Transition metal complexes with NHC based pincer ligands – Synthesis, Characterization, and Reactivity

M.Sc. Thesis

By

Dheeraj Kumar

DISCIPLINE OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Transition metal complexes with NHC based pincer 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
Dheeraj Kumar

DISCIPLINE OF CHEMISTRY

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CANDIDATE’S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Transition metal complexes with NHC based pincer 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 work carried out during the 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.

Dheeraj Kumar

Dheeraj Kumar

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

A Singh

Dr. Amrendra Kumar Singh

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

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Date: 23-10-2020

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Signature of PSPC Member #1

Date: 24-10-2020

Dipak Kumar Roy

Signature of PSPC Member #2

Date: 24.10.2020

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Dheeraj Kumar
Discipline of Chemistry IIT Indore

DEDICATED

TO……………………….

MY GRANDFATHER

For his unwavering belief in my potential!

ABSTRACT

NHC ligand precursors, 2,6-Bis(1-methylimidazolium pyridine)dibromide ($CNC^{Me}\cdot 2HBr$), 2,6-Bis(1-isopropylimidazoliumpyridine)dibromide ($CNC^{i\text{-}Pr}\cdot 2HBr$) were prepared by following literature procedures. Different metal precursors were synthesized by using a protocols recently developed in our group, starting from $RuCl_3\cdot 3H_2O$. Ru(II) complexes, $[Ru(CNC)^{\textit{i-}Pr}(PPh_3)_2Cl]PF_6$ **(1)**, $[Ru(CNC)^{\textit{i-}Pr}(DMSO)_2Cl]PF_6$ (**2**), $[Ru(CNC)^{\textit{i-}Pr}(COD)Cl]PF_6$ (**3**), $[Ru(CNC)^{\textit{i-}Pr}(PPh_3)(CO)Cl]PF_6$ **(4)**, $[Ru(CNC)^{\textit{i-}Pr}(PPh_3)_2H]PF_6$ **(5)**, and $[Ru(CNC)^{Me}(PPh_3)_2H]PF_6$ **(6)**, $[Ru(CNC)^{\textit{i-}Pr}(PPh_3)_2(N_3)]Cl$ **(7)** have been synthesized by reaction of NHC ligand precursors and other metal precursors under thermal condition.

All the synthesized ligands and complexes have been characterized by mass spectrometry and multinuclear NMR (^{1}H and ^{31}P NMR) and FTIR spectroscopic techniques. The molecular structure of complexes **1, 2,** and **5** was confirmed by single-crystal X-ray diffraction technique. The crystal structures reveal that the Ru (II) center is coordinated with one tridentate NHC donor ligands and other monodentate ligands forming a distorted octahedron.

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NOMENCLATURE

˚C	Degree Centigrade
%	Percentage
Mol	Mole
Mmol	Milli Mole
mL	Milli Litre
μL	Micro Litre
K	Kelvin
δ	Chemical Shift(N.M.R)

ACRONYMS

NHC	*N*-Heterocyclic carbene
ESI	Electrospray ionization
LCMS	Liquid chromatography-mass spectrometry
NMR	Nuclear magnetic resonance
DMSO	Dimethyl sulfoxide
ORTEP	Oak ridge thermal ellipsoid plot program
MeOH	Methanol
ACN	Acetonitrile
IPA	Propan-2-ol
Ru	Ruthenium
N	Nitrogen
DCM	Dichloromethane
Zn	Zinc
NH_4PF_6	Ammonium hexafluorophosphate
H_2O	Water

Chapter 1 Introduction

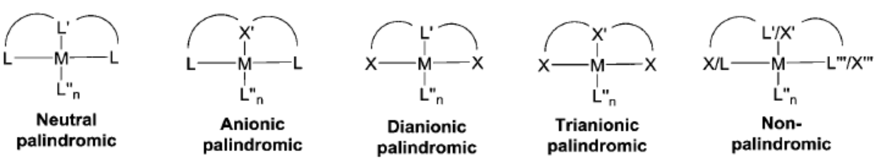
1.1. Aim of project

Our aim is to synthesize and characterize the electron-rich transition metal complexes with N-heterocyclic carbene based CNC pincer complexes and check their catalytic activities for different types of catalysis like hydroboration, hydrosilylation, hydrogenation, acceptor less dehydrogenation and N-alkylation of amines, etc. Due to the strong ability of σ donation of an electron pair by NHC, electron-rich complex is formed and it can be useful for activation of small molecules like oxidation of ammonia, water oxidation, and CO_2 reduction.

1.2. General introduction

Transition metal complexes with pincer ligands are found in all areas of transition-metal catalysis like hydrogenation and transfer hydrogenation reactions *[1]*. Pincer complexes have attracted large attention of research due to their high stability, rigidity, and their splendor catalytic activity *[8]*. Pincer complexes are also promoting the reaction like cross-coupling, polymerization, and Diel's alder reaction, etc. *[1]*. N-heterocyclic carbene based transition metal complexes have a wide range of use in organometallic chemistry and catalysis because of their stereoelectronic diversity and capability to make stable compounds *[2]*. Many methods have been developed to form the NHC's and their complexes. N-heterocyclic cyclic carbene containing pincer ligands are known as outstanding examples of strong electron donor ligands and provide a special environment around the metal complexes *[3]*. NHC's based pincer ligands and their complexes can be used in various catalysis like transfer hydrogenation, cross-coupling of alcohols, N-alkylation of amines, and acceptor less dehydrogenation *[4]*. These all are used as a homogeneous catalyst in catalysis. NHC bearing ligands are found as monodentate, bidentate, and tridentate (pincer ligand). NHC's pincer complexes are also used in the efficient and selective photolytic conversion of CO_2 to useful fuels and also fixation of CO_2 can be done by Ru(II) NHC pincer complexes *[15]*. The hydrogenation of esters is also catalyzed by ruthenium pincer complexes *[16]*. Herein, we have reported the CNC based N-heterocyclic ligands *[5-7]*. Pincer attached to metal center in mer-fashion and rarely found in fac fashion *[8-9]*. There are many moieties are found to construct a diverse range of pincer ligands and their complexes. Pincer ligands attached to the metal center via σ bond and it can be dative bonds. The pincer complex has come on a large scale of research due to its stability and splendor catalytic activity *[9]*. There are several types of pincer ligands are available and can be synthesized but our interest in CNC type pincer ligand. There is some common type of pincer ligands given below *[10]*.

Common types of pincer ligands

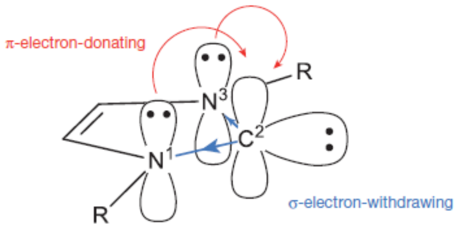


1.3. N-heterocyclic carbene(NHC’s)

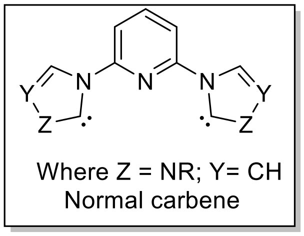
Carbene can be defined as neutral divalent carbon with 6 electrons. NHC’s are the special class of carbene having carbene carbon within the nitrogen-containing heterocyclic ring. Generally, there are two types of a carbene.

(1) Normal carbene

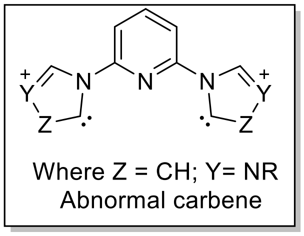
(2) Meso-ionic carbene or abnormal carbene



N-heterocyclic carbene

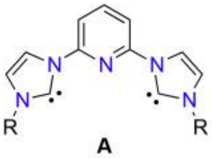


Where Z = NR; Y= CH
Normal carbene



Where Z = CH; Y= NR
Abnormal carbene

NHC's are also found as classical carbene (non-protic NHC's) and protic NHC (pNHC). NHC's are the strong σ-electron donor and form electron-rich metal complexes. Herein, our interested NHC's moieties are shown.



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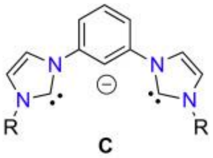

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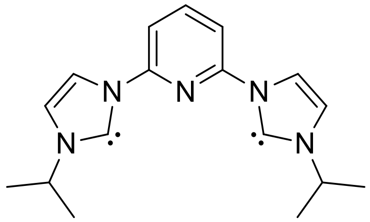

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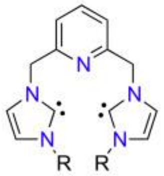

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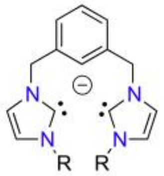


D

The σ donation ability of NHC's can be modified by using substituents at the ring nitrogen atom *[11]*. Bulky groups like iso-propyl, t-butyl, etc. on the ring nitrogen has a special additional feature on the steric diversity of NHC's in the coordination sphere of the metal atom which can play a special role in catalytic activity and selectivity *[11]*.

1.4. Pincer ligands. Why?

Pincer ligands are the chelating agent that binds to three co-planner sites on the metal (Fig.1). These ligands are mainly attached in mer fashion and rare to fac *[12]*.

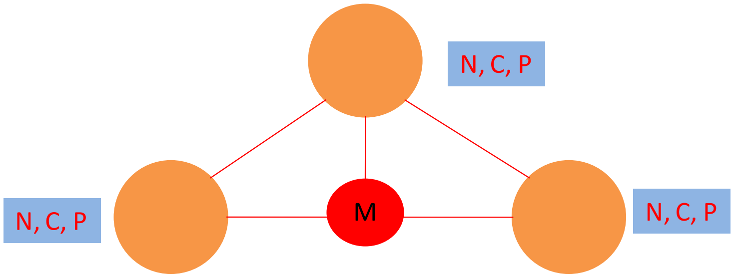


Fig.1: A Schematic diagram of pincer type complex

The attention of scientists has been attracted by pincer complexes due to their significant application in activating small molecules like NH_3, CO_2, etc. *[13]*. There are various types of pincer ligands such as NCN, CNC, and PNP, etc. but our interest in CNC type of pincer ligand. It forms two M-Carbon σ bonds. Complexes form by pincer ligands have tremendous research due to their splendor application in catalysis, medicinal chemistry, and chemical sensors. NHCs are a very strong electron donor, so it will definitely help to synthesized electron-rich metal complexes. Here, I have reported some metal complexes synthesized during this project using different ruthenium metal precursors.

