# Development of Efficient Molecular Catalysts for Hydrogen Production from C-1 Based Liquid Organic Hydrogen Carriers

Ph.D. Thesis

by

Soumyadip Patra

(Roll No. 1601231002)



# **DEPARTMENT OF CHEMISTRY**

# INDIAN INSTITUTE OF TECHNOLOGY INDORE

**DECEMBER 2021** 

# Development of Efficient Molecular Catalysts for Hydrogen Production from C-1 Based Liquid Organic Hydrogen Carriers

### A THESIS

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

of

# DOCTOR OF PHILOSOPHY

by

Soumyadip Patra



# **DEPARTMENT OF CHEMISTRY**

# INDIAN INSTITUTE OF TECHNOLOGY INDORE

**DECEMBER 2021** 



# INDIAN INSTITUTE OF TECHNOLOGY INDORE

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Development of Efficient Molecular Catalysts for Hydrogen Production from C-1 Based Liquid Organic Hydrogen Carriers" in the partial fulfilment 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 November 2016 to December 2021 under the supervision of Dr. Sanjay Kumar Singh, Professor, Department of Chemistry, IIT Indore.

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

Soumyadip Patra 07.04.2022

Signature of the student with date (NAME OF THE PhD STUDENT)

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

Dr. Sanjay K. Singh 27.12.2021 Signature of Thesis Supervisor #1 with date

(NAME OF THESIS SUPERVISOR)

Signature of Thesis Supervisor #2 with date (NAME OF THESIS SUPERVISOR)

Soumyadip Patra has successfully given his/her Ph.D. Oral Examination held on April 07, 2022.

\_\_\_\_\_

Dr. Sanjay K. Singh 07.04.2022 Signature of Thesis Supervisor #1 with date (NAME OF THESIS SUPERVISOR)

Signature of Thesis Supervisor #2 with date (NAME OF THESIS SUPERVISOR)

#### Acknowledgements

Good things happen in our life as a result of self-efforts, but it also needs help, motivation, guidance, support and love of various people at different stages. I would like to take this opportunity to acknowledge them all who have been instrumental in my journey to achieve this goal.

First and foremost, I would like to express my sincere gratitude to my respected **Ph.D. thesis supervisor**, **Dr. Sanjay Kumar Singh** who gave me the opportunity to join his research group at Department of Chemistry, Indian Institute of Technology (IIT) Indore in November 2016. I will always be grateful to him for his enormous help, support, guidance, insightful scientific discussions, critical comments and suggestions throughout my doctoral studies which helped me to improve my skills at different levels. He continues to inspire me with his vast knowledge, scientific thinking, innovative ideas, ethics and perfect management skills, which allowed me to become the researcher which I am today. His advice and constant encouragement was of immense help in enabling me to take up challenging tasks. I am thankful to him for his precious time and suggestions for my thesis corrections. Without his generous support and constant motivation, it would have been impossible to bring this thesis work towards completion. He is not only an ideal supervisor but also a complete human being and I could not have imagined a better mentor for my doctoral study.

I am thankful to my **PSPC members**, **Dr. Amrendra Kumar Singh** and **Dr. Pankaj R. Sagdeo** for their insightful and valuable suggestions at every comprehensive research progress seminar. I am thankful to **Convenor**, **DPGC** for his help during my doctoral study. I would like to acknowledge the Head, Department of Chemistry **IIT Indore** for providing infrastructure and lab facilities.

I would like to express my deep sense of gratitude to **Prof. Neelesh Kumar Jain** (Officiating Director, **IIT Indore**) and **Prof. Pradeep Mathur** (Former Director, IIT Indore) for providing me the opportunity to be a part of one of the most premiere institutes of India. I am grateful to them for providing all support and best research facilities at IIT Indore.

