Synthesis and Characterization of Ru(II) Complexes from a Ru(III)-NHC Complex as Precursor

M. Sc. Thesis

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Synthesis and Characterization of Ru(II) Complexes from a Ru(III)-NHC Complex as Precursor

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

> *by* **Priya R. Sharmesh**



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Synthesis and Characterization of Ru(II) Complexes from a Ru(III)-NHC Complex as Precursor" 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 2020 to June 2021 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.

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

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> Priya R Sharmesh Discipline of Chemistry IIT Indore

DEDICATED



MY PARENTS

For their unwavering belief in my potential!

ABSTRACT

Our main aim is to synthesize/mimic the well-known Ru(II) analogues by repurposing previously synthesized Ru(III) complex as a precursor. We have replaced two of the monodentate ligands in the original complexes with NHC-based bidentate ligand framework, i.e., 3isopropylimidazolium pyridine (**L**). The synthetic route followed is the same as reported with key modifications according to our chemical environment. We have synthesized three complexes with the metal precursor [RuCl₃(H₂O)(L)], which was synthesized using RuCl₃·3H₂O as starting material. Ru(II) complexes [RuCl₂(PPh₃)₂(L)] (**2**), [RuClCO(PPh₃)₂(L)] (**3**), [RuHCO(PPh₃)₂(L)] (**4**) were synthesized by the reaction of NHC ligand precursor and metal precursor under thermal conditions. All the synthesized ligands and complexes have been characterized by mass spectrometry and NMR spectroscopic techniques.

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NOMENCLATURE

°C	Degree Centigrade
%	Percentage
g	Gram
Mol	Mole
Mmol	Milli Mole
mL	Milli Litre
μL	Micro Litre
K	Kelvin
δ	Chemical Shift (NMR)

ACRONYMS

NHC	N-Heterocyclic Carbene
ESI.	Electrospray ionization
LCMS	Liquid chromatography-mass
	spectrometry
NMR.	Nuclear magnetic resonance
DMSO	Dimethylsulfoxide
MeOH	Methanol
ACN	Acetonitrile
Ru	Ruthenium
Ν	Nitrogen
DCM	Dichloromethane
H ₂ O	Water

CHAPTER 1

INTRODUCTION

1.1. Aim of the project

Our main aim is to mimic the well-known Ru(II) analogues with previously synthesized Ru(III)-NHC complex as a precursor. Because of NHC's excellent potential to donate an electron pair, an electron-rich complex will be formed. It can be advantageous for further derivatization and forming electron-rich complexes capable of performing numerous catalysis, including small-molecule activation such as ammonia oxidation, water oxidation, and CO_2 reduction.



Figure 1: General Schematic representation of our target complexes.

1.2. General introduction

In 1964, Wilkinson and co-workers reported the Wilkinson's catalyst, which served as a model for catalytic research, resulting in several breakthroughs in the scientific community, including the use of some of the first heteronuclear magnetic resonance studies for structural elucidation in solution (³¹P) [1], parahydrogen-induced polarization spectroscopy to analyze the nature of transient reactive species [2], and a pioneer detailed kinetic investigations by Halpern [3]. Later in 1967, they reported analogues of Wilkinson's catalyst using ruthenium as the metal center. Because this rhodium complex, i.e., RhCl(PPh₃)₃ and dichlorotris(triphenylphosphine) ruthenium, RuC1₂(PPh₃)₃ [4], both dissolve in the solution of benzene as a result of which a coordinatively unsaturated species is generated, it appeared to be plausible that the complexes of ruthenium would likewise operate as a catalyst [5]. The oxides of Rh and Ru predominantly exist in a distinctive oxidation state. Because of their excellent accessibility, stability, and efficiency towards CO oxidation at low-temperature, these transition metals, ruthenium and rhodium, are considered excellent alternatives to conventional metal oxide catalysts [6]. N-heterocyclic carbenes are gaining popularity as ligands for transition metals lately due to their exceptional performance in metathesis chemistry and coupling reactions [7]. Because of its stereo-electronic diversity and capacity to create stable molecules, N-heterocyclic carbene-based transition-metal complexes offer a large number of possible uses in organometallic chemistry and catalysis [8]. More extensive study of the effects of metal and ligand (steric and electronic variables) will result in more active catalysts in mild circumstances and catalysts with more selectivity, which is in accordance with the overarching principles representing the adaptability of transition-metal complexes as catalysts. Due to the range of valency states often participating in these catalytic reactions $(Ru^0 \rightarrow Ru^{IV})$, the ruthenium system appears to be particularly well suited for research [9].