2.1. Chemicals and reagents:

All the solvents were purchased from commercial sources and purified before use. All the chemicals were purchased and used as received without further purification. These chemicals includes imidazole (SRL, 99%), 2,6-dibromo pyridine (Alfa Aesar, 98%), potassium carbonate (SRL, 99.5%), sodium bicarbonate (SRL, 99.5%), sodium chloride (SRL, 99.9%), ruthenium trichloride trihydrate (SRL), magnesium sulphate (SRL, 99%), potassium hydroxide (Emplura, 85%), isopropyl bromide (Spectrochem, 99%), tertiary butylamine (Spectrochem, 99%).

2.2. Instrumentation:

NMR spectra were recorded on an ADVANCE 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 complexes:

2.3.2. Synthesis of iso-propylimidazole (L^1). L^1 was synthesized by using a reported procedure *[17]*. NaOH (60 mmol, 2.4 g) and Imidazole were taken with 20 mL of DMSO in a two neck RB. The solution was stirred for 2h at room temperature and converted into pale yellow. After that alkyl bromide was added and allowed to react. The reaction was monitored by TLC. The reaction mixture got solid like wax. After 4h, the reaction was completed. Water was added and solid got miscible into water. The mixture was extracted three times with ethyl acetate (100 mL) and the combined organic layer was washed several times with water and then brine solution. After that dried over Na_2SO_4 and solvent was evaporated under reduced vacuum and got the pale-yellow liquid as a compound.

Yield: 3.30 g, 75.2%. LCMS (ESI): calculated $[M+H]^+$ = 111.09, observed $[M+H]^+$ = 111.09.

2.3.2. Synthesis of CNC)$^{i\text{-}pr}$ ·2HBr (L^2).

L^1 was synthesized by a slight modification in the reported procedure *[18]*. 2, 6-dibromopyridine (2 g, 8.44 mmol), and 1-isopropylimidazole (1.86 ml, 16.88 mmol) were taken in a sealed pressure tube. The oil bath temperature was set to 150 ˚C and the reaction mixture was continuously stirred for 4 days. Brown solid was triturated with DCM to get the pure product. Yield: 2.49 g, 64.3%. ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 10.72 (s, 2H), 8.94 (d, 2H), 8.61 (dd, 1H), 8.36 (d, 4H), 5.01-4.78 ppm (m, 2H). LCMS (ESI): calculated $[M-H]^+$= 296.19 observed $[M-H]^+$ = 296.19.

2.3.3. Synthesis of complex 1: In a schlenk tube, Ag_2O (101.27 mg, 0.437 mmol) was added to a solution of (CNC)$^{i\text{-pr}}$·2HBr (200 mg, 0.437 mmol) in MeOH (10 mL) to generate carbene. The mixture was stirred under N_2 at rt for 1.5h. The color was changed dark brown to off white. After that $[RuCl_2(PPh_3)_3]$ was added and allowed to reflux the mixture for 16h. The color was changed into brown. The reaction mixture was filtered and the solvent was evaporated under reduced vacuum to afford greenish-brown solid $[Ru(CNC)^{i\text{-pr}}(PPh_3)_3Cl]Cl$. Solid was washed with diethyl ether to remove extra PPh_3. After that anion exchanged by one equivalent NH_4PF_6 in MeOH to afford $[Ru(CNC)^{i\text{-pr}}(PPh_3)_3Cl]PF_6$. Yield: 368.4 mg, 88%. ^{1}H NMR (400 MHz, DMSO-d6): LCMS (ESI): calculated $[M-PF_6]^+$ = 627.0, observed $[M-PF_6]^+$ = 627.0

2.3.4. Synthesis of complex 2: L^1·2HBr (200 mg, 0.437 mmol) was taken in a schlenk tube and dried under vacuum at 100 °C for half an hour and then cooled it to room temperature. Dry MeOH was injected under N_2. Ag_2O (110.92 mg, 0.437 mmol) was added and stirred the reaction mixture at rt for 1.5h. Schlenk tube was covered by aluminum foil. After this period, a change in color brown to off white was observed. The metal precursor $[RuCl_2(DMSO)_4]$ (212mg, 0.437mMol) was added and refluxed the reaction mixture overnight under N_2. After that reaction mixture was filtered and evaporated the solvent under reduced vacuum to afford [Ru(CNC)$^{i\text{-}pr}$(DMSO)$_2$Cl]Cl **(2)**. The solid was washed with diethyl ether. After that NH_4PF_6 (1 equivalent, 0.5 mL MeOH) was added to conc. solution of complex. The precipitated yellow powder was filtered, and washed with diethyl ether, and dried. Yield: 219.3 mg, 85.21%. ^{1}H NMR (400 MHz, DMSO-d6): δ 8.61(s, 2H, imidazolium CH), 8.25(t, H, pyridine top proton), 8.03(s, 2H, imidazolium CH), 7.96(d, 2H, Pyridine), 5.44-5.61(m, 2H, isopropyl), 2.69 (s, 9H, DMSO), 2.54(s, 3H, DMSO), 1.53(d, 12H, isopropyl). ESI-MS (MeOH, m/z) = 588.1 [M-Cl]$^+$. LCMS (ESI): calculated [M-PF$_6$]$^+$ = 588.78 observed [M-PF$_6$]$^+$ = 588.75

2.3.5. Synthesis of complex 3: In a standard schlenk tube, silver oxide (101.27 mg, 0.437 mmol) was added to a solution of (CNC)$^{i\text{-pr}}$·2HBr (200 mg, 0.437 mmol) in MeOH (10 mL). The mixture was stirred continuously under N_2 at rt for 1h to generate silver carbene. The color of the solution was changed from dark brown to off white. Then, [RuCl$_2$(COD)]$_n$ was added and allowed it to reflux the mixture for 15h. The color was changed into dark brown. The reaction mixture was filtered and the solvent was evaporated under reduced vacuum to afford dark brownish color [Ru(CNC)$^{i\text{-}pr}$(COD)$_2$Cl]Cl. Yield: 205.06 mg, 86.81%. ESI-MS (MeOH, m/z) = calculated [M-Cl]$^+$ = 540.1 observed [M-Cl]$^+$ = 540.1

2.3.6. Synthesis of complex 4: In a schlenk tube, Ag_2O (101.27 mg, 0.437 mmol) was added to a solution of (CNC)$^{i\text{-pr}}$·2HBr (200 mg, 0.437 mmol) in 10 mL MeOH under N_2. The mixture was stirred for 1h at rt results that formation of a silver carbene. The color was changed dark brown to off white. After that [Ru(H)(Cl)(CO)(PPh$_3$)$_3$] was added in *situ* and allowed to reflux the mixture for 15h. The color was changed into brown. The reaction mixture was filtered and the solvent was evaporated under reduced vacuum to afford orange-brown solid [Ru(CNC)$^{i\text{-}pr}$(PPh$_3$)(CO)Br]Cl. Solid was washed with diethyl ether to remove extra

PPh_3. Yield: 263.13 mg, 78.17%. ESI-MS (MeOH, m/z) = calculated $[M\text{-}Cl]^+$ = 766.09, observed $[M\text{-}Cl]^+$ = 766.1

2.3.7. Synthesis of complex 5: Complex $[Ru(CNC)^{i\text{-}pr}(PPh_3)_3Cl]Cl$ (200 mg, 0.209 mmol) and K_2CO_3 (28.88 mg, 0.209 mmol) were taken and dry propan-2-ol (10 mL) was injected under N_2 in schlenk tube. The reaction mixture was allowed to reflux overnight at 85 °C. The color of the reaction was changed greenish-brown to brownish orange. After completion of the reaction, reaction mixture was filtered by filter paper. The solvent was evaporated under a reduced vacuum to afford brownish solid of $[Ru(CNC)^{i\text{-}pr}(H)(PPh_3)_2]Cl$. To get the clean NMR, we did the anion exchange of this complex. Anion was exchanged with 1 Equiv. NH_4PF_6 in MeOH. The resulting complex was settled down in MeOH and removed the solvent to afford brown powder of complex. Yield: 136.8 mg, 70.9%. ^1H NMR (400 MHz, DMSO-d6): δ 8.27(d, 2H, imidazole), 7.69(t, 1 H, Pyridine), 7.44(d, 2H, imidazole), 7.39(d, 2H, Pyridine), 7.23(t, 6H, Phosphine), 7.11(t, 12H, Phosphine), 6.75(d, 12H, Phosphine) 4.18-4.35(m, 2H, isopropyl), 0.14(d, 12H, isopropyl), -8.69(t, 1H, Ru-H), ESI-MS (CH_3CN, m/z) = 922.3 [$M\text{-}Cl]^+$. Calculated $[M\text{-}Cl]^+$ = 922.3, observed $[M\text{-}Cl]^+$ = 922.3

2.3.8. Synthesis of complex 6: $[Ru(CNC)^{met}(PPh_3)_3Cl]Cl$ was synthesized and characterized earlier in our group by Dibya Yadav *et al* but not published yet. I took the $[Ru(CNC)^{met}(PPh_3)_3Cl]Cl$ (0.214 mmol, 200 mg) in a schlenk tube. K_2CO_3 (0.214 mmol, 29.54 mg) was added to schlenk and then *iso*-propanol was injected via the syringe. The reaction mixture was refluxed at 85-90 °C for overnight. The color was changed greenish-brown to brownish orange. After the completion of the reaction, the reaction mixture was filtered and the solvent was evaporated under a reduced vacuum to afford brown solid. Solid was washed with diethyl ether and dried under vacuum. Complex was obtained with a 77.8% yield. The complex was characterized by mass spectrometry and NMR spectroscopy. NMR spectrum of the complex was recorded after the exchange of chloride anion with PF^{6-}. 1 equivalent NH_4PF_6 in MeOH was added to the MeOH solution of complex to afford $[Ru(CNC)^{i-pr}(PPh_3)_3(H)]PF_6$ as a precipitate. Yield: 149.64 mg, 77.8%. ^1H NMR (400 MHz, DMSO-d6): δ 8.31(s, 2H, imidazole), 7.85(t, 1 H, Pyridine), 7.58(d, 2H, imidazole), 7.28(d, 6H, PPh_3), 7.24(d, 2H, Pyridine), 7.19(t, 12H, PPh_3), 6.79(d, 12H, P PPh_3) 2.47(s, 6H, methyl), -8.86(t, 1H, Ru-H), ESI-MS (CH_3CN, m/z) = 866.22 [M-Cl]$^+$. Calculated [M-Cl]$^+$ = 866.21, observed [M-Cl]$^+$ = 866.22

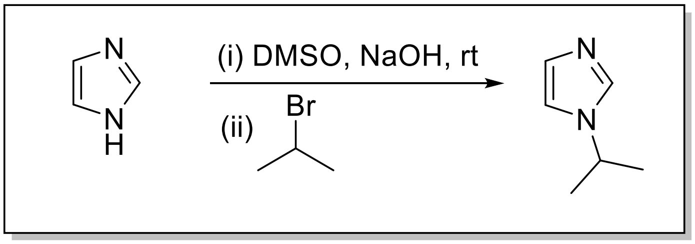
2.3.9. Synthesis of complex 7: $[Ru(CNC)^{i-pr}(PPh_3)_3Cl]Cl$ was taken (0.050mmol, 50 mg) in schlenk tube. Sodium azide (0.050 mmol, 3.27 mg) was added and 5 mL dry MeOH was added to schlenk by syringe. The reaction was continuously stirred and heated overnight at 50 °C. The color was changed greenish-brown to yellowish-orange. After completion of the reaction, reaction mixture was filtered and evaporated the solvent under reduced vacuum to afford $[Ru(CNC)^{i-pr}(PPh_3)_3(N_3)]Cl$ orange solid. Complex was obtained with a 48.86% yield. ESI-MS (MeOH, m/z) = 963.22 [M-Cl]$^+$. Calculated [M-Cl]$^+$ = 963.27, observed [M-Cl]$^+$ = 963.22.

