# Development of Ruthenium based Molecular Catalysts for Hydrogen Production from Formic Acid

Ph.D. Thesis

by

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# DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE APRIL 2024

# Development of Ruthenium based Molecular Catalysts for Hydrogen Production from Formic Acid

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

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By

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### INDIAN INSTITUTE OF TECHNOLOGY INDORE

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### INDIAN INSTITUTE OF TECHNOLOGY INDORE

### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Development of Ruthenium based Molecular Catalysts for Hydrogen Production from Formic Acid" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the Department of Chemistry, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2019 to April 2024 under the supervision of Prof. Sanjay Kumar Singh, Department of Chemistry, Indian Institute of Technology 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.

sanjeev kushwaha (May 13, 2024)

Signature of the student with date (SANJEEV KUSHWAHA)

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

Signature of Thesis Supervisor with date

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SANJEEV KUSHWAHA has successfully given his/her Ph.D. Oral Examination held on 09, August 2024.

Signature of Thesis (Prof. SANJ Y KUMAR SINGH)

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#### SYNOPSIS

The global energy demand is predicted to rise significantly in the coming decades due to various factors such as population growth, urbanization, industrialization, and increasing standards of living, meeting this demand with sustainable energy sources will be crucial in the near future. Traditional energy sources such as fossil fuels are major contributors to air and water pollution, as well as greenhouse gas emissions, which exacerbate climate change and its associated impacts such as global warming, extreme weather events, and sealevel rise. Hence, recent technological advancements have focused on developing a society that offers low environmental impact and high energy efficiency. In this context, hydrogen has been identified as a clean and ecofriendly alternative energy carrier with reduced greenhouse gas emissions. However, the flammable nature of hydrogen gas poses a challenge for its handling and storage, which in turn limits its application as a fuel source. Furthermore, the utilization of liquid organic hydrogen carriers (LOHCs) has emerged as a promising approach to address the challenges associated with the storage and transportation of hydrogen. LOHCs such as methanol (12.4 wt%), formaldehyde (8.4 wt%), and formic acid (4.4 wt%) have recently received significant attention as viable options for storing and transporting hydrogen safely and efficiently. Therefore, there is a growing need for cost-effective and sustainable methods to produce, store and distribute hydrogen, which can be facilitated with LOHCs.

Herein, this thesis deals with the ruthenium-based molecular catalysts for hydrogen production from formic acid in water. This thesis includes five chapters. The first chapter describes the brief advantages and drawbacks of hydrogen storage and production and focuses on the alternative energy source for the future. Particularly focused on the sustainable methods to produce, store, and distribute hydrogen, which can be facilitated with LOHCs and also focused on the structure-activity relationships which affects the catalytic activity in formic acid dehydrogenation. This chapter also describes the overview of noble and nonnoble metal-based molecular catalysts developed for hydrogen production from formic acid in water. The subsequent chapters include the synthesis, characterization and detailed discussion of catalytic activities of newly synthesized arene-Ru (II) complexes for hydrogen production from formic acid in water. The main motive of this thesis is to achieve hydrogen production from formic acid under ambient reaction conditions with the newly synthesized arene-Ru (II) catalysts for long-term and bulk-scale reactions. Further, to detect and isolate the crucial catalytic intermediates involve in formic acid dehydrogenation to understand the reaction pathway. In the last chapter, concluding remarks and the future scope of the present research work are briefly mentioned.

The content of each chapter are summarized below.

# Chapter 1: A comprehensive overview of formic acid dehydrogenation over molecular catalysts

This chapter highlights the sustainable, ecologically benign alternative renewable energy resources due to the depletion of the resources of fossil fuels and growing environmental concerns. Hence, utilizing hydrogen as a fuel may aid in reducing environmental pollution by emitting no hazardous emissions. However, the production, storage, and transportation of hydrogen gas pose numerous challenges and safety concerns due to its chemical and physical properties. Therefore, it is very crucial to develop sustainable and practical method for the hydrogen production, storage and transportation. Furthermore, a wide range of liquid organic hydrogen carriers (LOHCs) are also been extensively explored for hydrogen delivery, storage, and transportation. These liquid hydrogen carriers can release hydrogen under ambient conditions, with the suitable catalyst. Formic acid, which contains a volumetric hydrogen content of 4.4 wt%, has gained significant attention due to its accessibility, comparatively low toxicity and minimal danger of explosion or other hazardous mishaps.

However, several molecular catalytic systems have been well explored for formic acid dehydrogenation. Among them, Ir, Rh and Ru-based molecular catalysts have shown outstanding performance for the dehydrogenation of formic acid in water. Here, this chapter deals with a wide range of noble and non-noble metal-based catalysts reported for FA dehydrogenation. Among the literature reports, Ir-based complexes prove to be very efficient for the dehydrogenation of formic acid in water to achieve excellent catalytic activity in terms of turnover numbers (TONs) and turnover frequencies (TOFs). Due to the very high cost of Ir, Ru-based complexes, along with several other non–noble metal-based catalysts, attracted and proven to be effective for formic acid dehydrogenation in water. In this chapter, several noble and non-noble metal catalysed formic acid dehydrogenation are extensively explored with their structure-activity relationship in formic acid dehydrogenation based on literature.

The specific goal of this thesis is to improve the efficiency of rutheniumbased molecular catalysts for hydrogen production from formic acid. Based on the research gaps available in the literature reports, the prime objective the present work are:

- To develop an efficient catalytic system based on water-soluble Ruthenium-pyridyloxime catalyst and investigate the role of facile protonation – deprotonation of the catalysts in the catalytic cycle for the hydrogen production from formic acid in water. In addition, the detection and isolation of the various catalytic reaction intermediates to identify their crucial role of protonation-deprotonation in the catalytic dehydrogenation pathway.
- To synthesize a series of arene-Ru(II) complexes containing heterocyclic bis imidazole methane-based ligands and employ them for hydrogen production from formic acid in water to identify the effect of imidazole-based ligands and heterocyclic ring effect in the catalytic activity as compared to the oxime-based ligands. In addition, the detection and isolation of the various catalytic reaction intermediates to identify their crucial role in the catalytic dehydrogenation pathway.
- To synthesize diruthenium complexes containing bridged bis imidazole methane-based ligands and employ them for hydrogen production from formic acid in water and identify the effect of diruthenium catalyst as compared to monoruthenium catalyst in terms of activity, stability and recyclability. In addition, the detection and isolation of the various

catalytic reaction intermediates to identify their crucial role in the catalytic dehydrogenation pathway.





In this chapter, a series of water soluble (arene)Ru(II) complexes ([Ru]-1 - [Ru]-8) ligated with different N, N-based ligands (-pyridyloxime, pyridylmethyloxime, and -pyridylimines) were synthesized and explored for the formic acid dehydrogenation in water under mild conditions. Among the studied complexes, the Ru-pyridyloxime catalyst [Ru]-1 exhibited high catalytic performance for the FA dehydrogenation, where the oxime ligand played a crucial role in achieving enhanced catalytic performance, with TON ~13,000 and remarkably high long-term stability (~3 months) as well as recycled more than 25 catalytic runs for H<sub>2</sub> production from formic acid in water at 90 °C. The high catalytic activity of the catalyst was attributed to the -OH moiety present in the complex. Further, in-depth mass and NMR investigations with control kinetic experiments revealed the involvement of several intermediate species to establish the rate determining step over [Ru]-1 catalyst. Further, to detect the several crucial intermediates such as H<sub>2</sub>O coordinated, formate coordinate and hydride coordinate species, conducted several control experiments and analysed the species by mass and NMR. These findings inferred the plausible involvement of the proximal -N-OH in hydrogen release from the Ru-hydrido species resulted in the observed enhanced catalytic activity of [Ru]-1 catalyst. On the other hand, [Ru]-2 and [Ru]-3 catalysts having -OMe and -N<sup>n</sup>Pr,

respectively groups, may involve proton  $(H_3O^+)$  assisted hydrogen release, which contribute to the observed activity of these catalysts.

Based on experimental findings, the plausible reaction pathway for hydrogen gas generation from FA over the present catalytic system was proposed. Hence these findings helped us to establish the important role of catalytic intermediates on the efficient formic acid dehydrogenation over the **[Ru]-1** is an important development for aqueous-phase hydrogen release system.

Chapter 3: Heterocyclic Bis-imidazole Methane based Ruthenium Catalysts for Hydrogen Production from Formic Acid in Water



Based on the literature survey that imidazole ligated metal-based catalysts are highly active in the dehydrogenation of formic acid in water. This chapter deals with the synthesis of half sandwich arene-Ru(II) complexes ([Ru]-9–[Ru]-13) based on heterocyclic bis-imidazole methane based ligands and characterized them using various spectro analytical techniques and the molecular structures of the representative complexes [Ru]-10 and [Ru]-12 were established by single crystal X-ray diffraction. Furthermore, screened the synthesised complexes for the catalytic dehydrogenation of formic acid in water, where substitution of heterocyclic ring on the bis-imidazole methane ligands was found to exert significant impact on the catalytic activity of the complexes. Results inferred that, among the screened catalysts, thiophene substituted [Ru]-13 catalyst outperformed others with an initial turnover frequency (TOF) of 1831 h<sup>-1</sup> at 90 °C. One of the most notable features of **[Ru]**-13 was its exceptional long-term stability, as it maintained efficient  $H_2$ production from formic acid for 35 catalytic runs and remained active even after 60 days without any significant deactivation, reaching a turnover number (TON) of 35000, highlighting its long-term durability and potential for  $H_2$ 

production for FA in water. Further, reaction kinetics, the influence of various reaction parameters are thoroughly examined, and performed comprehensive mass and NMR investigations under both catalytic and control experimental conditions to gain more insights of the reaction pathway of FA dehydrogenation over the studied catalysts.

Chapter 4: Bis-imidazole Methane based Diruthenium Catalysts for Hydrogen Production from Formic Acid in Water



Based on the previous results obtained with arene-Ru(II) complexes containing N, N bidentate ligands where the facile protonation – deprotonation of the ligand and the heterocyclic bis-imidazole methane-based ligands where substitution of heterocyclic ring on the bis-imidazole methane ligands played a significant role in the catalytic cycle, herein assumed that bridged N, N donor ligands attached with the two Ru center might help in enhancing the catalytic activity and stability for the formic acid dehydrogenation reaction. Therefore, this chapter describes successfully synthesis of the first example of a watersoluble diruthenium (Ru-Ru) catalyst for formic acid dehydrogenation. Efforts were devoted towards evaluating and establishing the high catalytic performance and robustness of the studied Ru-Ru catalyst ([Ru]-14) for hydrogen production from formic acid in water. Further, [Ru]-14 catalyst structure was confirmed by a single crystal x-ray diffraction technique and explored to achieve efficient catalytic hydrogen production from formic acid in water. The catalytic efficacy and long-term stability of the [Ru]-14 catalyst for large-scale formic acid dehydrogenation was also investigated to evaluate the practical applicability of the studied catalytic system. Results inferred that the [Ru]-14 catalyst exhibited exceptionally high stability for over 30 h with no significant loss in activity during 25 consecutive catalytic runs for formic acid dehydrogenation, achieving a turnover number of 50000. Notably, the catalytic activity of the [Ru]-14 catalyst for formic acid dehydrogenation was not diminished even after employing the catalytic reaction mixture even after 60 days, suggesting the high stability of the [Ru]-14 catalyst. Moreover, the [Ru]-14 catalyst also displayed high activity for the dehydrogenation of formic acid under bulk scale. Interestingly, a TON of 93200 was achieved over the [[Ru]-14 catalyst for the dehydrogenation of formic acid in water. On the contrary, the analogous mononuclear catalysts [Ru]-9 and [Ru]-16 displayed lower activity with a substantial loss in activity during long-term stability evaluation, inferring the advantage of the diruthenium catalyst in achieving high catalytic activity for formic acid dehydrogenation. Moreover, a detailed mass and NMR investigation under catalytic and control experimental conditions revealed the possible involvement of Ru-aqua [Ru-(OH2)2], Ru-formato [Ru-(HCOO)2], and Ru-hydrido [Ru-(H)2] in the catalytic hydrogen production from formic acid. It is worth mentioning here that the high catalytic activity displayed by the [**Ru**]-14 catalyst is exceptional and is amongst the few high-yielding bimetallic catalysts reported to date.

#### **Chapter 5: Summary and future scope**

This thesis deals with the development of water-soluble arene-Ru(II) complexes with different N, N donor pyridylamine and bisimidazole methane based ligands for hydrogen production from formic acid under mild reaction conditions. Chapter 2 deals with the synthesis of several N, N donor pyridyl amine ligated arene-Ru(II) complexes for hydrogen production from formic acid in water, wherein studies revealed that the pyridyl oxime-based ligands attached to the Ru center had higher activity than having -OMe and -N<sup>n</sup>Pr groups. The high catalytic activity of the catalyst was attributed to the -OH moiety present in the complex. Further, in-depth mass and NMR investigations with control kinetic experiments revealed the involvement of several intermediate species to establish the rate determining step over [**Ru**]-1 catalyst and establish the crucial

role of these intermediates in formic acid dehydrogenation. After the exploration of complexes with pyridylamine substituted N, N donor ligands, Chapter 3 deals with the synthesis of a new series of arene-Ru(II) complexes containing heterocyclic bisimidazole methane based donor ligands [Ru]-9 - [Ru]-13 and employed them for hydrogen production from formic acid in water. Results inferred that the nature of the substituent on the heterocyclic arene ring had a pronounced effect in tuning the catalytic activities where the complex containing the thiophene substituted arene ring outperformed over all the other explored catalysts. Further, detailed mechanistic insights were provided by identifying and isolating the crucial reaction intermediates involved in the catalytic cycle. In Chapter 4, a detailed study of effect of bridging bisimidazole methane ligated diruthenium complex [Ru]-14 - [Ru]-15 explored for hydrogen production from formic acid in water, and utilize for recyclability and bulk scale hydrogen production from formic acid in water.

In summary, worldwide energy demand is continuously increasing day by day, In this context, hydrogen is now widely considered as a clean fuel for the future and therefore extensive efforts are being devoted by the scientific community globally to develop efficient catalytic systems for the green hydrogen production from various LOHCs. It seems beneficial to investigate LOHCs due to its accessibility, comparatively low toxicity, and minimal danger of explosion or other hazardous mishaps and in light of their possible uses in the creation, storage, and transportation of hydrogen. LOHCs, which contains a high volumetric hydrogen content, has gained significant attention due to its potential as a highly promising fuel for portable devices, vehicles, and various energy-related applications. Despite the extensive literature reports in this field, development of molecular catalytic systems for practical and industrial usage needs more attention. Moreover, the development of highly stable catalysts, stable in air, moisture and relatively inexpensive non-noble metal based catalytic systems also need special attention from the economic point of view for reversible formic acid dehydrogenation and CO<sub>2</sub> hydrogenation in water and further isolate and identified catalytic intermediates by crystallographic techniques for better understanding of their structure and the important role in the catalytic cycle which may further enhance the understanding the mechanistic pathway of these reactions. Though attempts have been made in this thesis work to evaluate to identify and isolate the crucial catalytic intermediates, catalyst recyclability and long-term stability with performance of bulk-scale hydrogen production, now the time is to separate the  $CO_2$  gas evolved in formic acid dehydrogenation and utilize them for further practical applications so that pure H2 can be utilized in the fuel cell applications to evaluate the practical application of the developed catalytic systems.

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## Nomenclature

α	Alpha
β	Beta
γ	Gamma
Å	Angstrom
λ	Wavelength
μ	Micro
σ	Sigma
π	Pi
η	Eta
δ	Delta
J	Coupling constant
Hz	Hertz
MHz	Mega hertz
K	Kelvin
D	Density
V	Volume
Μ	Molar
mM	Milli Molar
cm	Centimetre
0	Degree
°C	Degree centigrade
mL	Millilitre
μL	Microlitre

## Acronyms

L1	N-hydroxy-iminopyridine
L2	N-methoxy-iminopyridine
L3	N-propyl-iminopyridine
L4	N-isopropyl-iminopyridine
L5	4,4'-(phenylmethylene)bis(2-ethyl-5-methyl-1 <i>H</i> imidazole)
L6	2-(bis(2-ethyl-5-methyl-1H-imidazol-4-
	yl)methyl)pyridine
L7	4,4'-((1 <i>H</i> -imidazol-2-yl)methylene)bis(2-ethyl-5-
	methyl-1 <i>H</i> -imidazole)
L8	4,4'-(furan-2-ylmethylene)bis(2-ethyl-5-methyl-1H-
	imidazole)
L9	4,4'-(thiophen-2-ylmethylene)bis(2-ethyl-5-methyl-1H-
	imidazole)
L10	1,4-bis(bis(2-ethyl-5-methyl-1H-imidazol-4-yl)
	methyl)benzene (benztetraimd)
[Ru]-1	$[(\eta^6 - p$ -cymene)Ru(N-hydroxy-iminopyridine)Cl] <sup>+</sup>
[Ru]-2	$[(\eta^6 - p$ -cymene)Ru( <i>N</i> -methoxy-iminopyridine)Cl] <sup>+</sup>
[Ru]-3	$[(\eta^6 - p$ -cymene)Ru(N-propyl-iminopyridine)Cl] <sup>+</sup>
[Ru]-4	$[(\eta^6 - p$ -cymene)Ru(N-isopropyl-iminopyridine)Cl] <sup>+</sup>
[Ru]-5	$[(\eta^6$ -benzene)Ru(N-hydroxy-iminopyridine)Cl] <sup>+</sup>
[Ru]-6	$[(\eta^6$ -benzene)Ru(N-methoxy-iminopyridine)Cl] <sup>+</sup>
[Ru]-7	$[(\eta^6 - benzene)Ru(N - propyl - iminopyridine)Cl]^+$
[Ru]-8	$[(\eta^6$ -benzene)Ru(N-isopropyl-iminopyridine)Cl] <sup>+</sup>
[Ru]-9	$[(\eta^6 - p\text{-cymene})\text{Ru}(\text{L5})\text{Cl}]^+$
[Ru]-10	$[(\eta^6 - p\text{-cymene})\text{Ru}(\text{L6})\text{Cl}]^+$
[Ru]-11	$[(\eta^6 - p\text{-cymene})\text{Ru}(\text{L7})\text{Cl}]^+$
[Ru]-12	$[(\eta^6 - p\text{-cymene})\text{Ru}(\text{L8})\text{Cl}]^+$
[Ru]-13	$[(\eta^6 - p\text{-cymene})\text{Ru}(\text{L9})\text{Cl}]^+$
[Ru]-14	$[\{(\eta^6 - p - \text{cymene})\text{RuCl}\}_2(\mu - \kappa^2: \kappa^2 - \text{benztetraimd})]^{2+}$
[Ru]-15	$[{(\eta^6-\text{benzene})\text{RuCl}}_2(\mu-\kappa^2:\kappa^2-\text{benztetraimd})]^{2+}$
[Ru]-16	$[(\eta^6 - benzene)Ru(L5)Cl]^+$

UV-vis	UV - visible Spectroscopy
NMR	Nuclear Magnetic Resonance
ESI-MS	Electrospray Ionization- Mass Spectrometry
GC-TCD	Gas Chromatography-Thermal conductivity detector
TLC	Thin Layer Chromatography
SCXRD	Single crystal X-ray Diffraction
DFT	Density Functional Theory
GOOF	Goodness of fit
CDCl <sub>3</sub>	Chloroform-d
D <sub>2</sub> O	Deuterium oxide
Ar	Argon
<b>O</b> <sub>2</sub>	Oxygen
<b>H</b> <sub>2</sub>	Dihydrogen
<b>N</b> 2	Nitrogen
ру	Pyridine
NHC	N-heterocyclic carbene
PPh <sub>3</sub>	Triphenylphosphine
S	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
ppm	Parts per million
r.t.	Roomtemperature
temp.	Temperature
TON	Turnover number
TOF	Turnover frequency
DMOA	Dimethyloctylamine
Me	Methyl
br	br
Ph	Phenyl
mg	milligram
h	Hour

EtOH	Ethanol
MeOH	Methanol
DCE	Dichloroethane
CH <sub>3</sub> CN	Acetonitrile
Et <sub>2</sub> O	Diethyl ether
NEt <sub>3</sub>	Triethylamine
Calcd.	Calculated
atm	Atmospheres (pressure)
FA	Formic acid
SF	Sodium Formate

### **Chapter 1**

# A Comprehensive Overview of Formic Acid Dehydrogenation over molecular catalysts

#### **1.1. Introduction**

Hydrogen, the first element on the periodic table has become a very efficient chemical fuel and is becoming progressively more focus. Hydrogen is a tasteless and odourless chemical that is simple yet extremely combustible. In 16<sup>th</sup> century, Van Helmont discovered that although hydrogen could catch fire in air, it was not able to sustain combustion on its own without oxygen. In 1671 when Robert Boyle observed that iron filings with acid reacted to generate bubbles of gas. Further, Cavendish classified H<sub>2</sub> as "inflammable air" because of its unique characteristics, especially the way it burns when combined with oxygen to produce water. In 17<sup>th</sup> century, Lavoisier first used the term "hydro-gen" which is a Greek word that means "water-former.<sup>[1]</sup> Hydrogen is supposed to be a cleaner energy source, because of water as a by-product when it combines with oxygen in the fuel cell.<sup>[2]</sup> Global attention is now focused on investigating sustainable and, most importantly, ecologically benign alternative renewable energy resources due to the depletion of the resources of fossil fuels and growing environmental concerns. In this context, 'hydrogen gas' is supposed to be a clean fuel that carries significant potential for stationary and mobile applications with an exceptionally high energy density of approximately 120 MJ/kg, nearly three times that of gasoline.<sup>[3]</sup> Despite being the 3<sup>rd</sup> most common element in the universe, Hydrogen gas is an extremely rare atmosphere (< 1ppm) and mostly found in different chemical compounds.<sup>[4]</sup> Hence, utilizing hydrogen as a fuel may aid in reducing environmental pollution by emitting no hazardous emissions. However, the production, storage, and transportation of hydrogen gas pose numerous challenges and safety concerns due to its chemical and physical properties.<sup>[5]</sup> Therefore, it is very crucial to develop sustainable and practical method for the hydrogen production, storage and transportation. Currently, hydrogen gas is generated from non-renewable sources, mostly hydrogen in bulk-scale (96%) produced from the steam reforming process,

including coal and oil, as well as from the water gas shift reaction. In contrast, only 4% of hydrogen gas is produced using the more environmentally friendly process of water electrolysis. Therefore, developing new sources of sustainable and renewable energy for the generation of hydrogen gas that is free from greenhouse gases is a primary requirement of society. <sup>[5b]</sup>



*Figure 1.1.* Schematic representation of hydrogen storage, production and application.

However, attempts to store hydrogen gas at high pressures (300 bar) or as a liquid at cryogenic temperatures (-252.87 °C and 1.013 bar) with the low volumetric energy density (70.8 kg/m<sup>3</sup>) of hydrogen generates feasible safety issues to its transportation and storage.<sup>[5a]</sup> Furthermore, the storage and transportation of hydrogen gas have been investigated using porous structures and metal hydrides. On the other hand, worldwide interest in the storage of hydrogen in chemical bonds using an appropriate liquid hydrogen storage medium with a suitable catalyst, these liquid hydrogen storage materials can release hydrogen whenever is required and can be reverted back through hydrogenation. In this context, methanol (12.5 wt% H<sub>2</sub>), formaldehyde (8.4 wt% H<sub>2</sub>) and formic acid (4.4 wt% H<sub>2</sub>) have been extensively explored as efficient liquid hydrogen carriers.<sup>[6-7]</sup>

In addition, several liquid organic hydrogen carriers may be obtained from renewable sources, are affordable, ready to use and show noticeably high gravimetric hydrogen content. Advantageously, being liquid at room temperature makes these liquids suitable for the existing fossil fuel distribution system.<sup>[6-7]</sup> The current energy infrastructure is primarily dependent on renewable resources. Now, it's time to switch to renewable energy sources.<sup>[8]</sup> Hydrogen production can be achieved through various methods, including using thermal, electrical, and photochemical energy. It is also readily accessible in chemical form and may be generated by renewable energy sources.<sup>[9]</sup> Moreover, using hydrogen in fuel cells produces only water as an emission, which is acceptable for the environment and has no adverse impacts. Hydrogen is primarily used as an energy carrier in fuel cells, which are used to generate electricity for use in automobiles and buildings. Further, in the Haber process, hydrogen gas reacts with nitrogen gas to produce ammonia at a very high temperature and pressure with a suitable catalyst and ammonia is one of the major components in the fertilizer industry. Similarly, the hydrogenation of CO<sub>2</sub>, a major contributor to the greenhouse effect, which transforms into formic acid through hydrogenation, may minimize CO<sub>2</sub> (Figure 1.1.).<sup>[9]</sup>

#### 1.2. Hydrogen storage

The diverse physical and chemical properties of hydrogen make it challenging to transport and store safely.<sup>[5]</sup> It is considered risky to store by using conventional ways, such as in cylinders or tanks with high pressure (300 bar) or as liquid hydrogen (-252.87 °C), high-quality stainless-steel tanks are required to store the hydrogen and its transportation makes it very costly.<sup>[10]</sup> Therefore, in order to ensure the safe storage, efficient dispensing, and transportation of hydrogen on-site, it is highly desirable to investigate substitute carriers such as LOHCs. These LOHCs contain very high hydrogen in their reservoir and remain liquid at room temperature, making a safe and sustainable pathway to store and transport.<sup>[6-7]</sup>

An overview of various hydrogen storage techniques are provided here, classified according to their chemical and physical features (Figure 1.2.)



Figure 1.2. Overview of various hydrogen storage techniques.

#### 1.2.1. Physical Hydrogen Storage

Hydrogen can be stored in several ways, such as storing as liquid hydrogen (0.1 to 1 MPa pressure at -253 °C) as compressed hydrogen gas (35 to 70 MPa pressure at 25°C) and by cryo-adsorption on high-surface-area materials (0.2 to 0.5 MPa pressure at -193 °C) and over a variety of adsorbents, including carbon compounds, zeolites, and metal-organic frameworks, or MOFs. Despite encouraging advancements in the physisorption of hydrogen in porous materials, these systems continue to suffer from low hydrogen wt%.<sup>[10-12]</sup> Compressed hydrogen gas and liquid hydrogen are currently more efficient cutting-edge technologies for fuel-cell-powered cars, transportation of hydrogen, and so on.<sup>[5]</sup>

#### 1.2.2. Chemical Hydrogen Storage

There are several advantages as well as disadvantages of physical hydrogen storage, while chemical approaches are more effective because they can handle high hydrogen levels and allow for efficient release. Chemical storage methods include the storage of hydrogen in a variety of compounds, such as liquid organic hydrogen carriers, amides/imides, metal hydrides and so on.<sup>[5]</sup> The secure and practical storage and transportation of hydrogen gas becomes feasible by the chemical storage of hydrogen that are stable at room temperature, such as water, formic acid, and other liquid organic carriers.

LOHCs are able to store and release hydrogen reversibly through chemical processes. The advantages of these carriers include their high hydrogen density, ease of handling and compatibility with the current liquid fuel infrastructure. Moreover, LOHCs have the ability to regenerate, enabling repeated cycles of hydrogen release and storage. For example, formic acid has a high hydrogen content (4.4 wt%) and stability, making it a suitable hydrogen storage medium. Under mild conditions, it can easily release hydrogen through dehydrogenation processes, which makes it appropriate for on-demand hydrogen generation. Hydrocarbons are also an excellent source of hydrogen gas, where hydrogen can be released at very high temperature and pressure.<sup>[5]</sup>

Few of the chemical storage of hydrogen storage materials are briefly described in the following sections.

#### 1.2.2.1. Metal Hydride as Hydrogen Storage

Metal hydrides such as NaBH<sub>4</sub>, NaH, LiBH<sub>4</sub> and so on are good choices for storing hydrogen.<sup>[13]</sup> A key factor in assessing a metal hydride as a hydrogen storage system is its redox potential, which needs to be lower at a suitable pH than the H<sup>+</sup>/H<sub>2</sub> systems. Hydrogen and metal hydroxide or oxide are the results of the reaction between these metal hydrides and water. Metal hydrides also offers the favorable oxidation process that produces hydrogen gas and the high hydrogen storage capacity such as, LiBH<sub>4</sub>, which reacts with water to release 8.4 wt.% of hydrogen gas. However, the energy-intensive and costly procedure required to regenerate metal hydrides from metal hydroxides remains a major drawback for metal hydride storage systems.<sup>[13]</sup>

#### 1.2.2.2. Hydrocarbons as Hydrogen Storage

Steam reforming of hydrocarbons, particularly methane steam reforming, is a widely used process in industrial hydrogen production due to its effectiveness in producing bulk-scale hydrogen. Hydrocarbons are heated to high temperatures (700 °C -1000 °C) and pressures (3 - 25 bar) in this process.<sup>[14]</sup> Major disadvantage steam reforming process is due to very stable nature of methane, requires a high temperature and pressure to activate the methane molecule. Methane reforming (*approx.* 25 wt% of hydrogen) is a

process to produce hydrogen via the following pathway. 1) steam methane reforming reaction produces 3 equivalents of hydrogen and CO as well as CO<sub>2</sub> byproduct. 2) CO follows the water-gas shift process and produces 2 equivalents of hydrogen and CO<sub>2</sub>. Although steam methane reforming technology is well established and frequently used for producing hydrogen on a large scale, it's important to note that there are several disadvantages, including the need for high temperatures and high production costs.<sup>[15]</sup> There are several noble (Ru or Rh), non-noble metal (Ni/Al<sub>2</sub>O<sub>3</sub>) based catalysts are explored for the methane reforming, but no significant results for bulk scale hydrogen production are available due to several limitations and also the separation of mixture of gases increases production cost.<sup>[16-17]</sup>

#### 1.2.2.3. Liquid Organic Hydrogen Carriers (LOHCs)

In contrast to metal hydrides and other inorganic materials used for hydrogen storage, a wide range of liquid organic hydrogen carriers (LOHCs) are also been extensively explored as viable options for hydrogen delivery, storage, and transportation. These liquid hydrogen carriers can release hydrogen at room temperature with the suitable catalyst, under ambient conditions. These LOHCs can be delivered and transported securely and conveniently using the current infrastructure established for dispersing petroleum products because of their liquid nature. They also have a high hydrogen content (both gravimetrically and volumetrically). Interestingly, a large number of these liquid hydrogen carriers are capable of being effectively recycled via cycles of catalytic hydrogenation and dehydrogenation. Currently being thoroughly studied as potential options for liquid hydrogen storage materials (CH<sub>3</sub>OH, HCHO, and HCOOH). <sup>[18]</sup>

Since this thesis is focused on homogeneous catalysis for formic acid dehydrogenation, the following section provides an extensive overview of formic acid as a liquid organic hydrogen carrier and the catalysts crucial role that plays in this process.

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#### **1.3.** Formic acid as a hydrogen energy source: catalyst's crucial role

It seems beneficial to investigate liquid hydrogen carriers in light of their possible uses in the creation, storage, and transportation of hydrogen. Formic acid, which contains a volumetric hydrogen content of 4.4 wt%, has gained significant attention due to its potential as a highly promising fuel for portable devices, vehicles, and various energy-related applications.<sup>[19]</sup> Formic acid is a desirable choice for LOHCs due to its accessibility, comparatively low toxicity, and minimal danger of explosion or other hazardous mishaps. Formic acid (>10%) is corrosive to skin and eyes, it is volatile, and at hazards of exposure through inhalation.<sup>[20]</sup> High energy-intensive input is required for the activation of bonds during dehydrogenation of methanol, because of a positive  $\Delta H$  value (+130.7 kJ mol<sup>-1</sup>). But when a catalyst is added, it interacts with the substrate and causes a number of intermediates and transition states to arise. Through this approach, the reaction's Gibbs free energy is effectively decreased, allowing for the production of hydrogen in a more favourable reaction environment. <sup>[21]</sup> At the ambient temperature, the dehydrogenation of formic acid produces one equivalent of H<sub>2</sub> and CO<sub>2</sub> is thermodynamically favourable ( $\Delta G^{\circ} = -32.9$  kJ mol<sup>-1</sup>), but it has kinetic limitations. Formic acid's atom efficiency is one of its main benefits since it makes the stored hydrogen completely available without any loss. In addition, the thermodynamically possible dehydration reaction that produces hazardous CO gas and water, in addition to the intended dehydrogenation to produce H<sub>2</sub> and CO<sub>2</sub> reinforces the need for a catalyst that is selective in boosting hydrogen creation, thus preventing the unfavorable pathway.<sup>[22]</sup> Pure H<sub>2</sub> gas cannot be achieved from Formic acid as an equimolar amount of CO<sub>2</sub> is also produced during the process of releasing H<sub>2</sub>, although this does not pose a barrier for the use of fuel cells.<sup>[19]</sup> Further, the selective Formic acid dehydrogenation can result in the production of pressurized hydrogen gas and CO<sub>2</sub>, making it an attractive alternative to hydrogen storage and a promising solution for growing energy needs. Recently, a method for separating high-pressure hydrogen from the H<sub>2</sub>/CO<sub>2</sub> mixture gas produced by the breakdown of formic acid was devised. An appreciably high yield (85%) of pure hydrogen was achieved through the gas-liquid separation process, making formic acid a more attractive hydrogen carrier.<sup>[23]</sup>

Though, several homogeneous <sup>[24]</sup> and heterogeneous <sup>[25]</sup> catalytic systems have been well explored, it is essential to have efficient catalytic systems that can convert formic acid to release H<sub>2</sub> and CO<sub>2</sub> gas. Among them, Ru, Ir and Rh based molecular catalysts have shown outstanding performance for dehydrogenation of formic acid. This process offers the potential to create an H<sub>2</sub> storage/release system that can be controlled by a pH switch through the interconversion of CO<sub>2</sub> to formic acid and vice-versa.<sup>[24]</sup> However, the purification of gas mixture (H<sub>2</sub> and CO<sub>2</sub> in 1:1 molar ratio) produced from formic acid is challenging. Recent reports inferred that the separation of H<sub>2</sub> from H<sub>2</sub>/CO<sub>2</sub> mixed gas can be done by changing the gas mixture to gas-liquid phase under high-pressure condition. Moreover, lowering the temperature enabled the better separation while maintaining the high-pressure H<sub>2</sub> with 85% purity at -51 °C after gas-liquid separation process, endorsing the potential of formic acid as a promising hydrogen carrier.<sup>[26]</sup>

Here, in this chapter, we have briefly described a wide range of noble and nonnoble metal-based catalysts reported for formic acid dehydrogenation.