Herein we report the analogues of Wilkinson's catalyst incorporating ruthenium as the metal center bound with bidentate NHC ligand.

1.2.1. N-Heterocyclic carbene (NHC) donors

Carbenes can be defined as a neutral species with a divalent carbon bearing 6e⁻ in the valence shell. Due to an incomplete octet and unsaturated coordination environment, carbenes with no substitutions are usually unstable intermediates in many organic reactions. NHCs as a ligand for transition-metal catalysts have attracted a lot of interest in recent decades, especially as substitutes for phosphine. NHCs are a special class of carbenes containing one carbene carbon and at least one nitrogen atom in their ring structure [10,11]. σ -donation nature of Nitrogen atoms stabilizes the carbone carbon in both ways inductively and mesomerically by donating electrons into the empty p-orbital. The cyclic nature of NHC also leads to a more singlet state and stability by forcing carbone carbon into a bent form with a more sp^2 type arrangement. NHCs of our interest possess some extra stability because these are derived from heteroaromatic compounds and have a partial aromatic character, such as imidazolium salts. The first NHC-based transition metal compounds were reported by Wanzlick [12] and Ölefe [13]. Bertrand reported the first stable carbene, but Arduengo's isolation of 1,3 bis(diadamantyl)imidazol-2-ylidene as a stable NHC was the real breakthrough [14-16].



Figure 2: Imidazolylidene type NHCs of our interest.

We have used a carbene-based bidentate ligand framework for the generation of electron-rich, stable metal complexes during this project.

1.2.2. Target complex

We have proposed a complex of Ru metal conjugated with one bidentate NHC ligand occupying two coordination sites, and the remaining sites are occupied by halogen or other groups. The NHC ligand will increase electron density on the metal center and make it capable of forming its derivatives on binding with other ligand skeletons (X= PPh₃, Y= CO/CI/H).



Figure 3: Proposed Metal Complex Framework.

CHAPTER 2

EXPERIMENTAL SECTION

2.1 Chemicals and Reagents:-

All the solvents were obtained from commercial sources and purified before use. All of the chemicals were of analytical grade, and once obtained, they were used without further purification. Imidazole compound was obtained from SRL, with 99% purity, 2-bromopyridine was also used without further purification after purchasing from Spectrochem, and ruthenium trichloride trihydrate (RuCl₃·3H₂O) was procured from SRL, India. In addition, potassium hydroxide (Emplura, 85%), isopropyl bromide (Spectrochem, 99%), sodium chloride (SRL, 99.9%).

2.2 Instrumentation:-

NMR spectra were recorded on an AVANCE III 400 Ascend Bruker BioSpin machine at ambient temperature. Mass spectrometric analysis was done on Bruker-Daltonics, a microTOF-Q II mass spectrometer. The ligand and complexes were characterized using NMR spectroscopy and mass spectrometry as analytical methods.

2.3 Synthesis of ligand:-

2.3.1 Synthesis of iso-propylimidazole (L¹):-

 L^1 was synthesized by following a reported procedure [17]. 3g (44.067 mmol) imidazole, 2.64 g (66 mmol) in NaOH, and 40 ml DMSO were loaded into a two-neck bottom flask. The reaction mixture was stirred for 2 hours at room temperature until it became a pale-yellow solution. Then 6.205 mL (66.568 mmol) 2-isopropyl bromide was added to the solution after 2 hours and was allowed to react. The reaction was monitored by TLC. The reaction was completed later, after 12 hours, and water was introduced to stop the reaction. Then, the reaction mixture was extracted three times with ethyl acetate (100 mL). Organic layers were combined and were subsequently washed several times

with water and brine solution. It was then dried over sodium sulphate (Na_2SO_4) , and the solvent was evaporated under a reduced vacuum, yielding the pale-yellow liquid as the desired compound. This gives pure iso-propylimidazole L^1 in 3.952 g, 81.4% yield.

¹H NMR (CDCl₃, 400 MHz): $\delta = 7.55$ (s, 1H), 7.04 (s, 1H), 6.97 (s, 1H), 4.35 (m, 1H), 1.47ppm (d, 6H).¹³C NMR (CDCl₃, 100 MHz): $\delta = 133.79, 127.62, 115.24, 58.89, 22.30$ ppm.

LCMS (ESI): $[M+Na]^+$ observed = 133.0878, $[M+Na]^+$ calculated = 133.0736.