Crystallization was done for all the complexes in MeOH/ether via diffusion and layering method but crystals of only complex **1**, **2,** and **5** were obtained and found the expected structure of the complex. The structure is shown in **Fig. 19**, **Fig. 20** and **Fig. 21** respectively.

Chapter 3 Results and discussion

3.1. Synthesis of ligands and characterization

L^1 was prepared by dissolving NaOH in DMSO and stirred for 2h at rt. After that *iso*propyl bromide was added to the pale yellow solution and stirred continuously until converted in solid-like wax. Reaction conditions are shown in scheme 2. The final compound was obtained as a pale yellow liquid after work up with 75.2%. Obtained liquid was characterized by ^1H NMR spectroscopy and mass spectrometry.



Scheme 1: Synthesis of L^1

^1H NMR spectrum of L^2 is shown in **Fig. 3**. A singlet at 7.26 ppm for one proton of imidazole and another two imidazolium protons have doublets at 6.71 ppm were observed in the aromatic region. In the aliphatic region, there is a multiplet at 4.08 ppm for one proton of the isopropyl unit and a doublet was observed at 1.18 ppm. There are some other peaks for solvent like ethyl acetate and acetone.

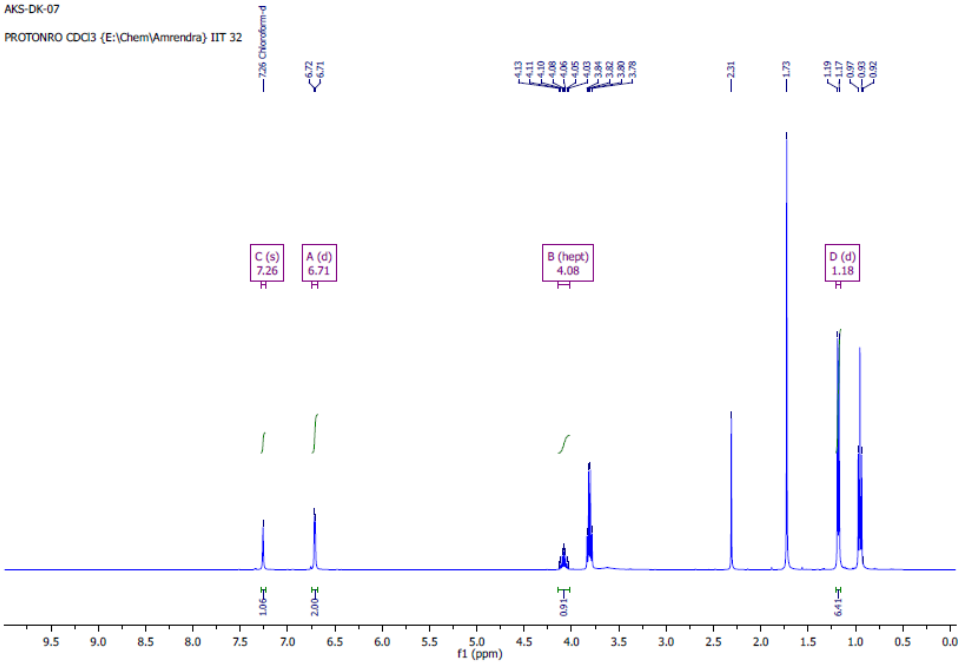


Fig. 1: ^{1}H NMR spectrum of L^1

LCMS of L^1 displayed a signal at m/z 111.092 (z=1) assigned to $[M+H]^+$ that could be seen from Figure 12. $[M+H]^+$ observed = 111.092, $[M]^+$ calculated = 111.0917

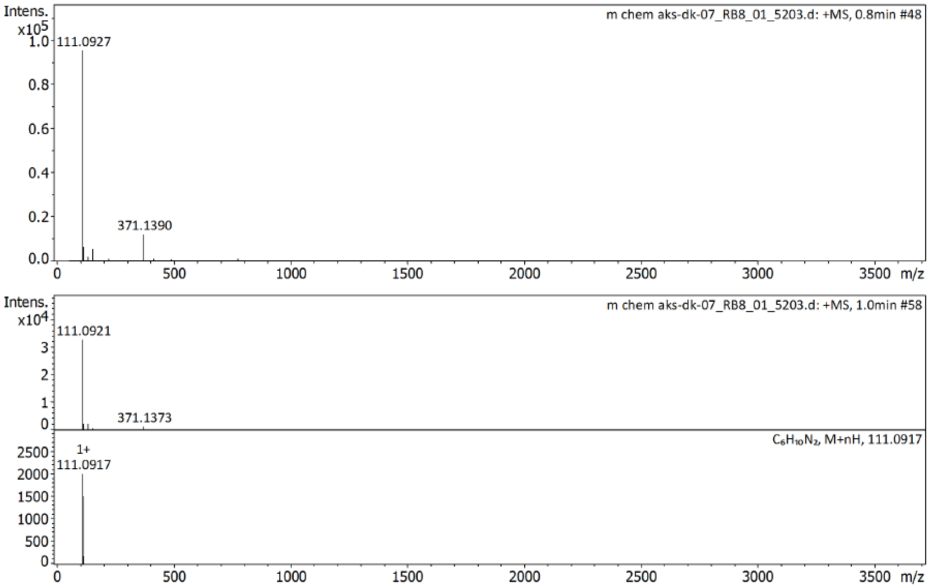
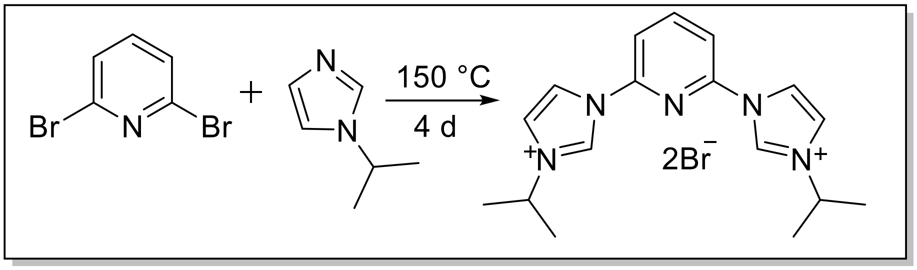


Fig. 2: Mass spectrogram of L^1

L^2 was synthesized by heating 2, 6-dibromopyridine with N-isopropyl imidazole at 150 °C. Reaction conditions are shown in Scheme 1. The product was obtained as a brown powder with 80% yield. The obtained product was characterized by ^1H NMR spectroscopy and mass spectrometry.



Scheme 2: Synthesis of L^2

^1H NMR spectrum of L^2 was shown in **Fig.1** from that we can see that a singlet at 10.72 is for two imidazolium protons and another singlet for 2 pyridine protons at 8.73 and one triplet at 8.61 for pyridine top proton and a doublet was observed at 8.35 for 2-2 protons of both imidazole units. Both *iso*propyl of iso-propyl imidazole were in the same environment and observed at 4.78-5.01 ppm as a septet with 12 protons. These 12 protons are observed for 6, 6 protons of both iso-propyl units. From the spectra, it is clear that the molecule is symmetric and both isopropyl imidazoles are identical.

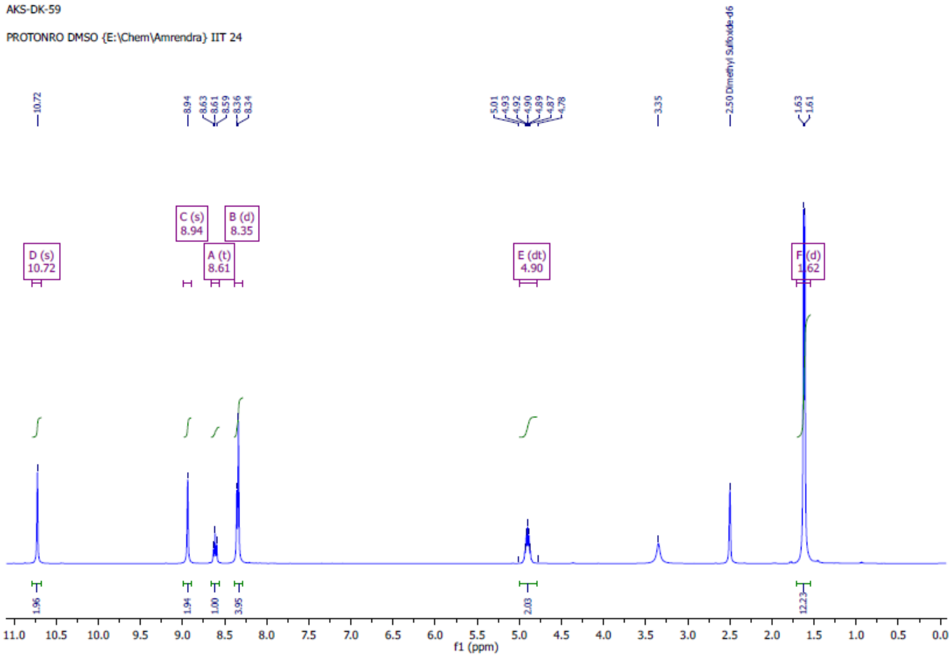


Fig. 3: ^{1}H NMR spectrum of L^2

ESI-MS spectrum of ligand L^1 showed a signal at m/z 296.19 (z=2) assigned to $[M/2]^+$ that could be seen from **Fig. 2**.