#### **1.3.1.** Noble metal-based molecular catalyst

Coffey et al. reported the first homogeneous catalysts for hydrogen production from formic acid, where they employed several transition metalbased complexes bearing phosphine ligands in acetic acid at 118 °C in 1967.<sup>[27]</sup> Further, several noble-metal based catalysts such as Ir, Rh and Ru were investigated for the dehydrogenation of formic acid in the recent past. In general, it was observed that these noble metal complexes displayed superior catalytic activity for formic acid dehydrogenation.<sup>[28]</sup> Literature reports show that Ir-based complexes are extensively explored for formic acid dehydrogenation reaction, where the role of pH responsive ligands is found to be crucial in achieving high catalytic activity (Scheme1.1.)<sup>[29]</sup> In 2009, Himeda et al. reported Cp\*Ir complexes (Cp\* is pentamethylcyclopentadienyl) containing 2,2'-bipyridine (bpy) ligands with different functional groups.<sup>[28a]</sup> The highest TOF value of 14000 h<sup>-1</sup> was obtained with 4, 4'-dihydroxy-2, 2'-bipyridine (DHBP) (**C-1**) with no loss in the activity during the five consecutive catalytic runs. In 2011, Tanaka et al. demonstrated an Ir-PNP-trihydride (C-2) as the most effective catalytic system for formic acid dehydrogenation. For the dehydrogenation of formic acid, a TON of 890 was achieved over the catalyst C-2. Catalytic activity was greatly enhanced when triethylammonium formate was employed, with the initial TOF of 120000 h<sup>-1</sup> at 80 °C. Performing formic acid dehydrogenation in 'BuOH in the presence of Et<sub>3</sub>N resulted in complete dehydrogenation of formic acid with a TON of 5000 at 80 °C.<sup>[30]</sup>



Scheme 1.1. Iridium based molecular catalysts (C-1-C-12) reported for formic acid dehydrogenation.

In 2012, Maenaka et al. reported a Cp\*Ir catalyst (C-3) based on [C, N] cyclometalated pyrazole benzoic acid ligand for formic acid dehydrogenation by controlling the pH of the reaction mixture under ambient reaction condition.<sup>[31]</sup> The catalyst C-3 catalysed the formic acid dehydrogenation to H<sub>2</sub> and CO<sub>2</sub> (1:1 molar ratio) in acidic water, where a maximum TOF of 1880 h<sup>-1</sup> was achieved at pH 2.8 at 25 °C. An increasing trend in TOF was observed with decreasing pH in the range of 9.0 to 2.8. Further decrease in pH below 2.8 resulted in the deactivation of the catalyst. This implies that C-3 has a higher

catalytic reactivity than the benzoate analogue (C-3A), which did not produce any hydrogen at pH 9.0 where C-3 was fully converted to (C-3A) and (benzoate analogue with Ru-hydroxo) (C-3B) at 298 K. The *rds* in the catalytic formic acid dehydrogenation was suggested to be the  $\beta$ -hydrogen elimination of the Cp\*Ir formato species (C-3C) to form the Cp\*Ir hydrido species (C-3D), particularly at lower pH, due to the relatively high concentration of protons (Scheme 1.2.).<sup>[31]</sup>



*Scheme 1.2.* CO<sub>2</sub> hydrogenation and formic acid dehydrogenation catalysed by Cp\*Ir catalyst (C-3). Adapted figure from ref. [31].

In 2015, Li et al. reported [Cp\*Ir(L)Cl]Cl (L=2,2'-bi-2-imidazoline) (C-4) for formic acid dehydrogenation in water without any additives, and achieved a TOF of 487500 h<sup>-1</sup> at 90 °C. They also reported a TON of 2400000 in [Cp\*Ir(L')Cl]Cl (L`=2,2'-bi-1,4,5,6over situ generated tetrahydropyrimidine) complex obtained from 2,2'-bi-1,4,5,6tetrahydropyrimidine and [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, for formic acid dehydrogenation at 80 °C.<sup>[28c]</sup> In 2017, Wang et al. explained new pyridylimidazoline-based Cp\*Ir catalysts, bearing two hydroxyl groups (C-5) and two methoxy groups (C-6) on the pyridyl moiety of the ligand, for formic acid dehydrogenation in water.<sup>23</sup> Notably, the catalysts (C-5) and (C-6) exhibited higher activity for the dehydrogenation of formic acid in water at 60 °C. Results inferred that catalyst (C-6) exhibited a maximum TOF of 19400  $h^{-1}$  at pH 1.7 but decreased activity at higher pH. Conversely, catalyst (C-5) (-OH group) displayed significantly increased catalytic activity at pH 3.0 with a maximum TOF of 56900 h<sup>-1</sup> and TON of 29000.<sup>[32]</sup> In same year, Siek et al. reported a comparative study on Cp\*Ir (C-7) bearing proton-responsive dihydroxybipyridine (6,6'-dhbp) based ligands for formic acid dehydrogenation.<sup>24</sup> Ruthenium complexes being less active compared to iridium complexes led to the variation in the catalytic activity. Among the catalysts explored, (C-7) demonstrated good activity for formic acid (1.02 M) dehydrogenation, yielding a TON of 3500 and a TOF of 1200 h<sup>-1</sup> at 60 °C for 3h. Furthermore, investigations involving the catalyst bearing dimethoxybipyridine (dmbp) [Cp\*IrCl(6,6'-dmbp)]OTf (C-8) were conducted, maintaining all other reaction conditions constant while employing an incredibly low catalyst loading (0.0028 mol %). Remarkably, this adjustment resulted in a TOF approximately 2.8 times higher (~ 3300 h<sup>-1</sup>), coupled with a formic acid conversion of 29% at 3 hours and achieved TON of 33,000 after 24 hours. Initially, a 10-fold increase in TOF was anticipated upon reducing the catalyst loading. However, it became apparent that at such low catalyst loading, the reaction progressed at a slower pace, potentially due to the saturation of all available catalyst sites or interference from catalyst decomposition.<sup>[33]</sup> In 2018. Semwal et al. reported a hybrid NHC carbene ligand-based Cp\*Ir catalyst (C-9) in a 5:2 mixture of HCO<sub>2</sub>H and NEt<sub>3</sub> at 90 °C resulted in a TOF of 58,000  $h^{-1}$  in 2 minutes (pH 3.7). Further carrying out the reactions in larger volume (4.5 mL) under analogous reaction condition, resulted in an increased TOF of value 96000  $h^{-1}$ . Further, in a multiple-charging experiment, highest TOF 100000 h<sup>-1</sup> was achieved at 90 °C, (pH 4.4) using 1 M FA/HCOONa solution. The observed activity was attributed to the imidazolylidene-based abnormal NHC ligand, a proton-responsive ligand framework enabling protonation and during the dehydrogenation process. This was facilitated by the proton transfer and strong sigma-donating ability of the abnormal NHC backbone for enhanced electron density required during dehydrogenation steps. Additionally, the robust bonding between iridium and the abnormal NHC ligand ensures structural

stability.<sup>[34]</sup> In same year, Fidalgo et al. developed Cp\*Ir (C-10) catalysts bearing 8-aminoquinoline ligand for the catalytic formic acid dehydrogenation in water. At initial pH 4.5, with (C-10) (0.04 mol %) catalyst achieved a TON of 3109 when a mixture of FA/HCOONa (1:2) was refluxed at 100 °C in water. Further, the mechanistic study revealed that the coordination of NH<sub>2</sub> group to the metal center had a positive effect on the reaction by assisting the proton transfer to the Ir-hydrido group.<sup>[35]</sup>

Subsequently, Li et al. also reported Cp\*Ir–diaminoglyoxime-based catalysts (C-11) to achieve a TON up to 3900000 and achieved a TOF of 65 000 h<sup>-1</sup> at 90 °C, and a TON of 5020000 at 70 °C.<sup>[36]</sup> Further, In 2020, Himeda et al. also explored the amine-substituted analogous Cp\*Ir–bipyridine catalyst (C-12 in Scheme 1.1.) exhibited the highest TOF of 115500 h<sup>-1</sup> at 80 °C and durability as compared to Cp\*Ir–DHBP (C-1) for the dehydrogenation of formic acid.<sup>16b</sup> However, imidazole–based ligands showed higher activity over the bipyridine ligands in the iridium-based complexes for formic acid dehydrogenation.<sup>[37]</sup>



*Scheme 1.3.* Iridium metal-based catalyst *C-13–C-20* explored for formic acid dehydrogenation.

Later, Himeda et al. reported Cp\*Ir catalysts (C-13) - (C-18) containing deprotonated pyridylamide-based ligands for formic acid dehydrogenation (Scheme 1.3.). They proposed that the higher catalytic activity of these catalyst for formic acid dehydrogenation was due the strong ability of the coordinated anionic nitrogen atom for electron-donation and the proton-responsive nature of the OH group close to the metal center. For formic acid dehydrogenation, the Cp\*Ir catalyst having N-phenyl-picolinamidate ligand without OH group (C-**14**) showed a TOF of 11800 h<sup>-1</sup> at 60 °C at pH 3.5. The catalyst activity was observed for formic acid dehydrogenation, attributed to the stability of catalysts in acidic conditions. However, introducing phenyl groups on the amido-N significantly improved the activity of the catalysts (TOF 61700 h<sup>-1</sup> over (C-15) at a 1 M FA/HCOONa (9:1) solution. Cp\*Ir catalyst with hydroxyl (OH) groups on the pyridine ring (C-15) and (C-17) could not show any significant improvement in the catalytic activity. Among imidazole, imidazoline, and pyrazole-based Cp\*Ir catalysts, imidazole-based Cp\*Ir catalyst (C-18) exhibited a TOF of 30100 h<sup>-1</sup>. Overall, the formic acid dehydrogenation rates were pH-dependent, and the durability of some of the catalysts in 1 M formic acid solutions was found to be low. After evaluating a set of catalysts, they analyzed the pH dependence of their catalytic activities in formic acid dehydrogenation. Substitutions on the amide-N were found to have a stronger impact on the pH-dependence and catalytic activity than OH groups substituted on the pyridine rings. Among the catalysts explored, (C-15) showed increased activity with increasing formic acid concentration and achieved complete conversion of formic acid at 6 M. The rate of released gases was stable, and the TOF reached 11,800 h<sup>-1</sup> in an 8 M FA/HCOONa (9:1) solution at 60 °C. The durability of (C-15) was also found to be higher, where almost complete consumption of formic acid and release of 51 L of mixed gases was observed in 100 h.<sup>[38]</sup>

In 2021, Mo et al. developed Cp\*Ir catalyst based on a protonresponsive N, N' pyridyl pyrrole ligand  $[Cp*Ir(N, N')X)]^{n+}$  (X = Cl, n = 0; X = H<sub>2</sub>O, n =1) for formic acid dehydrogenation.<sup>28</sup> The outstanding catalytic performance of (**C-19**) can be attributed to several factors, primarily the cooperative effect of the metal-ligand system, particularly the pyrrole group in the complex which accepts a proton in formic acid dehydrogenation (Scheme 1.4.). The catalyst (**C-19**) also demonstrated good catalytic activity for additivefree formic acid dehydrogenation, achieving a maximum TOF of 45900 h<sup>-1</sup> at 90 °C in water as compared to that observed in neat formic acid. A catalytic dinuclear hydride intermediate was proposed to be involved in the catalytic formic acid dehydrogenation. The pH of the reaction played a crucial role, where pH was tuned by the FA/HCOONa ratio in the formic acid dehydrogenation reaction, with fixed concentrations of formic acid and HCOONa at 2 M. At a pH of 1.81, higher activity was observed for formic acid dehydrogenation, achieving a maximum TOF of 45900 h<sup>-1</sup>. Further increasing the pH resulted in a decreased catalytic activity, while the reaction rate increased at higher reaction temperatures.<sup>[39]</sup>



**Scheme 1.4.** Catalytic formic acid dehydrogenation over the catalyst *C-19*. Reprinted with permission from ref [39]. Copyright 2015 American Chemical Society.

Later in 2022, Maji et al. further explored NHC-based Cp\*Ir catalyst (C-20) for formic acid dehydrogenation in water in the absence of additives or solvents. The observed prominent catalytic activity was attributed to the presence of RN-C(=O) group, and the  $\sigma$ -donor property of the NHC ligand, and the facile water solubility of the catalyst (C-20). The catalyst (C-20) exhibited high activity for formic acid dehydrogenation where a TOF of 70674 h<sup>-1</sup> was obtained at 80 °C within the first 5 minutes of the reaction. They concluded that the pH of the reaction mixture played a critical role in the dehydrogenation reactions (Scheme 1.5.). Moreover, the evolved H<sub>2</sub> and CO<sub>2</sub> gases from the formic acid dehydrogenation reactions were successfully reutilized in the hydrogenation reaction, indicating the suitability of the (C-20) catalytic system for utilizing formic acid as a typical H<sub>2</sub>/CO<sub>2</sub> storage liquid. Also, the dehydrogenation of formic acid was found to be highly dependent on the pH of the reaction mixture, with the maximum TON of 3600 h<sup>-1</sup> obtained at pH 3.5, while lower activity was observed at pH 2.75. The CO<sub>2</sub> released from the formic acid dehydrogenation reaction was captured in KOH (1M) solution to hydrogenate it to formate with a TON of 20 over the catalyst (C-20). They further reutilized the H<sub>2</sub> and CO<sub>2</sub> gas that evolved from formic acid dehydrogenation for the hydrogenation of quinoxaline, resulting in 88% yield of 1.2.3.4-tetrahydro quinoxaline at 50 °C in 1 h.<sup>[40]</sup>



Scheme 1.5. Catalytic cycle for the formic acid dehydrogenation over the catalyst C-20. Reprinted with permission from ref [40]. Copyright 2022 American Chemical Society.

In contrast to the extensively explored monometallic complexes, only a few bimetallic Ru-Ru, Ru-Mo, Ir–Ru, Ir–Ir and Ir–M (M= Co, Ni, Cu) (Scheme 1.6.) and complexes are explored for formic acid dehydrogenation. In 2000, Gao et al. utilized a binuclear Ru-based catalyst [Ru<sub>2</sub>( $\mu$ -CO)(CO)<sub>4</sub>( $\mu$ -dppm)<sub>2</sub>] (1,2-bis(diphenylphosphino) methane, dppm) (C-21) for the formic acid dehydrogenation.<sup>11</sup> The catalyst (C-21) also demonstrated the ability to dehydrogenate formic acid (0.35 M) with a TOF of 500 h<sup>-1</sup> at room temperature in acetone. Further, it was observed that increasing the catalyst amount led to a rise in the rate of formic acid dehydrogenation. Conversely, as the concentration

of formic acid was elevated, the rate of the reaction decreased. Notably, when the reaction was performed in more acidic conditions, the concentration of freeformate ions decreased significantly due to the formation of the adduct [(HCO<sub>2</sub>)<sub>2</sub>H].<sup>[41]</sup> Later, in 2003, Man et al. reported a Ru-Mo based heterobimetallic  $[(\eta^5-C_5H_5)Ru(CO)(\mu-dppm)Mo(CO)_2(\eta^5-C_5H_5)]$  complex (C-22) for the formic acid dehydrogenation.<sup>12</sup> Catalysts (C-22) also exhibited activity for the complete dehydrogenation of formic acid. Despite the relatively slow rate of formic acid dehydrogenation, monitoring the reaction by NMR spectroscopy suggests some interesting findings. In a THF-d<sub>8</sub> solution containing catalyst (C-22) and formic acid (25 µmol) within a sealed NMR tube, the mixture was heated to 80 °C for 2.5 hours, resulted in the formation of a formato complex, as confirmed by NMR.<sup>[42]</sup> In 2010, Heteronuclear Ir-Ru complex [Ir<sup>III</sup>(Cp\*)(H<sub>2</sub>O)(bpm)Ru<sup>II</sup>(bpy)](SO<sub>4</sub>)<sub>2</sub> (bpm is 2,2'-bipyrimidine) as reported by Suenobu et al. displayed an unusual hydrogen tunneling effect in the pH-dependent formic acid dehydrogenation (C-23) in Scheme 1.6.). In aqueous formic acid-sodium formate solution, the Ir-Ru catalyst exhibited a TOF of 426 h<sup>-1</sup> for formic acid dehydrogenation at 25 °C, where kinetic isotope effect (KIE) experiments inferred the hydrogen evolution step as the ratedetermining step instead of  $\beta$ -hydride elimination step.<sup>[43]</sup>



Scheme 1.6. Bimetallic catalysts explored for formic acid dehydrogenation.

In 2012, Fujita et al. developed a bimetallic catalyst of Cp\*Ir complex  $[(Cp*IrCl)_2(thbpym)]$  (thbpym is 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) (C-24) in Scheme 1.6.) for the efficient dehydrogenation of formic acid. The studied bimetallic Ir-Ir catalyst exhibited a TOF of 228,000 h<sup>-1</sup> at 90 °C and TON of 308,000 at 80 °C for CO-free hydrogen production from formic acid. Moreover, reversible H<sub>2</sub> storage using CO<sub>2</sub> in aqueous media under mild temperature and pressure was also achieved over the studied bimetallic Ir-Ir catalyst. The -OH moieties on the thbpym ligand of complex (C-24) were pH responsive, and hence facilitated the reversible H<sub>2</sub> storage and release by tuning the pH of the solution.<sup>[44]</sup> In 2020, Kojima et al. also reported heterodinuclear  $Ir^{III}-M^{II}$  complex (M = Co, Ni, Cu) based on 3.5-bis(2-pyridyl)-pyrazole (Hbpp) ligand for the catalytic formic acid dehydrogenation in water at 25 °C (C-25) - (C-27) in Scheme 1.6.).<sup>26</sup> Notably, the heterobimetallic Ir–M catalyst exhibited higher catalytic activities (in increasing order of activity: Ir<sup>III</sup>–Cu<sup>II</sup> < Ir<sup>III</sup>–Co<sup>II</sup> < Ir<sup>III</sup>–Ni<sup>II</sup>) as compared to the mononuclear Ir complex, attributed to the cooperative effect of the Ni metal.<sup>[45]</sup>

From extensive literature on dehydrogenation of formic acid using Cp\*Ir catalysts with various ligand moieties modifications in the substituents of the ligand moiety have a major impact on catalytic performance. More specifically, catalytic activity has been demonstrated to be enhanced by substituents that donate electrons, whereas catalytic performance was infrequently affected by steric hindrance. Because they promoted the production of particular intermediates that lowered the overall activation barrier, pendant OH groups were especially noteworthy for their impact on catalytic activity. Catalytic activity increased when pyridine was substituted with other coordinating N atoms that had a high electron-donating capacity. Thus, in the process of producing hydrogen by dehydrogenating formic acid, the design of ligands turned out to be a crucial element influencing the durability and activity of catalysts.

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Scheme 1.7. Rhodium based catalysts explored for formic acid dehydrogenation.

In 2008, Fukuzumi et al. was also explored a new class of Cp\*Rh complex  $[Rh^{III}(Cp^*)(bpy)(H_2O)]^{2+}$  (C-28) for formic acid dehydrogenation to achieve a TOF of 28 h<sup>-1</sup> at pH 3.8 (Scheme 1.7.).<sup>[46a]</sup> Later, Himeda el al. also explored 4,4'-dihydroxy-2,2'-bipyridine (4,4'-dhbp) ligated Cp\*Rh (C-29) for formic acid dehydrogenation to achieve moderate catalytic activity (initial TOF of 1340 h<sup>-1</sup>) at 60 °C. The significant catalytic activity was attributed to the electronic effect of oxyanions produced through the deprotonation of the -OH groups in the 4,4'-dhbp ligand.<sup>[47]</sup> In 2018, Fidalgo et al. reported Cp\*Rh (C-30) catalysts bearing 8-aminoquinoline ligand for the catalytic formic acid dehydrogenation in water. At initial pH 4.5, with C-30 (0.04 mol %) catalyst TON of 2109 was achieved when a mixture of FA/HCOONa (1:2) was refluxed at 100 °C.<sup>[35]</sup>

Ru-based catalysts displayed high catalytic activity and advantageously are comparatively less expensive than Ir and Rh, and therefore Ru based catalysts represent a class of the most extensively explored molecular catalysts for formic acid dehydrogenation (Scheme 1.8.).<sup>19</sup> For instance, Czaun et al. studied RuCl<sub>3</sub> with various phosphine (PPh<sub>3</sub>, tris(4-chlorophenyl) phosphine, and tris(2–tolyl)–phosphine) for the dehydrogenation of formic acid in an emulsion of water and organic solvents.<sup>[48a]</sup> Huang et al. reported ruthenium– PN<sup>3</sup> pincer complex for achieving high TON for formic acid dehydrogenation in non-aqueous solvents, where the role of the anime arm of the pincer ligand was found to be crucial in formic acid activation.<sup>[48b]</sup> Grützmacher et al. also reported several Ru-based catalysts for formic acid dehydrogenation, where they achieved a TOF of 2688 h<sup>-1</sup> over [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] in the presence of triethylamine at 40 °C. They also reported a TOF as high as 36000 h<sup>-1</sup> for formic acid dehydrogenation over RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> in THF at 60 °C.<sup>[48c]</sup> Further, to explore more sustainable processes, highly efficient catalytic systems for formic acid dehydrogenation in water were also developed.<sup>[49]</sup> Notably, unless otherwise observed, the majority of catalytic systems explored for formic acid dehydrogenation represent the CO-free hydrogen production process. In this direction, Laurenczy et al. developed hydrophilic Ru<sup>II</sup> phosphine-based complexes for the dehydrogenation of aqueous formic acid in the presence of sodium formate (n(HCOOH)/n(HCOONa) 9:1) at 100 °C.<sup>[49a]</sup>



*Scheme 1.8. Phosphine based Ruthenium catalysts* **C31–C36** *explored for the formic acid dehydrogenation.* 

In 2011, Boddien et al. utilized [{RuCl<sub>2</sub>(benzene)}<sub>2</sub>] precursor and 1,2bis(diphenylphosphino) methane (dppm) (C-31) for the catalytic formic acid dehydrogenation (Scheme 1.8.). Catalyst (C-31) exhibited high activity for hydrogen production from formate in H<sub>2</sub>O/DMF, where an initial TOF of 2923  $h^{-1}$  and 2592  $h^{-1}$  was achieved at 60 °C with lithium formate and HCOONa, respectively. Ammonium formate exhibited lower activity with a TOF of 126  $h^{-1}$ , while magnesium formate and calcium formate displayed good H<sub>2</sub> liberation activities with TOF of 420  $h^{-1}$  and 770  $h^{-1}$ , respectively. To facilitate the formation of H<sub>2</sub>, excess water was used to provide additional protons, resulting
in a selective dehydrogenation of formate. After H<sub>2</sub> release from formate, pH of the reaction medium shifts towards the higher (basic), as the released  $CO_2$  was captured in the basic solution as bicarbonate, which was recovered as a solid after the reaction.<sup>[50]</sup> In 2011, Papp et al. reported a charging/discharging hydrogen storage device using  $[RuCl_2(m-tppms)_2]_2$  catalyst (C-32) containing sodium diphenylphosphinobenzene-3-sulfonate (tppms) ligand.<sup>14</sup> Catalyst (C-32) catalyst also displayed good activity for the dehydrogenation of sodium formate at 80 °C with a TON of 120 in 1 h.<sup>[51]</sup> In 2014, Filonenko et al. developed a Ru-PNP pincer catalyst (C-33) for formic acid dehydrogenation (Scheme 1.8.). In DMF, catalyst (C-33) exhibited excellent stability and the highest reaction rate for formic acid dehydrogenation (Scheme 1.9.). Notably, the reaction followed first-order behaviour with respect to formate in the presence of DBU. This suggested that the base promoters actively participate in the elementary steps of the catalytic reaction. With triethylamine (Et<sub>3</sub>N), a maximum TOF of 257,000 h<sup>-1</sup> and TON of 326500 was achieved at 90 °C in DMF, inferred the significant promotional effect of Et<sub>3</sub>N on formic acid dehydrogenation.<sup>[52]</sup>



Scheme 1.9. Catalytic pathway for formic acid dehydrogenation over Ru-PNP catalyst C-33. Reproduced from ref [52]. Copyright 2014 WILEY-VCH Verlag GmbH.

In 2015, Kothandaraman et al. presented a novel approach for the hydrogen release system. This method utilized carefully characterized and readily accessible Ru-PNP complexes-based catalysts. The system is aminefree, efficient, with over 90% yield in dehydrogenation of formate (Scheme 1.8.). They used the Ru-MACHO-BH catalyst (C-34) for efficient dehydrogenation of formate, where MACHO ligands (HN(CH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>), with R group as isopropyl or phenyl. The catalysts (C-34) displayed high activity for the dehydrogenation of sodium formate, with an initial TOF of 286 h<sup>-1</sup> at 69 °C and 430 h<sup>-1</sup> at 68 °C, respectively. Further, an initial TOFs of 437 h<sup>-1</sup> and 290 h<sup>-1</sup> were observed for lithium formate and potassium formate dehydrogenation at 70 °C and 71 °C, respectively using the catalyst (C-34).<sup>[53]</sup> In 2018, Xin et al. also reported the successful application of Ru-triphos complex (C-35) combined with Al(OTf)<sub>3</sub> for the hydrogen release. To achieve exceptional performance, a lewis acid, Al(OTf)<sub>3</sub>, was utilized in a Ru-triphos complex (C-**35**) catalyst due to its ability to activate both the substrate and catalyst through a weak interaction. The process was observed to occur through two primary pathways: the first pathway involves promoting the formation of active cationic ruthenium species under acidic conditions, while the second involves accelerating the cleavage of polar C-O or C-N bonds through acid-base interactions. In the process of formic acid dehydrogenation, the rate was enhanced twofold (TOF from 550 to 1200 h<sup>-1</sup>) upon the incorporation of Al(OTf)<sub>3</sub>. In order to understand the promotion effect of Al(OTf)<sub>3</sub> on the reaction mechanism, in-situ NMR experiments were conducted. These experiments revealed that aluminum triflate activates both the precatalysts and formic acid by enhancing the activity of Ru-H species and the modulation of the polarity of the carbonyl group of formic acid through direct O-Al interaction, respectively, implying that the reaction proceed through a different mechanism as in the previously reported Ru-triphos complexes, no hydride signals were detected in the presence of organic base.<sup>[54]</sup>

Extensive literature revealed that the activity in phosphine-based catalytic systems for formic acid dehydrogenation is associated with the ligand's basicity. higher basicity ligands showed stronger  $\sigma$ -donating ability, which had a major impact on achieving higher catalytic activity. Furthermore, steric effects and the ligand's solubility in the employed solvent system were important

factors in increasing the catalytic activity for the dehydrogenation reaction. For the most particular, catalytic systems required the addition of an organic solvent because of poor solubility in water of phosphines-based complexes.



*Scheme 1.10.* (arene) Ruthenium catalysts C36–C40 explored for the Formic acid dehydrogenation.

In 2017, Huang et al. reported the aqueous formic acid/sodium formate dehydrogenation over the (arene)Ru-N,N-diimine complex (C-36) in the absence of any organic additive at 90 °C to achieve a TOF of 12000 h<sup>-1</sup> and a TON of 350000 (Scheme 1.10.).<sup>[55]</sup> Previously, we also investigated (arene)Ru<sup>II</sup> complexes with 8-(N-methylamino) quinoline (NHMeAmQ), pyridine-2-ylmethanol, and bis-imidazole methane-based ligands for the dehydrogenation of formic acid in water at 90 °C.<sup>[56]</sup> Over  $[(\eta^6-C_6H_6)Ru(\kappa^2-NHMeAmQ)Cl]^+$  (C-**37**) in Scheme 1.8.) catalyst, we achieved an initial TOF of 940  $h^{-1}$  in water with a TON of 2248 upon recycling the catalyst for 5 catalytic runs.<sup>[56a]</sup> Moreover, we observed an enhancement in the catalytic activity upon using (arene)Ru<sup>II</sup>-pyridine-2-yl-methanol complex (C-38) to achieve an initial TOF of 1548 h<sup>-1</sup> and a TON of 6050 for formic acid dehydrogenation in water at 90 °C.<sup>[56b]</sup> Further, (arene)Ru<sup>II</sup>–bis–imidazole methane complexes for catalytic dehydrogenation of formic acid in water were explored, where the (arene)Ru<sup>II</sup> complex having 4-methoxy phenyl substituted bis-imidazole methane (C-39) in Scheme 1.8.) showed high catalytic activity and long-term stability with an initial TOF of 1545 h<sup>-1</sup> and TON of 8830, attributed to the electron-donating effect of the ligand. It is expected that (arene)Ru-bis-imidazole methane with tuned substituents may effectively catalyse the aqueous-phase formic acid dehydrogenation[56c]. Recently, Verron et al. reported a dimeric tethered  $\pi$ -coordinated-phenoxy ruthenium precatalyst (**C-40**) for the formic acid dehydrogenation in DMSO under base-free condition. For formic acid dehydrogenation, the catalyst (**C-40**) (0.5 mol %), formic acid (2.4 M), and DMSO as solvent was used to achieve a conversion of 95% with the highest TOF of 202 h<sup>-1</sup> in 20 min.<sup>[57]</sup>

Extensive literature suggests that designing catalytic systems containing an arene ring as a polyhapto ligand has several advantages. The ability to precisely alter the catalytic activity by incorporating various substituents to the arene ring is a major advantage. These substituents have the ability to influence the ligand's steric and electronic characteristics, which may affect the interaction with the metal centre and, in turn, the complex's catalytic activity. Furthermore, complexes with arene rings as ligands frequently have high water solubility. This characteristic makes these complexes more useful in a variety of scientific fields, including aqueous-phase dehydrogenation of formic acid.

#### 1.3.2. Non-noble metal-based molecular catalyst

Despite the extensive reports on Ir, Rh and Ru based complexes in the literature, these metals are quite expensive owing to which researchers have also explored other inexpensive or comparatively less expensive metal-based molecular catalysts for the dehydrogenation of formic acid. Unlike noble metal-based catalysts, non-noble metal-based molecular catalysts (Scheme 1.11.) are less explored for formic acid dehydrogenation.



Scheme 1.11. Non-noble metal-based catalysts C-41–C-46 explored for formic acid dehydrogenation.

For instance, Enthaler et al. reported Ni-PCP-hydrido catalyst (C-41) to effectively catalyze formic acid dehydrogenation. The Ni-PCP catalyst (C-41) demonstrated formic acid dehydrogenation, wherein particularly Ni-PCP-hydrido (C-41) and Ni-PCP-formato species (C-41A) demonstrated high activity with TON of 626 for formic acid dehydrogenation using FA/NEt<sub>3</sub> at 80 °C in propylene carbonate solvent (Scheme 1.12.).<sup>[58]</sup>



Scheme 1.12. Ni-PCP (C-41) catalysed formic acid dehydrogenation. Reprinted with permission from ref [58]. Copyright 2015 WILEY-VCH Verlag GmbH.