2.3.2 Synthesis of Ligand (L·HBr):-

An ace pressure tube was charged with 461.8 μ L (765.3 mg, 5 mmol) 2-bromopyridine and 501.6 μ L (550.8 mg, 5 mmol) L¹and was sealed thoroughly. The reaction mixture was allowed to stir for 24 hours at 160 °C. After subsequent hours the colour of the solution noted was brown. After 24 hours, the reaction was completed, and the reaction mixture was treated and washed several times with hexane and DCM successively to get the solid brown product. The product was filtered to obtain the pure product (L·HBr) in 1210 mg, 84.2 % yield.

¹H NMR (CDCl₃, 400 MHz): δ = 11.64 (s, 1H), 8.71 (d, 1H), 8.49 (s, 1H), 8.33 (s, 1H), 8.02 (t, 1H), 7.65 (s, 1H), 7.43 (t, 1H), 5.21 (dq, 1H), 1.72ppm (d, 6H).

LCMS (ESI): $[M-Br]^+$ observed = 188.1261, $[M-Br]^+$ calculated = 188.1182.

2.4 Synthesis of complexes:-

2.4.1 Synthesis of metal precursor complex C1:-

To 200 mg (0.7458 mmol) of ruthenium trichloride trihydrate (RuCl₃·3H₂O), and 195.01 mg (0.7458 mmol) of the prepared ligand **L·HBr**, 3-4 mL of THF was added in Schlenk tube under N₂ atmosphere. For 12 hours, the reaction mixture was refluxed at 65 °C. The resulting reaction mixture was filtered out to obtain a brown-

colour precipitate. The precipitate was washed with THF 4-5 times and kept for drying, and the pure product was isolated in a significant amount in 206 mg, 66.76 % yield.

LCMS (ESI): $[M-C1]^+$ observed = 376.9623, $[M-C1]^+$ calculated = 376.9627.

2.4.2. Alternate synthesis of complex C1-

To 200 mg (0.7458 mmol) of ruthenium trichloride trihydrate (RuCl₃·3H₂O) and 195.0194 mg (0.7458 mmol) of the prepared ligand **L·HBr**, 5.0 mL of 1.0 N HCl were added. The mixture was allowed to stand in a 15mL vial for 15 days. The reaction was filtered, washed with water and ether, and allowed to dry in the air to yield 71.6 mg, 23.10% of red wine solid crystals.

2.4.3. Synthesis of complex C2:-

Under N₂ atmosphere, a Schlenk tube was charged with 3-4 mL methanol and degassed for some time. Then, at room temperature, 30 mg (0.0725 mmol) of **C1** and 57.025 mg (0.21765 mmol) of PPh₃ were added, then the mixture was refluxed for 6 hours at 65 °C. On completion, a fine yellow precipitate was obtained in the reaction vessel, which was filtered out to obtain **C2**. The product was washed with methanol 3-4 times and kept for drying, and the pure product was obtained in 26 mg, 40.27 % yield.

LCMS (ESI): $[M-Cl]^+$ observed = 848.1199, $[M-Cl]^+$ calculated = 848.1668.

2.4.4. Synthesis of complex C3:-

Under N₂ atmosphere, a Schlenk tube was charged with 95.26 mg (0.3632 mmol) of PPh₃, 3.617 mL of 2-methoxy ethanol, and degassed for some time. A solution of 50 mg (0.1210 mmol) of C1, 3.82 mL of 2-methoxy ethanol, and 3.82 mL of formaldehyde were prepared and added dropwise in the reaction vessel. For 10 minutes, the reaction mixture was refluxed at 100°C. After forming the precipitate, the

reaction was stopped and was allowed to rest under an N_2 atmosphere for 12 hours. The reaction mixture was filtered out to obtain yellow precipitate by washing it with ethanol, water, ethanol, and hexane and was kept for drying to isolate the product in 25 mg, 22.31% yield.

LCMS (ESI): $[M-Cl-CO]^+ = 848.1083$ observed $[M-Cl-CO]^+$ calculated = 848.1668.