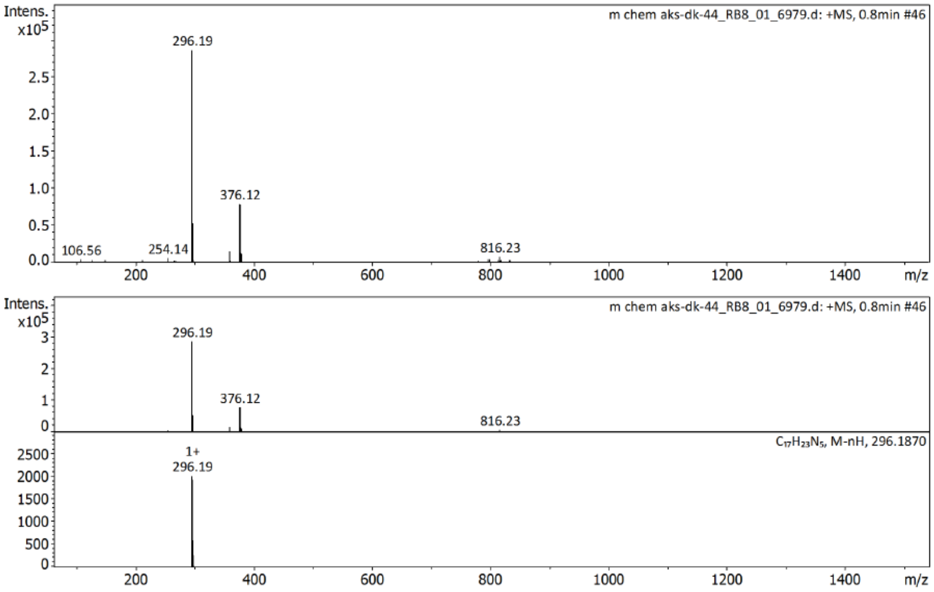
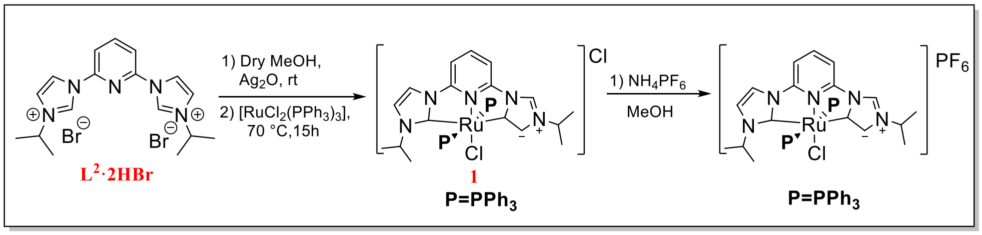


Fig. 4: Mass spectrogram of L^2

3.2. Synthesis of complexes and characterization

All the complexes were synthesized by using the reaction condition that is shown in corresponding in the scheme. Complex **1** was synthesized under N_2 atm. Initially, silver carbene was generated on ligand precursor **L^1** by using mild base Ag_2O at rt. After that transmetallation was done by ruthenium precursor $[RuCl_2(PPh_3)_3]$ and refluxed the reaction mixture overnight. Reaction conditions are shown in **scheme 3**.



Scheme 3: Synthesis of complex **1**

Ligand precursor (**L^2**) binds with the Ruthenium Metal center in meridional fashion and occupies three adjacent co-planner positions. It was confirmed by SCXRD. In the complex, three co-planner sites were occupied by pincer ligand (L^2) in meridional fashion and the other three sites of this octahedral complex were occupied by two PPh_3 and one Cl ligand. Both triphenylphosphine ligands are trans to each other and Cl is trans to nitrogen of pyridine. By the NMR of this complex, we found that a mixture of three complexes was formed during the reaction because we got the 4 septet and 4 doublets for the isopropyl unit on the imidazole ring. That indicates three sets of isomers were formed during the reaction. It is tough to separate each. We tried but till now we couldn't separate all of these. One complex formed by attaching both abnormal carbene of imidazolium unit and another one is with both normal carbene and third complex has one normal and one abnormal carbene of the imidazolium unit. We found one of these crystal structures which is with one normal and one abnormal carbene **Fig.5.**

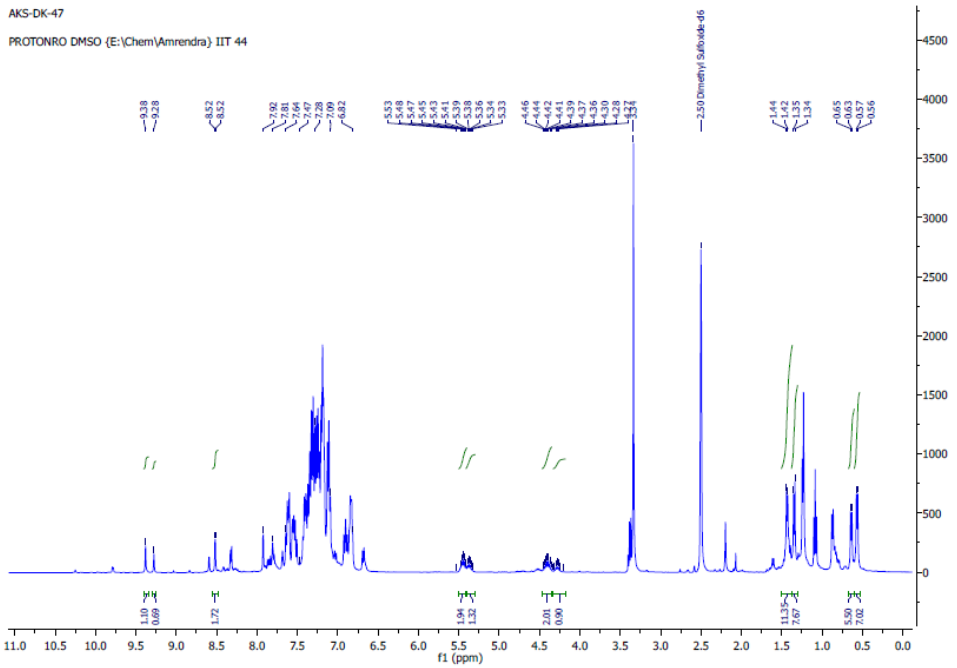


Fig. 5: ^{1}H NMR spectrum of complex **1**

Crystal data of this complex is not publishable but we can see the atom to atom connectivity. It shows that attachment of one imidazole based carbene unit to Ru (II) is normal and the other is in abnormal mode. But when we go to make **(5)** all the three mixtures get converted to the normal carbene that is clear by 1H NMR of complex 5. The crystal data of complex **5** also confirms that only normal mode of carbene binding is present. Crystallization was done by layering method where the complex was dissolved in MeOH and layering was done by diethyl ether and put the sample in the freezer.

LCMS of complex **1** displayed a signal at m/z 627.0 (z=1) assigned to $[M\text{-}PF_6]^+$ that could be seen from Fig. 21. Observed mass $[M\text{-}PF_6]^+$ = 627.0 Calculated mass $[M\text{-}PF_6]^+$ = 627.0

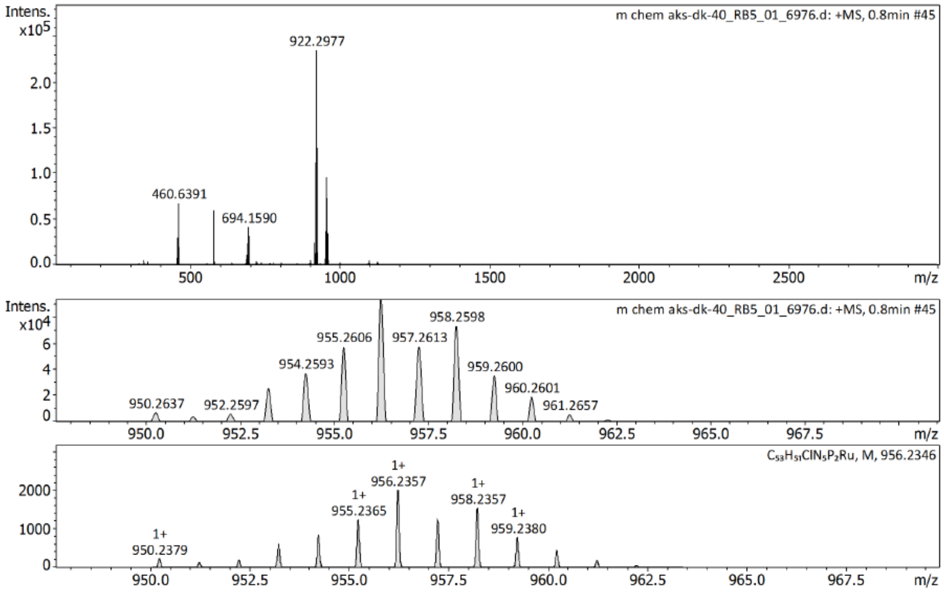
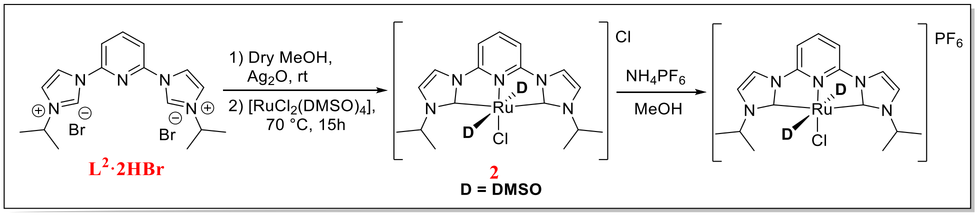


Fig. 6: Mass spectrogram of complex **1**

The reaction of $\mathbf{L}^2$ with [RuCl$_2$(DMSO)$_4$] was done with the same reaction conditions shown in **Scheme 4**. The reaction was carried out under the N_2 atmosphere result that the formation of the octahedral complex. In this complex, ruthenium exhibits a +2 oxidation state as ruthenium has in metal precursors. The reaction was carried out in methanol by using silver oxide as a base to generate the NHC carbene.



Scheme 4: Synthesis of complex **2**

Tridentate ligand $\mathbf{L}^2$ facially attached to metal with three adjacent co-planner sites and two DMSO and one Cl ligand complete the octahedral geometry around the metal center. Anion Cl$^-$ was exchanged with PF$_6$ by adding 1 Equiv. ammonium hexafluorophosphate (NH$_4$PF$_6$) to methanolic solution of complex [Ru(CNC)$^{i\text{-}pr}$ (DMSO)$_2$Cl]Cl to afford [Ru(CNC)$^{i\text{-}pr}$ (DMSO)$_2$Cl]PF$_6$. Crystallization of Complex [Ru(CNC)$^{i\text{-}pr}$ (DMSO)$_2$Cl]Cl was done by the layering method. The complex was dissolved in MeOH and layering was done by diethyl ether. We got the yellow cubical type crystal for this complex. The molecular structure of this complex was confirmed by the X-ray single-crystal crystallographic determination (**Fig.20**). Ruthenium is present in distorted octahedral geometry in the solid-state structure of complex which has Cl as *trans* of the pyridyl nitrogen atom and both the dimethyl sulphoxide (DMSO) are trans to each other. The complex was also characterized by mass and NMR. It is found that the 12 protons of both DMSO molecules are present as a peak of 9 and 3 protons in NMR spectra. It can be possible due to the exchange rate of DMSO with deuterated solvent and complex during recording NMR. NMR spectrum shows that a doublet at 8.61 is observed for two protons of imidazole, triplet at 8.25 for pyridine top proton, doublet at 8.03 for imidazolium protons and a doublet of two protons of pyridine was observed in aromatic region. A septet (multiplet) at 5.54 for CH proton of both *iso*propyl group in the aliphatic region. DMSO protons are observed as two singlets for 9protons and three protons. These two singlets are observed due to the exchange of the solvent during NMR recording. Also, a doublet at 1.53 ppm was observed for 12 protons of both *iso*propyl groups. From this doublet and heptet of 2 protons, we can say that both imidazole units are attached in the same manner i.e. the complex have a plane of symmetry.