In 2015, Bertini et al. developed an Fe (II) complex (C-42) for formic acid dehydrogenation. Formic acid dehydrogenation was performed over the *in situ* generated (C-42) species by using [Fe(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with tetraphos (tetraphosphine 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane), in propylene carbonate under base-free condition, which resulted in considerably enhanced catalytic activity with initial TOF of 1737 h<sup>-1</sup> and a TON of 6061 in 6 h at 60 °C. A 5-coordinated Fe species was dominating the formic acid dehydrogenation reaction. Notably, the Fe-hydrido species (C-42A) was also found to pay a crucial role in the catalytic formic acid dehydrogenation, where it facilitated the fast elimination of H<sub>2</sub> to regenerate the Fe-formato species (C-42D). The Fe-formato species after undergoing a  $\eta^2 \rightarrow \eta^1$  coordination shift and rearrangement, followed by  $\beta$ -hydride elimination to form Fe-hydrido species (C-42A) (Scheme 1.13.).<sup>[59a]</sup>



Scheme 1.13. Reaction pathway for the Catalytic formic acid dehydrogenation over C42. Reprinted with permission from ref [59]. Copyright 2015 American Chemical Society.

Furthermore, Gonsalvi et al. reported, Fe–PNP catalyst (C-43) in Scheme 1.11.) exhibited a TOF of 9425 h<sup>-1</sup> and a TON over 92000 for formic acid dehydrogenation at 80 °C.<sup>[59b]</sup> Later, Beller et. al reported a phosphine-free Mn-based catalyst (C-44 in Scheme 1.11.) was also explored for the dehydrogenation of aqueous formic acid with an initial rate of 7 mL/min and a TON of 5763 at 92.5 °C.<sup>[60a]</sup> Further, Wei et al. employed a Mn-PNP catalyst (C-45) for formic acid dehydrogenation. For formic acid dehydrogenation, the Mn-PNP catalyst (C-45) exhibited good stability and reusability with high productivity to achieve a TON of 600000. In order to understand the feasibility of reusing the catalyst and base, a biphasic solvent system was used to easily recycle the catalyst (C-45) and organic solvent, where >89% of the theoretical H<sub>2</sub> productivity for the formic acid dehydrogenation was achieved with a total TON of 676700 (Scheme 1.14.).<sup>[60b]</sup>



Scheme 1.14. Mn-PNP (C-45) catalysed formic acid dehydrogenation. Reprinted with permission from ref [60b]. Copyright 2022 Springer Nature Limited.

Wei et al. also reported a similar Mn-PNP catalyst with a methyl substituent (**C-46**) for the dehydrogenation of formate.<sup>31(b)</sup> Catalyst, (**C-46**) catalyzed the dehydrogenation of various formate salts (Li<sup>+</sup>, Na<sup>+</sup>, NH4<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) resulted in the generation of hydrogen gas with low purity (67-95%) in the absence of lysine. However, in the presence of lysine, high yields of H<sub>2</sub> (>91%) with high purity (>98%) was achieved.<sup>[60c]</sup>

# 1.4. Research gaps in formic acid dehydrogenation over transition metal catalysts

- Extensive research indicates that iridium-based catalysts are highly efficient for hydrogen production from formic acid in water. However, due to the high cost associated with iridium, therefore alternative catalytic systems for both cost-effective and equally efficient are required.
- Several studies have explored the use of alternative metals such as ruthenium, rhodium, iron, nickel and manganese for formic acid dehydrogenation. However, in many instances, the addition of organic

solvents or additives is necessary, posing challenges to the sustainability of the process.

- Catalysts with high recyclability for bulk-scale hydrogen production have not received extensive research attention, highlighting the need for further investigation in this crucial area.
- The majority of reported catalysts for formic acid dehydrogenation in water are monometallic systems. However, the exploration of bimetallic systems could offer significant advantages.

#### 1.5. Objective of thesis

Hydrogen, with its high energy density and environmental friendliness when produced from renewable sources, holds great promise as a future energy carrier. One efficient method for hydrogen production involves the use of Liquid Organic Hydrogen Carriers (LOHCs), stable organic compounds that can reversibly store and release hydrogen. However, to make this process economically viable and scalable, efficient catalysts are crucial. Rutheniumbased complexes, with their versatile activities and lower cost compared to iridium-based complexes, have emerged as attractive candidates for this purpose.

This thesis is dedicated to advancing the efficiency of ruthenium-based molecular catalysts for hydrogen production from Formic acid. The specific objectives are as follows:

- To design and synthesis of ruthenium-based catalysts targeted for formic acid dehydrogenation reactions under ambient reaction conditions in water. This may involve the incorporation of various ligands and functional groups to enhance catalytic activity, stability, and selectivity.
- To characterize the ligands and molecular catalysts through various spectro analytical techniques such as Single Crystal X-ray diffraction (SC-XRD) and spectroscopic methods are employed to analyse the structure of the ligand and catalyst.
- To study the ligand-tuned activities of the different catalysts toward the dehydrogenation reactions.

- To study the different reaction parameters such as pH, temperature, and base effect by which these reactions kinetics affected.
- To scale up the catalytic activities of the developed catalysts by performing recyclability, long-term stability and bulk-scale reactions.
- To detect and isolate different active catalytic reaction intermediates involved in the catalytic cycle for better understanding the reaction pathway.

#### **1.6. Organization of thesis**

- In *Chapter 1*, provides an overview of relevant literature concerning hydrogen storage, production, and application, with a specific focus on the formic acid as a liquid organic hydrogen carriers and catalyst's role in formic acid dehydrogenation reactions.
- In *Chapter 2*, discusses the synthesis and characterization of *N*, *N* donor schiff-based ligated Ruthenium (II) complexes and the role of ligand-tuned activity for the catalytic dehydrogenation of formic acid in water.
- In *Chapter 3*, discusses the synthesis and characterization of bisimidazole methane-based ligand-tuned catalytic activity of halfsandwich Ruthenium (II) complexes for the catalytic dehydrogenation of formic acid in water.
- In *chapter 4*, discusses the synthesis and characterization of bisimidazole methane-based diruthenium metal complex and their ligandtuned catalytic activity for the dehydrogenation of formic acid in water.
- In *chapter 5*, presents a summary of the thesis work, including achievements and future scope of the current work.

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### Chapter 2 Ruthenium-Oxime Catalyst for Hydrogen Production from Formic acid in Water

#### **2.1. Introduction**

With the developing strategy of finding an alternate greener energy source for reducing greenhouse gas emissions in the environment, hydrogen has emerged as a strong contender for a carbon-free energy carrier, particularly for mobile applications when paired with proton-exchange membrane fuel cells.<sup>[1]</sup> In this context, H<sub>2</sub>, a clean energy carrier, is gaining attention as it can be produced using renewable resources (e.g. water), and it released water and energy in fuel cells.<sup>[1-7]</sup> However, the practical use of hydrogen is limited by storage and delivery issues due to the low volumetric density of  $H_2$ . Several solid and liquid H<sub>2</sub> carriers have been extensively explored, which can safely store high H<sub>2</sub> content for a long duration, enabling easy and safe transportation of H<sub>2</sub> gas. Among several liquid hydrogen carriers explored, formic acid (FA) displays unique characteristics as it can store and release 4.4 wt% (53.4 g/L) of  $H_2$  gas and can be produced by the hydrogenation of  $CO_2$ .<sup>[8]</sup> Hence, FA dehydrogenation with high efficiency under mild condition is highly desirable for a H<sub>2</sub>-based energy system. Researchers have developed various practical methods for the large-scale production of CO-free hydrogen gas from FA by following: HCOOH  $\rightleftharpoons$  H<sub>2</sub> + CO<sub>2</sub> and avoiding the undesirable dehydration step: HCOOH  $\rightarrow$  H<sub>2</sub>O + CO.<sup>[9-17]</sup> The entropy driven FA dehydrogenation to CO<sub>2</sub>, is more feasible for reversible H<sub>2</sub> production and storage.<sup>[18]</sup> Which is crucial for the development of a reversible hydrogen release system.

Over the past few decades, numerous homogeneous molecular catalysts have been reported for FA dehydrogenation.<sup>[17], [19]</sup> Analogous to that, only a limited number of studies have been focused on the development of homogeneous molecular catalysts for the reversible hydrogen storage and release over the same catalytic system.<sup>[20-33]</sup> Among the noble metal-based catalyst, Ir-based catalysts have shown exceptional performance in the FA dehydrogenation. For instance, Nozaki et al. developed Ir-PNP trihydride complex to achieve high efficiency in FA dehydrogenation with a TON of 890

and TOF of 120,000 h<sup>-1</sup> at 80 ° C in H<sub>2</sub>O/THF.<sup>[20]</sup>Fujita et al. reported a protonswitchable hydroxy substituted Cp\*Ir-bipyrimidine catalyst demonstrating a remarkable performance in aqueous medium for FA dehydrogenation with a TON of 165,000 and TOF of 228,000 h<sup>-1</sup> at 90 °C.<sup>[21]</sup> Fukuzumi et al. also developed a pH-controllable cyclometalated Cp\*Ir-pyrazolyl benzoic acid complex for FA dehydrogenation with TOF of 1880 h<sup>-1</sup>, pH 2.8 at 25 °C in aqueous medium.<sup>[22]</sup> Himeda et al. investigated imidazoline-based Cp\*Ir catalysts for hydrogen release, achieving efficient FA dehydrogenation with maximum TOF of 56900 h<sup>-1</sup> (pH 3.0) at 60 °C.<sup>[23]</sup> Choudhury et al. also reported a hybrid NHC carbene-based Cp\*Ir catalyst for FA dehydrogenation with TOF of 100,000 h<sup>-1</sup> (pH 4.4) at 90 °C in water at 30 °C.<sup>[24]</sup> The observed high activity was attributed to the presence of a strong  $\sigma$ -donating ability of the imidazolylidene-based NHC ligand. Yi et al. synthesized a Cp\*Irpyrrolylpyridine catalyst that efficiently dehydrogenated HCOOH/HCOONa (3:1) with TOF<sub>max</sub> of 45900 h<sup>-1</sup>) at 90 °C.<sup>[25]</sup> Choudhury et al. reported Cp\*Ir based catalyst containing cyclic amide-NHC ligand for the FA dehydrogenation with TOF of 70600  $h^{-1}$  and TON of 5889 at 80 °C.<sup>[26]</sup>

Notably, Ru catalysts have also offered promising potential for the formic acid dehydrogenation and hence, have undergone significant exploration in this field as a cost-effective alternative to Ir catalysts. For instance, Beller et al. first demonstrated HCOO<sup>-</sup> based H<sub>2</sub>-release system over [{Ru( $\eta^{6}$ -C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>}<sub>2</sub>] with 1,2-bis(diphenylphosphino)methane (dppm) in water-DMF. Dehydrogenation of sodium formate in water-DMF was achieved with 100% conversion at 40 °C and achieved initial TOF 377 h<sup>-1</sup> with TON 885 (3h).<sup>[27]</sup> Joó et al. also reported a [RuCl<sub>2</sub>(*m*-tppms)<sub>2</sub>]<sub>2</sub> catalyst containing sodium diphenylphosphinobenzene-3-sulfonate (tppms) ligand for the dehydrogenation of sodium formate at 80 °C with TON of 120 in water.<sup>[28]</sup> Olah et al. explored Ru-MACHO-BH complex for sodium formate dehydrogenation with 100% yield of H<sub>2</sub> with an initial TOF of 430 h<sup>-1</sup> in dioxane-water at 70 °C.<sup>[29]</sup>

Hirose et al. reported a Ru catalyst containing 4,4'-dihydroxy-2,2'bipyridine (DHBP) ligand exhibiting remarkable performance for the interconversion of FA dehydrogenation with an initial TOF of 94 h<sup>-1</sup> and achieved TON of 3700 at 60 °C in H<sub>2</sub>O.<sup>[30]</sup> Plietker et al. reported [Ru(Cl)(CH<sub>3</sub>CN)(PNNP)]PF<sub>6</sub> catalyst, a rechargeable hydrogen battery for dehydrogenation of FA at 100 °C in toluene using DBU as a base.<sup>[31]</sup> Pidko et al. reported a Ru-PNP catalyst with excellent stability and high catalytic activity for FA dehydrogenation with TOF of 257,000 h<sup>-1</sup> at 90 °C. Advantageously, FA dehydrogenation was also achieved during the cyclic operations without any need to introduce additional base between cycles, and without catalyst deactivation throughout the process.<sup>[32]</sup> Li et al. used a combination of a Ru-triphos complex with Al(OTf)<sub>3</sub> for FA dehydrogenation, where the highest TOF of 1200 h<sup>-1</sup> was achieved using HCOOH/HCOONa ratio of 9:1. Under the same reaction condition.<sup>[33]</sup> Nilsen et al. used a Ru-PNP pincer complex for the dehydrogenation of FA with a TON of 18,000,000 and TOF of 11,134 h<sup>-1</sup> at 80 °C in the presence of an ionic liquid 1-ethyl-3 methylimidazolium acetate (EMIM OAc).<sup>[34]</sup> Recently, Fischmeister et al. developed an arene-based Ru complex for FA dehydrogenation with TOF of 84 h<sup>-1</sup> and TON of 173 at 90 °C in DMSO.<sup>[35]</sup>

It is evident from these reports that Cp\*Ir-based catalysts are the most active catalyst, and these Cp\*Ir catalysts are also active in aqueous condition. On the other hand, Ru-based catalysts are mostly explored for FA dehydrogenation in organic solvents, while the development of active Ru-catalyst in aqueous condition for FA dehydrogenation is yet to be extensively explored. Herein, we report water-soluble (arene)Ru -pyridyloxime, - pyridylmethyloxime, and -pyridylimines complexes for FA dehydrogenation in water under mild reaction condition. In our catalytic system, the role of ligand was found to be crucial in achieving efficient FA dehydrogenation cycles over the same catalytic system. Further, extensive investigations are performed to identify the crucial catalytic intermediate species to elucidate their role in the observed activity. Attempts are also made to replicate the observed results to dehydrogenation over the studied catalytic system.

#### 2.2. Results and discussion

## 2.2.1. Catalytic formic acid dehydrogenation in water over ruthenium catalysts

Catalysts  $[(\eta^6 - p \text{-cymene}) \text{Ru}(N \text{-hydroxy-iminopyridine}) \text{Cl}]^+$  (**[Ru]-1**),  $[(\eta^6 - p \text{-cymene}) \text{Ru}(N \text{-methoxy-iminopyridine}) \text{Cl}]^+$  (**[Ru]-2**),  $[(\eta^6 - p \text{-cymene}) \text{Ru}(N \text{-propyl-iminopyridine}) \text{Cl}]^+$  (**[Ru]-3**),  $[(\eta^6 - p \text{-cymene}) \text{Ru}(N \text{-isopropyl-iminopyridine}) \text{Cl}]^+$  (**[Ru]-4**  $[(\eta^6 \text{-benzene}) \text{Ru}(N \text{-hydroxy-iminopyridine}) \text{Cl}]^+$ 

([**Ru**]-5),  $[(\eta^6-\text{benzene})\text{Ru}(N-\text{methoxy-iminopyridine})\text{Cl}]^+$  ([**Ru**]-6),  $[(\eta^6$ benzene)Ru(N-propyl-iminopyridine)Cl]<sup>+</sup> ([Ru]-7) and  $[(\eta^6-benzene)Ru(N-benzene)$ isopropyl-iminopyridine)Cl]<sup>+</sup> ([**Ru**]-8), were synthesized following earlier reports (Figure 2.1).<sup>[36]</sup> Initially, we investigated FA dehydrogenation over [Ru]-1, [Ru]-2, [Ru]-3 and [Ru]-4 under additive free condition in water at 90 °C. Results inferred that Ru-pyridyloxime [Ru]-1 outperformed others with H<sub>2</sub> vield over 99% besides CO<sub>2</sub> with a turnover of 500 (TOF 134 h<sup>-1</sup>) (Table 2.1., entry 1, and Figure 2.1.). In contrast to [Ru]-1, [Ru]-2, [Ru]-3 and [Ru]-4 showed less H<sub>2</sub> yield, 65%, 81% and 63% respectively (Table 2.1., entries 2-4 and Figure 2.1.). These results suggesting the crucial role of the OH group of pyridyloxime in achieving high catalytic activity for H<sub>2</sub> production from FA. Further electron-deficient N-isopropyl pyridylimine accounts for the lower H<sub>2</sub> yield observed for **[Ru]-4** (TOF of 54 h<sup>-1</sup>) as compared to **[Ru]-3** (TOF of 120 h<sup>-1</sup>). Further, the conversion of **[Ru]-2** and **[Ru]-4** appears comparable, but [**Ru**]-4 (TOF of 54  $h^{-1}$ ) took 3 times more time than [**Ru**]-2 (TOF of 120  $h^{-1}$ ) to achieve this conversion (Table 2.1., entries 2 and 4). Notably, the analogous (benzene)Ru complexes ([Ru]-5 – [Ru]-8) were found to be less active than the (p-cymene)Ru complexes ([Ru]-1 – [Ru]-4). However, analogous to (pcymene)Ru-pyridyloxime complexes, (benzene)Ru-pyridyloxime complex [Ru]-5 outperformed others ([Ru]-6 – [Ru]-8). Literature reports also revealed that usually, the (*p*-cymene)Ru-based catalysts displayed higher activity than the analogous (benzene)Ru-based catalysts, attributed to the electronwithdrawing property of the  $\eta^6$ -benzene causing more electron-deficient ruthenium centre.<sup>[37]</sup>



*Figure 2.1.* Catalytic dehydrogenation of FA in water over [*Ru*]-1–[*Ru*]-8 catalysts. Reaction Conditions: FA (2 M, in 2.5 mL water), catalysts (10 μmol), 90 °C.

Table 2.1. Optimization of reaction condition for FA dehydrogenation in water<sup>a</sup>

			<b>Ru-catalysts</b>	Ha	+ C	0_	
	п	СООП	H <sub>2</sub> O, 90 °C	2 112			
Entry	Catalyst	HCOONa	<i>n</i> (H <sub>2</sub> +CO <sub>2</sub> )/	Time	TON	TOF	FA
	(µmol)	(mmol)	n(FA)	(min)		( <b>h</b> -1)	Conv.
							(%)
1	[Ru]-1	-	2.0	490	500	134	>99
2	[Ru]-2	-	1.3	500	326	120	65
3	[Ru]-3	-	1.6	480	404	107	81
4	[Ru]-4	-	1.25	1400	314	54	63

5	[Ru]-5	-	1.4	420	357	80	71
6	[Ru]-6	-	1.2	1400	306	75	61
7	[Ru]-7	-	1.0	840	244	75	50
8	[Ru]-8	-	0.8	900	204	54	40
9	[Ru]-1	0.10	2.0	180	500	161	>99
10	[Ru]-1	0.25	2.0	163	500	188	>99
11	[Ru]-1	0.50	2.0	125	500	215	>99
12	[Ru]-1	1	2.0	110	500	242	>99
13	[Ru]-1	2	2.0	94	500	296	>99
14	[Ru]-1	5	2.0	160	490	188	>99
15	[Ru]-1	10	1.6	195	408	160	80

<sup>*a*</sup>Reaction Condition: FA (2 M, in 2.5 mL water), sodium formate (0–10 mmol), catalysts (10  $\mu$ mol), 90 °C. TONs at the completion of reaction as per the mentioned time (min). TOFs per Ru (initial 10 min). TON and TOF values are average of at least two runs with an error of less than 5%. Calculation of FA Conversion = [(evolved volume of gas)/(expected volume of gas) x 100.

It is evident from the literature that, pH of the reaction has a significant influence on the rate of hydrogen production from FA. Therefore, pH-dependent H<sub>2</sub> production from FA (2 M, in 2.5 mL water) was performed over **[Ru]-1**, where the pH of the reaction (1.9 - 5.9) was tuned by varying the amount of sodium formate (0.10 - 10 mmol) at 90 °C. An increasing trend in the catalytic activity was observed with the increase in pH, where initial TOF increased from 134 h<sup>-1</sup> (at pH 1.4) to 296 h<sup>-1</sup> (at pH 3.9) (n(FA)/n(sodium formate) = 5:2). Further, the increase in pH to 5.0 and 5.9 resulted in a drastic decrease in the initial TOF to 188 h<sup>-1</sup> and 160 h<sup>-1</sup>, respectively (Figure 2.2.).<sup>[38-39]</sup>



**Figure 2.2.** Turn Over Frequency (h<sup>-1</sup>) vs pH plot for the catalytic dehydrogenation of FA over **[Ru]-1**. Reaction condition: FA (2 M, in 2.5 mL water), sodium formate (0-10) mmol, **[Ru]-1** (10 µmol), 90 °C.

In all the experiments, the FA fraction was completely decomposed to  $H_2$  and  $CO_2$ . This was further confirmed by GC-TCD analysis of the released gas, where an equimolar ratio of  $H_2$  and  $CO_2$  was only observed with no detectable traces of CO, which is in line with the expected  $H_2$  to  $CO_2$  ratio for FA dehydrogenation. Notably, complete catalytic FA dehydrogenation over [**Ru**]-1 was also achieved at 70 °C, but the rate of evolution of  $H_2$  gas decreased with the lowering in the reaction temperature (5 °C intervals) from 90 to 60 °C ( $E_a$  79.78 kJ/mol) (Figure 2.3.).<sup>[40]</sup>



*Figure 2.3.* (*a*) *Temperature-dependent FA dehydrogenation over* [*Ru*]-1. (*b*) *Corresponding Arrhenius plot. Reaction condition: FA (2 M, in 2.5 mL water), sodium formate (2 mmol), [Ru]-1 (10 μmol), 60-90 °C.* 

The observed pH-dependent trend in the catalytic activity inferred the involvement of formate species in the catalytic reaction. It was further noticed that neat anhydrous FA showed no gas evolution in the absence of water, suggesting the importance of hydronium ions in the release of H<sub>2</sub> gas from FA. The dependence of the initial rates of the catalytic H<sub>2</sub> production from FA (2 M, in 2.5 mL water) on the concentration of [**Ru**]-1 (5- 20 µmol) at 90 °C was also determined. Results inferred that the catalytic reaction is a first-order reaction with respect to the catalyst concentration (Figure 2.4.(a)).<sup>[41]</sup> This observation is consistent with the possible involvement of the active Ru-formato species in the catalytic H<sub>2</sub> production from FA in water. Moreover, a linear dependence of the reaction rate for H<sub>2</sub> production from FA with that of FA concentration (0.5 – 2 M) was also observed, suggesting the involvement of an equilibrium between [**Ru**]-1+ HCOOH and [**Ru-HCOOH**] species (Figure 2.4.(b)).<sup>[41]</sup>



**Figure 2.4.** Plot of (a) ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs ln[cat] (mmol  $L^{-1}$ ). Reaction condition: FA (2 M, in 2.5 mL water), **[Ru]-1** (5-20 µmol), 90 °C. (b) Plot of ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: FA (0.5 M - 2 M, in 2.5 mL water), **[Ru]-1** (10 µmol), 90 °C.

#### 2.2.2. Reusability and recyclability for FA dehydrogenation over [Ru]-1

The catalytic efficacy and long-term stability of [**Ru**]-1 for large-scale reaction for hydrogen production from FA was investigated to evaluate the practical applicability of the studied catalytic system. Results inferred that [**Ru**]-1 (10  $\mu$ mol) exhibited exceptionally high stability with no significant loss in the activity during 26 consecutive catalytic runs, till 50 h for continuous hydrogen production with the recharging of FA (5 mmol) in each cycle to achieve a turnover number of ~13,000 (Figure 2.5.(a)). Notably, **[Ru]-1** catalyst displayed exceptional stability over 90 days with no loss in the catalytic activity for hydrogen production from FA in water, suggesting the high stability of the **[Ru]-1** catalyst. Moreover, **[Ru]-1** also displayed high activity for the complete conversion of 50 mmol FA to H<sub>2</sub> and CO<sub>2</sub> and with the subsequent addition of 50 mmol FA more, a total TON of ~8000 was achieved at 90 °C (Figure 2.5.(b)). Further, the catalytic reaction performed with **[Ru]-1**, where **[Ru]-1** (10 µmol) was stirred in 2.5 mL water with an excess of elemental Hg (0) prior to the reaction at 90 °C, inferred no noticeable loss in the catalytic activity, suggesting the homogeneous nature of the active catalytic species.



*Figure 2.5.* Recyclability plot for the catalytic dehydrogenation of FA in water. Reaction Conditions: FA (2 M, in 2.5 mL water), sodium formate (2 mmol), [*Ru*]-1 (10 μmol), 90 °C. FA (5 mmol) was added after each catalytic run.



**Figure 2.6.** Recharging experiment for hydrogen production from FA over [**Ru**]-1 in water at 90 °C. Reaction condition: FA (2 M, in 25 mL water) and sodium formate (20 mmol), [**Ru**]-1 (10 µmol), 90 °C. Subsequent addition of 50 mmol of FA after complete conversion of initial 50 mmol of FA.

#### 2.2.3. Reutilizing CO<sub>2</sub> released from FA dehydrogenation

Further, to reutilize CO<sub>2</sub> produced during the catalytic FA dehydrogenation in water over [**Ru**]-1, we adopted a one-step CO<sub>2</sub> capture process.<sup>[25]</sup> Initially, the gas released from the reaction (containing an equimolar ratio of CO<sub>2</sub> and H<sub>2</sub>) was passed through KOH (1 mmol) in water (5 mL), till the reaction ceases. As a result, CO<sub>2</sub> is captured by KOH in the form of K<sub>2</sub>CO<sub>3</sub> as confirmed by <sup>13</sup>C NMR spectra, showing a peak at 168.1 ppm corresponding to CO<sub>3</sub><sup>2-</sup> (Figure 2.7.), while the effluent gas was analysed to have only H<sub>2</sub> gas confirmed by GC-TCD confirming the complete capture of CO<sub>2</sub> released during FA dehydrogenation.



**Figure 2.7.** (a) Reutilization of the generated  $H_2$  and  $CO_2$  gas from the catalytic FA dehydrogenation reaction setup. (b) Reaction condition: Dehydrogenation-FA (2 M, in 2.5 mL water), sodium formate (2 mmol), **[Ru]-1** (10 µmol), 90 °C.

#### 2.2.4. Kinetic Isotope Effect

To gain insights into the plausible reaction pathway for the FA dehydrogenation over **[Ru]-1**, we attempted to detect crucial reaction intermediates by performing several control and kinetic experiments. The Kinetic Isotope Effect (KIE) studies were performed to investigate the role of formate activation *vs* hydrogen evolution on the reaction rate for the hydrogen production from FA, by using FA/D<sub>2</sub>O, *d*<sub>2</sub>-formic acid/H<sub>2</sub>O, and *d*<sub>2</sub>-formic acid/D<sub>2</sub>O systems. The observed trend in KIE studies indicated that the *d*<sub>2</sub>-formic acid (DCOOD) was more influential than D<sub>2</sub>O for the reaction rate of the catalytic reaction over **[Ru]-1** under the optimized reaction conditions (Table 2.2.). These results inferred that the reaction rate for FA dehydrogenation over **[Ru]-1** was greatly influenced by the step involving the decarboxylation of the Ru-formato species with the formation of Ru-hydrido species, rather than the H<sup>+</sup>-assisted evolution of hydrogen gas.<sup>[39], [42]</sup> Despite that FA dehydrogenation reaction in presence of DCOOD and/or D<sub>2</sub>O may involve a complex combination of kinetics, equilibrium, and isotope exchange process, the observed trend in the KIE studies suggesting that the rate determining step (RDS) in the studied catalytic cycle may involve the cleavage of the formyl C–H bond with decarboxylation. The observed trend corroborating well with the literature reports. For instance, Huang et al. also observed a KIE of 2.1 when DCOOH was utilized, while a maximum KIE of 3.0 with DCOOD in D<sub>2</sub>O.<sup>[40]</sup> Li et al. also noted that the KIE was 2.3 when DCOOH replaced HCOOH, while it was only 1.7 when HCOOD replaced HCOOH. Additionally, they obtained a KIE of 4.0 with DCOOD in D<sub>2</sub>O in their study.<sup>[43]</sup> Himeda et al. reported a KIE of 1.6 for the D<sub>2</sub>O substituting H<sub>2</sub>O and a KIE of 2.3 for the DCOOD substituting HCOOH.<sup>[43]</sup>

Tab	le 2	2.2.	KIE.	for	FA	del	iyd	rog	gena	tion	over	[ <b>R</b> u]	-1	
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Entry	Substrate	Solvent	<b>TOF</b> ( <b>h</b> <sup>-1</sup> )	KIE
1	НСООН	H <sub>2</sub> O	134	-
2	НСООН	$D_2O$	107	1.25
3	DCOOD	H <sub>2</sub> O	80	1.67
4	DCOOD	$D_2O$	54	2.48

Reaction Condition: HCOOH/DCOOD (2 M, in 2.5 mL of  $D_2O/H_2O$ ), **[Ru]-1** (10 µmol), 90 °C. Initial TOF at 10 min. KIE = TOF (entry 1) / TOF (entry n) (n = 2, 3, 4).

#### 2.2.5. Mechanistic Investigation for FA dehydrogenation

Further, to detect the intermediate species, we conducted several control experiments and analysed the species by mass and NMR. Initially, we dissolved **[Ru]-1** (10 µmol) in 2.5 mL water and stirred for 10 minutes at 50 °C, analysis of the aliquots by mass spectrometry revealed the presence of Ru-aqua species **[Ru-OH2]** at m/z of 375.0659 ([M]<sup>+</sup>) corresponding to the monocationic Ru-aqua species with deprotonated oxime group (Figure 2.8.). In contrast to **[Ru]-1**, we observed the Ru-aqua species of **[Ru]-2** and **[Ru]-3** appeared as dicationic species ([M]<sup>2+</sup>) with mass peak at m/z =195.0458 and m/z = 201.0637, respectively (Figures 2.8. and 2.9.). Moreover, mass peaks corresponding to the [M-1]<sup>+</sup> species for **[Ru]-2** and **[Ru]-3** appeared at m/z 389.0810 and m/z = 401.1146, respectively (Figures 2.9. and 2.10.).<sup>[44]</sup>



*Figure 2.8. HRMS showing the Ru-aqua species for the reaction of [Ru]-1* (10  $\mu$ mol) stirred in 2.5 mL water for 10 minutes at 50 °C.


*Figure 2.9. HRMS showing the Ru-aqua species for the reaction of [Ru]-2* (10  $\mu$ mol) stirred in 2.5 mL water for 10 minutes at 50 °C.



*Figure 2.10. HRMS showing the Ru-aqua species for the reaction of* [*Ru*]-3 (10  $\mu$ mol) stirred in 2.5 mL water for 10 minutes at 50 °C.

Further, sodium formate plays a vital role to maintain the equilibrium between formato and aqua species in the FA dehydrogenation. Ru-formato species [**Ru-HCOO**] (m/z 403.0618) is observed by stirring [**Ru**]-1 with FA (0.5 mmol) and sodium formate (0.1 mmol) at 50 °C for 10 minutes (Figure 2.11.). Analogously, mass peaks corresponding to the Ru-formato species of [**Ru**]-2 (m/z 417.10) and [**Ru**]-3 (m/z 429.13) became more prominent in the presence of sodium formate, suggesting that formate ions facilitate the formation of the Ru-formato species (Figures 2.12. and 2.13.).<sup>41, 42(c)</sup>



Figure 2.11. HRMS showing the Ru-formato species for the reaction of [Ru]-1 (10  $\mu$ mol) with sodium formate (0.1 mmol) and FA (0.5 mmol) stirred in 2.5 mL water for 10 minutes at 50 °C.



Figure 2.12. (a) ESI-MS showing the Ru-aqua species for the reaction of [Ru]-2 (10  $\mu$ mol) stirred in water (2.5 mL) for 5 minutes at 50 °C. (b) ESI-MS showing the Ru-formate species for the reaction of [Ru]-2 (10  $\mu$ mol) with FA (0.5 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature. (c) ESI-MS showing the Ru-formate species for the reaction of [Ru]-2 (10  $\mu$ mol) with FA (0.5 mmol) and sodium formate (1.0 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature.



Figure 2.13. (a) ESI-MS showing the Ru-aqua species for the reaction of [Ru]-3 (10  $\mu$ mol) stirred in water (2.5 mL) for 5 minutes at 50 °C. (b) ESI-MS showing the Ru-formate species for the reaction of [Ru]-3 (10  $\mu$ mol) with FA (0.5 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature. (c) ESI-MS showing the Ru-formate species for the reaction of [Ru]-3 (10  $\mu$ mol) with FA (0.5 mmol) and sodium formate (1.0 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature.