I would also like to thank all faculty members, Prof. Rajneesh Misra, Prof. Suman Mukhopadhyay, Dr. C. Venkatesh, Dr. Apurba K. Das, Dr. Sampak Samanta, Dr. Tridib K. Sarma, Dr. Anjan Chakraborty, Dr. Tushar Kanti Mukherjee, Dr. Satya S. Bulusu, Dr. Biswarup Pathak, Dr. Abhinav Raghuvanshi, Dr. Selvakumar Sermadurai, Dr. Umesh A. Kshirsagar and Dr. Dipak K. Roy for their guidance and help during various activities in the Department of Chemistry, IIT Indore.

I am grateful to my institute **IIT Indore** for providing the best infrastructure and **SIC facilities**. I am also thankful to **IIT Indore** and **Ministry of Human Resource Development** (**MHRD**), government of **India** for providing the research scholarships (JRF and SRF grants) for my doctoral studies.

I wish to thank the technical staff from Sophisticated Instrumentation Center (SIC), IIT Indore, Mr. Kinny Pandey and Mr. Ghanshyam Bhavsar for their timely technical support without which it would never have been possible to complete my work. I am also thankful to Mr. Tapesh Parihar for his timely help. I would like to acknowledge Mr. Manish Kushwaha for all his help throughout the five years. I am thankful to Ms. Vinita, Mr. Rameshwar, Mr. Dayaram, Mr. Manoj, Mr. Pinkesh, Mr. Aditya, Mr. Santosh, Mr. Ram and other technical and non-technical staff for all their help during my stay at IIT Indore.

I am very much thankful to my former labmates cum seniors Dr. Rohit Kumar Rai, Dr. Deepika Tyagi, Dr. Ambikesh Dhar Dwivedi, Dr. Kavita Gupta, Dr. Chinky Binnani, Dr. Dharmendra Kumar Panchariya and Dr. Debashis Panda from whom I have learnt a lot and received enormous support and guidance. A special mention for Dr. Hemanta Deka, who joined our lab as a National Post-Doctoral (N-PDF) fellow and was more like a friend to me. His contribution is immense in several of my projects. Coming to my present labmates, I would first like to thank Mr. Mahendra Kumar Awasthi who has been my constant companion from the beginning of PhD and always extended his help and support whenever I required. I extend my acknowledgement to all my other lab mates Mr. Vinod K. Sahu, Mr. Ankit Kumar, Ms. Bhanupriya, Ms. Vaishnavi Kulkarni, Mr. Sanjeev Kushwaha, Mr. Tushar Kharde and Ms. Jayashree Parthiban for all their help and pleasant company. I also wish to acknowledge present and past members (M.Sc. students and interns) from our group, Mr. Nazmul, Ms. Vanitha, Ms. Chanchal, Ms. Nirupama, Mr. Pranav, Ms. Ankita, Mr. Manoj, Mr. Abhay, Ms. Aswathi, Ms. Nivedha, Ms. Meenu, Ms. Poonam and Ms. Sayma with whom I spent a pleasant time.

I would like to sincerely thank all my seniors, juniors and friends at IIT Indore, Dr. Amit, Dr. Ankan, Dr. Sayan, Dr. Soumya, Dr. Yogajivan, Dr. Madhurima, Mr. Bijesh, Mr. Pravin, Ms. Anupama, Ms. Dibya, Mr. Tapas, Mr. Shyama, Ms. Manju, Mr. Shambhu Nath, Mr. Avijit, Ms. Reena, Mr. Amitabh, Mr. Surya, Mr. Arghya, Mr. Sayantan, Mr. Sourav, Mr. Chinthakuntla, Mr. Bhanuprakash and Mr. Rajarshi for their company and help.

I would like to express my gratitude to all my **teachers** who have taught me and guided me in my life starting from my school days.

I would like to express my sincere thanks to three most amazing persons in my life, my family! Words cannot express my gratitude towards my respected father **Dr. Dadhichi Patra** and my loving mother **Mrs. Suparna Patra** for all their sacrifice in bringing me up. Their faith in me, affection for me and support in all forms encouraged me to achieve this success which would hopefully make them feel proud. I would like to thank my beloved sister, **Ms. Anwesha Patra** for all the beautiful memories that we shared since childhood.