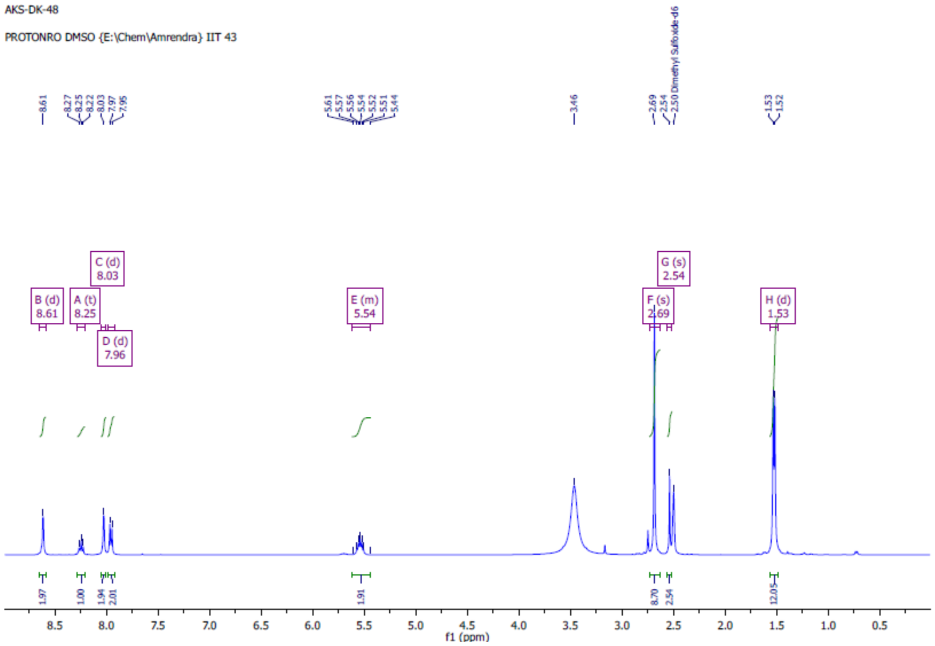


Fig. 7: ^{1}H NMR spectrum of complex **2**

LCMS of complex **2** displayed a signal at m/z 711.1 (z=1) assigned to [M-Cl]$^+$ that could be seen from **Fig.8**. Observed mass [M-Cl+CH_3OH]$^+$ = 620.15 Calculated mass [M-Cl+ CH_3OH]$^+$ = 620.10, another fragment for this complex also matched. [M-Cl]$^+$ = 588.08, [M-Cl-DMSO]$^+$= 510.07 and [M-Cl- 2 DMSO +CH_3OH]$^+$= 464.0 are observed for these specified fragments.

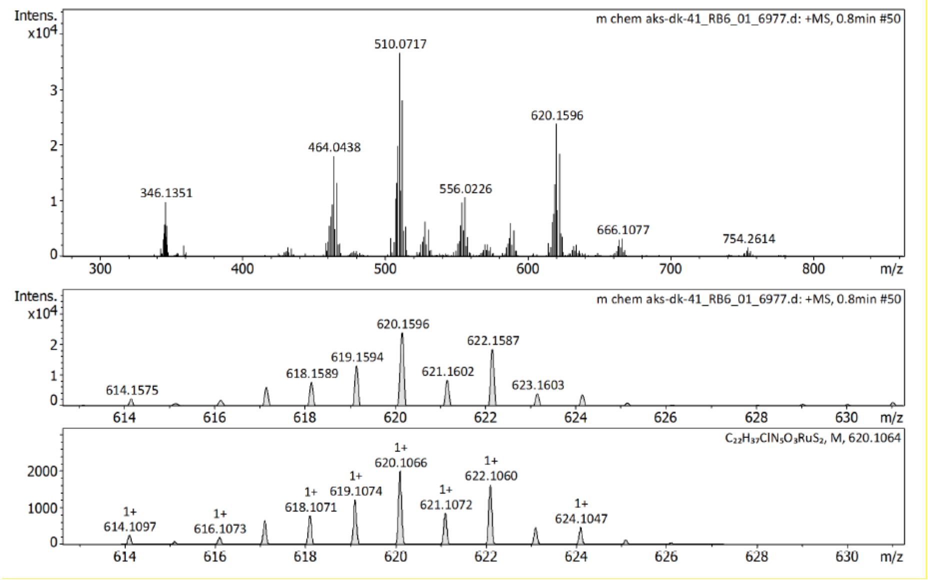
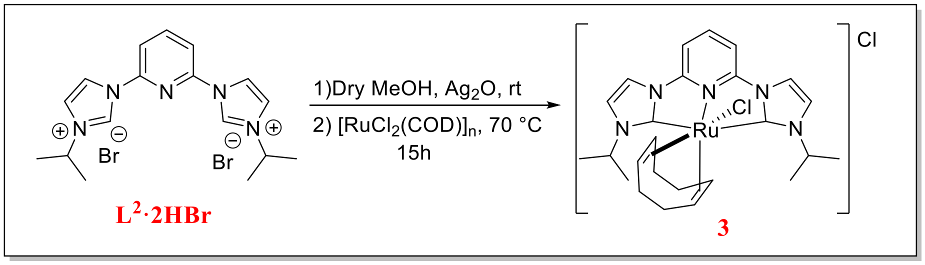


Fig.8: Mass spectrogram of complex **2**

Complex **3** was synthesized under the reaction conditions that are shown in the reaction scheme. In this reaction, the same reaction procedure was followed to generate the NHC carbene. $[RuCl_2(COD)]_n$ metal precursor was used to synthesize the complex **3.** We have done the characterization by ESI-MS only for this complex. The crystal structure is not obtained yet after many attempts.



Scheme 5: Synthesis of complex **3**

LCMS of complex **3** displayed a signal at m/z 540.1 (z=1) assigned to $[M-Cl]^+$ that could be seen from **Fig.9**. Observed mass $[M-Cl]^+$ = 540.1 Calculated mass $[M-Cl]^+$ = 540.1, another fragment at 464.0 is observed for $[M-Cl-COD+ CH_3OH]^+$.

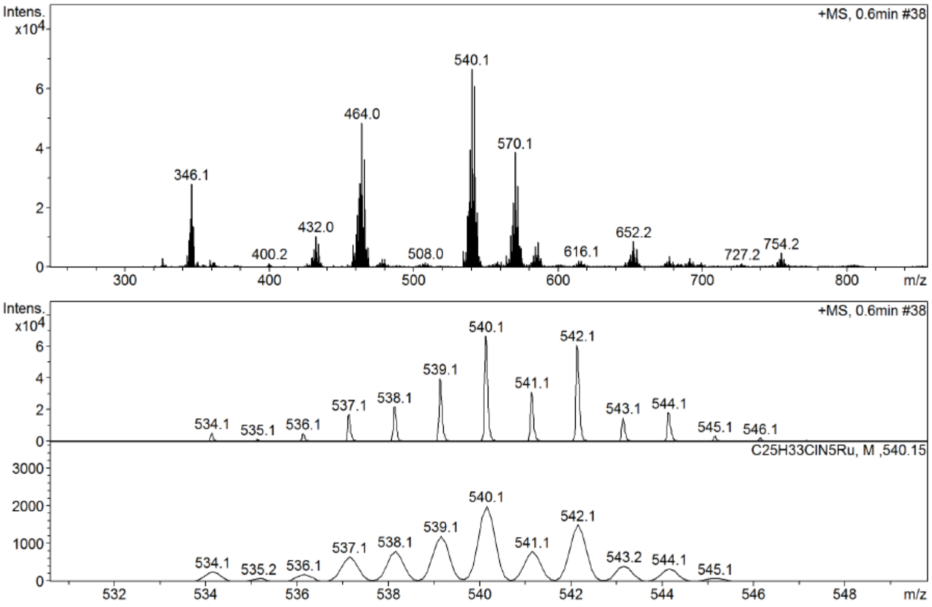
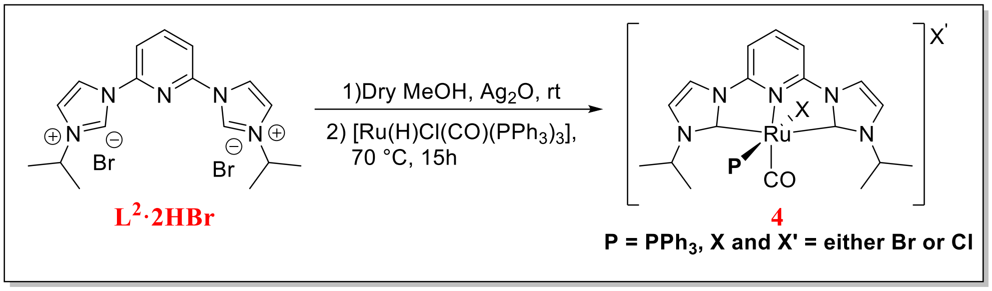


Fig. 9: Mass spectrogram of complex **3**

Complex **4** was synthesized in dry MeOH by using metal precursor $[Ru(H)(Cl)(CO)(PPh_3)_3]$. Firstly, we generate the silver carbene in ligand **L^1** after that same procedure was done for transmetallation as we've done earlier for complex 1, 2, and 3 by using different metal precursors $[Ru(H)(Cl)(CO)(PPh_3)_3]$. Reaction conditions are shown in **scheme 6**.



Scheme 6: Synthesis of complex **4**

LCMS of complex **4** displayed a signal at m/z 768.1 (z=1) assigned to $[M-X']^+$ "where X is Br" that could be seen from **Fig. 10**. Another peak was observed at 722.1 to $[M-X']^+$ "where X is Cl" Observed mass $[M-X']^+$ = 768.1 Calculated mass $[M-X']^+$ = 768.1, another fragment at 688.2 is observed for $[M-X'-X+ H]^+$.