On the other hand, Ru-hydrido species [**Ru-H**] (m/z 359.0667) was detected by mass spectrometry by treating [**Ru**]-1 with sodium formate (1 mmol) in 2.5 mL water at 50 °C for 10 min, and then immediately cooled at 0 °C (Figure 2.14.). The peak at -6.14 ppm appeared in the <sup>1</sup>H NMR of the

reaction aliquot containing is also consistent with the formation of Ru-hydride species (Figure 2.15.).



Figure 2.14. HRMS showing the Ru-hydride species for the reaction of [Ru]-1 (10  $\mu$ mol) with sodium formate (1 mmol) in 2.5 mL water for 10 minutes at 50 °C and cooled to 0 °C.



**Figure 2.15.** <sup>1</sup>*H*-*NMR* spectra showing the generation of Ru-hydride species during the treatment of [**Ru**]-1 (20  $\mu$ mol) with sodium formate (0.5 mmol) in  $D_2O$  (0.5 mL) after heating at 50 °C for 10 minutes.

Hence, these findings inferred the plausible involvement of the proximal -N-OH in hydrogen release from the Ru-hydrido species resulted in the observed enhanced catalytic activity of **[Ru]-1** catalyst. Based on our findings and literature reports, the plausible reaction pathway for hydrogen gas generation from FA over the present catalytic system may involve the following steps: a) in an aqueous solution, Ru-aqua species is formed from [**Ru**]-1, b) Ru-formato species was formed by replacing H<sub>2</sub>O with formate in the presence of FA/formate, c) subsequently, decarboxylation of the Ru-formato species resulted in the generation of Ru-hydrido species and d) finally, with the release of hydrogen gas from Ru-hydrido species, the active Ru-aqua species was regenerated to complete the catalytic cycle (Scheme 2.1.). On the other hand, [**Ru**]-2 and [**Ru**]-3 catalysts having -OMe and -N<sup>n</sup>Pr, respectively groups, may involve proton (H<sub>3</sub>O<sup>+</sup>) assisted hydrogen release, which contribute to the observed activity of these catalysts (Scheme 2.2.).



Scheme 2.1. Proposed reaction pathway for FA dehydrogenation over [Ru]-1 catalyst



Scheme 2.2. Proposed reaction pathway for FA dehydrogenation over [Ru]-2-[Ru]-4 catalyst

## 2.3. Conclusion

Herein, we report a promising (arene)Ru-pyridyloxime-based catalyst for hydrogen generation from FA in water at 60 °C – 90 °C in water, where the oxime ligand played a crucial role in achieving enhanced catalytic performance. The Ru-pyridyloxime [**Ru**]-1 catalyst exhibited an appreciably good turnover number of ~13,000 with high long-term stability (upto 26 catalytic runs) for H<sub>2</sub> production from FA in water with no detectable CO content. Notably, the [**Ru**]-1 catalyst displayed no significant deactivation even after 90 days in water. On this basis, we successfully demonstrated the formic acid/formate dehydrogenation cycles over [**Ru**]-1 catalyst. Moreover, attempts were made to detect crucial Ru-aqua, Ru-formato, and Ru-hydrido intermediate species involved in FA dehydrogenation reactions. Hence our findings on the efficient dehydrogenation of formic acid/formate achieved over the **[Ru]-1** is an important development for aqueous-phase dehydrogenation system.

## **2.4. Experimental Section**

**2.4.1. Materials and Instrumentation**. All reactions are performed without any inert gas protection using high–purity chemicals purchased from sigma Aldrich (Merck). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are recorded using CDCl<sub>3</sub> and D<sub>2</sub>O as solvents Brucker Ascend 500 MHz spectrometers. pH values are measured on a Eutech pH meter, Model Eco TestrpH2. ESI mass spectra are recorded on a micrOTF-Q II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a shin carbon- ST packed column.

**2.4.2. General process for FA dehydrogenation**. An aqueous solution (2.5 mL) containing the catalyst, sodium formate, and FA in an appropriate molar ratio in a two necked 5 mL reaction tube, fitted with a condenser and a gas buret, is stirred at 90 °C over a preheated oil bath. The evolved gas is measured as the displacement of water in the burette with respect to time. The composition of the produced gas is confirmed by GC-TCD. The turnover number (TON) is calculated by the formula [(substrate/catalyst)  $\times$  (conversion/100)]. The turnover frequency (TOF) is calculated as TON/time.

2.4.3. Mechanistic investigation for FA dehydrogenation under catalytic and controlled reaction conditions. FA (2 M, in 2.5 mL water) and [**Ru**]-1 (10  $\mu$ mol) are taken in a 5 mL two-necked test tube and heated at 90 °C. Reaction aliquots are taken in every 5 min and analysed by mass spectrometry to identify the catalytic aqua species [**Ru–H**<sub>2</sub>**O**] involved in the base-free dehydrogenation of FA. [**Ru**]-1 (10  $\mu$ mol) is dissolved in 2.5 mL water, stirred at room temperature and the reaction mixture is analysed by mass spectrometry to detect the Ru-aqua species [**Ru–OH**<sub>2</sub>]. Further, [**Ru**]-1 (10  $\mu$ mol) is dissolved in 2.5 mL of water, and FA (0.5 mmol) is added to it. The reaction aliquots are then analyzed by mass spectrometry to detect the Ru-formato species [**Ru–HCOO**]. To the above solution, sodium formate (1 mmol) is added and analysed by mass spectrometry to gain insights in to the effect of higher concentration of formate ions over the formation of Ru-formato species. [**Ru**]- **1** (10  $\mu$ mol) is dissolved in 2.5 mL of water, sodium formate (1 mmol) is added to it and heated it at 50 °C, after cool the reaction aliquots, analysed by mass spectrometry to detect the Ru-hydrido species [**Ru–H**]. The Ru-hydrido species [**Ru-H**] was also identified by <sup>1</sup>H NMR by heating [**Ru]-1** (20  $\mu$ mol) with sodium formate (0.5 mmol) in D<sub>2</sub>O (0.5 mL) at 50 °C for 10 minutes.

2.4.4. Long-term stability and recyclability experiment of [Ru]-1 for FA dehydrogenation in water. FA (2 M, in 2.5 mL water) and sodium formate (2 mmol) are stirred at 90 °C in the presence of [Ru]-1 (10  $\mu$ mol) catalyst in a two-necked 5 mL reaction tube fitted with a condenser and a gas burette. Further, 5 mmol of FA is added to the reaction mixture for 19 more times between 1.5 h to 50 h, and the produced gas is measured as displacement of water in the burette with respect to time. After that sealed reaction tube are kept in the refrigerator for 15 days and after that again added 5 mmol of FA to H<sub>2</sub> and CO<sub>2</sub>. Similarly, we have repeated the reaction after 30, 45, 60, 75 and 90 days by adding additional 5 mmol of FA in the reaction vessel.

**2.4.5. Recharging experiment for FA dehydrogenation in water**. FA (2 M, in 25 mL water) and sodium formate (20 mmol) are stirred at 90 °C in the presence of **[Ru]-1** (10  $\mu$ mol) catalyst in 50 mL round bottom flask fitted with a condenser and a gas burette. Evolved gas is measured as the displacement of water in the burette per unit time. Further, 50 mmol of FA is recharged in the reaction mixture to generate a total ~4 L of gas in 68 h.

**2.4.6. Reutilizing CO<sub>2</sub> released from FA dehydrogenation**. FA (2 M, in 2.5 mL water) and **[Ru]-1** (10  $\mu$ mol) are taken in a 5 mL two-necked test tube and heated at 90 °C. The complete FA dehydrogenation set-up was deaerated before starting the reaction to ensure the complete removal of any residual air contamination (as ascertained by GC-TCD. The released gases CO<sub>2</sub> and H<sub>2</sub>, (confirmed by GC-TCD analysis), are passed through the deaerated KOH (1 mmol) in water (5 mL) for 3 h to capture CO<sub>2</sub> (as CO<sub>3</sub><sup>2-</sup>). The effluent gas was analysed to have only H<sub>2</sub> gas (as confirmed by GC-TCD) confirming the complete capture of CO<sub>2</sub> released during FA dehydrogenation.

**2.4.7.** Synthesis of ligand N-hydroxy-iminopyridine [L1]. A mixture of pyridine-2-carboxaldehyde (95  $\mu$ L, 1.0 mmol) and hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) (0.075 g, 1.1 mmol) in 30 mL of methanol was

stirred for 8 h at room temperature. Formation of corresponding iminopyridine ligand **[L1]** was confirmed by TLC through consumption of pyridine-2-carboxaldehyde. After completion of the reaction, the resulting solution was evaporated to dryness. The obtained white solid was dissolved in water (3 mL) and extracted with dichloromethane (3x15 mL). The combined organic layer was dried in *vacuo* to obtain **[L1]** as white solid. Further, the ligand **[L1]** was characterized by NMR spectroscopy and mass spectrometry.

**[L1]**. White powder (80 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  8.71-8.70 (d, J = 4 Hz, 1H), 8.59-8.55 (t, J = 8 Hz, 1H), 8.37 (s, 1H), 8.15-8.13 (d, J = 4 Hz, 1H), 8.01-7.98 (t,  $J_1 = 8$  Hz,  $J_2 = 4$  Hz, 1H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  147.22, 144.53, 142.40, 141.86, 126.98, 126.01; ESI-HRMS calcd for [M+H]<sup>+</sup> [C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O] 123.0553, observed 123.0554.



HRMS spectrum of ligand [L1].



<sup>1</sup>H NMR spectrum of ligand [L1] with  $D_2O$  as solvent.



 $^{13}C$  NMR spectrum of ligand [L1] with  $D_2O$  as solvent.

2.4.8. Synthesis of ligand N-methoxy-iminopyridine [L2]. A mixture of pyridine-2-carboxaldehyde (95  $\mu$ L, 1.0 mmol) and methoxylamine hydrochloride (NH<sub>2</sub>OMe.HCl) (0.090 g, 1.1 mmol) in 30 mL of methanol was stirred for 8 h at room temperature. Formation of corresponding iminopyridine ligand [L2] was confirmed by TLC through consumption of pyridine-2-carboxaldehyde. After completion of the reaction, the resulting solution was evaporated to dryness. The obtained white solid was dissolved in water (3 mL) and extracted with dichloromethane (3x15 mL). The combined organic layer was dried in *vacuo* to obtain [L2] as white solid. Further, the ligand [L2] was characterized by NMR spectroscopy and mass spectrometry.

[L2]. White powder (75 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  8.68-8.67 (d, J = 4 Hz, 1H), 8.56-8.52 (t, J = 8 Hz, 1H), 8.28 (s, 1H), 8.10-8.08 (d, J = 4 Hz, 1H), 7.99-7.95 (t, J = 8 Hz, 1H), 4.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  147.46, 143.63, 141.96, 141.22, 127.24, 126.35, 63.70; ESI- HRMS calcd for [M+H]<sup>+</sup> [C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O] 137.0709, observed 137.0705.



HRMS spectrum of ligand [L2].



 $^{13}C$  NMR spectrum of ligand [L2] with  $D_2O$  as solvent.

**2.4.9. Synthesis of ligand N-propylamine-iminopyridine [L3]**. A mixture of pyridine-2-carboxaldehyde (95  $\mu$ L, 1.0 mmol) and *n*-propylamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) (245  $\mu$ L, 3 mmol) in 30 mL of methanol was stirred for 8 h at room temperature. Isolation and purification of the product were carried out according to the procedure for the synthesis of ligands [L1] and [L2] to obtain brown colour liquid [L3]. Further, the ligand [L3] was characterized by NMR spectroscopy and mass spectrometry.

**[L3]**. Brown liquid (83 %); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.56-8.55 (d, *J* = 4 Hz, 1H), 8.29 (s, 1H), 7.91-7.90 (d, *J* = 4 Hz, 1H), 7.66-7.62 (t, *J* = 8 Hz, 1H), 7.22-7.20 (t, *J* = 4 Hz, 1H), 3.57-3.54 (t, *J*<sub>1</sub> = 4 Hz, *J*<sub>2</sub> = 8 Hz, 2H), 1.70-1.63 (sext, *J*<sub>1</sub> = 4 Hz, *J*<sub>2</sub> = 8 Hz, *J*<sub>3</sub> = 8 Hz, 2H), 0.89-0.86 (t, *J*<sub>1</sub> = 4 Hz, *J*<sub>2</sub> = 8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.55, 154.45, 149.18, 136.33, 124.40, 120.99, 63.09, 23.66, 11.64; ESI-HRMS calcd for [M+H]<sup>+</sup> [C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>] 149.1073, observed 149.1075.



HRMS spectrum of ligand [L3].





**2.4.10. Synthesis of ligand N-isopropylamine-iminopyridine [L4]**. A mixture of pyridine-2-carboxaldehyde (95  $\mu$ L, 1.0 mmol) and isopropylamine (NH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>) (245  $\mu$ L, 3 mmol) in 30 mL of methanol was stirred for 8 h at room temperature. Isolation and purification of the product were carried out according to the procedure for the synthesis of ligands **[L3]** to obtain yellow colour liquid **[L4]**. Further, the ligand **[L4]** was characterized by NMR spectroscopy and mass spectrometry.

**[L4].** Yellow liquid (74%); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  8.65-8.64 (d, *J* = 4 Hz, 1H), 8.45 (s, 1H), 8.09-8.08 (d, *J* = 4 Hz, 1H), 7.80-7.77 (t, *J*<sub>1</sub> = 4 Hz, *J*<sub>2</sub> = 8 Hz, 1H), 7.37-7.34 (t, *J*<sub>1</sub> = 4 Hz, *J*<sub>2</sub> = 8 Hz, 1H), 3.72-3.64 (m, 1H), 1.33-1.32 (d, *J* = 4 Hz, 6H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  158.94, 153.96, 148.65, 136.41, 124.40, 120.93, 60.97, 49.00, 23.29; ESI- HRMS calcd for [M+H]<sup>+</sup> [C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>] 149.1073, observed 149.1073.







## 2.4.11. General procedure for the Synthesis of complex [Ru]-1 - [Ru]-8.

Ru<sup>II</sup>–arene complexes [**Ru**]-1 – [**Ru**]-8 were synthesized by previous reports from our laboratory.<sup>51</sup> [( $\eta^6$ –arene)RuCl<sub>2</sub>]<sub>2</sub> (arene = C<sub>6</sub>H<sub>6</sub> and C<sub>10</sub>H<sub>14</sub>) (0.5 mmol) was dissolved in 30 mL of methanol, and the corresponding ligand (1.05 mmol) dissolved separately in 5 mL methanol, was subsequently added dropwise in the above solution. Stirring the above reaction mixture at room temperature for 18 h resulted in the dark orange-colored solution, which was filtered to remove the undesired insoluble solid, the filtrate was dried in *vacuo* to remove the solvent till 1 mL, further an excess of diethyl ether is poured to reprecipitate a yellow to brown color solid. The obtained solid was dried in an oven overnight.

[**Ru**]-1. Yellow powder (74%); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.21-9.20 (d, *J* = 4 Hz, 1H), 8.32 (s, 1H), 8.05-8.01 (t, *J* = 8 Hz, 1H), 7.81-7.79 (d, *J* = 8 Hz, 1H), 7.58-7.54 (t, *J* = 8 Hz, 1H), 6.11-6.09 (d, *J* = 8 Hz, 1H), 5.98-5.96 (d, *J* = 8 Hz, 1H), 5.84-5.53 (d, *J* = 4 Hz, 1H), 5.67-5.65 (d, *J* = 8 Hz, 1H), 2.67-2.60 (m, 1H), 2.18 (s, 3H), 1.06-1.04 (d, *J* = 8 Hz, 3H), 1.00-0.98 (d, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  155.08, 152.03, 139.88, 126.79, 105.29, 104.95, 87.33, 86.92, 85.01, 83.95, 30.82, 21.02, 18.24; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>ORuCl] 393.0302, observed 393.0304.



<sup>1</sup>*H* NMR spectrum of complex [Ru]-1 with  $D_2O$  as solvent.



<sup>13</sup>C NMR spectrum of complex [Ru]-1 with D<sub>2</sub>O as solvent.

[**Ru**]-2. Brown powder (76 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.30-9.29 (d, *J* = 4 Hz, 1H), 8.70 (s, 1H), 8.15-8.11 (t, *J* = 8 Hz, 1H), 7.97-7.95 (d, *J* = 8 Hz, 1H), 7.71-7.68 (t, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 4 Hz, 1H), 6.16-6.14 (d, *J* = 8 Hz, 1H), 6.08-6.07 (d, *J* = 4 Hz, 1H), 5.91-5.89 (d, *J* = 8 Hz, 1H), 5.81-5.80 (d, *J* = 4 Hz, 1H), 4.20 (s, 3H), 2.71-2.64 (m, 1H), 2.19 (s, 3H), 1.08-1.04 (t, *J* = 8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  155.36, 152.19, 140.24, 128.31, 128.09, 105.88, 104.55, 87.16, 86.73, 85.14, 84.49, 63.36, 30.81, 21.08, 18.16; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>ORuCl] 407.0460, observed 407.0468.





<sup>13</sup>C NMR spectrum of complex [Ru]-2 with  $D_2O$  as solvent.

**[Ru]-3**. Brown powder (68 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.38-9.37 (d, *J* = 4Hz, 1H), 8.56 (s, 1H), 8.17-8.14 (t, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 4 Hz, 1H), 8.04-8.02 (d, *J* = 8 Hz, 1H), 7.76-7.72 (t, *J* = 8 Hz, 1H), 6.12-6.11 (d, *J* = 4 Hz 1H), 6.04-6.03 (d, *J* = 4 Hz, 1H), 5.84-5.82 (d, *J* = 8 Hz, 1H), 5.81-5.79 (d, *J* = 8 Hz, 1H), 4.29-4.22 (m, 2H), 2.62-2.52 (m, 1H), 2.17 (s, 3H), 2.03-1.98 (q, *J* = 4 Hz, 1H), 1.89-1.80 (m, 1H) 1.05-1.03 (d, *J* = 8 Hz, 3H), 0.94-0.92 (t, *J* = 8 Hz, 6H); <sup>13</sup>C NMR

(100 MHz, D<sub>2</sub>O)  $\delta$  167.44, 155.32, 154.45, 140.17, 128.83, 104.58, 103.61, 87.75, 85.27, 84.83, 84.52, 68.38, 30.70, 22.61, 21.57, 20.64, 18.10, 10.57; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>RuCl] 419.0824, observed 419.0815.





<sup>13</sup>C NMR spectrum of complex [Ru]-3 with  $D_2O$  as solvent.

**[Ru]-4**. Brown powder (65 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.38-9.37 (d, *J* = 4 Hz, 1H), 8.64 (s, 1H), 8.18-8.14 (t, *J* = 8 Hz, 1H), 8.04-8.02 (d, *J* = 8 Hz, 1H), 7.76-7.73 (t, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 4 Hz, 1H), 6.15-6.13 (d, *J* = 8 Hz, 1H), 6.0-6.06 (d, *J* = 8 Hz, 1H), 5.85-5.84 (d, *J* = 4 Hz, 1H), 5.80-5.78 (d, *J* = 8 Hz, 1H), 4.92-4.85 (m, 1H), 2.61-2.54 (m, 1H), 2.20 (s, 3H), 1.63-1.62 (d, *J* = 4 Hz, 3H), 1.46-1.45 (d, *J* = 4 Hz, 3H) 1.05-1.03 (d, *J* = 8 Hz, 3H), 0.95-0.93 (d, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  165.38, 155.12, 140.17, 129.09, 128.80, 104.15, 82.24, 85.00, 84.77, 66.25, 30.72, 23.32, 21.59, 20.69, 18.16; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>RuCl] 419.0824, observed 419.0839.



<sup>1</sup>*H* NMR spectrum of complex [Ru]-4 with  $D_2O$  as solvent.



<sup>13</sup>C NMR spectrum of complex [Ru]-4 with  $D_2O$  as solvent

[**Ru**]-5. Yellow powder (71 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.33-9.32 (d, J = 4 Hz, 1H), 8.37 (s, 1H), 8.11-8.07 (t, J = 8 Hz, 1H), 7.86-7.84 (d, J = 8 Hz, 1H), 7.64-7.60 (t, J = 8 Hz, 1H), 6.10 (s, 6H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  185.37, 152.90, 140.11, 128.51, 127.02, 126.90, 87.40; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>ORuCl] 336.9676, observed 336.9660.





<sup>13</sup>C NMR spectrum of complex [Ru]-5 with  $D_2O$  as solvent.

[**Ru**]-6. Light green powder (65 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.38-9.36 (d, J = 8 Hz, 1H), 8.68 (s, 1H), 8.16-8.12 (t, J = 8 Hz, 1H), 7.97-7.95 (d, J = 8 Hz, 1H), 7.71-7.68 (t,  $J_1 = 8$  Hz,  $J_2 = 4$  Hz, 1H), 6.13 (s, 6H), 4.12 (s, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  153.41, 150.57, 150.15, 138.15, 126.06, 125.76, 85.22, 61.29; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>ORuCl] 350.9833, observed 350.9817.





<sup>13</sup>C NMR spectrum of complex [Ru]-6 with  $D_2O$  as solvent.

[**Ru**]-7. Brown powder (70 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.44-9.42 (d, *J* = 8 Hz, 1H), 8.53 (s, 1H), 8.17-8.13 (t, *J* = 8 Hz, 1H), 8.03-8.01 (d, *J* = 8 Hz, 1H), 7.74-7.71 (t, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 4 Hz, 1H), 6.08 (s, 6H), 4.30-4.25 (q, *J* = 4 Hz, 2H), 2.06-1.99 (m, 1H), 1.93-1.84 (m, 1H), 0.95-0.91 (t, *J* = 8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  167.71, 155.47, 154.60, 150.28, 128.86, 128.60, 86.93, 68.53, 22.69, 10.57; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>RuCl] 363.0196 , observed 363.0208.





<sup>13</sup>C NMR spectrum of complex [Ru]-7 with  $D_2O$  as solvent.

**[Ru] -8**. Brown powder (74 %); <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  9.44-9.43 (d, J = 4 Hz, 1H), 8.62 (s, 1H), 8.18-8.14 (t, J = 8 Hz, 1H), 8.03-8.02 (d, J = 4 Hz, 1H), 7.74-7.71 (t,  $J_1$  = 4 Hz,  $J_2$  = 8 Hz, 1H), 6.10 (s, 6H), 4.95-4.90 (m, 1H), 1.64-

1.62 (d, J = 8 Hz, 3H), 1.49-1.48 (d, J = 4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O)  $\delta$  165.64, 155.32, 155.21, 140.30, 129.00, 128.58, 87.03, 66.44, 23.36, 21.74; ESI-HRMS calcd for [M]<sup>+</sup> [C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>RuCl] 363.0196, observed 363.0205.





2.4.12. GC-TCD analysis for FA dehydrogenation



**Figure 2.16.** GC-TCD analysis of the (a) evolved gas  $(H_2:CO_2 \approx 1:1)$  gas for the catalytic dehydrogenation of FA over **[Ru]-1**. Reaction condition: FA (2 M, in 2.5 mL water), sodium formate (2 mmol), **[Ru]-1** (10 µmol), 90 °C. (Analysis is performed using Argon as the carrier gas). (b) Pure mixture of gases.

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# Chapter 3

# HeterocyclicBis-imidazoleMethane-basedRutheniumCatalysts for Hydrogen Production from Formic Acid in Water

## **3.1 Introduction**

The need for sustainable energy solutions is highlighted by the projected increase in global energy demand. As a result, new developments in technology have made building a hydrogen-focused infrastructure a top priority, with the promise of low environmental impact and maximum energy efficiency.<sup>[1-5]</sup> Under these circumstances, hydrogen emerges as a clean, green, and sustainable alternative energy source that will reduce greenhouse gas emissions for the advantage of future generations.<sup>[6-7]</sup> However, the flammable nature of hydrogen gas poses a challenge for its handling and storage, which in turn limits its application as a fuel source.<sup>[8]</sup> To overcome these safety concerns, ongoing research and development efforts are aimed at enhancing the design and materials used for hydrogen storage and transportation systems. In this regard, the utilization of liquid organic hydrogen carriers (LOHCs) has emerged as a promising approach to address the challenges associated with the storage and transportation of hydrogen. Recently, there has been a lot of interest in liquid organic hydrogen carriers (LOHCs), such as methanol (12.4 wt%), formaldehyde (8.4 wt%), and formic acid (4.4 wt%), as potential alternatives for effective and efficient storage and transportation of hydrogen.<sup>[9-10]</sup> Furthermore, reducing the cost of supplying hydrogen at hydrogen stations is crucial for promoting the widespread adoption of hydrogen energy. Therefore, there is a growing need for cost-effective and sustainable methods to produce, store, and distribute hydrogen, which can be facilitated with LOHCs.<sup>[11]</sup> Formic acid (FA) has been identified as a practical hydrogen carrier, with several methods developed for producing hydrogen gas using this LOHC. However, to utilize FA as a suitable hydrogen carrier, a highly stable and active catalyst is required.<sup>[12-20]</sup> Therefore, research efforts are focused on developing highly efficient catalysts to enable the effective use of FA as a hydrogen carrier. Particularly, Molecular catalysts are currently more significant for hydrogen

production from FA compared to heterogeneous catalysts due to several advantages. Firstly, molecular catalysts release less or negligible amounts of CO contamination, which is a critical consideration for fuel cell applications. Secondly, molecular catalysts can operate at lower reaction temperatures, which reduces energy consumption and enhances safety.<sup>[21]</sup>

Recent developments have produced an extensive range of molecular catalysts for the dehydrogenation of formic acid (FA), employing noble metals like  $Ir^{(22)}$  and  $Ru^{(23)}$  as well as non-noble metals like  $Fe^{(24)}$  and  $Mn^{(25)}$ . These studies have shown that noble metal-based catalysts exhibit superior activity for hydrogen production from FA. A review of the literature suggests that molecular catalysts based on Ir have been extensively studied for hydrogen production from FA reactions. Himeda et al. developed Cp\*Ir (Cp\* = pentamethylcyclopentadienyl) complexes ligated with N, N-type ligands such as 2,2'-bipyridine with a variety of functional groups. They reported a maximum turnover frequency (TOF) of up to 14000 h<sup>-1</sup> over five consecutive catalytic runs without any significant loss of catalytic activity, using a 4,4'dihydroxy-2,2'-bipyridine ligand (DHBP).<sup>[22(a)]</sup> In addition, the Cp\*Irbipyridine complex functionalized with amines showed longer catalytic lifetime than the Cp\*DHBP catalyst and an even higher Turnover Frequency (TOF) of 115,500 h-1 at 80 °C.<sup>[22(e)]</sup> However, imidazole-based ligands with Ir metal demonstrated better catalytic activity than bipyridine-substituted ligands in Cp\*Ir complexes used for hydrogen production from FA. For instance, Li et al. developed a novel Cp\*Ir-based molecular catalyst, ligated with 2,2'-bi-2imidazoline, for hydrogen production from FA in water without the use of any additives. They reported impressive TOFs of up to 487500 h<sup>-1</sup> at a reaction temperature of 90 °C.<sup>[22(j)]</sup> Again, Same research group, reported the synthesis of Cp\*Ir-metal-based catalysts [Cp\*Ir(2,2'-tetrahydrobipyrimidine)Cl]Cl through in situ generation using 2,2'-tetrahydrobipyrimidine and [Ir(Cp\*)Cl<sub>2</sub>]<sub>2</sub>, which exhibited a TON of up to 3900000 and an initial TOF of 65000  $h^{-1}$  at 90 °C for hydrogen production from FA and at 70 °C reported a maximum TON of 5020000.<sup>[22(k)]</sup>

Researchers have extensively studied iridium-based complexes due to their remarkable catalytic activity in hydrogen production from FA.<sup>[22]</sup> However, their high cost has motivated to investigate alternative molecular catalysts incorporating more affordable metals. For instance, an iron-based pincer-type catalyst has been studied as a more cost-effective alternative to nonnoble metal-based catalysts for hydrogen production from FA. The catalyst demonstrated a high activity with an initial TOF up to 9425 h<sup>-1</sup> and achieved a maximum TON up to 92000 at a reaction temperature of 80 °C.<sup>[23(a)]</sup> Additionally, phosphine-free complexes based on Mn metal were studied for their potential in hydrogen production from FA in aqueous conditions, resulting in a TON of 5763 and an initial reaction rate of 7 mL/min at 92.5 °C.<sup>[24(a)]</sup> Analogous to Cp\*Ir catalysts, Ru-based catalysts have been extensively studied for hydrogen production from FA under optimized reaction conditions, owing to their relatively lower cost compared to Ir catalysts.<sup>[25]</sup> Using acetic acid as a solvent and transition metals along with phosphine ligands, Coffey et al. reported a variety of molecular catalysts that generated hydrogen from FA at 118 °C.<sup>[26]</sup> Laurenzy et al. thoroughly investigated the efficiency of Ru (II) phosphine-based complexes for the production of hydrogen from formic acid in water with a base at 100 °C (with a ratio of n(FA)/n(SF) of 9:1.<sup>[25]</sup> Further, they described the use of  $Ru(H_2O)_6$  (tos = toluene-4-sulfonate) and meta-tri sulfonated triphenylphosphine in the identical ratio of n(FA)/n(SF) to produce hydrogen from FA in water. At 100 °C, they were able to attain a TON of up to 40,000. Beller et al. elucidated various Ru-based molecular catalysts for hydrogen production from formic acid, including [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>], which exhibited a TOF of 2,688 h<sup>-1</sup> in the presence of the organic solvent trimethylamine at 40 °C. With catalyst [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] reported a TOF of 36000  $h^{-1}$  for the hydrogen production from FA at 60 °C. [RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] catalyst also showed long-term stability for up to 120 days.<sup>[27]</sup> Olah et al. investigated the suitability of RuCl<sub>3</sub> precursor along with varity of phosphine ligands such as tris(2-tolyl)-phosphine), triphenylphosphine and tris(4-chlorophenyl) for hydrogen production from FA in a water-organic solvent emulsion.<sup>[23(f)]</sup>

In the pursuit of more sustainable processes, researchers have investigated highly efficient catalytic systems for aqueous hydrogen production from FA. Huang *et al.* reported a system, where the ( $\eta^6$ -*p*-cymene)Ru-N, N'diimine complex was used for FA/sodium formate dehydrogenation in water without any additive at 90 °C. This system achieved the highest TOF up to 12000 h<sup>-1</sup> and a maximum TON up to 350000.<sup>[28]</sup> Recently, we have also explored previously investigated the (arene)Ru (II) [arene = ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>) or ( $\eta^6$  - C<sub>10</sub>H<sub>14</sub>)] complexes with various N, N' and N, O donor ligands such as 8-(N-methylamino) quinoline,<sup>[13]</sup> pyridine-2-yl-methanol<sup>[14]</sup> and bis-imidazole methane <sup>[29]</sup> for hydrogen production from FA in water at 90 °C. Using the [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru( $\kappa^2$ -NpyNHMe-MAmQ)Cl]<sup>+</sup> catalyst<sup>[13]</sup>, attained an initial TOF up to 940 h<sup>-1</sup> and by utilizing the pyridine-2-yl-methanol ligated Ru(II) complex<sup>[14]</sup>, attained an increased initial TOF up to 1548 h<sup>-1</sup> and a maximum TON up to 6050 in the hydrogen production from FA in water at 90 °C. By employing an ( $\eta^6$ -*p*-cymene)Ru(II) complex featuring a bis-imidazole methane ligand with a 4-methoxy phenyl substitution, we attained a maximum TON up to 8830 with an initial TOF up to 1545 h<sup>-1</sup> attributed to the electron-donating effect of the ligand.<sup>[29]</sup>

In this study, we introduce a range of water-soluble ( $\eta^6$ -*p*-cymene)Ru(II) catalysts with heterocyclic bis-imidazole methane ligands for hydrogen production from FA in water. The crucial component of our study involves evaluating and establishing the catalytic performance of these catalysts for hydrogen production from FA. We discuss the role of substituents in tuning the performance and stability of these catalysts for the co-generation of H<sub>2</sub> and CO<sub>2</sub> from FA in water. Moreover, we also identify and characterize all potential catalytic intermediates to shed light on the possible reaction pathway for hydrogen production from FA over the reported catalysts.