2.4.5. Synthesis of complex C4:-

Complex C4 was synthesized by following a reported procedure [18]. Under N₂ atmosphere, a Schlenk tube was charged with 8.4 mL of ethanol, 30 mg (0.0725 mmol) of metal precursor, and kept for deaeration. After 1 hour of degassing, 76 mg (0.26 mmol) of PPh₃ was added to the Schlenk tube and was heated up to the boiling. After the reaction mixture was cooled down to room temperature, 13.626 mg (0.2428 mmol) of KOH was added and kept for continuous stirring for 1 hour at room temperature. Then it was stirred for another hour at 60 °C, then again heated to the boiling for the next 5 hours. After cooling the reaction mixture to room temperature, the slightly yellowish precipitate was separated by filtration and then was washed with ethanol (2x10mL), deionized water (2x10mL), and ethanol (2x10mL) and allowed to dry under vacuum to obtain the product C4 in 11.5 mg, 18.5% yield.

LCMS (ESI): $[M-Cl-CO]^+$ observed = 814.2093, $[M-Cl-CO]^+$ calculated = 814.2061.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Synthesis of Ligands and Characterization:-

The L^1 was prepared by dissolving NaOH in DMSO and stirred for 2 hours at room temperature. After that, isopropyl bromide was added to the pale-yellow solution and stirred continuously until converted into solid-like wax. Reaction conditions are shown in **scheme 1**. The final compound was obtained as a pale-yellow liquid after workup, with an 81.42% yield. The pale-yellow liquid was characterized as (L^1) by ¹H NMR, ¹³C NMR spectroscopy, and mass spectrometry.



Scheme 1: Synthesis of L¹

Figure 4 shows the ¹H NMR spectrum of L^1 , which shows a singlet at 7.55 ppm for one proton of imidazole and another two imidazolium protons at 7.04 ppm, 6.97 ppm respectively were observed in the aromatic region. There is a multiplet at 4.35 ppm in the aliphatic region for one proton of the isopropyl unit, and a doublet is observed at 1.47 ppm. There are some other peaks for solvent like ethyl acetate and acetone.



Figure 4: ¹H NMR Spectrum of L¹.

Figure 5 represents the ¹³C NMR spectrum of L^1 , which shows that each carbon of imidazole is different. The two carbon of isopropyl unit shows a single peak at 22.30 ppm, and the imidazolium carbon shows the peak at 133.79 ppm.



Figure 5: ¹³C NMR Spectrum of L¹.

ESI-MS of L^1 displayed a signal at m/z 133.0878 assigned to $[M+Na]^+$ ($C_6H_{10}N_2$) $[M+Na]^+$ observed mass = 133.0878, $[M+Na]^+$ calculated mass = 133.0736.



Figure 6: Mass spectrogram of L¹.

Ligand L·HBr was synthesized by heating 2-bromopyridine in neat condition with L^1 , as shown in scheme 2. The final compound was obtained with an 84.2% yield. The obtained solid (L·HBr)was characterized by ¹H NMR and mass spectrometry.



Scheme 2: Synthesis of Ligand L·HBr.

Figure 7 showing the ¹H NMR spectrum of ligand **L**·**HBr**; from there, we can see that a singlet at 11.64 ppm for the imidazolium proton and

one triplet at 8.02 ppm for pyridine top proton, a doublet at 8.71 ppm, a triplet at 8.02 ppm, and a singlet at 7.65 ppm of pyridine protons. A doublet at 1.72 ppm and a multiplet at 5.20 ppm were observed of the isopropyl protons.



Figure 7: ¹H NMR Spectrum of Ligand L·HBr.

ESI-MS of **L**•**HBr** displayed a signal at m/z 188.1261 assigned to [M-Br]⁺ ($C_{11}H_{14}N_3$). [M-Br]⁺ observed mass = 188.1261, [M-Br]⁺ calculated mass = 188.1182.



Figure 8: Mass spectrogram of Ligand L·HBr.

3.2. Synthesis of complexes and characterization

The metal precursor complex C1 was synthesized by reacting L·HBr and ruthenium trichloride trihydrate (RuCl₃·3H₂O) in THF at the reflux temperature of 65 °C for 12 hours, as shown in scheme 3, the product (C1) was obtained with 66.76% yield. Complex C1 was then characterized by mass spectrometry.



Scheme 3: Synthesis of complex C1.

ESI-MS of C1 displayed a signal at m/z 376.9623 assigned to $[M-C1]^+$ (C₁₁H₁₆C₁₂N₃ORu). $[M-C1]^+$ observed mass = 376.9623, $[M-C1]^+$ calculated mass = 376.9627.



Figure 9: Mass spectrogram of complex C1.

Alternatively, complex C1 was synthesized by adding L·HBr and ruthenium trichloride trihydrate (RuCl₃·3H₂O) to HCl and kept for 15 days as shown in scheme 5, and the final product was obtained with 23.10% yield.