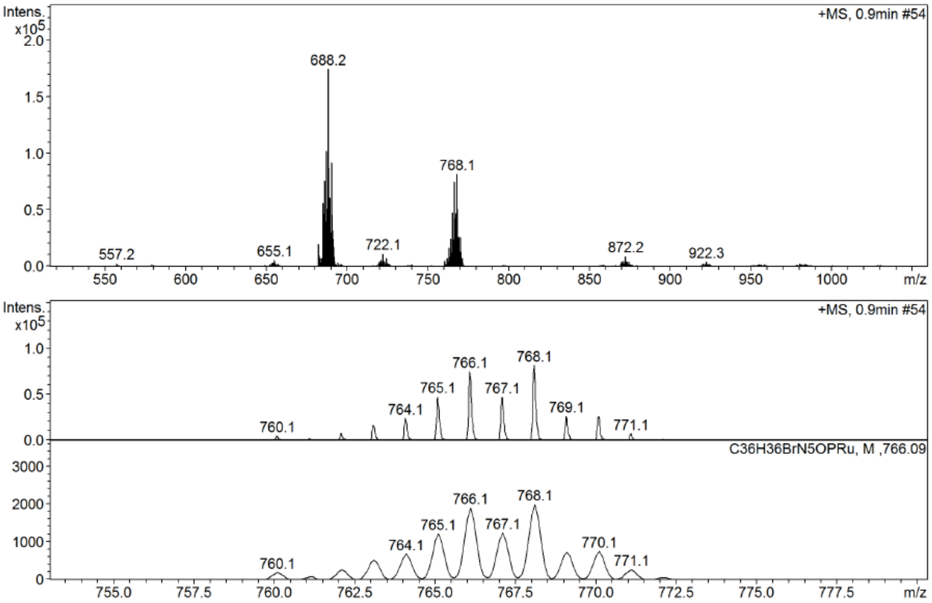
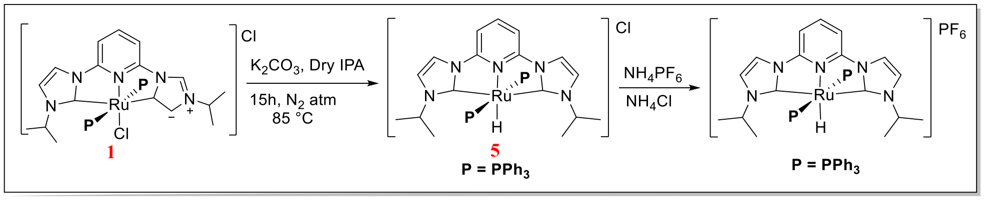


Fig. 10: Mass spectrogram of complex **4**

NMR and crystal were not obtained clean yet after many attempts.

Complex **5** is a ruthenium hydride complex that is synthesized by taking

$[Ru(CNC)^{i\text{-}pr}(PPh_3)_3Cl]Cl$ as a complex precursor. The reaction of Complex $[Ru(CNC)^{i\text{-}pr}(PPh_3)_3Cl]Cl$ **(1)** with K_2CO_3 was done in isopropanol which was used as a solvent as well as the hydrogen donor under N_2 atm. The reaction scheme as shown in **scheme 7**.



Scheme 7: Synthesis of complex **5**

Complex **5** is obtained as a greenish-brown solid. The charge of the complex ion is countered by an outer sphere chloride ion. ^1H and ^{31}P NMR reveals that complex attain an octahedral geometry in which three co-planner sites are occupied by pincer ligand $\mathbf{L^1}$ in meridional fashion and two PPh_3 are *trans* to each other. The *trans* geometry of PPh_3 was confirmed by ^{31}P NMR which shows a doublet peak at 66 ppm. ^1H NMR shows a triplet in the negative region at -8.69 ppm that indicates that a Ru-H is formed during the reaction. The co-ordination mode is also confirmed by X-ray diffraction analysis. Complex **5** is highly soluble in MeOH and DMSO but when anion was exchanged it loses the solubility in MeOH and became highly soluble in ACN. A doublet is observed at 8.27 ppm for two imidazole protons, triplet at 7.69 for pyridine top proton, another doublet for two protons of imidazole was observed at 7.44ppm and one doublet is for two protons of pyridine at 7.39 ppm. ^1H NMR also reveals that three peaks for PPh_3 proton are observed in region 6.75-7.25 ppm. A heptet and doublet were observed in the aliphatic region for the *iso*propyl group. ^1H and $^{31}P\{^1H\}$ NMR spectrums are shown in **Fig. 11** and **Fig. 12** respectively.

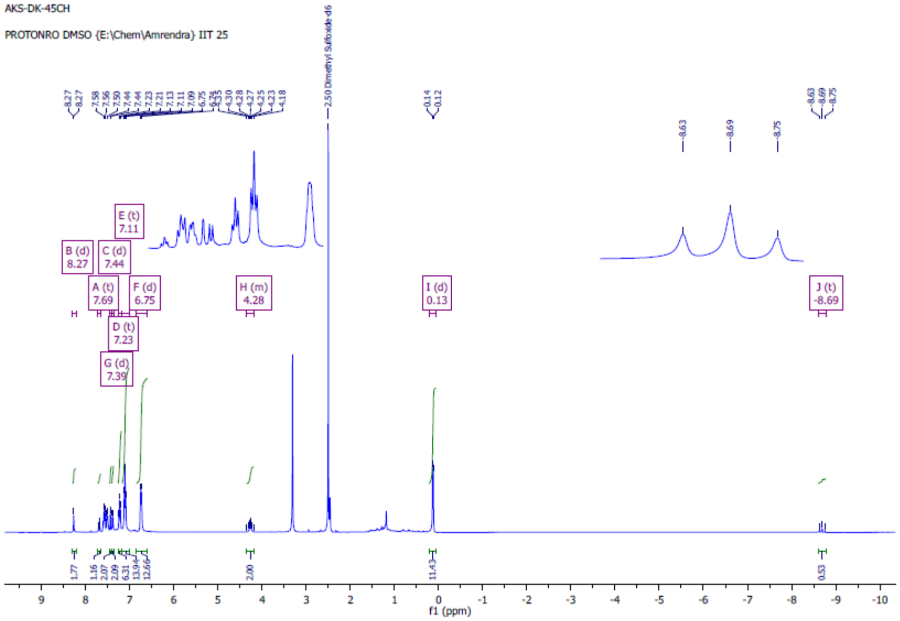


Fig. 11: ^{1}H NMR spectrum of complex **5**

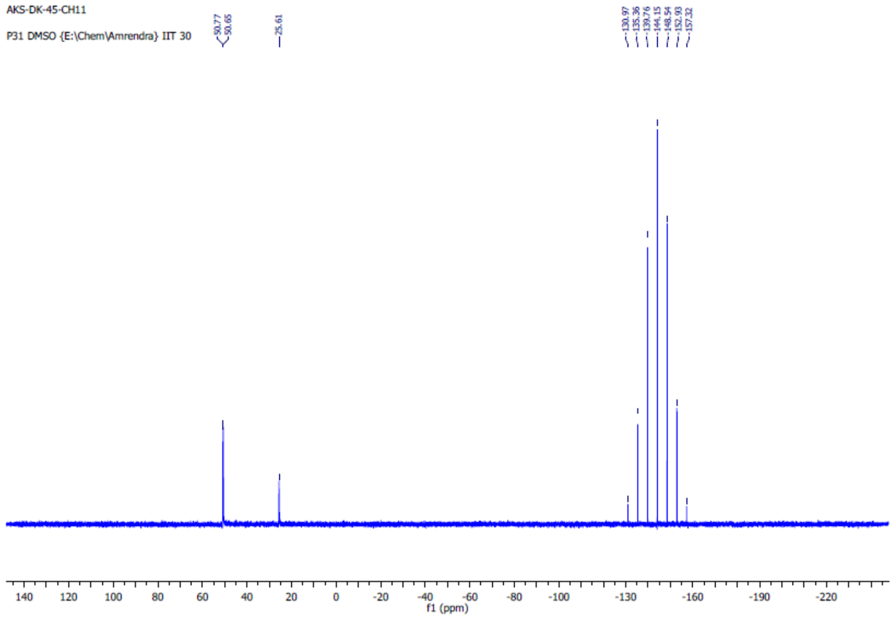


Fig. 12: ^{31}P NMR spectrum of complex **5**

It is confirmed by ^{1}H NMR that all normal and abnormal complex mixture which we have got in Complex **1** is completely converted into Complex **5** and due to one heptet in NMR, it can be sat that complex is found in a normal carbene manner.

LCMS of complex **5** displayed a signal at m/z 922.23 (z=1) assigned to

$[M-Cl]^+$ that could be seen from **Fig. 13**. There is no other peak higher than that of 922.23. Observed mass $[M-Cl]^+$ = 922.23 Calculated mass $[M-Cl]^+$ = 922.27.

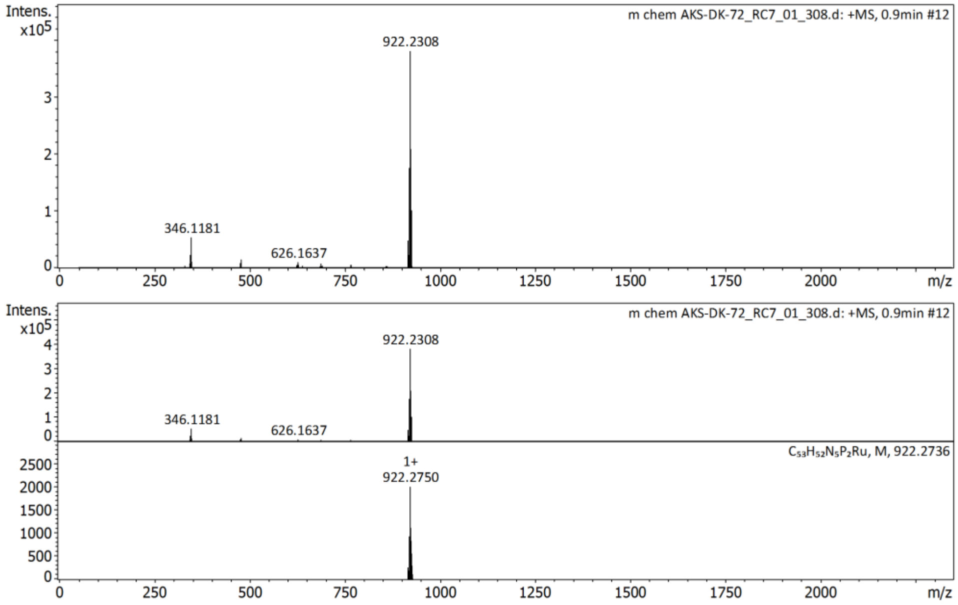
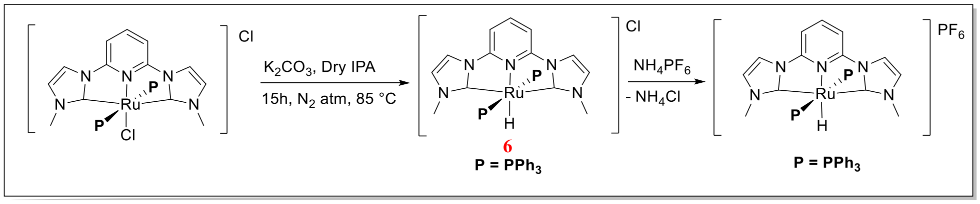


Fig. 13: Mass spectrogram of complex **5**

Complex **6** was synthesized by the treatment of complex precursor $[Ru(CNC)^{met}(PPh_3)_3Cl]Cl$ with K_2CO_3 in IPA. IPA is used as a solvent as well as H-donor to the metal center. Reaction conditions and procedures are shown in the reaction scheme.