#### 3.2. Result and Discussion

#### 3.2.1. Synthetic, Structural and Spectroscopic aspects

Herein, four bis-imidazole methane-based ligands (**L-6** – **L-9**) were successfully synthesized. Where different heterocyclic aldehydes such as 2pyridine carboxaldehyde, 2-imidazole carboxaldehyde, 2-furan carboxaldehyde, and 2-thiophene carboxaldehyde were taken under reflux conditions with 2-ethyl-4-methyl-imidazole for 3 days in a mixture of methanol and highly basic water solvent. After successful synthesis of ligand 2-(bis(2ethyl-5-methyl-1*H*-imidazol-4-yl)methyl)pyridine (**L-6**), complex  $[(\eta^6-p$ cymene)Ru(**L-6**)Cl]Cl, [**Ru**]-10 was synthesized with Ru metal precursor  $[(\eta^6-p$ cymene)Ru(**L**-6)Cl]Cl, [**Ru**]-10 under reflux conditions for 24 h. Similarly, complex [**Ru**]-11 with ligand 4,4'-((1*H*-imidazol-2-yl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole) (**L-7**), [**Ru**]-12 with ligand 4,4'-(furan-2ylmethylene)bis(2-ethyl-5-methyl-1*H*-imidazole) (**L-8**) and [**Ru**]-13 with 4,4'-(thiophen-2-ylmethylene)bis(2-ethyl-5-methyl-1*H*-imidazole) (**L-9**) were synthesized. Several spectro-analytical methods, including HRMS and NMR, were used to determine the structures of these ligands (**L-6** – **L-9**) and further complexes [**Ru**]-10, [**Ru**]-11, [**Ru**]-12 and [**Ru**]-13 (Scheme 3.1). Complex [**Ru**]-9, was successfully synthesized with ligand 2-(bis(2-ethyl-5-methyl-1*H*imidazol-2-yl)methylene)phenyl by previously reported literature. <sup>[29]</sup>

Further, observed mass spectra of the complexes [Ru]-10, [Ru]-11, [Ru]-12, and [Ru]-13 strongly support that all the complexes were monocationic in nature. Moreover, in the <sup>1</sup>H NMR spectra of [Ru]-10 displayed a slight upshift in the resonance position of the methylene proton in the Rucoordinated ligand at 5.33 ppm, as compared to the Ru-free ligand (L-6) at 5.42 ppm. The <sup>1</sup>H NMR spectra of **[Ru]-11**, the methylene proton of the Rucoordinated ligands exhibited a slight upshift at 5.35 ppm, compared to the Rufree ligand (L-7) at 5.37 ppm. Similarly, the <sup>1</sup>H NMR spectra of [Ru]-12 revealed a slight upshift in the resonance position of the methylene proton in the Ru-coordinated ligands, with 5.35 ppm, compared to the Ru-free ligand (L-8) at 5.27 ppm. Additionally, the <sup>1</sup>H NMR spectra of **[Ru]-13**, the methylene proton of the ligands coordinated to the Ru exhibited a slightly higher resonance frequency at 5.42 ppm, indicating a slight upshift compared to the Ru-free ligand (L-9) at 5.35 ppm. The  ${}^{13}$ C NMR spectra of the methylene carbon peak also show a similar pattern in the shifting of the peak position of [Ru]-10, [Ru]-11, [Ru]-12, and [Ru]-13. Further, proton signals corresponding to the  $\eta^6$ -pcymene ring in [Ru]-10, [Ru]-11, [Ru]-12 and [Ru]-13 complexes were detected within the anticipated region in the NMR spectra.<sup>[29-30]</sup>



Scheme 3.1. Synthetic scheme of heterocyclic bis-imidazole methane ligands L-5—L-9 and their Ru-bis-imidazole methane complexes [Ru]-9, [Ru]-10, [Ru]-11, [Ru]-12, [Ru]-13.

Moreover, light brown colored crystals of **Ru]-10** and [**Ru]-12** were also obtained in a concentrated methanolic solution layered with diethyl ether at atmospheric temperature. From obtained crystals, suitable crystals were well characterized by X-ray diffraction techniques. Results inferred that [**Ru]-10** crystallized in the monoclinic crystal system with the P21/c space group. The crystal structure confirms the orientation of the ligands with ruthenium metal center and  $\eta^6$ –*p*–cymene ring and a Cl atom (Figure 3.1.). It was calculated that the bond distance between the center of the  $\eta^6$ –*p*–cymene ring (Centroid, C<sub>t</sub>) to be 1.699 Å and also observed that bond distance of Ru with N atoms of the 2ethyl 4-methyl imidazole ring 2.132 Å (Ru–N<sub>1</sub>) and 2.116 Å (Ru–N<sub>3</sub>) and observed that the Ru-Cl bond distance was 2.4202 Å for **[Ru]-10.** The calculated bond angles from the  $\eta^6$ –*p*–cymene ring centroid (C<sub>t</sub>) with Ru metal and N of the 2-ethyl 4-methyl imidazole ring were C<sub>t</sub>–Ru–N<sub>3</sub> (127.50°), C<sub>t</sub>–Ru–N<sub>1</sub> (131.21°), and bond angles from the  $\eta^6$ –*p*–cymene ring centroid (C<sub>t</sub>) with Ru metal and Cl atom were C<sub>t</sub>–Ru–Cl (121.17°), whereas calculated bite angle between the two N atoms (N<sub>1</sub> and N<sub>3</sub>) of the 2-ethyl 4-methyl imidazole ring and the Ru center was to be 84.20° for **[Ru]-10**.



Figure 3.1. Single Crystal X-ray structures of [Ru]-10.

Similarly, it was observed that **[Ru]-12** crystallized in the triclinic crystal system with the P-1 space group. It was calculated that the bond distance between the center of the  $\eta^6$ –p–cymene ring (Centroid, C<sub>t</sub>) to be 1.445 Å and observed that the bond distance between Ru and N atom of the 2-ethyl 4-methyl imidazole ring 2.111 Å (Ru–N<sub>1</sub>) and 2.104 Å (Ru–N<sub>3</sub>) for **[Ru]-12** whereas the Ru-Cl bond distance was 2.4107 Å for **[Ru]-12** (Figure 3.2.). The calculated bond angles from the  $\eta^6$ –p–cymene ring centroid (C<sub>t</sub>) with Ru metal and N of the 2-ethyl 4-methyl imidazole ring were C<sub>t</sub>–Ru–N<sub>3</sub> (126.93°), C<sub>t</sub>–Ru–N<sub>1</sub> (129.35°), and bond angles from the  $\eta^6$ –p–cymene ring centroid (C<sub>t</sub>) with Ru metal and Cl atom were C<sub>t</sub>–Ru–Cl (129.52°) for **[Ru]-12**. The calculated bite

angle between the two N atoms (N<sub>1</sub> and N<sub>3</sub>) of the 2-ethyl 4-methyl imidazole ring and the Ru center was calculated to be  $82.44^{\circ}$  for [**Ru**]-12.



Figure 3.2. Single Crystal X-ray structures of [Ru]-12.

# 3.2.2. Catalytic hydrogen production from FA in water

Screening of all the catalysts [**Ru**]-9, [**Ru**]-10, [**Ru**]-11, [**Ru**]-12 and [**Ru**]-13 was performed for FA dehydrogenation in water. It was observed that all the synthesized catalysts were efficient for FA dehydrogenation at 90 °C in water under the absence of sodium formate (SF). Initially, a catalytic hydrogen production reaction of an aqueous solution of FA (2 M, 2.5 mL) was performed at 90 °C with catalyst loading (5 µmol) under an atmospheric environment. Results inferred that [**Ru**]-13 catalyst, containing an electron-rich ( $\eta^6$ -p-cymene) group, substituted with 4,4'-(thiophen-2-ylmethylene)bis(2-ethyl-5-methyl-1*H*-imidazole) (**L**-5) ligand, showed a maximum TOF of 754 h<sup>-1</sup>, [**Ru**]-12 catalyst, substituted with furan-based ligand (**L**-4) achieved a TOF of 696 h<sup>-1</sup>, [**Ru**]-11 catalyst, substituted with imidazole-based ligand (**L**-3) achieved a TOF of 484 h<sup>-1</sup>, [**Ru**]-10 catalyst, substituted with pyridine-based ligand (**L**-2) achieved a maximum TOF of 216 h<sup>-1</sup>, whereas phenyl- based (**L**-1) ligated ruthenium catalyst [**Ru**]-9, showed a TOF of 372 h<sup>-1</sup> at 90 °C without the

addition of SF for FA dehydrogenation (Table 3.1., entries 1-5, Figure 3.2.).<sup>[29]</sup> Further, it was observed that addition of SF (1 mmol), a noticeable change in initial TOF value for all catalysts; where **[Ru]-13**, having thiophene-substituted bis-imidazole methane ligand achieved a maximum TOF of 1831  $h^{-1}$  and **[Ru]-10**, having pyridine-substituted bis-imidazole methane ligand, achieved a maximum TOF of 538  $h^{-1}$  which was least TOF observed among all the catalysts for FA dehydrogenation (2 M, 2.5 mL H<sub>2</sub>O) at 90 °C (Table 3.1., entries 6-10, Figure 3.3.).

Entry	Catalyst	SF	V(H2+CO2)	t	<b>TON</b> <sup>b</sup>	TOF <sup>c</sup>
		(mmol)	(mmol)	<b>(h)</b>		( <b>h</b> -1)
$1^a$	[Ru]-9	-	10	2	1000	372
$2^a$	[ <b>Ru</b> ]-10	-	7	6	522	216
3 <sup><i>a</i></sup>	[Ru]-11	-	10	3.08	1000	484
$4^a$	[Ru]-12	-	10	2.58	1000	696
5 <sup><i>a</i></sup>	[Ru]-13	-	10	1.41	1000	754
$6^d$	[Ru]-9	1	10	0.76	1000	1239
$7^d$	[ <b>Ru</b> ]-10	1	10	4.08	1000	538
$8^d$	[Ru]-11	1	10	1.05	1000	1023
$9^d$	[Ru]-12	1	10	0.63	1000	1508
$10^d$	[Ru]-13	1	10	0.53	1000	1831

*Table 3.1. Hydrogen production from FA in water with/without any additive.*<sup>*a,d*</sup>

<sup>*a*</sup>*Reaction Condition*: FA (2 M, 2.5 mL H<sub>2</sub>O), catalysts (0.005 mmol), 90 °C. <sup>*b*</sup>TONs per mmol of catalyst (After the reaction). <sup>*c*</sup>TOFs per mmol of catalyst (initial 10 min). <sup>*d*</sup>Reaction Condition: FA (2 M, 2.5 mL H<sub>2</sub>O), SF (1 mmol), catalysts (0.005 mmol), 90 °C.



*Figure 3.3.* A comparative graph illustrates FA dehydrogenation over [*Ru*]-9–[*Ru*]-13 catalysts with and without additive. Reaction conditions: FA (2 M, 2.5 mL H<sub>2</sub>O), catalysts (0.005 mmol), SF (1 mmol), 90 °C.

After optimization of the reaction condition, further, the hydrogen production reaction was carried out with [**Ru**]-13 catalyst with varying SF concentration under the optimized reaction condition (2 M, 2.5 mL H<sub>2</sub>O) at 90 °C with 0.005 mmol catalyst loading. It was observed that a small amount of SF addition influenced the catalytic activity for FA dehydrogenation (Table 3.2., entry 1-8). Notably, the maximum TOF of 1831 h<sup>-1</sup> for FA dehydrogenation (2 M, 2.5 mL H<sub>2</sub>O) was achieved when 1 mmol of SF was added at 90 °C (Table 3.2, entry 5). Further, addition of more than 1 mmol of SF, the TOF of the reaction decreased, shows the significant role of SF for FA dehydrogenation in water (Table 3.2., entries 6-8).

Entry	Catalyst	SF	V(H2+CO2)	t	TON <sup>b</sup>	TOF <sup>c</sup>
		(mmol)	(mmol)	<b>(h)</b>		
1	[Ru]-13	-	10	1.41	1000	754
2	[Ru]-13	0.1	10	1.03	1000	915
3	[Ru]-13	0.25	10	1.0	1000	969

*Table 3.2. Optimization table for the hydrogen production from FA in water with SF.<sup>a</sup>* 

4	[Ru]-13	0.5	10	0.86	1000	1077
5	[Ru]-13	1	10	0.53	1000	1831
6	[Ru]-13	2	10	0.73	1000	1346
7	[Ru]-13	5	10	0.83	1000	1293
8	[Ru]-13	10	8	3.11	775	1023

<sup>*a*</sup>Reaction Condition: FA (2 M, 2.5 mL H<sub>2</sub>O), SF (0.1–10 mmol), **[Ru]-13** (0.005 mmol), 90 °C. <sup>*b*</sup>TONs per mmol of catalyst (end of the reaction). <sup>*c*</sup>TOFs per mmol of catalyst (initial 10 min).

The catalytic performance of the reaction was notably affected by the reaction temperature. Results inferred that, as the temperature was raised from 60 °C to 90 °C, the reaction rate for the hydrogen production from FA increased, resulting in the maximum TOF being attained at 90 °C (Figure 3.3.). Furthermore, by analyzing the corresponding Arrhenius plot, the calculated activation energy ( $E_a$ ) was determined to be 21.45 kcal mol<sup>-1</sup> (89.75 kJ mol<sup>-1</sup>) (Figure 3.4.). This value is in the acceptable range with earlier reported catalysts that have similar characteristics. <sup>[28-30]</sup> Therefore, further optimization of the reaction conditions for the hydrogen production from FA was performed over [**Ru**]-13 catalyst with (n(FA)/n(SF) ratio of 5:1 in water at 90 °C.



*Figure 3.4.* Activation Energy calculation by Arrhenius plot for hydrogen production from FA. Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O), SF (1 mmol), [*Ru*]-13 (0.005 mmol),  $60^{\circ}$ C – 90 °C.

Notably, the TOF of the hydrogen production from FA reaction over the [Ru]-13 catalyst was found to be significantly influenced by the reaction medium pH (Figure 3.5.). With an increase in pH, the TOF for the hydrogen production from FA reaction over the [Ru]-13 catalyst exhibited a corresponding increase, ultimately reaching its maximum value of 1831 h<sup>-1</sup> at pH 2.9. However, lower TOF values were observed for pH levels exceeding 2.9. The decrease in TOF for hydrogen production from FA over [Ru]-13 with increasing SF amount from 1 mmol to 10 mmol resulted because of enhancement in the concentration of HCOO<sup>-</sup> species and hence pH of the reaction solution was also increased from 2.9 to 4.1, suggesting the crucial role of the  $H_3O^+$  concentration in the FA dehydrogenation. Conversely, with a decrease in the amount of SF (<1 mmol), the TOF of the reaction was decreased from 1.8 to 2.9, showing the importance of formato species in the FA dehydrogenation. These results indicate that the participation of both H<sub>3</sub>O<sup>+</sup> and HCOO<sup>-</sup> ions is crucial for hydrogen production from FA.<sup>[32]</sup> Additionally, it is important to note that in all these experiments, the quantity of H<sub>2</sub> and CO<sub>2</sub> released corresponds solely to the content of FA used. The reaction ceases once all the FA has been completely consumed. Furthermore, the analysis of double logarithmic plots relating the initial change in the gas evolution rate of the **[Ru]-13** catalyst concentration revealed a linear correlation, suggesting that the reaction follows a reaction order of 0.93 with respect to the **[Ru]-13** catalyst (Figure 3.6.).<sup>[33]</sup>



*Figure 3.5.* FA dehydrogenation over the catalyst [*Ru*]-13 at different pH. Reaction condition: FA (2 M, 2.5 mL H<sub>2</sub>O), SF (0–10 mmol), [*Ru*]-13 (0.005 mmol), 90 °C. TOF at initial 10 min.



*Figure 3.6.* Plot of ln [rate] (mmol L<sup>-1</sup> h<sup>-1</sup>) vs ln[catalyst] (mmolL<sup>-1</sup>). Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O), SF (1 mmol), [C-5] (2.5 μmol – 10 μmol), 90 °C.

Further, in identical conditions, controlled experiments with **[Ru]-10** and **[Ru]-13** were performed to show the active species generated during FA dehydrogenation. Mass study revealed that molecular ion peaks intensity remains unchanged in case of **[Ru]-10** compared to **[Ru]-13**, stirred in water at 50 °C for 5 minutes. In other hand, Ru-aqua species intensity was lower with **[Ru]-10** compared to **[Ru]-13** (Figure 3.7.). Notably, mass peaks corresponding to Ru-aqua and Ru-formato species was further confirmed by aqueous catalyst solutions with FA at 50 °C for 5 minutes. Interestingly, compared to **[Ru]-10**, the molecular ion mass peak for **[Ru]-13** was significantly lower, showing the activity of **[Ru]-13** is more compared to **[Ru]-10** (Figure 3.8.).



Figure 3.7. Controlled mass experiments for catalytic Ru-aqua species generated with (a) [Ru]-10 and (b) [Ru]-13. Reaction condition: Catalysts (0.010 mmol),  $H_2O$  (2.5 mL), stirred at 50 °C for 5 minutes.



*Figure 3.8.* Controlled mass experiments for catalytic Ru-aqua and Ru-formato species generated with (a) [*Ru*]-10 and (b) [*Ru*]-13. Reaction condition: Catalysts (0.010 mmol), H<sub>2</sub>O (2.5 mL), stirred at 50 °C for 5 minutes.

Remarkably, the crystal structure of [**Ru**]-10 and [**Ru**]-12 showed that the orientation of the heterocyclic ring was quite different, possibly the reason for the coordination of the formate species at the vacant site at the Ru centre, potentially impeding the catalytic FA dehydrogenation reaction. In the X-ray structure of [**Ru**]-10, the Ru centre with N<sub>py</sub> was 4.925 Å, which was lower than the bond distance of Ru centre with the O<sub>furan</sub> (5.603 Å), because of furan ring was parallel and the pyridine ring was perpendicular with respect to the methylene carbon of the catalyst. These findings highlighted the crucial role of the ligand tuned activity for the FA dehydrogenation (Figure 3.9.).



*Figure 3.9. X-ray structures of (a) [Ru]-10 and (b) [Ru]-12, showing the bond lengths of heterocyclic ring with Ru center and orientation of with respect to the Ru center respectively.* 

Gas generated during the dehydrogenation of FA was analyzed using GC-TCD, revealing the presence of  $H_2$  and CO<sub>2</sub>. Notably, no traces of CO were detected in these experiments (Figure 3.10.). It's crucial to emphasize that the amounts of  $H_2$  and CO<sub>2</sub> released were directly proportional to the quantity of FA utilized, and the reaction concluded upon complete consumption of FA.



Figure 3.10. GC-TCD analysis of the (a) reaction mixture of catalytic hydrogen production from FA over [Ru]-13 catalyst (Analysis is performed using Argon as the carrier gas). (b) Pure mixture of gases.

# **3.2.3.** Mechanistic Investigation

A comprehensive investigation employing mass spectrometry, NMR and kinetic isotope effect (KIE) methodologies was undertaken to enhance comprehension of the potential pathway engaged in FA dehydrogenation over [**Ru**]-13. It was observed that Ru-aqua species ([**Ru-(aqua)**]) (m/z = 567.1735) and Ru-formato species ([**Ru-(formato)**] + H<sup>+</sup>) (m/z = 595.1682) (Figure 3.11, 3.12, and 3.13) during the catalytic activity for FA dehydrogenation in mass analysis of reaction aliquots. It was observed that when the catalyst [**Ru**]-13 treated only with water at 90 °C, Ru-aqua species ([**Ru-(aqua)**]) (m/z = 567.1735) observed as base peak in mass spectrum (Figure 3.12.). Further, addition of FA in above solution showed, a noticeable peak of ([**Ru-(aqua)**]) and ([**Ru-(formato)**] + H<sup>+</sup>) in mass spectra at 50 °C (Figure 3.13.). Notably, addition of SF enhances the intensity of Ru-formato species, which was clearly observed in mass analysis of the reaction aliquots (Figure 3.14.). Additionally, if DCOOD was added instead of HCOOH in H<sub>2</sub>O at 90 °C, increment in m/z value from (**[Ru-(formato)]** +  $\mathbf{H}^+$ ) (m/z = 595.1682) to (**[Ru-(DCOO)]** +  $\mathbf{H}^+$ ), (m/z 596.1), confirms the coordination of formato species with Ru centre (Figure 3.15.).



**Figure 3.11.** Mass analysis of reaction aliquots extracted during the catalytic FA dehydrogenation over **[Ru]-13**. Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O), SF (1 mmol), **[Ru]-13** (0.005 mmol), 90 °C.



*Figure 3.12. Ru-aqua species observed during HRMS analysis for the reaction* of [*Ru*]-13 (0.005 mmol) stirred in 2.5 mL H<sub>2</sub>O for 5 minutes at 50 °C.



**Figure 3.13.** Ru-formato species observed during HRMS analysis. Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O) and **[Ru]-13** (0.005 mmol) stirred for 5 minutes at 50 °C.



**Figure 3.14.** Effect of SF on mass investigations for the Ru-formato species. Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O), SF (0.5 mmol) and **[Ru]-13** (0.005 mmol) stirred for 5 minutes at 50 °C.



**Figure 3.15.** Deuterated Ru-formato species observed during mass analysis over [**Ru**]-13 (0.005 mmol) with DCOOD (1 mmol) in 2.5 mL D<sub>2</sub>O stirred for 30 minutes at 90 °C.

Subsequently, in a controlled experiment where [**Ru**]-13 was first dissolved in water and exposed only with SF for 5 minutes at 50 °C, mass analysis revealed that formation Ru-hydrido species ([**Ru-(hydrido**)] +  $H^+$ ) at m/z = 551.1, which was further confirmed by the <sup>1</sup>H NMR spectroscopy, where a proton peak observed in highly shielded region at -7.33 ppm (Figure 3.16 and 3.17). Further, when the Ru-hydrido species was treated with 1 M HCl, it got back to the parent species [**Ru**]-13, which was clearly visible from the brown color changed to the original yellow color, also confirmed by the mass analysis of the reaction aliquotes. (Figure 3.18.)



*Figure 3.16.* Ru-hydrido species observed during mass analysis over [*Ru*]-13 (0.005 mmol) with SF (1 mmol) and stirred in 2.5 mL of  $H_2O$  for 5 minutes at 50 °C.



Figure 3.17 Ru-hydrido species observed in <sup>1</sup>H NMR analysis. Reaction condition: SF (0.1 mmol) and [Ru]-13 (0.010 mmol) stirred in 0.5 mL of H<sub>2</sub>O for 10 minutes at 50 °C. (D<sub>2</sub>O used as an NMR solvent).



*Figure 3.18. Restoration of the molecular peak with HCl.* [*Ru*]-13 (0.005 mmol) *treated with SF (1 mmol) in water (1 mL) stirred at 50 °C for 5 min in step 1, and further with 1 M HCl (0.5 mL) in the step 2.* 

Furthermore, the findings from the kinetic isotope effect (KIE) studies revealed a trend under the optimized reaction conditions, it was observed that the deuterated FA (DCOOD) had a more influence on the reaction rate of the catalytic hydrogen production of HCOOH/DCOOD in D<sub>2</sub>O/H<sub>2</sub>O over [**Ru**]-13 catalyst compared to deuterated water (D<sub>2</sub>O) (Table 3.3.). Results obtained from KIE studies inferred that the carbon release (decarboxylation) step from Ruformato species is possibly the rate-determining step in the catalytic hydrogen production from FA over [**Ru**]-13 catalyst.

Table 3.3 KIE for hydrogen production from FA over [Ru]-13 catalyst					
Entry	Substrate/	<b>TOF</b> ( <b>h</b> <sup>-1</sup> )	KIE		
	Solvent				
1	HCOOH/H <sub>2</sub> O	269	-		
2	HCOOH/ D <sub>2</sub> O	233	1.15		
3	DCOOD/ H <sub>2</sub> O	215	1.25		
4	DCOOD/ D <sub>2</sub> O	161	1.67		

Reaction Condition: HCOOH/DCOOD (0.4 M, 2.5 mL H<sub>2</sub>O/D<sub>2</sub>O), **[Ru]-13** (5  $\mu$ mol), 90 °C. TOFs per mmol of catalyst (initial 30 min). KIE = TOF (entry 1) / TOF (entry n) (n = 2, 3, 4).

Based on several identified catalytic intermediates namely Ru-aqua ([**Ru-(aqua**)]), Ru-formato [**Ru-(formato**)], and Ru-hydrido [**Ru-(hydrido**)] species, observed in mass spectrometry and NMR spectroscopy under controlled and catalytic experiments for FA dehydrogenation, a plausible reaction mechanism for hydrogen production from FA can be proposed, which involves the four steps to dehydrogenate the FA. (i) Ru-aqua species ([**Ru-(aqua**)]) generated from [**Ru]-13**, after dissociation of H<sup>+</sup>Cl<sup>-</sup> with addition of water (ii) Ru–formato species [**Ru-(formato**)] generated by the reaction of FA/formate with [**Ru-(aqua**)], (iii) subsequently CO<sub>2</sub> release of [**Ru-(formato**)] by the  $\beta$ - hydride elimination step resulted in the generation of Ru–hydrido species [**Ru-(hydrido**)], and (iv) finally with the proton assisted hydrogen gas release from [**Ru-(hydrido**)], the active [**Ru-(aqua**)] was reproduced to complete the catalytic pathway (Scheme 3.2.).



Scheme 3.2. A plausible mechanism for hydrogen production from FA over [*Ru*]-13 catalyst.

The catalytic efficiency and long-term stability of the [**Ru**]-13 catalyst was evaluated for large-scale hydrogen production from FA to figure out the practical use of the studied catalytic system. The [**Ru**]-13 catalyst (5  $\mu$ mol) demonstrated remarkable stability, maintaining its high activity during thirty-five consecutive catalytic runs for hydrogen production from FA. This corresponded to a turnover number of 35000, with no significant loss in activity observed (Figure 3.18.). In the recyclability experiment, after the completion of each catalytic cycle, 5 mmol of FA was introduced to maintain the pH at approximately ~2.9, ensuring that the catalytic activity remained stable without any notable alteration. It is noteworthy that the activity of the catalyst [**Ru**]-13 for hydrogen production from FA was not diminished even after 60 days, suggesting the high stability of the [**Ru**]-13 catalyst. Moreover, a control experiment involving Hg poisoning was conducted using [**Ru**]-13 in the presence of an excess of elemental Hg (0). There was no notable decrease in

catalytic activity observed, indicating that the catalytic species exhibits homogeneity (Figure 3.19.).



**Figure 3.19.** Plot for the cumulative TON vs volume of released gas during the Recyclability experiment for the catalytic hydrogen production from FA over [**Ru**]-13 catalyst in water at 90 °C. Reaction condition: FA (2 M, 2.5 mL H<sub>2</sub>O), SF (1 mmol), [**Ru**]-13 (0.005 mmol), 90 °C, where FA (5 mmol) was added after each catalytic run for 34 consecutive catalytic runs.



*Figure 3.20.* Hg (0) poisoning experiment of [*Ru*]-13 catalyst for hydrogen production from FA. Reaction condition: FA (2 M, in 2.5 mL H<sub>2</sub>O), SF (1 mmol), [*Ru*]-13 (0.005 mmol), 90 °C. without and with 200 equivalent of elemental Hg (0).

## **3.3.** Conclusion

We have successfully synthesized water-soluble ( $\eta^6$ -p-cymene)Ru(II) complexes [Ru]-10, [Ru]-11, [Ru]-12, and [Ru]-13 with different heterocyclic bis-imidazole methane-based ligands. These complexes demonstrate remarkable catalytic activity in producing hydrogen from FA in aqueous environment. Specifically, we achieved a maximum initial TOF of 1831 h<sup>-1</sup> at 90 °C and with a total TON of 35000 using [Ru]-13 catalyst. One of the most notable features of [Ru]-13 is its exceptional long-term stability, as it maintained efficient H<sub>2</sub> production from FA for 35 catalytic runs and remained active even after 60 days without any significant deactivation. To gain further insight into the catalytic mechanism, we conducted comprehensive mass and NMR studies under both catalytic and control experimental conditions. These investigations suggested the participation of Ru-aqua [Ru-(aqua)], Ruformato [Ru-(formato)], and Ru-hydrido [Ru-(hydrido)] species in the catalytic process of hydrogen production from FA. Additionally, a kinetic isotope effect (KIE) study indicated that the carbon dioxide release from Ruformato species is likely the rate-determining step in the catalytic hydrogen production over the [Ru]-13 catalyst. Overall, we consider the catalytic performance exhibited by these ruthenium catalysts to be a remarkable advancement in the development of more efficient molecular catalysts for hydrogen production from FA in water.

#### **3.4. Experimental Section**

**3.4.1. Materials and Instrumentation**. The reactions were carried out under standard atmospheric conditions, without the use of inert gas protection. high-purity chemicals were sourced from Sigma Aldrich (Merck). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using CD<sub>3</sub>OD and D<sub>2</sub>O solvents on Brucker Advance III 400 MHz and Brucker Ascend 500 MHz spectrometers, respectively. pH measurements were carried out using a Eutech pH meter, specifically the Model Eco TestrpH2. ESI mass spectra were recorded on a micrOTF-Q II mass spectrometer. GC-TCD analyses were performed on a Shimadzu GC-2014 system equipped with a shin carbon-ST packed column. **3.4.2. General procedure for the Synthesis of ligands L6, L7, L8 and L9** 

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A solution containing 2-ethyl-4-methyl imidazole (2.2 g, 20 mmol) and various aldehydes (2-pyridine carboxaldehyde, 2-imidazole carboxaldehyde, furfural, and 2-thiophene carboxaldehyde) in methanol (3 mL) was mixed with an aqueous solution (27 mL) of potassium hydroxide (3.36 g, 60 mmol). The resulting mixture was stirred at 80 °C for three days to yield a solid product. Afterward, the solid product was filtered, washed multiple times with water to eliminate excess base, and finally rinsed with diethyl ether. The resulting solid was then dried overnight in an oven.

**L6**, Yellow powder (74% yield); <sup>1</sup>**H NMR** (500 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 8.37-8.38 (d, J=5 Hz, 1H), 7.66-7.70 (t, J= 10 Hz, 1H), 7.16-7.19 (t,  $J_1$ = 10 Hz,  $J_2$ = 5 Hz, 2H), 5.44 (s, 1H), 2.52-2.57 (q,  $J_1$ = 10 Hz,  $J_2$ = 5 Hz, 4H), 1.79 (s, 6H), 1.13-1.17 (t, J= 10 Hz, 6H), <sup>13</sup>**C NMR** (125 MHz, MeOH- $d_4$ ):  $\delta$  (ppm):163.27, 149.87, 139.05, 125.25, 123.58, 67.26, 22.67, 15.79, 13.81, 10.83. **HRMS** calcd. For [**L6**]<sup>+</sup>[C<sub>18</sub>H<sub>23</sub>N<sub>5</sub>]: 310.2026, Observed: 310.2023.





<sup>1</sup>*H* NMR spectrum of ligand *L6*.



<sup>13</sup>C NMR spectrum of ligand L6.

**L7**, white powder (78% yield); <sup>1</sup>**H NMR** (500 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 6.82 (s, 2H), 5.37 (s, 1H), 2.48-2.53 (q, J= 10 Hz), 1.73 (s, 6H), 1.09 -1.13 (t, J= 10 Hz, 6H) <sup>13</sup>**C NMR** (125 MHz, MeOH- $d_4$ ):  $\delta$  (ppm):149.05, 129.86, 126.65, 122.04, 36.25, 21.85, 12.86, 9.62 **ESI-MS** calcd. For **[L7]**<sup>+</sup> [C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>]: 299.1979, Observed: 299.2202.







 $^{13}C$  NMR spectrum of ligand L7.

**L8**, Brown powder (70% yield); <sup>1</sup>**H NMR** (500 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) 7.33 (s, 1H), 6.24 (s, 1H), 5.84 (s, 1H), 5.27 (s, 1H), 2.52-2.55 (q, *J*= 5 Hz, 4 H), 1.82 (s, 6H), 1.13-1.16 (t, *J*<sub>1</sub>= 10 Hz, *J*<sub>2</sub>= 5 Hz, 6H) <sup>13</sup>**C NMR** (125 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm):156.06, 149.12, 148.80, 142.53, 112.12, 108.03, 66.74, 36.00, 22.13, 13.26, 10.09. **HRMS** calcd. For **[L8]**<sup>+</sup> [C<sub>17</sub>H<sub>22</sub>N<sub>4</sub>O]: 299.1866, Observed: 299.1882.



HRMS spectra of ligand L8.



**L9**, white powder (75% yield); <sup>1</sup>**H NMR** (500 MHz, MeOH-*d*<sub>4</sub>): δ (ppm) 7.11-7.12 (d, 1H, *J* = 5 Hz), 6.79-6.81 (t, 1H, *J*= 5 Hz), 6.55-6.56 (d, 1H, *J*= 5 Hz), 5.45 (s, 1H), 2.50-2.56 (q, *J* =10 Hz, 4H), 1.90 (s, 6H), 1.11-1.15 (t, *J*= 10 Hz, 6H), <sup>13</sup>**C NMR** (125 MHz, MeOH-*d*<sub>4</sub>): δ (ppm):149.84, 148.57, 132.03, 127.86,

126.62, 125.64, 67.25, 36.90, 22.71, 13.73, 10.92. **HRMS** calcd. For **[L9]**<sup>+</sup> [C<sub>17</sub>H<sub>22</sub>N<sub>4</sub>S]: 315.1638, Observed: 315.1648.