Scheme 5: Alternate synthesis of complex C1.

Complex C2 was synthesized by reacting complex C1 and PPh₃ in MeOH at the reflux temperature of 65°C for 6 hours, as shown in scheme 4, and the final product was obtained as with a 40.27% yield. Complex C2 was then characterized by ¹H NMR, ³¹P NMR, and mass spectrometry.



Scheme 4: Synthesis of complex C2.

Figure 10 shows the ¹H NMR spectrum of complex **C2**, which shows the absence of the imidazolium proton from the ligand framework, suggesting a Ru-C bond formation. Also, there is no hydride peak in the negative region of the NMR, indicating that the complex formed does not have a metal-hydride bond.



Figure 10: ¹H NMR Spectrum of complex **C2**.



Figure 11: ³¹P NMR Spectrum of complex C2.

ESI-MS of C2 displayed a highest intensity peak assignable to [M-Cl-PPh₃]⁺ at m/z 586.0487 signal and additional peak at m/z 848.1199 (z=1) assigned to $[M-Cl]^+$ (C₄₇H₄₄C₁₂N₃P₂Ru). [M-Cl]⁺ observed mass = 848.1199, [M-Cl]⁺ calculated mass = 848.1668.



Figure 12: Mass spectrogram of complex C2.

Complex C3 was synthesized by reacting complex C1, PPh₃, and formaldehyde in 2-methoxy ethanol at the reflux temperature of 100 °C for 10 minutes as shown in scheme 6, and the final product was obtained with 22.31% yield. Complex C3 was then characterized by ¹H NMR, ³¹P NMR, and mass spectrometry.



Scheme 6: Synthesis of complex C3.

Figure 13 shows the ¹H NMR spectrum of complex **C3**, in which the absence of the imidazolium proton from the ligand framework suggests forming a Ru-C bond. Also, there is no hydride peak in the negative region of the NMR, indicating that the complex formed does not have a metal-hydride bond.



Figure 13: ¹H NMR Spectrum of complex C3.



Figure 14: ³¹P NMR Spectrum of complex C3.

ESI-MS of C3 displayed an intense signal at m/z = 586.0388 which is assignable to [M-Cl-PPh₃-CO]⁺. Additional signals have been observed due to the presence of variety of ligands and the attachment of the solvent molecule. A signal at m/z = 655.0488, appeared for [M-Cl-

 $PPh_3+CH_3CN]^+$. The molecular ion peak observed at m/z = 848.1083is assignable to $[M-Cl-CO]^+$. Calculated $[M-Cl-CO]^+ = 848.1083$ observed $[M-Cl-CO]^+ = 848.1668$.



Figure 15: Mass spectrogram of complex C3.

Since the mass data of this complex **C3** corresponds exactly to the mass data of complex **C2**, it might be possible that this reaction can eventually lead to the production of the complex **C2**.

Complex C4 was synthesized by reacting complex C1 and PPh₃ with EtOH and KOH at the reflux temperature of 25-78°C for 8 hours as shown in scheme 7, and the final product was obtained with 18.5% yield. Complex C4 was then characterized by ¹H NMR, ³¹P NMR, and mass spectrometry.



Scheme 7: Synthesis of complex C4.

Figure 16 shows the ¹H NMR spectrum of complex **C4**, which shows the absence of the imidazolium proton from the ligand framework, suggesting the formation of a Ru-C bond.



Figure 16: ¹H NMR Spectrum of complex C4.



Figure 17: ³¹P NMR Spectrum of complex C4.

ESI-MS of C4 displayed a signal at m/z 814.2093 (z=1) assigned to $[M-Cl-H]^+$. Calculated $[M-Cl-H]^+ = 814.2093$ observed $[M-Cl-H]^+ = 814.2061$



Figure 18: Mass spectrogram of complex C4.



Figure 19: Mass spectrogram of complex C4.

CHAPTER FOUR

CONCLUSION AND FUTURE PROSPECTIVE

4.1 Conclusion

In summary, we have successfully synthesized electron-rich Ru(II) complexes C2, C3, and C4 with NHC donor bidentate ligands. These Ru(II) complexes have been synthesized using ruthenium metal precursor C1 and characterized by NMR and ESI-MS techniques.

4.2 Future Prospective

Ruthenium complexes have already demonstrated a wide variety of uses, such as ester hydrogenation, CO_2 fixation, etc., and our synthesized complexes 2 to 4 are expected to demonstrate a wide variety of catalytic uses in the near future.

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