Scheme 8: Synthesis of complex **6**

Hydride complexes mostly generate as intermediate in transfer hydrogenation and another catalysis. These hydride complex can also use for base free catalysis. Complex $[Ru(CNC)^{met}(PPh_3)_3Cl]Cl$ was synthesized earlier by Dibya Yadav *et al* in our group and not published yet. Characterization has been completed for this complex. Complex **6** was characterized by mass spectrometry and NMR techniques. Still, we are little bit far away from the crystal structure of **6.** For NMR, we exchanged the anion with PF_6 by treating complex **6** with NH_4PF_6 in MeOH. The structure can be predicted by ^1H and ^{31}P NMR. There is one doublet at 51.76 ppm is observed that reveals that both PPh_3 are trans to each other and another septet is for PF_6 that is an anion of the complex. A peak was observed at -8.86 ppm which shows that a Ru-H bond is present. The singlet was observed at 8.31 for two protons of imidazole, a triplet for pyridine top proton at 7.85, the doublet is found at 7.85 for another two imidazole protons and another doublet of two protons of pyridine was observed at 7.24 ppm. Three peaks of doublet, triplet, and doublet were found for PPh_3 protons. In the aliphatic region, a doublet of 6 protons was observed that is for the methyl group. Since the conclusion is that ruthenium adopted octahedral geometry in complex 6. Three co-planner sites are occupied by pincer ligand $(CNC)^{met}\cdot 2HBr$, two sites are occupied by the two PPh_3 and another is by hydride trans to pyridyl nitrogen.

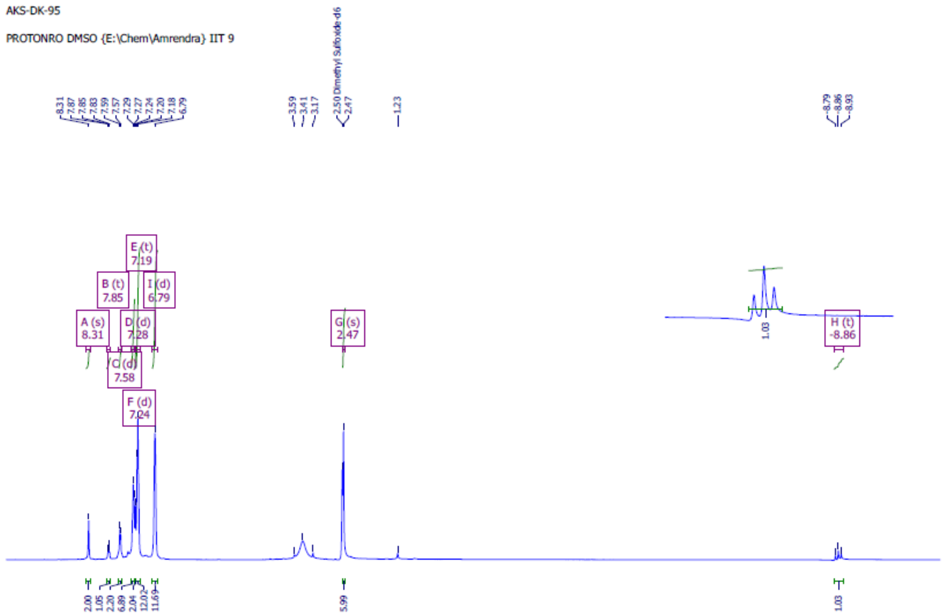


Fig. 14: ^1H NMR spectrum of complex **6**

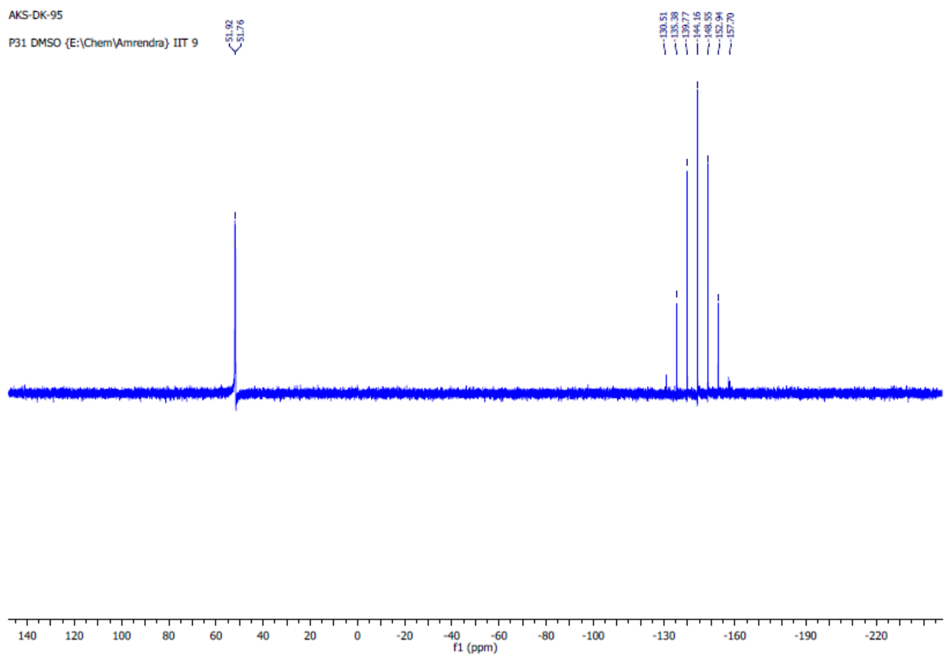


Fig. 15: ^{31}P NMR spectrum of complex **6**

LCMS of complex **6** displayed a signal at m/z 866.22(z=1) assigned to [M-Cl]$^+$ that could be seen from **Fig.16**. There is no other peak higher than that of 866.22. Observed mass [M-Cl]$^+$ = 866.22Calculated mass [M-Cl]$^+$ = 866.21

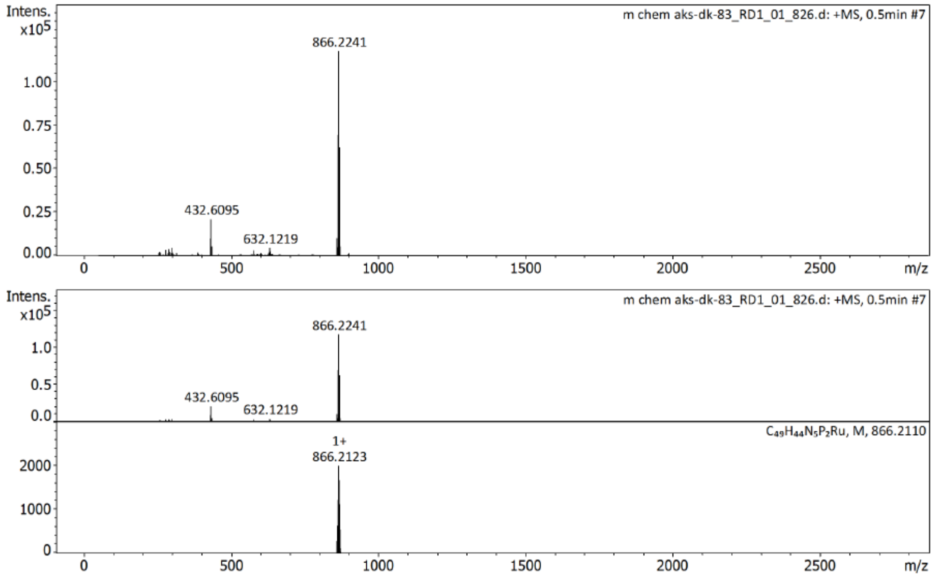
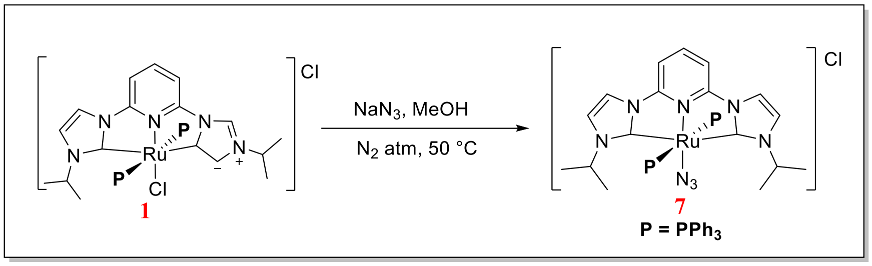


Fig. 16: Mass spectrogram of complex **6**

Complex **7** was synthesized by using complex precursor **1**. Complex 1was treated with sodium azide (NaN_3) in methanol. Reaction conditions are shown in **scheme 9**.



Scheme 9: Synthesis of complex **7**

The complex is characterized by ESI-MS and IR techniques. IR spectroscopy reveals that azide is attached to a metal center that can be confirmed by IR frequency at 2041.80 is of N_3 bond stretching frequency. IR spectrum was recorded by KBr pallets. Complex **7** was highly sensitive towards moisture.

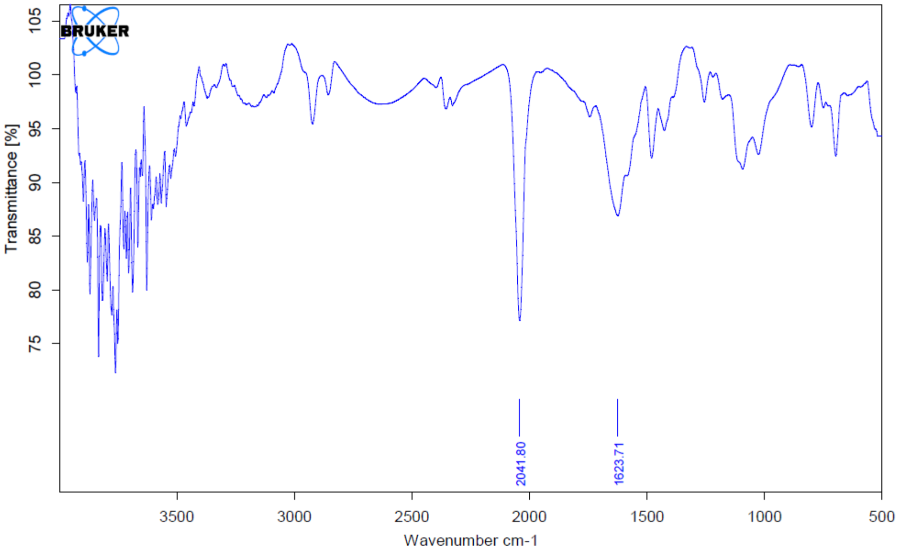


Fig. 17: FTIR spectrum of complex **6**

We have done many attempts to convert this azido complex to nitrido complex but we didn’t get success to synthesize the nitrido complex.