<sup>1</sup>H NMR spectrum of ligand L9.





To a solution of  $[(\eta^6-p\text{-cymene})\text{RuCl}_2]_2$  (0.5 mmol)] in methanol (30 mL), the respective solution of ligands (**L6-L9**) (1.10 mmol) in methanol (5 mL) were added dropwise. The reaction mixture was refluxed for 16 hours and then the reaction volume reduced to 1 mL using a rotatory evaporator. Excess diethyl ether was added to the above solution, resulting in the precipitation of a solid product, which was reprecipitated twice and dried overnight in an oven at room temperature.

**[Ru]-10**. Light green powder (65% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 8.50-8.51 (d, J= 5 Hz, 1H), 7.73-7.77 (t, J= 5 Hz, 1H), 7.25-7.27 (t, J= 5 Hz, 1H), 7.12-7.14 (d, J=10 Hz, 1H), 5.35 (s, 1H), 5.25-5.26 (d, J= 5 Hz, 2H), 5.20-5.21 (d, J= 5 Hz, 2H), 3.18-3.22 (q, J= 10 Hz, 4 H), 2.89-2.97 (m, 8H), 2.27 (s, 6H), 1.85 (s, 3H), 1.26-1.29 (t,  $J_1$ = 10 Hz,  $J_2$ = 5 Hz, 6H), 0.72-0.73 (d, J= 5 Hz, 6H) <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm): 162.03, 153.50, 150.36, 138.47, 131.13, 126.36, 123.62, 106.50, 101.26, 85.33, 82.51, 40.54, 31.29, 24.30, 22.82, 17.86, 12.96, 9.39. HRMS calcd. For [M]<sup>+</sup>[C<sub>28</sub>H<sub>37</sub>RuN<sub>5</sub>Cl]: 580.1780, Observed: 580.1778.



<sup>1</sup>H NMR spectrum of complex [Ru]-10.



<sup>13</sup>C NMR spectrum of complex [Ru]-10.

**[Ru]-11.** Yellow powder (70% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 7.14-7.17 (d, J= 12 Hz, 2H), 5.62-5.63 (d, J= 4 Hz, 2H), 5.42-5.43 (d, J= 4 Hz, 2H), 5.35 (s, 1H), 3.00-2.95 (s, 1H), 2.63-2.58 (q,  $J_1$ = 4 Hz,  $J_2$ = 8 Hz, 4H), 2.24 (s, 3H), 1.72 (s, 6H), 1.30-1.27 (t,  $J_1$ = 8 Hz,  $J_2$ = 4 Hz, 6H), 1.20-1.18 (d, J= 8 Hz, 6H) <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm): 130.23, 127.53, 118.81, 104.77, 102.85, 85.66, 83.82, 82.13, 32.22, 24.93, 23.87, 22.78, 18.76, 14.15, 13.31. HRMS calcd. For [M]<sup>+</sup>[C<sub>26</sub>H<sub>36</sub>RuN<sub>6</sub>Cl]: 569.1732, Observed: 569.1743.



HRMS spectra of complex [Ru]-11.


<sup>13</sup>C NMR spectrum of complex [Ru]-11.

[**Ru**]-12. Brown powder (60% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 7.57 (s, 1H), 6.53-6.54 (d, J= 4 Hz, 1H), 6.50-6.51 (d, J= 4 Hz, 1H), 5.58-5.59 (d, J= 4 Hz, 2H), 5.50-5.51 (d, J= 4 Hz, 2H), 5.35 (s, 1H), 2.88-2.94 (q, J= 8 Hz, 4H), 2.59-2.66 (m, 1H), 2.27 (s, 3H), 2.10 (s, 3H), 1.39 (s, 6H), 1.19-1.23 (t, J= 8 Hz, 6H), 1.03-1.05 (d, J= 8 Hz, 6H), <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 153.66, 151.29, 143.55, 131.54, 124.88, 116.94, 112.94, 112.50,

106.72, 101.31, 86.10, 83.36, 38.75, 33.32, 24.23, 22.94, 18.55, 13.58, 9.51. HRMS calcd. For [M]<sup>+</sup> [C<sub>27</sub>H<sub>36</sub>RuN<sub>4</sub>ClO]: 569.1620, Observed: 569.1624.



<sup>1</sup>H NMR spectrum of complex [Ru]-12.



<sup>13</sup>C NMR spectrum of complex [Ru]-12.

**[Ru]-13.** Yellow powder (68% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 7.30-7.31 (d, J= 4 Hz, 1H), 6.95-6.96 (d, J= 4 Hz, 1H), 6.59-6.60 (d, J= 4 Hz, 2H), 5.42 (s, 1H), 5.38-5.39 (d, J= 4 Hz, 2H), 5.22-5.23 (d, J=4 Hz, 2H), 3.23-3.27 (q,  $J_1$ =4 Hz,  $J_2$ = 8 Hz), 2.92-2.97 (m, 1H), 2.27 (s, 6H), 1.91 (s, 3H), 1.26-1.29 (t,  $J_1$ = 4 Hz,  $J_2$ = 8 Hz, 6H), 0.82-0.83 (d, J= 4 Hz, 6H), <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 153.78, 148.80, 132.04, 128.49, 126.30, 125.99, 125.46, 106.60, 101.95, 84.93, 83.11, 34.51, 31.33, 24.24, 23.07, 17.99, 12.98, 9.19. HRMS calcd. For [M]<sup>+</sup> [C<sub>27</sub>H<sub>36</sub>RuN<sub>4</sub>ClS]: 585.1391, Observed: 585.1395.



HRMS spectra of complex [Ru]-13.



## **3.4.4. Single-Crystal X-ray Diffraction Studies**

Single crystals of **[Ru]-10** and **[Ru]-12** were obtained by slow diffusion of diethyl ether into the respective methanolic solution of the complexes **[Ru]-10** and **[Ru]-12**. X-ray structural analysis was conducted using a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. The diffraction data of **[Ru]-10** was collected at 298 K and the diffraction data of [**Ru**]-12 was collected at 99 K by the standard "phi-omega" scan techniques using a SuperNova (Mo) X-ray source with a wavelength of 0.71073 Å. The data was processed and reduced using CrysAlisPro RED software, and the extracted data was evaluated using CrysAlisPro CCD software. The structure was solved using direct methods with SHELEX-2018/1 and refined using the full-matrix least-squares method, refining on F<sup>2</sup>. The positions of all atoms, except for hydrogen, were determined using direct methods and refined anisotropically. Hydrogen atoms were positioned in geometrically constrained positions. The [**Ru**]-10 and [**Ru**]-12 structures had been assigned a CCDC deposition number of 2260743 and 2310926, respectively. Tables 3.4., 3.5., 3.6., 3.7., and 3.8. provide an overview of the crystallographic information of [**Ru**]-10 and [**Ru**]-12.

	[Ru]-10	[Ru]-12		
Formula	$C_{28}H_{37}RuCl_2N_5$	C27H36RuCl2N4O		
Molecular weight	615.59	636.61		
Crystal System	Monoclinic	Triclinic		
Space group	P 21/c	P -1		
Temperature/K	298	99		
Wavelength	0.71073	0.71073		
<i>a</i> /Å	20.7451(8)	9.1590(3)		
<i>b</i> /Å	11.5813(7)	12.9646(4)		
c/Å	13.3922(5)	14.5494(5)		
$\alpha/^{\circ}$	90.00	68.484(3)		
$eta/^{\circ}$	92.768(4)	85.369(3)		
γ/ <sup>0</sup>	90.00	72.489(3)		
$V/Å^3$	3213.8(3)	1531.91(9)		
Ζ	4	2		
Density/gcm <sup>-1</sup>	1.272	1.380		
Absorption Coefficient	0.677	0.716		
Absorption Correction	spherical harmonics-	multi-scan		
	Frame scaling			
F(000)	1272.0	660		
Total no of reflections	39846	21437		
Max. $2\theta/^{\circ}$	29.131	27.009		
Ranges (h, k, l)	$-28 \le h \le \!\!28$	$-10 \le h \le 10$		
	-15 ≤k ≤15	$-15 \le h \le 15$		
	-17 ≤l ≤17	-17 ≤l ≤17		
Complete to $2\theta$ (%)	99.8	100		
Refinement method	CrysAlisPro	CrysAlisPro		
	1.171.41.115a (Rigaku	1.171.41.115a		
	OD, 2021)	(Rigaku OD, 2021)		
Goof $(F^2)$	1.100	1.043		
R Indices (all data)	0.1116	0.0745		

 Table 3.4. Single crystal X-ray refinement data for [Ru]-10 and [Ru]-12.

 Table 3.5. Selected bond lengths (Å) for [Ru]-10.

	Bond Length (Å)
Ru1 Cl1	2.4202(15)
Ru1 N1	2.132(5)
Ru1 N3	2.116(5)
Ru1 C2	2.224(5)
Ru1 C3	2.196(6)
Ru1 C4	2.184(6)
Ru1 C5	2.259(6)
Ru1 C6	2.187(7)
Ru1 C7	2.189(6)

# Table 3.6. Selected bond lengths (Å) for [Ru]-12.

	Bond Length (Å)
Ru1 Cl1	2.4107(11)
Ru1 N1	2.111(3)
Ru1 N3	2.104(3)
Ru1 C1	2.246(4)
Ru1 C2	2.201(4)
Ru1 C3	2.192(4)
Ru1 C4	2.202(4)
Ru1 C5	2.183(4)
Ru1 C6	2.190(4)

	Bond Angle (°)			
N1 Ru1 Cl1	84.31(13)			
N1 Ru1 C4	155.5(2)			
N1 Ru1 C3	159.0(2)			
N1 Ru1 C2	121.3(2)			
N1 Ru1 C5	118.9(2)			
N1 Ru1 C6	95.3(2)			
N1 Ru1 C7	96.0(2)			
N3 Ru1 Cl1	85.90(13)			
N3 Ru1 N1	84.19(18)			
N3 Ru1 C4	119.7(2)			
N3 Ru1 C3	92.7(2)			
N3 Ru1 C2	90.5(2)			
N3 Ru1 C5	156.7(2)			
N3 Ru1 C6	153.8(2)			
N3 Ru1 C7	116.4(2)			
C4 Ru1 Cl1	91.50(16)			
C4 Ru1 C2	67.8(2)			
C4 Ru1 C5	37.0(2)			
C4 Ru1 C6	66.1(2)			
C4 Ru1 C7	78.9(2)			
C3 Ru1 C2	37.8(2)			
C3 Ru1 C5	67.0(2)			
C2 Ru1 C5	80.4(2)			

Table 3.7. Selected bond angles (°) for [Ru]-10.

C5 Ru1 Cl1	92.83(17)
C6 Ru1 Cl1	120.1(2)
C6 Ru1 C3	78.5(2)
C6 Ru1 C2	67.4(3)
C6 Ru1 C5	36.8(2)
C6 Ru1 C7	37.6(3)
C7 Ru1 Cl1	157.7(2)
C7 Ru1 C3	66.7(3)
C7 Ru1 C2	37.0(3)
C7 Ru1 C5	67.4(2)

Table 3.8	Selected	bond	angles	(°)	for	[Ru]-12.
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	Bond Angle (°)
N1 Ru1 Cl1	86.51(10)
N1 Ru1 C1	113.22(15)
N1 Ru1 C2	150.02(16)
N1 Ru1 C3	162.34(16)
N1 Ru1 C4	124.65(14)
N1 Ru1 C5	96.03(14)
N1 Ru1 C6	91.30(14)
N3 Ru1 Cl1	86.34(10)
N3 Ru1 N1	82.43(13)
N3 Ru1 C1	163.93(15)
N3 Ru1 C2	127.24(15)

N3 Ru1 C3	96.05(15)
N3 Ru1 C4	87.21(14)
N3 Ru1 C5	107.96(15)
N3 Ru1 C6	144.81(14)
C1 Ru1 Cl1	97.85(11)
C2 Ru1 Cl1	90.90(11)
C2 Ru1 C1	37.65(15)
C2 Ru1 C4	67.80(15)
C3 Ru1 Cl1	111.01(12)
C3 Ru1 C1	67.94(16)
C3 Ru1 C2	37.29(16)
C3 Ru1 C4	37.77(16)
C4 Ru1 Cl1	146.92(12)
C4 Ru1 C1	80.82(16)
C5 Ru1 Cl1	165.68(12)
C5 Ru1 C1	68.17(15)
C5 Ru1 C2	79.84(15)
C5 Ru1 C3	67.59(16)
C5 Ru1 C4	37.40(16)
C5 Ru1 C6	38.07(15)
C6 Ru1 Cl1	127.99(11)
C6 Ru1 C1	37.16(15)
C6 Ru1 C2	67.08(15)
C6 Ru1 C3	79.78(16)
C6 Ru1 C4	68.05(16)

C21 O1 C20	104.7(4)
C12 N1 Ru1	123.7(3)
C14 N1 Ru1	129.1(3)
C14 N1 C12	107.1(3)
C2 C1 Ru1	69.5(2)
C2 C1 C8	123.0(4)
C6 C1 Ru1	69.3(2)
C6 C1 C2	116.7(4)
C6 C1 C8	120.2(4)
C8 C1 Ru1	135.7(3)
C14 N2 C13	109.3(4)
C1 C2 Ru1	72.9(2)
C3 C2 Ru1	71.0(2)
C3 C2 C1	121.7(4)
C25 N3 C22	106.7(3)
C2 C3 Ru1	71.7(2)
C4 C3 Ru1	71.5(2)
C3 C4 Ru1	70.7(2)
C5 C4 Ru1	70.6(2)
C7 C4 Ru1	128.8(3)
C4 C5 Ru1	72.0(2)
C6 C5 Ru1	71.2(2)
C1 C6 Ru1	73.6(2)
C5 C6 Ru1	70.7(2)

#### 3.4.5. General process for FA dehydrogenation

In a two-necked 5 mL reaction tube, equipped with a condenser and a gas burette, an aqueous solution (2.5 mL) containing the catalyst, FA and SF in a suitable molar ratio was stirred. The reaction tube was placed in a preheated oil bath at the designated reaction temperature. The gas evolved during the reaction was measured by observing the displacement of water in the burette over time, and the composition of the produced gas was established by GC-TCD. The Turnover number (TON) was calculated using the formula [(FA/catalyst) × (FA conversion/100)], while the Turnover frequency (TOF) was calculated TON/time.

# **3.4.6.** Mechanistic investigation for FA dehydrogenation under catalytic and controlled reaction conditions

In a control experiment, aqueous solution of [**Ru**]-13 (5  $\mu$ mol, 2.5 mL) was heated at 50 °C for 5 minutes, then reaction aliquot was analysed by mass spectrometry to detect the Ru-aqua species [**Ru-(OH**<sub>2</sub>)]. To the above solution, FA (2 M) was added and heated at 50 °C for 5 minutes, reaction aliquot showed Ru-formato species ([**Ru-(HCOO**)]) in mass spectrometry. Further, in the aqueous solution of [**Ru**]-13 (5  $\mu$ mol, 2.5 mL), SF (0.5 mmol) was added and heated at 50 °C for 5 minutes, Ru-hydrido species [**Ru-(H**)] was detected in mass spectrometry.

# **3.4.7. Recyclability and long-term durability for FA dehydrogenation over** [Ru]-13 catalyst

In a two-necked 5 mL reaction tube equipped with a condenser and a gas burette, FA (2 M, 2.5 mL) and SF (1 mmol) were stirred at 90 °C in the presence of **[Ru]-13** (5  $\mu$ mol) catalyst. Further, 5 mmol of FA was added to the reaction mixture during each subsequent catalytic run. The gas produced during the reaction was measured by observing the displacement of water in the burette over time.

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## **Chapter 4**

# **Bis-imidazole Methane based Diruthenium Catalyst for Hydrogen Production from Formic Acid in Water**

### 4.1. Introduction

In the coming decades, global energy demand is expected to continue to rise. As a result, accepting the challenge of providing sustainable energy to the world will be critical in the near future.<sup>[1-6]</sup> In this regard, hydrogen is considered an efficient chemical energy carrier that can meet rising energy demand by lowering greenhouse gas emissions.<sup>[7-8]</sup> Liquid organic hydrogen carriers (LOHCs) carrying a high gravimetric content of hydrogen, such as methanol (12.5 wt% of H<sub>2</sub>), formaldehyde (8.4 wt% of H<sub>2</sub>), formic acid (4.4 wt% of H<sub>2</sub>) can provide a solution for the safe storage and transportation of hydrogen gas.<sup>[9-13]</sup> Among these LOHCs, formic acid (53 g of H<sub>2</sub>/L), which is a simple C1 carboxylic acid found in nature or can be easily produced in the laboratory, can release hydrogen gas in the presence of an appropriate catalyst under mild reaction conditions.<sup>[11], [14]</sup>

In this context, Coffey et al. reported the first homogeneous catalysts for hydrogen production from formic acid, where they employed several transition metal-based complexes bearing phosphine ligands in acetic acid at 118 °C.<sup>[15]</sup> Further, several noble-metal based catalysts such as Ir,<sup>[16-17]</sup> Rh<sup>[18]</sup> and Ru<sup>[19]</sup> were investigated for the dehydrogenation of formic acid in the recent past. In general, it was observed that these noble metal complexes displayed superior catalytic activity for formic acid dehydrogenation.<sup>[16-19]</sup> Literature reports show that Ir-based complexes are extensively explored for formic acid dehydrogenation reactions, where the role of pH-responsive ligands is found to be crucial in achieving high catalytic activity.<sup>[17]</sup> In 2009, Himeda et al. reported Cp\*Ir complexes (Cp\* is pentamethylcyclopentadienyl) containing 2,2'– bipyridine (bpy) ligands with different functional groups.<sup>[16a]</sup> The highest TOF value of 14000 h<sup>-1</sup> was obtained with 4,4'–dihydroxy–2,2'–bipyridine (DHBP) (**C-1**) (Scheme 4.1.) with no loss in the activity during the five consecutive catalytic runs. Further, the amine-substituted analogous Cp\*Ir–bipyridine

catalyst (C-12) (Scheme 4.1.) exhibited the highest TOF of 115500 h<sup>-1</sup> at 80 °C and durability as compared to Cp\*Ir–DHBP (C-1) for the dehydrogenation of formic acid.<sup>[16b]</sup> However, imidazole–based ligands showed higher activity over the bipyridine ligands in the iridium-based complexes for formic acid dehydrogenation. In 2015, Li et al. reported [Cp\*Ir(L)Cl]Cl (L=2,2'–bi–2– imidazoline) (C-4) (Scheme 4.1.) for formic acid dehydrogenation in water without any additives, and achieved a TOF of 487500 h<sup>-1</sup> at 90 °C.<sup>16c</sup> They also reported a TON of 2400000 over *in situ* generated [Cp\*Ir(L')Cl]Cl (L`=2,2'– bi–1,4,5,6–tetrahydropyrimidine) complex obtained from 2,2'–bi–1,4,5,6–tetrahydropyrimidine) complex obtained from 2,2'–bi–1,4,5,6–tetrahydropyrimidine and [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, for formic acid dehydrogenation at 80 °C.<sup>[16c]</sup> Subsequently, Li et al. also reported Cp\*Ir–diaminoglyoxime based catalysts (C-11) (Scheme 4.1.) to achieve a TON up to 3900000 (TOF 65 000 h<sup>-1</sup>) at 90 °C, and a TON of 5020000 at 70 °C.<sup>[16d]</sup> Furthermore, a new class of Cp\*Rh complex [Rh<sup>III</sup>(Cp\*)(bpy)(H<sub>2</sub>O)]<sup>2+</sup> was also explored by Fukuzumi et al. for formic acid dehydrogenation to achieve a TOF of 28 h<sup>-1</sup> at pH 3.8.<sup>[18a]</sup>

Despite the extensive reports on Ir<sup>[16-17]</sup> and Rh<sup>[18]</sup> based complexes in the literature, these metals are quite expensive owing to which researchers have also explored other inexpensive or comparatively less expensive metal-based molecular catalysts for the dehydrogenation of formic acid.<sup>[19-22]</sup> For instance, Fe–PNP catalyst (C-43) (Scheme 4.1.) exhibited a TOF of 9425 h<sup>-1</sup> and a TON over 92000 for formic acid dehydrogenation at 80 °C.<sup>[20b]</sup> Further, phosphinefree Mn-based catalyst (C-44) (Scheme 4.1.) was also explored for the dehydrogenation of aqueous formic acid with an initial rate of 7 mL/min and a TON of 5763 at 92.5 °C.<sup>[21c]</sup> In this regard, Ru-based catalysts displayed high catalytic activity and advantageously are comparatively less expensive than Ir and Rh, and therefore Ru based catalysts represent a class of the most extensively explored molecular catalysts for formic acid dehydrogenation.<sup>[19]</sup> For instance, Czaun et al. studied RuCl<sub>3</sub> with various phosphine (PPh<sub>3</sub>, tris(4chlorophenyl) phosphine, and tris(2-tolyl)-phosphine) for the dehydrogenation of formic acid in an emulsion of water and organic solvents.<sup>[19f]</sup> Huang et al. reported ruthenium-PN<sup>3</sup> pincer complex for achieving high TON for formic acid dehydrogenation in non-aqueous solvents, where the role of the anime arm of the pincer ligand was found to be crucial in formic acid activation.<sup>[19g]</sup> Grützmacher et al. also reported several Ru-based catalysts for formic acid dehydrogenation, where they achieved a TOF of 2688 h<sup>-1</sup> over [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] in the presence of triethylamine at 40 °C.<sup>[19h]</sup> They also reported a TOF as high as 36000 h<sup>-1</sup> for formic acid dehydrogenation over RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> in THF at 60 °C.

Further, to explore more sustainable processes, highly efficient catalytic systems for formic acid dehydrogenation in water were also developed.<sup>[22]</sup> Notably, unless otherwise observed, the majority of catalytic systems explored for formic acid dehydrogenation represent the CO-free hydrogen production process. In this direction, Laurenczy et al. developed hydrophilic Ru<sup>II</sup> phosphine-based complexes for the dehydrogenation of aqueous formic acid in the presence of sodium formate (n(HCOOH)/n(HCOONa) 9:1) at 100 °C.<sup>[22a]</sup> On the other hand, Huang et al. reported the aqueous formic acid/sodium formate dehydrogenation over the (arene)Ru-N,N-diimine complex in the absence of any organic additive at 90 °C to achieve a TOF of 12000 h<sup>-1</sup> and a TON of 350000 (C-36) (Scheme 4.1.).<sup>[22d]</sup> Previously, we also investigated (arene)Ru<sup>II</sup> complexes with 8-(N-methylamino) quinoline (NHMeAmQ), pyridine-2-yl-methanol and bis-imidazole methane based ligands for the dehydrogenation of formic acid in water at 90 °C. Over  $[(\eta^6-C_6H_6)Ru(\kappa^2-$ NHMeAmQ)Cl]<sup>+</sup> (C-37) (Scheme 4.1.) catalyst, we achieved an initial TOF of 940 h<sup>-1</sup> in water with a TON of 2248 upon recycling the catalyst for 5 catalytic runs.<sup>[23a]</sup> Moreover, we observed an enhancement in the catalytic activity upon using (arene)Ru<sup>II</sup>-pyridine-2-yl-methanol complex (**C-38**) to achieve an initial TOF of 1548 h<sup>-1</sup> and a TON of 6050 for formic acid dehydrogenation in water at 90 °C.<sup>[23b]</sup> Recently, we explored (arene)Ru<sup>II</sup>-bis-imidazole methane complexes for catalytic dehydrogenation of formic acid in water, where the (arene)Ru<sup>II</sup> complex having 4-methoxy phenyl substituted bis-imidazole methane (C-39) (Scheme 4.1.) showed high catalytic activity and long-term stability with an initial TOF of 1545 h<sup>-1</sup> and TON of 8830.<sup>[23c]</sup>



*Scheme 4.1.* Literature known molecular catalysts for formic acid dehydrogenation.

In contrast to the extensively explored monometallic complexes, only a few bimetallic Ir–Ir<sup>(24)</sup>, Ir–Ru<sup>(25)</sup> and Ir–M<sup>(26)</sup> (M= Co, Ni, Cu) complexes

(Scheme 4.1.) are explored for formic acid dehydrogenation. Fujita et al. developed a bimetallic catalyst of Cp\*Ir complex [(Cp\*IrCl)<sub>2</sub>(thbpym)] (thbpym is 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) for the efficient dehydrogenation of formic acid.<sup>24</sup> The studied bimetallic Ir–Ir catalyst (C-24) exhibited a TOF of 228,000 h<sup>-1</sup> at 90 °C and TON of 308,000 at 80 °C for CO-free hydrogen production from formic acid. Moreover, reversible H<sub>2</sub> storage using CO<sub>2</sub> in aqueous media under mild temperature and pressure was also achieved over the studied bimetallic Ir-Ir catalyst. The -OH moieties on the thbpym ligand of complex (C-24) were pH responsive, and hence facilitated the reversible H<sub>2</sub> storage and release by tuning the pH of the solution. Heteronuclear Ir–Ru complex [Ir<sup>III</sup>(Cp\*)(H<sub>2</sub>O)(bpm)Ru<sup>II</sup>(bpy)](SO<sub>4</sub>)<sub>2</sub> (bpm is 2,2'-bipyrimidine) as reported by Fukuzumi et al. displayed an unusual hydrogen tunneling effect in the pH-dependent formic acid dehydrogenation (C-23).<sup>[25]</sup> In aqueous formic acid-sodium formate solution, the Ir–Ru catalyst exhibited a TOF of 426 h<sup>-1</sup> for formic acid dehydrogenation at 25 °C, where kinetic isotope effect (KIE) experiments inferred the hydrogen evolution step as the rate-determining step instead of  $\beta$ -hydride elimination step. Recently, Kojima et al. also reported heterodinuclear  $Ir^{III}-M^{II}$  complex (M = Co, Ni, Cu) based on 3,5-bis(2-pyridyl)-pyrazole (Hbpp) ligand for the catalytic formic acid dehydrogenation in water at 25 °C (C-25- C-26).<sup>[26]</sup> Notably, the heterobimetallic Ir-M catalyst exhibited higher catalytic activities (in increasing order of activity:  $Ir^{III}-Cu^{II} < Ir^{III}-Co^{II} < Ir^{III}-Ni^{II}$ ) as compared to the mononuclear Ir complex, attributed to the cooperative effect of the Ni metal.<sup>[26]</sup>

It is, therefore, evident that developing more efficient catalytic systems for CO-free formic acid dehydrogenation in water is essential to explore the hydrogen storage properties of formic acid. Herein, we report the first example of a water-soluble diruthenium (Ru–Ru) catalyst for formic acid dehydrogenation in water. Efforts are devoted towards evaluating and establishing the high catalytic performance and robustness of the studied Ru– Ru catalyst for hydrogen production from aqueous formic acid. Further, we probed computational studies for NBO charge calculation, and extensive mass and NMR investigations to identify crucial catalytic species and reaction steps to elucidate the possible reaction pathway for formic acid dehydrogenation over the reported diruthenium (Ru–Ru) catalyst.

### 4.2. Result and Discussion

4.2.1. Synthesis and characterization of the diruthenium complexes. At the outset, a new bridging bis-imidazole methane-based ligand 1,4-bis(bis(2ethyl-5-methyl-1H-imidazol-4-yl) methyl)benzene (benztetraimd) was synthesized by stirring 2-ethyl-4-methyl-imidazole with terephthaldehyde in the presence of KOH in a methanol-water (1:1 v/v) mixture under reflux condition (Figure 4.1.). The structural identity of the benztetraimd ligand was established by probing various spectro-analytical techniques. Subsequently, diruthenium (arene)Ru<sup>II</sup>-benztetraimd water-soluble  $[\{(\eta^6 - p$ complexes cymene)RuCl}<sub>2</sub>( $\mu$ - $\kappa^2$ : $\kappa^2$ -benztetraimd)]<sup>2+</sup>[**Ru**]-14, [{( $\eta^6$ -benzene)RuCl}<sub>2</sub>( $\mu$ - $\kappa^2$ : $\kappa^2$ -benztetraimd)]<sup>2+</sup> [**Ru**]-15 were obtained in good yields by stirring a mixture of benztetraimd ligand and the respective (arene)Ru<sup>II</sup> precursors  $[(\eta^6$ arene)RuCl<sub>2</sub>]<sub>2</sub> (arene =  $C_6H_6$  and  $C_{10}H_{14}$ ) in acetonitrile at room temperature (Figure 4.1.). The analogous monoruthenium complexes  $[(\eta^6 - p - \text{cymene})\text{RuCl}(\kappa^2 - \text{benzbisind})]^+$ [Ru]-9 and  $[(\eta^6-\text{benzene})\text{RuCl}(\kappa^2-\text{benzbisimd})]^+$  **[Ru]-16** were synthesized by previously reported method by our group.<sup>[23c]</sup>



*Figure 4.1.* Synthesis of (a) benztetraimd ligand and (b) diruthenium complexes [*Ru*]-14 and [*Ru*]-15 (c) mononuclear complexes [*Ru*]-9 and [*Ru*]-16, and (d) X-ray crystal structure of [*Ru*]-14 with 30 % ellipsoid probability. The counterion Cl<sup>-</sup> and all the hydrogen atoms are omitted for clarity.

The mass data of the obtained yellow to brown colored complexes appeared as the dicationic diruthenium (arene)Ru<sup>II</sup>–benztetraimd complexes [**Ru**]-14 and [**Ru**]-15 corroborate well with the proposed molecular structures. In the <sup>1</sup>H NMR spectra of the complexes [**Ru**]-14 and [**Ru**]-15, the methylene proton of the metal coordinated benztetraimd ligand resonated at a slightly upshifted position of 5.19 ([**Ru**]-14) and 5.24 ppm ([**Ru**]-15) as compared to the free ligands 5.28 ppm. An analogous trend in the shifting of the peak position of the methylene carbon is also observed in the <sup>13</sup>C NMR spectra of [**Ru**]-14 and [**Ru**]-15. All the protons corresponding to the  $\eta^6$ -arene ring were also observed in the expected region for the complexes [**Ru**]-14 and [**Ru**]-15.<sup>[23c]</sup> The slow diffusion of diethyl ether into a methanolic solution of [**Ru**]-14 at room temperature resulted in the growth of the crystals suitable for X-ray diffraction (Figure 4.1.). The complex [**Ru**]-14 crystalized in the monoclinic crystal system with the P 21/c space group. The crystal structure shows the formation of a diruthenium complex, where each ruthenium atom is coordinated to a  $\eta^6$ -*p*-cymene ligand, two nitrogen atoms of the bridging benztetraimd ligand, and a chloro ligand. The  $\eta^6$ -*p*-cymene ring centroid (Ct) is displaced from the Ru(II) centre by 1.719 Å. The Ru-N bond lengths are 2.132 Å (Ru-N<sub>1</sub>) and 2.125 Å (Ru-N<sub>3</sub>), and the Ru-Cl bond distance is 2.4457 Å. The bond angles from the  $\eta^6$ -*p*-cymene ring centroid (Ct) to each of the legs are Ct-Ru-N<sub>3</sub>, Ct-Ru-N<sub>1</sub>, and Ct-Ru-Cl are 130.54°, 129.05°, and 116.98°, respectively. The N<sub>3</sub>-Ru-N<sub>1</sub> bite angle is observed to be 84.7°.

# 4.2.2. Catalytic dehydrogenation of formic acid in water over Ruthenium catalyst

Initially, the diruthenium complexes [Ru]-14 and [Ru]-15 (0.05 mol%) were employed for the catalytic dehydrogenation of Formic acid 2 M in 2.5 mL of water solution under additive-free (in the absence of sodium formate) condition at 90 °C. Notably, dehydrogenation of formic acid over [Ru]-14 and [**Ru**]-15 catalysts were achieved with respective initial TOFs of 754  $h^{-1}$  per Ru and 220 h<sup>-1</sup> per Ru (Table 4.1., entries 1 and 2). These results inferred that the [**Ru**]-14 catalyst having the electron-rich  $\eta^6$ -p-cymene group is more influential in achieving higher efficiency for the dehydrogenation of formic acid as compared to the  $\eta^6$ -benzene based [Ru]-15 catalyst. It is worth mentioning that the [Ru]-14 catalyst exhibited significantly higher activity than the analogous mononuclear [Ru]-9 and [Ru]-16 catalysts for the dehydrogenation of formic acid under analogous reaction condition (Table 4.1., entries 3 and 4). Notably, the dehydrogenation of formic acid performed in solvents other than water, such as acetonitrile, methanol, tetrahydrofuran (THF), and toluene over [Ru]-14, [Ru]-15, [Ru]-9 and [Ru]-16 catalysts resulted in no gas evolution, presumably due to the poor solubility of the catalysts in these solvents.