At last but not the least, I would like to acknowledge **Ms. Santa** for always being there in my hard times during the journey of PhD. Staying so far away from each other was difficult for both of us in many ways but we have completed the journey together. Her willingness to help whenever I required despite her own busy schedule and constant moral support has helped me in achieving this thesis. I am thankful to the almighty **GOD**, who always blessed me with wonderful people in my life and provided me the strength and patience to accomplish the challenging goals.

Words are not enough to express my deep sense of gratitude but at the end of this journey, it is my great pleasure to thank them all who contributed in many ways to my success and made it an unforgettable experience for me.

Thank You!!!

Soumyadip Patra



#### **SYNOPSIS**

Owing to the global energy crisis at present, there is an urgent need to develop and popularize alternative and renewable sources of energy to replace the fossil fuels. In this context, hydrogen energy is one of the most popular choices, but unfortunately it is not available freely on the earth's surface and needs to be produced from water or other biomass sources. In addition, the low energy density of hydrogen makes it difficult to store and the handling is also an issue due to its highly explosive nature. C-1 based liquid organic hydrogen carriers (LOHCs) such as formic acid, formaldehyde and methanol are attractive candidates for on-demand hydrogen production, as they are liquid in nature and hence safe to handle and transport. Herein, this thesis deals with the designing and development of homogeneous ruthenium-based complexes for hydrogen production from C-1 based LOHCs, particularly formic acid and formaldehyde. This thesis comprises of six chapters. The first chapter describes the general scenario of global energy crisis at present thereby focusing on the importance of alternative and renewable energy resources, among which hydrogen energy is one of the most popular choices for the future. It also describes the background of metal based homogeneous catalysts developed for hydrogen production from formic acid and formaldehyde which are two of the most popular LOHCs for on demand hydrogen production. In the subsequent chapters, synthesis, characterisation and catalytic activities of newly synthesized arene-Ru(II) complexes for hydrogen production from formic acid and formaldehyde have been discussed. Main goal of this thesis is to achieve the production of hydrogen under environmentally benign reaction conditions with the developed catalysts and understand the catalytic dehydrogenation pathway in detail. In the last chapter, concluding remarks and future scope of the present research work are briefly mentioned.

The content of each of the chapters included in the thesis are summarized as follows:

#### Chapter 1. Introduction: The need of liquid organic hydrogen carriers and transition metal catalysed hydrogen production from formic acid and formaldehyde

This chapter highlights the need to develop and popularize alternative and renewable sources of energy in the current world scenario. In this context, hydrogen energy is one of the most popular choices which needs to be produced from water or other biomass sources. The chapter particularly focuses on the background of hydrogen production from formic acid and formaldehyde with different transition metal-based catalysts reported in literature. It describes the gradual progress in the field of hydrogen production from formic acid and formaldehyde by the development of efficient catalytic systems and role of different ligands attached to the metal center in achieving enhanced catalytic activity with a particular focus on water based catalytic systems due to its importance in the sustainability of the process. Among the studied complexes, Ir based complexes prove to be very promising candidates for hydrogen production from formic acid to achieve excellent turnover numbers (TONs) and turnover frequencies (TOFs), but the very high price of iridium is drawing the attention of the researchers globally to develop cheaper yet efficient catalysts for this kind of reactions. Ruthenium based complexes along with several other non – noble metal-based catalysts prove to be promising and effective in this direction.

Ligand design plays a crucial role in tuning the catalytic activities by controlling the electronic and steric environment around the metal center. Specific examples of catalytic systems active in aqueous medium along with the reaction mechanism from literature have been discussed in this chapter. Although there is a significant advancement in this field of metal catalyzed hydrogen production from C-1 based LOHCs, several challenges related to the development of efficient catalysts for waterbased reactions, reducing the cost of the catalytic system and identifying important reaction intermediates needs to be addressed properly. In this direction, this thesis describes the design and synthesis of several bidentate N,N/N,O donor ligand based arene-Ru(II) complexes and their catalytic activities towards hydrogen production from formic acid and formaldehyde in aqueous medium along with detailed mechanistic investigations.

