C2 can also show various applications in near future if explored some possibilities are shown in Figure 29.

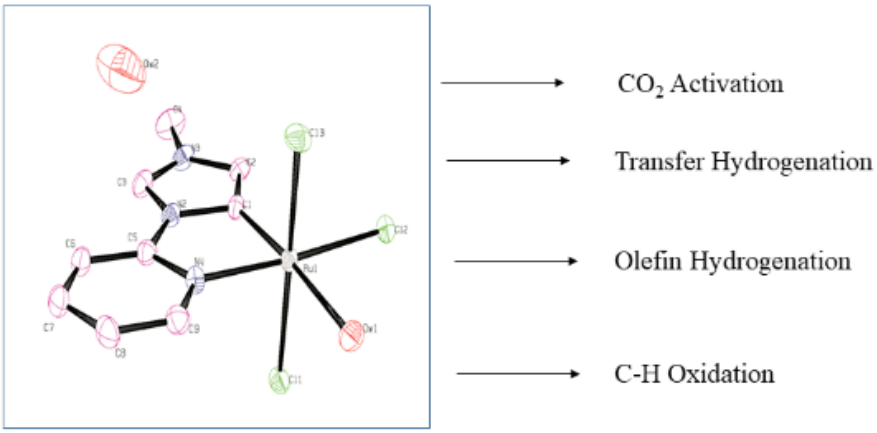


Figure 30: Future Aspects of Complex C2

Our Complex can be reacted with some Pincer type ligands to attain robustness and attached abnormal carbene will facile the multi-electron transfer reactions like CO_2 activation.

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