Entry	Catalyst	Sodium	Volume	Time	TON <sup>c</sup>	TOF <sup>d</sup>
	(mmol)	formate	of gas	(min)		
		(mmol)	( <b>mL</b> )			
1	[Ru]-14	-	245	157	1980	1508 (754)
2	[Ru]-15	-	198	396	1616	440 (220)
3	[Ru]-9 <sup>b</sup>	-	244	192	990	323 (323)
4	[Ru]-16 <sup>b</sup>	-	184	342	751	215 (215)
5	[Ru]-14	0.1	242	94	1975	1724 (862)
6	[Ru]-14	0.25	246	62	2000	1938 (969)
7	[Ru]-14	0.5	246	48	2000	2800 (1400)
8	[Ru]-14	1	246	42	2000	3340 (1670)
9	[Ru]-14	2	246	35	2000	3986 (1993)
10	[Ru]-14	5	233	50	1902	2800 (1400)
11	[Ru]-14	10	194	65	1583	2400 (1200)

*Table 4.1. Optimization of reaction condition for the dehydrogenation of formic acid in water.*<sup>*a*</sup>

<sup>*a*</sup>Reaction Condition: Formic acid (2 M, 2.5 mL), sodium formate (0–10 mmol), catalysts (0.0025 mmol), 90 °C. <sup>*b*</sup>catalyst loading 0.05 mmol. <sup>*c*</sup>TONs at the completion of reaction. <sup>*d*</sup>TOFs per mmol of catalyst (initial 10 min) (Parenthesis shows TOFs per Ru atom for initial 10 min). Initial pH 1.3 (entry 1), 2.1 (entry 5), 2.6 (entry 6), 2.8 (entry 7), 3.0 (entry 8), 3.9 (entry 9), 4.6 (entry 10), and 5.1 (entry 11). TON and TOF values are average of at least two runs with an error of less than 5%.

Further, upon performing the dehydrogenation of formic acid 2 M in 2.5 mL of water solution over [**Ru**]-14 catalyst in the presence of 0.1 mmol sodium formate (n(HCOOH)/n(HCOONa) = 5/0.1), an enhancement in the initial TOF of the reaction was observed (Table 4.1., entry 5). Investigation of the effect of the varying sodium formate (0 – 10 mmol) over the catalytic efficiency of [**Ru**]-14 catalyst inferred an increasing trend in the TOF with the increase in sodium formate amount (Figure 4.2.). Notably, [**Ru**]-14 catalyst exhibited an initial TOF of 1993 h<sup>-1</sup> per Ru atom for the dehydrogenation of formic acid in the presence of 2 mmol of sodium formate (n(HCOOH)/n(HCOONa) ratio =

5:2) at 90 °C (Table 4.1., entries 6-9). However, a further increase in sodium formate amount resulted in a decrease in the catalytic activity (Table 4.1., entries 10 and 11).



**Figure 4.2.** pH-dependent dehydrogenation of formic acid over **[Ru]-14** catalyst in water, where the pH is altered by tuning the ratio of formic acid and sodium formate. Reaction condition: Formic acid 2 M in 2.5 mL of water solution, sodium formate (0–10 mmol), **[Ru]-14** (0.0025 mmol), 90 °C.

The reaction temperature also significantly influenced the catalytic performance, where with the increase in reaction temperature from 60 °C to 90 °C, an increase in the reaction rate for formic acid dehydrogenation was also observed, and hence the highest TOF was achieved at 90 °C (Figure 4.3.). The observed activation energy (E<sub>a</sub>) of 17 kcal mol<sup>-1</sup> (71 kJ mol<sup>-1</sup>), as estimated from the corresponding Arrhenius plot, is in good agreement with the earlier reported analogous catalysts (Figure 4.3.).<sup>[19], [22], [23], [27a]</sup> Notably, GC-TCD analysis of the gas produced during the catalytic formic acid dehydrogenation confirmed the presence of a mixture of H<sub>2</sub> and CO<sub>2</sub> (in 1:1 molar ratio) no detectable traces of CO (Figure 4.4.). Therefore, further optimization of the reaction conditions for the dehydrogenation of formic acid was performed over [**Ru**]-14 catalyst with *n*(HCOOH)/*n*(HCOONa) ratio of 5:2 at 90 °C in water.



Figure 4.3. (a) Temperature dependent formic acid dehydrogenation over [Ru]-14 and (b) the corresponding Arrhenius plot of the initial TOF values for formic acid. Reaction condition: Formic acid 2 M in 2.5 mL of water solution sodium formate (2 mmol), [Ru]-14] (0.0025 mmol),  $60^{\circ}C - 90^{\circ}C$ .



**Figure 4.4.** GC-TCD analysis of the (a) evolved gas  $(H_2:CO_2 \approx 1:1)$  gas for the catalytic dehydrogenation of formic acid over **[Ru]-14** catalyst (Analysis is performed using Argon as the carrier gas). (b) Pure  $H_2$  gas. (c) Pure  $CO_2$  gas. (d) Pure CO gas (detection limit 10 ppm).

Notably, TOF for formic acid dehydrogenation over [Ru]-14 was highly influenced by the pH of the reaction medium (Figure 4.2.). TOF increased with the increase in pH to achieve the highest TOF of 1993 h<sup>-1</sup> per Ru atom at pH 3.9, while lower TOF was observed at pH > 3.9. The decrease in TOF for formic acid (5 mmol) dehydrogenation over [Ru]-14 with increasing sodium formate amount from 2 mmol to 10 mmol resulted due to the increase in the concentration of HCOO<sup>-</sup> species (pH increased from 3.9 to 5.1), suggesting the importance of the  $H_3O^+$  concentration in the formic acid dehydrogenation process. On other hand, with the increase in pH from 1.2 (without sodium formate) to 3.9 (2 mmol of sodium formate) TOF also increased, presumably because it could facilitate the formation of formato intermediate. These findings suggesting the involvement of both H<sub>3</sub>O<sup>+</sup> and HCOO<sup>-</sup> ions is essential for formic acid dehydrogenation reaction.<sup>16c</sup> Further, it is to be noted that for all these experiments, the amount of H<sub>2</sub> and CO<sub>2</sub> released is only corresponding to the formic acid content, and the reaction stops after the complete consumption of formic acid.<sup>[17d]</sup>

Further, the double logarithmic plots of the initial change in hydrogen evolution rate with respect to catalyst concentration and formic acid show linear dependence for [Ru]-14. These results inferred that the reaction proceeds with an order of 0.84 with respect to [**Ru**]-14 catalyst and 0.32 with respect to formic acid concentration (Figure 4.5.). Beller et al. also observed a linear relation of reaction rate with formic acid concentration (lower concentration, with a order of 0.44 for formic reaction acid dehydrogenation over iron(II)hydridophosphine complexes.<sup>[20a]</sup> Li et al. also reported a reaction order of 0.41 for formic acid dehydrogenation over a Cp\*-Ir complex.<sup>16c</sup> They implied these observations to the coordination of one formic acid with the catalyst and that an equilibrium is involved between [Catalyst] + HCOOH and [catalyst-HCOOH] species. Therefore, in line with the literature reports, the observed reaction order of 0.32 implies that an equilibrium is probably involved between  $[cat] + HCO_2^-$  and  $[cat-HCO_2^-]$  species. <sup>[16c], [20a], [23c]</sup> The rate dependence on [Ru]-9 catalyst concentration and formic acid concentration was also determined under analogous conditions, where the reaction proceeds with an order of 0.75 with respect to the catalyst and 0.50 with respect to formic acid concentration (Figure 4.6.). For **[Ru]-15** and **[Ru]-9** catalysts, the reaction proceeds with an order of 0.87 and 0.75, respectively, with respect to the catalyst, while the rate was independent of formic acid concentration for both **[Ru]-15** and **[Ru]-16** (Figures 4.7. and 4.8.).



**Figure 4.5.** (a) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[cat] (mmol  $L^{-1}$ ). Reaction condition: formic acid (2 M, 2.5 mL), **[Ru]-14** (0.0025 mmol – 0.0100 mmol), 90 °C. (b) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: formic acid (0.4 – 1.5 M), **[Ru]-14** (0.0025 mmol), 90 °C.



**Figure 4.6.** (a) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[cat] (mmol  $L^{-1}$ ). Reaction condition: formic acid (2 M, 2.5 mL), **[Ru]-9** (0.0025 mmol – 0.0100 mmol), 90 °C. (b) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: formic acid (0.10 – 0.80 M), **[Ru]-9** (0.0025 mmol), 90 °C.



**Figure 4.7.** (a) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[cat] (mmol  $L^{-1}$ ). Reaction condition: formic acid (2 M, 2.5 mL), **[Ru]-15** (0.0025 mmol – 0.0100 mmol), 90 °C. (b) Plot of  $ln(d[H_2/dt)]$  9(mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: formic acid (0.05 – 0.80 M), **[Ru]-15** (0.0025 mmol), 90 °C.



**Figure 4.8.** (a) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[cat] (mmol  $L^{-1}$ ). Reaction condition: formic acid (2 M, 2.5 mL), **[Ru]-16** (0.0025 mmol – 0.0100 mmol), 90 °C. (b) Plot of  $ln(d[H_2/dt)]$  (mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: formic acid (0.10 – 0.80 M), **[Ru]-16** (0.0025 mmol), 90 °C.

### 4.2.3. Mechanistic Investigation

Extensive mass, NMR, and KIE measurements were probed to gain further insights into the possible pathway for formic acid dehydrogenation over the active catalyst **[Ru]-14**. At the outset, mass analysis of the aliquots taken during the catalytic formic acid dehydrogenation over the **[Ru]-14** catalyst inferred the presence of crucial Ru-aqua species (**[Ru-(OH<sub>2</sub>)<sub>2</sub>]**) (m/z 522.2) and

Ru-formato species ([Ru-(HCOO)<sub>2</sub>]) (m/z 550.2), suggesting the involvement of these species in the dehydrogenation process (Figure 4.9.). Further, the Ruaqua ([Ru-(OH<sub>2</sub>)<sub>2</sub>]) and Ru-formato [Ru-(HCOO)<sub>2</sub>] species were also observed upon treating [Ru]-14 with water and aqueous formic acid at room temperature under control reaction condition (Figure 4.10.). Moreover, with the subsequent addition of sodium formate to the reaction mixture at room temperature, the mass peak corresponding to the Ru-formato species ([Ru-(HCOO)<sub>2</sub>] (m/z 550.2) became more prominent, suggesting that formate ions facilitate the formation of the Ru-formato species (Figure 4.10.).



**Figure 4.9.** Ru-aqua and Ru-formato species observed during mass investigation of the catalytic reaction aliquots. Reaction conditions: Formic acid 2 M in 2.5 mL of water solution, sodium formate (2 mmol), **[Ru]-14** (0.0025 mmol), 90 °C.



Figure 4.10. Mass analysis showing the Ru-aqua species for the reaction of (a) [Ru]-14 (0.0025 mmol) stirred in water (2.5 mL) for 5 minutes at room temperature, (b) formic acid (5 mmol) and [Ru]-14 (0.0025 mmol) stirred in water (2.5 mL) for 5 minutes at room temperature, and (c) formic acid (5 mmol), sodium formate (2.0 mmol) and [Ru]-14 (0.0025 mmol) stirred in water (2.5 mL) for 5 minutes at room temperature.

In a subsequent controlled experiment, [Ru]-14 (0.0025 mmol) was stirred with HCOONa (0.05 mmol) in water for 15 minutes at 50 °C and then cooled to 0 °C. The obtained brown-colored solid showed an intense mass peak at m/z = 506.2, corresponding to the Ru-hydrido species ([Ru-(H)<sub>2</sub>]) (Figure 4.11. and Figure 4.12.). The formation of Ru-hydrido species was further confirmed by the <sup>1</sup>H NMR signal observed at  $\delta = -6.80$  ppm, corresponding to ruthenium hydrido species ([Ru-(H)2]) (Figure 4.12.) and along with ([Ru-(H)<sub>2</sub>]) two more hydride species were also observed in <sup>1</sup>H NMR spectroscopy consistent with the mass analysis of the same support the presence of three  $[Ru-(H)(H_2O)]^+$ hydride species assigned as  $[Ru-(H)_2],$ and [Ru-(H)(HCOO)]. Among these, [Ru-(H)<sub>2</sub>] with m/z 506.2 ([M] + 2H<sup>+</sup>) is observed as the major species, along with [Ru-(H)(H<sub>2</sub>O)] at m/z 513.7 ([M] + H<sup>+</sup>) and
[**Ru**-(**H**)(**HCOO**)] at m/z 528.2 ([M] + 2H<sup>+</sup>) (Figure 4.12.). Additionally, the mass analysis of the reaction of DCOOD with [**Ru**]-14 in water at 90 °C also revealed the presence of [**Ru**-(**DCOO**)<sub>2</sub>] (m/z 551.2) (Figure 4.13.). Interestingly, a noticeable color change from the initial light brown (for Ruhydrido species) to light yellow color (analogous to the color of the parent catalyst [**Ru**]-14 was observed upon addition of 1 M HCl (1 mL) in Ru-hydrido [**Ru**-(**H**)<sub>2</sub>]. Mass analysis of the reaction aliquot also inferred the regeneration of the [**Ru**]-14 species from Ru-hydrido species upon adding HCl (Figure 4.14.).



*Figure 4.11.* Mass investigations for the Ru-hydrido species. Reaction condition: sodium formate (0.05 mmol) and [*Ru*]-14 (0.005 mmol) stirred in water (2.5 mL) for 15 minutes at 50 °C.



*Figure 4.12.* (a) <sup>1</sup>*H* NMR analysis (b) mass analysis of identification of Ruhydrido species. Reaction condition: sodium formate (0.05 mmol) and [*Ru*]-14 (0.005 mmol) stirred in water (2.5 mL) for 15 minutes at 50 °C.



*Figure 4.13.* Mass analysis showing the Ru-formato (deuterated) species for the reaction of [*Ru*]-14 (0.0025 mmol) with deuterated formic acid (5 mmol) in deuterated water (2.5 mL) stirred for 30 minutes at 90 °C.



*Figure 4.14. Mass investigation of the reaction mixture of [Ru]-14* (0.005 *mmol) treated with sodium formate* (2 *mmol) in water* (1 *mL) stirred at* 50 °*C for 5 min in step 1, and further with 1 M HCl* (1 *mL) in step 2.* 

Moreover, the trend in kinetic isotope effect (KIE) studies indicated that the deuterated formic acid (DCOOD) was more influential than deuterated water (D<sub>2</sub>O) for the reaction rate of the catalytic dehydrogenation of HCOOH/DCOOD in D<sub>2</sub>O/H<sub>2</sub>O over [**Ru**]-14 under the optimized reaction conditions (Table 4.2.).

Table 4.2. KIE for formic acid dehydrogenation over [Ru]-14				
Entry	Substrate	Solvent	<b>TOF</b> ( <b>h</b> <sup>-1</sup> )	KIE
1	НСООН	H <sub>2</sub> O	754	-
2	НСООН	$D_2O$	592	1.27
3	DCOOD	H <sub>2</sub> O	538	1.40
4	DCOOD	$D_2O$	431	1.75

Reaction Condition: HCOOH/DCOOD (2 M, 2.5 mL), **[Ru]-14** (0.0025 mmol), 90 °C. Initial TOF at 10 min. KIE = TOF (entry 1) / TOF (entry n) (n = 2, 3, 4).

Though the KIE value of DCOOD is not very high compared to those observed in D<sub>2</sub>O, the overall trend in KIE clearly inferred that the decarboxylation of Ru-formato species is possibly the rate-determining step in the catalytic formic acid dehydrogenation over [**Ru**]-14 catalyst.<sup>[22], [23], [27]</sup> Notably, for the reactions with the hydrogen evolution step as the rate-determining step, earlier reports suggested higher KIE values for HCOOH in D<sub>2</sub>O than those observed for DCOOD in H<sub>2</sub>O.<sup>[25]</sup> Moreover, Fukuzumi et al. also demonstrated the H/D exchange in their bimetallic Ru–Ir system, and hence, Ir–D species were also observed in D<sub>2</sub>O. In this regard, we performed a control experiment by treating [**Ru**]-14 with HCOONa in H<sub>2</sub>O and D<sub>2</sub>O separately. Results inferred the formation of only Ru-hydrido species [**Ru-(H)**<sub>2</sub>] with no observable incorporation of deuterium, suggesting the  $\beta$ -hydride elimination of Ru-formato to Ru-hydrido (Figure 4.15.).





**Figure 4.15.** Mass analysis of the reaction mixture showing the Ru-hydrido species in water and in Deuterated water. Reaction Condition: **[Ru]-14** (0.0025 mmol), (a) H<sub>2</sub>O (1 mL) (b) D<sub>2</sub>O (1 mL), HCOONa (1 mmol), 50 °C, 3 min.

Further, the rate of the reaction of the diruthenium catalyst [**Ru**]-14 (k= 0.0333 min<sup>-1</sup>) is high than that of the mononuclear catalyst [**Ru**]-9 (k = 0.0218 min<sup>-1</sup>), while [**Ru**]-15 (k = 0.0085 min<sup>-1</sup>) and [**Ru**]-16 (k = 0.0112 min<sup>-1</sup>) have comparable rates (Figure 4.16. and Figure 4.17.). The observed trend is consistent with the literature reports, where the Ru–p–cymene-based catalysts were usually found to display higher activity as compared to the analogous Rubenzene-based catalyst, which can be attributed to the electron-donating nature of  $\eta^6$ –p-cymene compared to  $\eta^6$ –benzene, causing more electron rich Ru center.<sup>[28]</sup> Notably, the Ru-formato and Ru-hydrido species play a crucial role in formic acid dehydrogenation reaction, where the  $\eta^6$ –p-cymene bound electron rich Ru<sup>II</sup> center favours the facile transformation of Ru-formato to the Ru-hydrido species.<sup>[28]</sup>



*Figure 4.16.* (a) Gas generation profile and (b) corresponding reaction rate for formic acid dehydrogenation in water over [*Ru*]-14 and [*Ru*]-9. Reaction conditions: Formic acid 2 M in 2.5 mL of water solution, sodium formate (2 mmol), [*Ru*]-14 (0.0025 mmol)/[*Ru*]-9 (0.005 mmol), 90 °C.



Figure 4.17. Reaction rate for formic acid dehydrogenation in water over (a) [*Ru*]-15 and (b) [*Ru*]-16. Reaction conditions: Formic acid 2 M in 2.5 mL of water solution, sodium formate (2 mmol), [*Ru*]-15 (0.0025 mmol)/ [*Ru*]-16 (0.005 mmol), 90 °C. [(a)  $R^2 = 0.99$ , (b)  $R^2 = 0.99$ ]

In line with the experimental findings, the computationally calculated average NBO charges of the Ru center in the Ru-formato species of **[Ru]-14**, and **[Ru]-15** complexes also inferred that the Ru center in **[Ru]-14** (-0.564) is more negatively charged compared to **[Ru]-15** (-0.395) (Figure 4.18.). Hence, these results are consistent with the high catalytic activity of the  $\eta^6$ -p-cymene-based diruthenium complex **[Ru]-14** compared to the  $\eta^6$ -benzene-based diruthenium **[Ru]-15** complex.



Figure 4.18. The calculated NBO charges for Ru-formato species of (a) [Ru]-14 and (b) [Ru]-15.

Identification of several important catalytic intermediate species, Ru– aqua ([**Ru-(OH**<sub>2</sub>)<sub>2</sub>]), Ru–formato [**Ru-(HCOO**)<sub>2</sub>], and Ru–hydrido [**Ru-(H**)<sub>2</sub>] species, under catalytic and controlled reaction conditions, inferred the crucial role of these species in the formic acid dehydrogenation reaction. Consequent to the above findings, a plausible reaction pathway (Scheme 4.2.) for formic acid dehydrogenation may involve the following steps: (i) formation of Ru-aqua species ([**Ru-(OH**<sub>2</sub>)<sub>2</sub>]) from [**Ru**]-14, (ii) formation of Ru–formato species [**Ru-(HCOO**)<sub>2</sub>] by the reaction of formic acid/formate with Ru-aqua species ([**Ru-(OH**<sub>2</sub>)<sub>2</sub>]), (iii) subsequently decarboxylation of Ru–formato species [**Ru-**(**HCOO**)<sub>2</sub>] resulted in the generation of Ru–hydrido species [**Ru-(H**)<sub>2</sub>], and (iv) finally with the proton assisted hydrogen gas release from Ru–hydrido species **[Ru-(H)**<sub>2</sub>] the active Ru–aqua species (**[Ru-(OH**<sub>2</sub>)<sub>2</sub>]) was regenerated to complete the catalytic cycle.



*Scheme 4.2.* A plausible pathway for formic acid dehydrogenation over diruthenium catalyst [*Ru*]-14.

The catalytic efficacy and long-term stability of the **[Ru]-14** catalyst for large-scale formic acid dehydrogenation was also investigated to evaluate the practical applicability of the studied catalytic system. Results inferred that the **[Ru]-14** catalyst (0.0025 mmol) exhibited exceptionally high stability for over 30 h with no significant loss in activity during twenty-five consecutive catalytic runs for formic acid dehydrogenation, achieving a turnover number of 50000 (Figure 4.19a.). During the recyclability experiment, 5 mmol of formic acid was added after the end of each catalytic cycle to maintain the pH (~4.0) without significant change in the catalytic activity. Notably, the catalytic activity of the

**[Ru]-14** catalyst for formic acid dehydrogenation was not diminished even after employing the catalytic reaction mixture even after 60 days, suggesting the high stability of the **[Ru]-14** catalyst (Figure 4.19b.).



Figure 4.19. (a) Recyclability and (b) Long-term stability experiment for the catalytic dehydrogenation of formic acid over [Ru]-14 catalyst in water at 90 °C. Reaction condition: Formic acid (2 M, 2.5 mL), sodium formate (2 mmol), [Ru]-14 (0.0025 mmol), 90 °C, where formic acid (5 mmol) was added after each catalytic run for 25 consecutive catalytic runs.

Further, a control Hg poisoning experiment was performed during the recyclability experiment for 10 consecutive catalytic runs with **[Ru]-14** in the presence of an excess of elemental Hg (0), where no significant loss in the activity was observed, suggesting the homogeneous nature of the catalytic species (Figure 4.20.).



Figure 4.20. Control Hg (0) poisoning experiment during recyclability of [Ru]-14 catalysts for formic acid dehydrogenation for 10 consecutive catalytic runs. Reaction conditions: Formic acid 2 M in 2.5 mL of water solution, sodium formate (2 mmol) and [Ru]-14 (0.0025 mmol) at 90 °C, without and with 400 equivalent of elemental Hg (0), after each cycle added 5 mmol of Formic acid.

Moreover, the [**Ru**]-14 catalyst (0.0025 mmol) also displayed high activity for the dehydrogenation of formic acid under bulk scale (150, 200, and 300 mmoles of formic acid) at 90 °C. Interestingly, a TON of 93200 was achieved over the [**Ru**]-14 catalyst (0.0025 mmol) at 90 °C for the dehydrogenation of formic acid 2 M in 100 mL of water solution (Figure 4.21.). It is worth mentioning here that the high catalytic activity displayed by the [**Ru**]-14 catalyst is exceptional and is amongst the few high-yielding bimetallic catalysts reported to date.<sup>[19], [22-26]</sup>



**Figure 4.21.** Bulk-scale catalytic dehydrogenation of formic acid over **[Ru]-14** catalyst in water at 90 °C. Reaction condition: Formic acid 2 M in 100 mL of water solution, and sodium formate (40 mmol), **[Ru]-14** (0.0025 mmol), 90 °C with the subsequent addition of formic acid (100 mmol) twice after complete conversion.

Consistent with the higher activity of the diruthenium catalyst [Ru]-14 over the mononuclear **[Ru]-9** under the base-free condition, as evident from the observed higher TOF (754  $h^{-1}$  per Ru) of **[Ru]-14** vs **[Ru]-9** (323  $h^{-1}$  per Ru) (Table 4.1., entries 1 and 3), the diruthenium catalyst [Ru]-14 also exhibited higher activity (TOF 1993 h<sup>-1</sup> per Ru) over the mononuclear **[Ru]-9** (TOF 1239  $h^{-1}$  per Ru) for the formic acid dehydrogenation in the presence of sodium formate. Further, to rigorously evaluate the high performance of the diruthenium catalyst [Ru]-14, the long-term stability of the [Ru]-14 was compared with that of [Ru]-9 over the recyclability experiment of formic acid dehydrogenation over these catalysts for consecutive 15 catalytic runs (Figure 4.22.). Results inferred the robustness and high stability of the diruthenium catalyst [Ru]-14, where a TOF of 1455 h<sup>-1</sup> was observed even after the 10<sup>th</sup> catalytic run for the catalytic formic acid dehydrogenation over [Ru]-14. On the contrary, a significant loss in the catalytic activity of the monometallic [Ru]-9 was observed under an analogous condition, where reaction TOF dropped (by >56%) from the initial value of 1239 h<sup>-1</sup> to 538 h<sup>-1</sup> after the 10<sup>th</sup> cycle and further dropped by ~70% after 15<sup>th</sup> catalytic run (Figure 4.22.). Notably, a cumulative 3.5 L of gas during 15 consecutive catalytic runs of formic acid dehydrogenation was released in 10 h over the diruthenium catalyst **[Ru]-14**. In contrast, twice the time (~20 h) was required for the mononuclear catalyst **[Ru]-9** under analogous conditions (Figure 4.22.). These observations inferred the advantage of the diruthenium catalyst **[Ru]-14** over monometallic Ru–*p*–cymene catalyst **[Ru]-9** and the Ru–benzene catalysts (**[Ru]-15** and **[Ru]-16**) for formic acid dehydrogenation in water under analogous condition.



Figure 4.22. TOF for formic acid dehydrogenation in water over [Ru]-14 and [Ru]-9 in recyclability experiment. (a) TOF per catalyst (b) TOF per Ru Reaction conditions: formic acid 2 M in 2.5 mL of water solution, sodium formate (2 mmol), [Ru]-14 (0.0025 mmol)/ [Ru]-9 (0.005 mmol), 90 °C (c) Cumulative gas generation profile for formic acid dehydrogenation in water over [Ru]-14 and [Ru]-9. Reaction conditions: formic acid 2 M in 2.5 mL of water solution and subsequently 5 mmol of formic acid was added for the next 14 runs), sodium formate (2 mmol), [Ru]-14 (0.0025 mmol), [Ru]-14 (0.0025 mmol)/ [Ru]-9 (0.005 mmol), 90 °C.

Moreover, catalytic performance for formic acid dehydrogenation of the diruthenium complex **[Ru]-14** was compared with those of the mononuclear **[Ru]-9** under strictly identical conditions, using the Eyring equation while keeping the catalyst concentration constant in the temperature range of 90 °C-

60 °C (Figure 4.23.). The corresponding activation parameters for [**Ru**]-14 ( $\Delta H^{\neq}$  = 18.82 kcal mol<sup>-1</sup> and  $\Delta S^{\neq} = -7.09$  calK<sup>-1</sup>mol<sup>-1</sup>) and [**Ru**]-9 ( $\Delta H^{\neq} = 19.81$  kcal mol<sup>-1</sup> and  $\Delta S^{\neq} = -5.48$  calK<sup>-1</sup>mol<sup>-1</sup>) are obtained from the Eyring equation analyses of the kinetic data for both [**Ru**]-14 and [**Ru**]-9 catalysts. Results inferred that the free energy barrier estimated for [**Ru**]-14 ( $\Delta G^{\neq} = 20.93$  kcal mol<sup>-1</sup>) is lower than that for [**Ru**]-9 ( $\Delta G^{\neq} = 21.45$  kcal mol<sup>-1</sup>), suggesting the favourable pathway for formic acid dehydrogenation over [**Ru**]-14 compared to [**Ru**]-9.<sup>[29]</sup> In addition, we have also calculated the values of activation parameters for [**Ru**]-15 ( $\Delta H^{\neq} = 24.26$  kcal mol<sup>-1</sup> and  $\Delta S^{\neq} = 3.968$  cal K<sup>-1</sup>mol<sup>-1</sup>). Results inferred that the free energy barrier estimated for [**Ru**]-15 ( $\Delta G^{\neq} = 23.07$  kcal mol<sup>-1</sup>) is higher than that for [**Ru**]-14 ( $\Delta G^{\neq} = 20.93$  kcal mol<sup>-1</sup>) is higher than that for [**Ru**]-14 ( $\Delta G^{\neq} = 20.93$  kcal mol<sup>-1</sup>) and that for [**Ru**]-9 ( $\Delta G^{\neq} = 21.45$  kcal mol<sup>-1</sup>), suggesting the favourable pathway for formic acid dehydrogenation over [**Ru**]-15 ( $\Delta G^{\neq} = 23.07$  kcal mol<sup>-1</sup>) is higher than that for [**Ru**]-14 ( $\Delta G^{\neq} = 20.93$  kcal mol<sup>-1</sup>) and that for [**Ru**]-9 ( $\Delta G^{\neq} = 21.45$  kcal mol<sup>-1</sup>), suggesting the favourable pathway for formic acid dehydrogenation over [**Ru**]-15 ( $\Delta G^{\neq} = 23.07$  kcal mol<sup>-1</sup>) is higher than that for [**Ru**]-14 ( $\Delta G^{\neq} = 20.93$  kcal mol<sup>-1</sup>) and that for [**Ru**]-9 ( $\Delta G^{\neq} = 21.45$  kcal mol<sup>-1</sup>), suggesting the favourable pathway for formic acid dehydrogenation over [**Ru**]-15.<sup>[29]</sup>



Figure 4.23. Eyring plots of ln(k/T) vs 1/T for formic acid dehydrogenation in water over (a) [Ru]-14 (b) [Ru]-15 and (c) [Ru]-9. Reaction conditions: (a) formic acid (2 M, 2.5 mL), sodium formate (2 mmol), [Ru]-14 (0.0025 mmol), 363–333 K. (b) formic acid (2 M, 2.5 mL), sodium formate (2 mmol), [Ru]-15 (0.0025 mmol), 363–343 K. (c) formic acid (2 M, 2.5 mL), sodium formate (2 mmol), [Ru]-9 (0.0025 mmol), 363-333 K.

Further, literature revealed that the two distinct metal centres bridged through a flexible ligand in a dinuclear complex may approach each other and hence may help in achieving high activity and durability with the cooperation of both metal centers.  $^{[29(a)]}$  Therefore, though the solid-state structure of **[Ru]**-14 shows a Ru-Ru distance of 10.1 Å, the two Ru centers can approach in close proximity as a cis-form with a much smaller Ru-Ru distance, facilitated by the rotation of C<sub>Ph</sub>-C<sub>CH</sub> bond, connecting the bridging phenyl and the bisimidazole methane moiety of the ligand in the diruthenium complex (Figure 4.24.). This arrangement may help in achieving enhanced catalytic activity with the cooperation of both metal centers in the activation of formic acid. Kirillov et al. also had a similar observation for the aluminum complex, which shows a transform in the solid state with Al-Al distance of 8.0 Å. Further, the two Al centers could approach as close as 2.8 Å due to the favorable aryl-aryl bond rotation and hence facilitate the cooperation of the two metal centers.<sup>[29(a)]</sup> The room temperature <sup>1</sup>H NMR spectrum of the [**Ru**]-14 in CD<sub>3</sub>OD- $d_4$  shows a singlet at +7.11 ppm corresponding to the phenyl group of the bridging ligand. At  $-50^{\circ}$ C, the phenyl group in <sup>1</sup>H NMR resonances appeared as two peaks of equal integration ratio at +7.21 and +7.48 ppm in CD<sub>3</sub>OD- $d_4$  (Figure 4.24.), which may be due to the isomers of the [Ru]-14. A similar trend was also observed in the <sup>1</sup>H NMR spectrum of [**Ru**]-15, showing a singlet at +7.00 ppm corresponding to the phenyl group of the bridging ligand at room temperature, while at -50 °C, two peaks of equal integration ratio at +7.11 and +7.45 ppm appeared for the phenyl group in CD<sub>3</sub>OD- $d_4$ . Since the crystal structure of **[Ru]**-14 revealed the *trans*-arrangement of the arene-Ru moieties, the new peaks that appeared at low-temperature <sup>1</sup>H NMR can be assigned to this isomer. Though more detailed investigations in this regard will be required to ascertain this, the preliminary low-temperature NMR results suggest that the two-ruthenium center in the studied diruthenium complexes presumably may interact by the possible transformation of its *trans*-form to *cis*-form (Figure 4.24.). Despite that, a *cis-trans* transformation is possibly observed for both [Ru]-14 and [Ru]-15, the kinetic data and computational investigations inferred that the electronrich Ru center of the Ru-p-cymene-based [Ru]-14 catalysts, due to the electron-donating nature of  $\eta^6$ -p-cymene compared to  $\eta^6$ -benzene favouring facile  $\beta$ -hydride elimination of Ru-formato species to Ru-hydrido species, and hence attributed to the observed higher activity of **[Ru]-14** as compared to the analogous Ru-benzene-based diruthenium **[Ru]-15** catalyst.