LCMS of complex **7** displayed a signal at m/z 963.22(z=1) assigned to $[M\text{-}Cl]^+$ that could be seen from **Fig.18**. There is no other peak higher than that of 963.22. Observed mass $[M-Cl]^+$ = 866.22 Calculated mass $[M-Cl]^+$ = 963.27

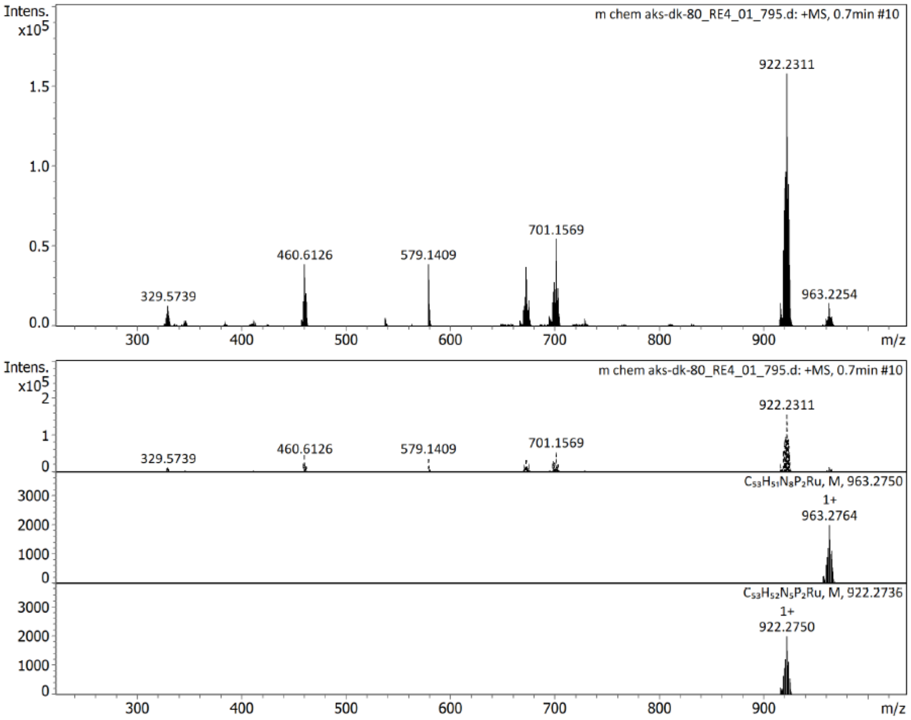


Fig. 18: Mass spectrogram of complex **6**

3.3. Molecular structure of complexes

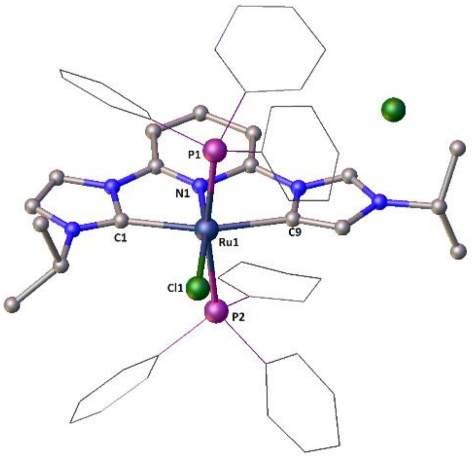


Fig.19: Structure of Complex 1

Table 1: The selected bond lengths (Å) and bond angles (º) of complex **2**

Ru1-S1	2.2936(11)
Ru1-Cl1	2.4300(11)
Ru1-S1	2.3130(12)
Ru1-N1	1.996(4)
Ru1-C1	2.073(5)
Ru1-C11	2.062(5)
S1- Ru1-Cl1	87.57(4)
S1-Ru1-S2	175.97(5)
S2-Ru1-Cl1	93.40(5)
N1-Ru1-S1	89.79(11)
N1 Ru1-Cl1	177.26(12)
N1-Ru1-S2	89.28(11)
N1-Ru1-C1	77.99(17)
N1-Ru1-C11	78.15(18)
C1-Ru1-S1	91.83(12)
C1-Ru1-Cl1	101.34(13)
C1-Ru1-S2	91.81(13)
C11-Ru1-S1	88.01(13)
C11-Ru1-Cl1	102.49(14)
C11-Ru1-S2	87.96(13)
C11-Ru1-C1	156.14(18)

Table 2: Crystal refinement data for complex **2**

Empirical formula	$C_{21}H_{39}Cl_2N_5O_5RuS_2$
Formula weight	677.66
Crystal system	Monoclinic
Space group	*P2₁/n*
a (Å)	11.3897(2)

b (Å)	11.0142(2)
c (Å)	24.3549(5)
α (°)	90
β (°)	96.689(2)
γ (°)	90
V (Å^3)	3034.49(10)Å^3
ρcalcd (mg/m^3)	1.483mg/m^3
Z	4
μ (mm^{-1})	7.411mm^{-1}
θ ranges (°)	7.31 to 142.434
Reflections collected/ unique	13716
Goodness-of-fit (GOF) on F^2	1.014
Final R indices[I > 2σ(I)]	R_1 = 0.0756, wR_2 = 0.1989
R indices (all data)	R_1 = 0.0814, wR_2 = 0.2083

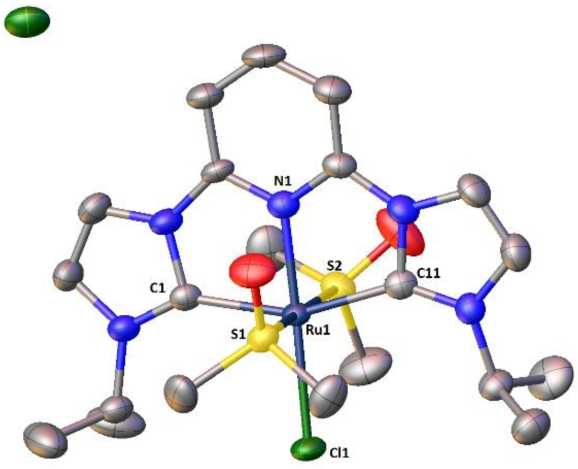


Fig.20: Structure of Complex 2

Table 5: The selected bond lengths (Å) and bond angles (º) of complex **5**

Ru1-C1	2.015(7)
Ru1-C11	2.045(7)
Ru1-N1	2.052(6)
Ru1-P2	2.3334(19)
Ru1-P1	2.3502(18)
C1-Ru1-C11	154.6(3)
C1-Ru1-N1	77.7(3)
C11-Ru1- N1	76.9(3)
C1-Ru1-P2	91.8(2)
C11-Ru1-P2	88.7(2)
N1-Ru1-P2	94.31(18)
C1-Ru1-P1	91.5(2)
C11Ru1-P1	94.5(2)
N1-Ru1-P1	100.71(18)
P2-Ru1-P1	164.98(7)

Table 2: Crystal refinement data for complex **2**

Empirical formula	$C_{53}H_{51}ClN_5P_2Ru$
Formula weight	956.45
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.3384(3)
b (Å)	26.5703(15)
c (Å)	14.8808(6)
α (°)	90
β (°)	92.582(3)
γ (°)	90
V (Å^3)	4873.5(4)Å^3

ρcalcd (mg/m^3)	1.483mg/m^3
Z	4
μ (mm^{-1})	4.035 mm^{-1}
θ ranges (°)	3.407 to 71.420
Reflections collected/ unique	9229
Goodness-of-fit (GOF) on F^2	1.162
Final R indices[I > 2σ(I)]	R_1 = 0.1253, wR_2 = 0.3274
R indices (all data)	R_1 = 0.1032, wR_2 = 0.2955

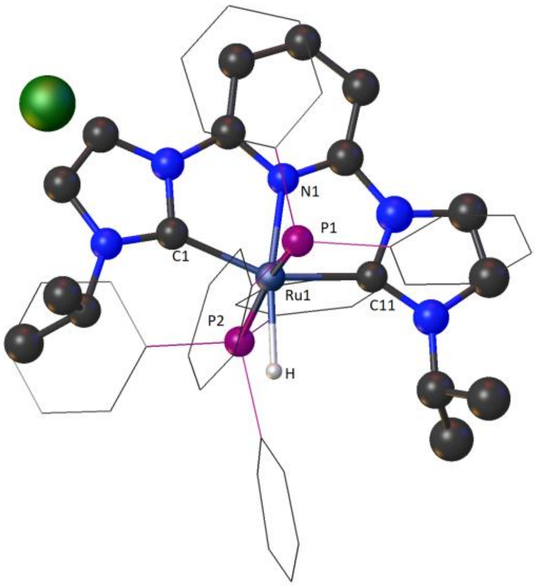


Fig.21: Structure of Complex 5

Chapter 4: Conclusion and Future Prospective

4.1 Conclusion: In summary, we have successfully synthesized some electron-rich Ru(II) complexes with NHC donor tridentate ligands. These Ru(II) complexes have been synthesized by using different ruthenium metal precursors and characterized by NMR, ESI-MS, and XRD techniques. Structures of complexes **1**, **2,** and **5** were confirmed by single-crystal XRD. It was found that NHC tridentate pincer ligand bonded abnormally in complex **1** and normal fashion in complexes **2** and **5**. As we have seen Ru(II) pincer complexes have been shown in a vast range of applications in the near past. So, our synthesized Ru(II) complexes can be explored for various types of catalysis in the near future.

4.2 Future prospective: Ruthenium complexes have shown a wide range of applications like ester hydrogenation, CO_2 fixation, etc. in past and our synthesized complexes **1** to **7** can also show various catalytic applications in near future.

(1) CO_2 reduction
(2) N-alkyl amination
(3) Ester hydrogenation
(4) Base free catalysis
(5) Transfer hydrogenation
(6) C-H activation

References:

(1) Huang K.W., Lupp D. (2020), The importance of metal−ligand cooperativity in the phosphorus nitrogen PN^{3}P platform: A computational study on mn-catalyzed pyrrole synthesis, Organometallic*s*, *39* (1), 18-24.

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