*Figure 4.24.* (*a-b*) <sup>1</sup>*H* NMR spectra of (*a*) [*Ru*]-14 and (*b*) [*Ru*]-15 at room temperature and -50 °C, and the corresponding (*c*) pictorial presentation for the possible transformation of trans-form of [*Ru*]-14 to its cis-form.

After establishing the high catalytic activity of [Ru]-14 for formic acid dehydrogenation, we performed preliminary experiments to investigate and demonstrate the potential of [Ru]-14 for the catalytic hydrogenation of CO<sub>2</sub> to formic acid. We considered reutilizing the H<sub>2</sub> and CO<sub>2</sub> gas generated during the catalytic dehydrogenation of formic acid in water over [Ru]-14 under the optimized reaction condition. Initially, the released CO<sub>2</sub> and H<sub>2</sub> gas, during the dehydrogenation of formic acid over [Ru]-14 at optimized reaction condition, was passed through an aqueous KOH solution (1 M in 5 mL water) till the gases ceased. The captured CO<sub>2</sub> was confirmed as carbonate (<sup>13</sup>C NMR (D<sub>2</sub>O) 168.1 ppm) (Figure 4.25.). The solution containing captured CO<sub>2</sub> (as carbonate) was further subjected to hydrogenation under 30 bar H<sub>2</sub> pressure over [Ru]-14 catalyst at 80 °C for 24 h in a high-pressure reactor. The <sup>1</sup>H NMR (in D<sub>2</sub>O) of the reaction aliquot shows a peak at 8.34 ppm, confirming the formation of formate (Figure 4.25.). Though these preliminary results demonstrated that [Ru]-14 catalyst might also be active for the hydrogenation of CO<sub>2</sub> to formate, our further investigations are focused on performing extensive and elaborative studies to establish the activity of these diruthenium catalysts.



Figure 4.25. Reutilization of  $CO_2$  gas generated during the catalytic dehydrogenation of formic acid in water by capturing the  $CO_2$  as carbonate in KOH at room temperature and hydrogenating it under  $H_2$  pressure at 80 °C over [Ru]-14 catalyst. Reaction Condition: Dehydrogenation: [Ru]-14 (0.0025 mmol),  $H_2O$  (5 mL), 90 °C, 1 h; Capturing of  $CO_2$ : Passing the  $CO_2$  released during the dehydrogenation reaction to aqueous KOH solution (1 M in 5 mL water) for 1 h; Hydrogenation: The aqueous KOH solution (1 M, 5 mL) containing captured  $CO_2$  (as carbonate) is transferred to a high-pressure reactor in the presence of [Ru]-14 (0.0025 mmol) with  $H_2$  (30 bar) at 80 °C for 24 h.

## 4.3. Conclusion

We report the synthesis of diruthenium complexes to achieve efficient catalytic hydrogen production from formic acid in aqueous media. We observed a TOF of 1993 h<sup>-1</sup> per Ru atom at 90 °C and a TON of 93200. Notably, the catalyst [**Ru**]-14 exhibits appreciably high long-term stability for H<sub>2</sub> production from formic acid up to 29 catalytic runs and displays no significant sign of deactivation even after 60 days. On the contrary, the analogous mononuclear catalysts displayed lower activity with a substantial loss in activity during long-term stability evaluation, inferring the advantage of the diruthenium catalyst in achieving high catalytic activity for formic acid dehydrogenation. Moreover, a detailed mass and NMR investigation under catalytic and control experimental conditions revealed the possible involvement of Ru–aqua [**Ru-(OH**<sub>2</sub>)<sub>2</sub>], Ru–

formato [**Ru**-(**HCOO**)<sub>2</sub>], and Ru–hydrido [**Ru**-(**H**)<sub>2</sub>] in the catalytic hydrogen production from formic acid. Further, the kinetic data and charge calculations suggest that the electron-rich diruthenium-*p*-cymene [**Ru**]-14 displayed higher activity compared to the analogous diruthenium-benzene [**Ru**]-15 catalyst. Unless otherwise reported, we believe the high catalytic performance displayed by the studied diruthenium catalyst is a significant development toward the development of more efficient molecular catalysts for hydrogen production from formic acid in aqueous media.

## 4.4. Experimental Section

**4.4.1. Materials and Instrumentation.** All reactions are performed without inert gas protection using high–purity chemicals purchased from sigma Aldrich (Merck). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are recorded using CD<sub>3</sub>OD and D<sub>2</sub>O as solvents on Brucker Advance III 400 MHz and Brucker Ascend 500 spectrometers. The pH values are measured on a Eutech pH meter, Model Eco TestrpH2. ESI mass spectra are recorded on a micrOTF-Q II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using a shin carbon- ST packed column.

**4.4.2. General procedure for the Synthesis of Ligands L10.** To a solution of 2-ethyl-4-methyl imidazole (2.2 g, 20 mmol) in 3 mL methanol and terephthaldehyde (5 mmol), an aqueous solution of potassium hydroxide (3.36 g, 60 mmol) is added. The reaction mixture is stirred for three days at 80 °C to obtain the solid product, which is filtered and washed several times with water to remove the excess base and finally with diethyl ether. The obtained solid is dried in an oven overnight to obtain yellow color solid.

**L10**, Yellow powder (70% yield); <sup>1</sup>**H NMR** (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 6.96 (s, 4H), 5.28 (s, 2H), 2.55-2.50 (q, J=8 Hz, 8H), 1.84 (s, 12H), 1.15-1.11 (t, J=8 Hz, 12H), <sup>13</sup>**C NMR** (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm):149.13, 141.58, 129.59, 129.21, 127.92, 40.40, 22.12, 13.26, 10.62 **ESI-MS** calcd. For [L]<sup>+</sup> [C<sub>32</sub>H<sub>42</sub>N<sub>8</sub>]: 539.3605, Observed: 539.3684.



<sup>1</sup>H NMR spectrum of complex L10.



<sup>13</sup>C NMR spectrum of complex L10.

4.4.3. General procedure for the Synthesis of complex [Ru]-14 and [Ru]-15. [ $(\eta^6$ -arene)RuCl<sub>2</sub>]<sub>2</sub> (arene = C<sub>6</sub>H<sub>6</sub> and C<sub>10</sub>H<sub>14</sub>) (0.5 mmol) is dissolved in 30 mL of acetonitrile, and the corresponding ligand L10 (0.51 mmol) dissolved separately in 3 mL methanol, was subsequently added dropwise in the above solution. Stirring the above reaction mixture at room temperature for 20 h resulted in the precipitation of a yellow solid, which was filtered through the crucible. Further, in 1 mL methanolic solution of the precipitate, an excess of diethyl ether is poured to reprecipitate a yellow colour solid. The obtained solid is dried in an oven overnight to obtain a yellow color solid.

[**Ru**]-14. Yellow powder (68% yield); <sup>1</sup>H NMR (400 MHz, MeOH-*d<sub>4</sub>*): δ (ppm) 7.11 (s, 4H), 5.38-5.37 (d, J= 4Hz, 4H), 5.28-5.27 (d, J= 4Hz, 4H), 5.19 (s, 2H), 3.24-3.20 (m, 8H), 2.98-2.94 (m, 2H), 2.25 (s, 12H), 2.02 (s, 6H), 1.31-1.28 (t, J1=8 Hz, J2= 4Hz, 12H), 0.72 (s, 12H), <sup>13</sup>C NMR (100 MHz, MeOH-*d<sub>4</sub>*): δ (ppm) 153.67, 141.71, 131.19, 128.85, 125.30, 106.31, 100.85, 85.75, 81.65, 36.84, 30.50, 24.01, 22.73, 17.65, 12.57, 9.11. **ESI-MS** calcd. For  $[M]^{2+}$ [C<sub>52</sub>H<sub>70</sub>Ru<sub>2</sub>N<sub>8</sub>Cl<sub>2</sub>]: 540.1596. Observed: 540.1648. Elemental analysis Calcd. (%) for  $[M]^{2+}2Cl^{-}$ .2H<sub>2</sub>O [C<sub>52</sub>H<sub>74</sub>Ru<sub>2</sub>N<sub>8</sub>Cl<sub>4</sub>O<sub>2</sub>]: C, 52.61; H, 6.28; N, 9.44; Observed (%); C, 52.88; H, 6.16; N, 9.82.





<sup>13</sup>C NMR spectrum of complex [Ru]-14

[**Ru**]-15. Light green powder (65% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ ):  $\delta$  (ppm) 7.01 (s, 4H), 5.24 (s, 12H), 5.23 (s, 2H), 3.32-2.95 (m, 8H), 2.25 (s, 12H), 1.31-1.27 (t, J1=8Hz, J2=4 Hz, 12H), <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ ):  $\delta$  (ppm): 154.02, 131.49, 128.64, 125.55, 86.23, 36.93, 23.93, 15.10, 12.71, 8.89, ESI-MS calcd. For [M]<sup>2+</sup>[C<sub>44</sub>H<sub>54</sub>Ru<sub>2</sub>N<sub>8</sub>Cl<sub>2</sub>]: 484.0962, Observed: 484.0696.



Elemental analysis Calcd. (%) for [M]<sup>2+</sup>.5H<sub>2</sub>O [C<sub>44</sub>H<sub>64</sub>Ru<sub>2</sub>N<sub>8</sub>Cl<sub>4</sub>O<sub>5</sub>: C, 46.81; H, 5.71; N, 9.93; Observed (%); C, 46.94; H, 5.36; N, 9.96.



<sup>13</sup>C NMR spectrum of complex [Ru]-15

**4.4.4. Single-Crystal X-ray Diffraction Studies.** Single crystals are obtained by slow diffusion of diethyl ether into a methanolic solution of **[Ru]-14**. X-ray structural are executed on a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. Using SuperNova (Mo) X-ray Source ( $\lambda = 0.71073$  Å) based diffraction, data are collected at 293 K by the standard "phiomega" scan techniques and are scaled and reduced using CrysAlisPro RED software. The extracted data are evaluated using CrysAlisPro CCD software. The structures are solved by direct methods using SHELEX-2018/1 and refined

by the full-matrix least-squares method, refining on  $F^2$ . The positions of all of the atoms are determined by direct methods. All non-hydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions. The CCDC deposition number for [**Ru**]-14 is 2131753. Crystallographic details and selected bond parameters of [**Ru**]-14 are summarized in Tables 4.3. 4.4. and 4.5.

**4.4.5. General process for the formic acid dehydrogenation:** An aqueous solution (2.5 mL) containing the catalyst, sodium formate, and formic acid in an appropriate molar ratio in a two-necked 5 mL reaction tube, fitted with a condenser and a gas buret, is stirred at 90 °C over a preheated oil bath. The evolved gas is measured as the displacement of water in the buret with respect to time. The composition of the produced gas is confirmed by GC-TCD. The turnover number (TON) is calculated by the formula [(substrate/catalyst) × (conversion/100)]. The turnover frequency (TOF) is calculated as TON/time.

## 4.4.6. Mechanistic investigation for Formic acid dehydrogenation under catalytic and controlled reaction conditions.

Formic acid (2 M, 2.5 mL) and [Ru]-14 (0.0025 mmol) are taken in a 5 mL twonecked test tube and heated at 90 °C. Reaction aliquots are taken every 5 min and analyzed by mass spectrometry to identify the catalytic aqua species ([Ru-(OH<sub>2</sub>)<sub>2</sub>) involved in the base-free dehydrogenation of formic acid. Formic acid (2 M, 2.5 mL), [Ru]-14 (0.0025 mmol), and sodium formate (2 mmol) are taken in a 5 mL test tube and heated at 90 °C. Reaction aliquots are taken out from the reaction mixture every 5 minutes for mass analysis to identify the catalytic ([Ru-(HCOO)<sub>2</sub>]) involved in the sodium formate-assisted species dehydrogenation of formic acid over [Ru]-14. [Ru]-14 (0.0025 mmol) is dissolved in 2.5 ml water, stirred at room temperature, and the reaction mixture is analyzed by mass spectrometry to detect the Ru-aqua species [Ru-(OH<sub>2</sub>)<sub>2</sub>]. Further, [Ru]-14 (0.0025 mmol) is dissolved in 2.3 mL of water, and formic acid (5 mmol) is added to it. The reaction aliquots are then analyzed by mass spectrometry to detect the Ru-formato species [Ru-(HCOO)2]. To the above solution, sodium formate (2 mmol) is added and analyzed by mass spectrometry to gain insights into the effect of a higher concentration of formate ions over the formation of Ru-formato species. [Ru]-14 (0.0025 mmol) is dissolved in 2.5 mL of water, sodium formate (2 mmol) is added to it and heated at 50 °C, and a solid part is precipitated out after cooling the reaction aliquots. Solid part is analyzed by mass spectrometry to detect the Ru-hydrido species [**Ru-(H)**<sub>2</sub>].

**4.4.7.** Long-term stability and recyclability experiment of [Ru]-14 for dehydrogenation of formic acid. Formic acid (2 M, 2.5 mL) and sodium formate (2 mmol) are stirred at 90 °C in the presence of [Ru]-14 (0.0025 mmol) catalyst in a two-necked 5 mL reaction tube fitted with a condenser and a gas burette. Further, 5 mmol of formic acid is added to the reaction mixture 24 more times between 0.5 h to 29.5 h, and the produced gas is measured as displacement of water in the burette with respect to time.

**4.4.8.** Bulk reaction for the dehydrogenation of Formic acid in water. Formic acid (2 M, 25 mL) and sodium formate (20 mmol) are stirred at 90 °C in the presence of **[Ru]-14** (0.0025 mmol) catalyst in a 50 mL round bottom flask fitted with a condenser and a gas burette. Evolved gas is measured as water displacement in the burette per unit time. Further, 50 mmol of Formic acid is added twice in the reaction mixture to generate ~4.9 L of gas in 30 h. A similar reaction was also performed using a higher concentration of formic acid (2 M, 50 mL) and the sodium formate (40 mmol) over **[Ru]-14** (0.0025 mmol) catalyst in a 100 mL round bottom flask fitted with a condenser and a gas burette are stirred at 90 °C. Further, an additional 100 mmol of formic acid was added twice to the reaction mixture to yield a total of 11.3 L of gas in 68 h. An analogous reaction using an even higher concentration of formic acid (2 M, 100 mL) and sodium formate (80 mmol) was performed at 90 °C in the presence of **[Ru]-14** (0.0025 mmol) catalyst in a 250 mL round bottom flask with a condenser and a gas burette are a gas burette to generate over 8 L of gas in 60 h.

**4.4.9. Computational details.** All the density functional theory (DFT) based calculations were carried out using Becke's three-parameter exchange and the Lee–Yang–Parr correlation functional (B3LYP) implemented in Gaussian 09 package.<sup>[30]</sup> Geometry optimizations were performed using the 6-31++G(d,p) basis set for nonmetals (C, H, O, and N), and LANL2DZ effective core potential (ECP) for Ru.<sup>[31]</sup> Grimme's DFT-D3 potential were incorporated to consider all the non-covalent interactions (NCI) present.<sup>[32]</sup> All the structures were optimized using the implicit solvation model based on density (SMD) for the water solvent (e = 78.35) in order to mimic the experimental conditions.<sup>[33]</sup>

Natural bond orbital (NBO) analysis is done to understand the charge distribution of different atoms.<sup>[34]</sup>

<b>Table 4.3</b> . Single crystal X-ray refl	nement aata jor [ <b>Ku]-14</b>	
Formula	Ru <sub>2</sub> Cl <sub>4</sub> N <sub>8</sub> C <sub>52</sub> H <sub>70</sub>	
Molecular weight	1150	
Crystal System	Monoclinic	
Space group	P 21/c	
Temperature/K	293(2)	
Wavelength	0.71073	
a/Å	12.4074(11)	
<i>b</i> /Å	12.0600(8)	
c/Å	20.8633(19)	
$\alpha/^{\circ}$	90.00	
$\beta/^{\circ}$	105.569(9)	
$\gamma/^{\circ}$	90.00	
$V/Å^3$	3007.3(4)	
Z	2	
Density/gcm <sup>-1</sup>	1.271	
Absorption Coefficient	0.243	
Absorption Correction	spherical harmonics- Frame scaling	
Total no of reflections	38144	
Max. 20/°	26.400	
Ranges (h, k, l)	$\text{-15} \le h \le \! 15$	
	-15 ≤k ≤15	
	-26 ≤l ≤24	
Complete to $2\theta$ (%)	99.7	
Refinement method	CrysAlisPro 1.171.41.115a (Rigaku	
	OD, 2021)	
Goof (F <sup>2</sup> )	1.565	

Table 4.4. Selected bond lengths (Å) for [Ru]-14.

Bond	Length
------	--------

Ru01 Cl1	2.4457(17)
Ru01 N1	2.132(5)
Ru01 N3	2.125(5)
Ru01 C3	2.204(7)
Ru01 C7	2.251(7)
Ru01 C4	2.211(6)
Ru01 C2	2.255(7)
Ru01 C6	2.219(6)
Ru01 C5	2.246(6)

\_

Table 4.5 Selected bond angles (°) for [Ru]-14.	
	Bond Angle
N1 Ru01 Cl1	84.36(14)
N1 Ru01 C3	153.8(2)
N1 Ru01 C7	93.3(2)
N1 Ru01 C4	158.2(2)
N1 Ru01 C2	117.6(3)
N1 Ru01 C6	93.8(2)
N1 Ru01 C5	120.6(2)
N3 Ru01 Cl1	84.89(14)
N3 Ru01 N1	84.7(2)
N3 Ru01 C3	120.6(2)

N3 Ru01 C7	157.1(2)
N3 Ru01 C4	95.2(2)
N3 Ru01 C2	157.1(3)
N3 Ru01 C6	119.0(2)
N3 Ru01 C5	93.9(2)
C4 C3 Ru01	71.7(4)
C2 C3 Ru01	73.6(4)
C2 C7 Ru01	72.1(4)
C6 C7 Ru01	69.7(3)
C3 C4 Ru01	71.1(4)
C5 C4 Ru01	72.5(4)
C3 C2 Ru01	69.6(4)
C7 C2 Ru01	71.8(4)
C1 C2 Ru01	128.8(5)
C7 C6 Ru01	72.0(3)
C5 C6 Ru01	72.4(3)
C4 C5 Ru01	69.9(3)
C6 C5 Ru01	70.3(3)
C8 C5 Ru01	135.3(4)

Note: The contents of this chapter is published as Kushwaha et al., Inorg. Chem., 2023, 62, 8080–8092 (DOI: 10.1021/acs.inorgchem.2c04079) and reproduced with the permission from American Chemical Society.

## 4.5. References

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## Chapter 5

## **Summary and Future Scope**

## 5.1. Summary of this thesis

In my thesis work, I focused on creating novel arene-Ru(II) complexes using bidentate N, N donor ligands and investigating their potential for catalysing hydrogen production from formic acid in water. Further, analysed the impact of the coordinated ligands on the catalytic activity of the Ru center, and also examined various factors influencing the reaction kinetics of these dehydrogenation processes in details. Additionally, to gain a deeper understanding of the catalytic pathways involved in these reactions conducted several control experiments and characterize well thorough mass spectrometry and NMR spectroscopy.

*Chapter 1* describes the brief advantages and drawbacks of hydrogen storage and production and focuses on the alternative energy source for the future. This chapter highlights the sustainable, ecologically benign alternative renewable energy resources due to the depletion of the resources of fossil fuels and growing environmental concerns. Hence, utilizing hydrogen as a fuel may aid in reducing environmental pollution by emitting no hazardous emissions. However, the production, storage, and transportation of hydrogen gas pose numerous challenges and safety concerns due to its chemical and physical properties. Therefore, it is very crucial to develop sustainable and practical method for the hydrogen production, storage and transportation. Furthermore, a wide range of liquid organic hydrogen carriers (LOHCs) are also been extensively explored for hydrogen delivery, storage, and transportation. Furthermore, focused on the structure-activity relationships which affects the catalytic activity in formic acid dehydrogenation. Several molecular catalytic systems have been well explored for formic acid dehydrogenation. Among them, Ir, Rh and Ru-based molecular catalysts have shown outstanding performance for the dehydrogenation of formic acid in water. Here, this chapter deals with a wide range of noble and non-noble metal-based catalysts reported for FA dehydrogenation.

Cchapter 2, deals with the synthesis of series of water soluble (arene)Ru(II) complexes ([Ru]-1 – [Ru]-8) ligated with different N, N-based ligands (-pyridyloxime, -pyridylmethyloxime, and -pyridylimines) and explored for the formic acid dehydrogenation in water under mild reaction conditions. Among the studied complexes, the Ru-pyridyloxime catalyst [Ru]-1 exhibited high catalytic performance for the FA dehydrogenation, where the oxime ligand played a crucial role in achieving enhanced catalytic performance, with TON ~13,000 and remarkably high long-term stability (~3 months) as well as recycled more than 25 catalytic runs for H<sub>2</sub> production from formic acid in water at 90 °C. The high catalytic activity of the catalyst was attributed to the deprotonation of -OH moiety present in the complex. Further, in-depth mass and NMR investigations with control kinetic experiments revealed the involvement of several intermediate species to establish the rate determining step over [Ru]-1 catalyst. Further, to detect the several crucial intermediates, conducted several control experiments and analysed the species by mass and NMR. These findings inferred the plausible involvement of the proximal -N-OH in hydrogen release from the Ru-hydrido species resulted in the observed enhanced catalytic activity of [Ru]-1 catalyst. On the other hand, [Ru]-2 and [Ru]-3 catalysts having -OMe and -N<sup>n</sup>Pr, respectively groups, may involve proton  $(H_3O^+)$  assisted hydrogen release, which contribute to the observed activity of these catalysts. Based on experimental findings, the plausible reaction pathway for hydrogen gas generation from FA over the present catalytic system was proposed. Hence these findings helped us to establish the important role of catalytic intermediates on the efficient formic acid dehydrogenation over the [Ru]-1 is an important development for aqueousphase hydrogen release system.

*Chapter 3*, deals with the synthesis of new series of half sandwich arene-Ru(II) complexes ([**Ru**]-9–[**Ru**]-13) based on heterocyclic bis-imidazole methane based ligands and characterized them using various spectro analytical techniques and the molecular structures of the representative complexes [**Ru**]-10 and [**Ru**]-12 were established by single crystal X-ray diffraction. Furthermore, screened the synthesised complexes for the catalytic dehydrogenation of formic acid in water, where substitution of heterocyclic ring on the bis-imidazole methane ligands was found to exert significant impact on the catalytic activity of the complexes. Results inferred that, among the screened catalysts, thiophene substituted [**Ru**]-13 catalyst outperformed others with an initial turnover frequency (TOF) of 1831 h<sup>-1</sup> at 90 °C. One of the most notable features of [**Ru**]-13 was its exceptional long-term stability, as it maintained efficient H<sub>2</sub> production from formic acid for 35 catalytic runs and remained active even after 60 days without any significant deactivation, reaching a turnover number (TON) of 35000, highlighting its long-term durability and potential for H<sub>2</sub> production for FA in water. Further, reaction kinetics, the influence of various reaction parameters are thoroughly examined, and performed comprehensive mass and NMR investigations under both catalytic and control experimental conditions to gain more insights of the reaction pathway of FA dehydrogenation over the studied catalysts.

*Chapter 4*, deals with the synthesis of bridged N, N donor ligands and successfully synthesis of the first example of a water-soluble diruthenium (Ru-Ru) catalyst for formic acid dehydrogenation. Efforts were devoted towards evaluating and establishing the high catalytic performance and robustness of the studied Ru–Ru catalyst [Ru]-14 for hydrogen production from formic acid in water. Further, [Ru]-14 catalyst structure was confirmed by a single crystal Xray diffraction technique and explored to achieve efficient catalytic hydrogen production from formic acid in water. The catalytic efficacy and long-term stability of the [Ru]-14 catalyst for large-scale formic acid dehydrogenation was also investigated to evaluate the practical applicability of the studied catalytic system. Results inferred that the **[Ru]-14** catalyst exhibited exceptionally high stability for over 30 h with no significant loss in activity during 25 consecutive catalytic runs for formic acid dehydrogenation, achieving a turnover number of 50000. Notably, the catalytic activity of the [Ru]-14 catalyst for formic acid dehydrogenation was not diminished even after employing the catalytic reaction mixture even after 60 days, suggesting the high stability of the **[Ru]-14** catalyst. Moreover, the [Ru]-14 catalyst also displayed high activity for the dehydrogenation of formic acid under bulk scale. Interestingly, a TON of 93200 was achieved over the [Ru]-14 catalyst for the dehydrogenation of formic acid in water.



*Figure 5.1.* Comparative turnover numbers for different Ru(II)-based catalytic systems developed in this thesis work for hydrogen production from formic acid.

<b>Table 5.1</b> . Comparative table for the denyarogenation of formic acta in water.	water. <sup><i>a,b,</i></sup>	icid in	formic	of fe	rogenation	dehydi	• the	for	table.	arative	Comp	<b>5.1</b> .	Table
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		Ru-	catalysts	H_	+ 00		
	нсоон	H <sub>2</sub>	O, 90 °C			2	
Entry	Catalyst	SF	<i>n</i> (H <sub>2</sub> +C	Time	TON	TOF	FA
	(µmol)	(mmol)	<b>O</b> <sub>2</sub> )/	(min)		( <b>h</b> -1)	Conv.
			n(FA)				(%)
$1^a$	[Ru]-1	-	2.0	490	500	134	>99
$2^a$	[Ru]-2	-	1.3	500	326	120	65
3 <sup><i>a</i></sup>	[Ru]-3	-	1.6	480	404	107	81
4 <sup><i>a</i></sup>	[Ru]-4	-	1.25	1400	314	54	63
5 <sup><i>a</i></sup>	[Ru]-5	-	1.4	420	357	80	71
6 <sup><i>a</i></sup>	[Ru]-6	-	1.2	1400	306	75	61
$7^a$	[Ru]-7	-	1.0	840	244	75	50
8 <sup><i>a</i></sup>	[Ru]-8	-	0.8	900	204	54	40
$9^b$	[Ru]-9	-	2.0	120	1000	372	>99

$10^{b}$	[Ru]-10	-	1.4	360	522	216	70
$11^{b}$	[Ru]-11	-	2.0	185	1000	484	>99
$12^{b}$	[Ru]-12	-	2.0	154	1000	696	>99
13 <sup>b</sup>	[Ru]-13	-	2.0	85	1000	754	>99
14 <sup>c</sup>	[Ru]-14	-	2.0	157	1980	1508	>99
15 <sup>c</sup>	[Ru]-15	-	0.8	396	1616	440	>40
16 <sup><i>c</i></sup>	[Ru]-16	-	0.75	342	990	323	>38
$17^{a}$	[Ru]-1	1	2.0	110	500	242	>99
$18^b$	[Ru]-9	1	2.0	46	1000	1239	80
19 <sup>b</sup>	[Ru]-10	1	2.0	245	1000	538	>99
$20^b$	[Ru]-11	1	2.0	63	1000	1023	>99
21 <sup><i>b</i></sup>	[Ru]-12	1	2.0	38	1000	1508	>99
$22^b$	[Ru]-13	1	2.0	32	1000	1831	>99
$23^b$	[ <b>R</b> u]-14	1	2.0	42	2000	3340	>99

Reaction Condition: FA (2 M, in 2.5 mL water), SF (0–1 mmol), catalysts<sup>*a*</sup> (10 µmol), catalysts<sup>*b*</sup> (5 µmol), catalysts<sup>*c*</sup> (2.5 µmol), 90 °C. TONs at the completion of reaction as per the mentioned time (min). TOFs at initial 10 min. TON and TOF values are average of at least two runs with an error of less than 5%. Calculation of FA Conversion = [(evolved volume of gas)/(expected volume of gas) x 100.

Therefore, it is evident from our studies that half-sandwich areneruthenium catalysts (where arene =  $\eta^6$ -*p*-cymene and  $\eta^6$ -benzene) are widely favored due to their ability to stabilize Ru(II) complexes. Typically, Ru-*p*-cymene-based catalysts exhibit greater activity compared to their Ru-benzene-based counterparts. This discrepancy arises from the electron-withdrawing nature of  $\eta^6$ -benzene, which induces a more electron-deficient Ru center. Additionally, variations in the substituents within the ligand moiety alter the catalytic activity, with more electron-donating substituents correlating with increased activity. Furthermore, the presence of mono- or bidentate ligands and the choice of leaving group have a substantial impact on tuning the catalytic activity. In a few instances, steric hindrance also impacts tuning the catalytic activities. Furthermore, the ligand's alignment, as well as the substitution of functional groups, heterocyclic rings (thiophene, furan, imidazole, pyridine), and pendant base group, had a significant effect on catalytic activity. For instance, in *Chapter 2*, we explored the catalysts [Ru]-1–[Ru]-8, where the pendent -OH of oxime played a very crucial role in dehydrogenation of FA. The proton responsive nature of this -OH group and its possible interaction with Ru-coordinated hydrido or formato group had a positive impact in improving the catalytic efficacy to achieve a TON of ~13000. Using the rigid bis-imidazole ligands with pendent heterocyclic group also significantly tuned the catalyst activity and durability during FA dehydrogenation, as we reported catalyst [Ru]-9 – [Ru]-13 in *Chapter 3*, where the thiophene substituted bis-imidazole methane ligated catalysts showed the superior catalytic activity for FA dehydrogenation achieving an enhanced TON of 35000. Further, while working with diruthenium catalyst [Ru]-14, in Chapter 4, we demonstrated that two Ru metals work simultaneously to achieve the higher catalytic activity for FA dehydrogenation. Our study evidenced that the binuclear effect may result from the possible proximity of two ruthenium centers connected by a flexible bridged ligand, enhances durability and activity for FA dehydrogenation achieving a significantly enhanced TON of 93200. Hence, the arene-ruthenium(II) complexes with pH responsive ligands or ligands with pendent groups may represent a class of highly active and durable catalysts for achieving high catalytic activity for large scale and long-term hydrogen production from formic acid, where the strong metal-ligands electronic interactions plays a crucial role in extending the catalyst life by preventing the catalytic deactivation.

Furthermore, the spacer aryl ring in a ligand acts as a component of structure, which assists in the ligand's rigidification. In coordination chemistry, this rigidity may be essential to ensuring the proper orientation of functional groups interacting with the metal centre. The metal centre and other ligand components may be significantly affected electronically by the aryl ring. As substituents on the aryl ring that donate or withdraw electrons can change the electron density surrounding the metal centre, which in turn can change the catalytic activity of the metal. The metal complex's geometry may be determined by steric limitations established by the aryl ring's size and shape. The aryl ring's steric barrier may affect the accessibility of the metal center to substrates, thereby influencing reaction pathways and rates. Consequently, the spacer aryl ring in a ligand is not just a linker but a crucial functional component that contributes to the overall stability, reactivity, and selectivity of metal complexes in various chemical applications.

## 5.2. Future Scope

The global energy demand is predicted to rise significantly in the coming decades due to various factors such as population growth, urbanization, industrialization, and increasing standards of living, meeting this demand with sustainable energy sources will be crucial in the near future. Conventional energy sources, led by fossil fuels, significantly contribute to pollution and climate change, prompting a shift towards cleaner options. Hydrogen emerges as a promising clean energy carrier among diminishing fossil fuel reservoirs and mounting environmental concerns. Hence, recent technological advancements have focused on developing a society that offers low environmental impact and high energy efficiency. Therefore, exploring new molecular catalysts efficient for hydrogen generation from various liquid hydrogen carriers is highly desirable. There's a pressing need to enhance productivity in hydrogen production processes, particularly at low temperatures, while ensuring catalysts are highly efficient and durable. Efforts can be directed towards isolating and refining the identified reaction intermediates to gain a deeper understanding of their structure and pivotal role within the catalytic cycle. This endeavour could significantly enhance the mechanistic comprehension of dehydrogenation reactions. While this thesis has already explored the catalyst's recyclability and performance in bulk hydrogen production, as well as the potential reutilization of CO<sub>2</sub> from formic acid dehydrogenation, there remains a need to develop a suitable technique

for separating  $CO_2$  from the gas mixture. This separation would enable the direct utilization of pure H<sub>2</sub> in fuel cells, thus assessing the practical application of the developed catalytic systems. Despite significant progress, creating a reliable catalytic system remains paramount for transitioning laboratory successes to industrial scales. Similarly, there's an untapped potential in developing molecular catalysts using costeffective and air-stable metals for hydrogen production from diverse liquid hydrogen carriers.

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## Reversible hydrogenation of carbon dioxide to formic acid using a Mn-pincer complex in the presence of lysine

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