Based on the research gaps identified from the available literature reports, the prime objectives of the present research work are:

- To design and synthesize an efficient catalytic system based on water soluble arene-Ru(II) complexes bearing N,N bidentate aminoquinoline based ligands for hydrogen production from formic acid and study the mechanistic pathway.
- To develop water soluble arene-Ru(II) complexes containing N,O bidentate pyridine based ligands for efficient and robust hydrogen production from formic acid and formaldehyde under mild reaction conditions and investigate the role of facile protonation – deprotonation of the oxygen atom in the catalytic cycle.
- To synthesize a series of arene-Ru(II) complexes containing bisimidazole methane based ligands and employ them for hydrogen production from formic acid in aqueous solution to decipher the effect of imidazole based ligands in the catalytic activity as compared to the pyridine based ligands. In addition, the detection and isolation of the various catalytic reaction intermediates to decipher their crucial role in the catalytic dehydrogenation pathway.
- To employ the synthesized bis-imidazole methane based arene-Ru(II) complexes for highly efficient, selective and robust hydrogen production from formaldehyde-water solution under additive and base free reaction conditions and detection of various catalytic reaction intermediates to propose a plausible reaction mechanism.

Chapter 2. Hydrogen production from formic acid over water soluble arene ruthenium (II) complexes based on bidentate N,N donor ligands



In this chapter, we have synthesised and employed several arene-Ru(II) complexes based on N,N bidentate donor ligands for the catalytic dehydrogenation of formic acid in water, where the complexes having aminoquinoline based ligands were found to be more active than the complexes having ethylenediamine ligand and the complex  $[(\eta^6 C_6H_6$ )Ru( $\kappa^2$ -NpyNHMe-MAmQ)Cl]<sup>+</sup> (MAmQ 8-(N-= methylamino)quinoline) proved to be the most efficient catalyst and a TON of 2248 was achieved with this catalytic system. The high activity of the complex could be attributed to the availability of the -NH moiety. Furthermore, extensive mass investigations were carried out which evidenced the formation of several important catalytic reaction intermediates, such as the H<sub>2</sub>O coordinated dicationic ruthenium species  $[(\eta^6-C_6H_6)Ru(\kappa^2-NpyNHMe-MAmQ)(H_2O)]^{2+}$  and the coordinatively unsaturated species  $[(\eta^6-C_6H_6)Ru(\kappa^2-NpyNMe-MAmQ)]^+$  involved in the catalytic cycle. These findings helped us to establish the important role of these reaction intermediates in the catalytic dehydrogenation of formic acid with this catalytic system. Most importantly, the plausible catalyst resting state was isolated and characterized as a dicationic diruthenium species  $[{(\eta^6-\text{benzene})\text{Ru}(\kappa^2-\text{NpyNH-AmQ})}_2]^{2+}$  by single crystal X-ray diffraction technique.

Chapter 3. Hydrogen production from formic acid and formaldehyde over N,O donor ligand based arene-ruthenium (II) catalysts in water



Based on the previous results obtained with arene-Ru(II) complexes containing N,N bidentate donor ligands where the facile protonation – deprotonation of the ligand played a significant role in the catalytic cycle, we assumed that more acidic N,O donor ligands attached to the Ru center might help in enhancing the catalytic activity for the dehydrogenation reaction. Therefore, we have synthesized and employed several arene-Ru(II) complexes containing N,O donor bidentate ligands for the catalytic dehydrogenation of formic acid in water. Results inferred that the complex  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-NpyOH L_2Cl$ ]<sup>+</sup> ( $L_2$  = pyridine-2-ylmethanol) outperformed all the other complexes to achieve an initial TOF of 1548 h<sup>-1</sup>. The analogous arene-Ru(II) complex containing the N,N bidentate donor ligand pyridine-2ylmethanamine was found to be much less active. The catalyst  $[(\eta^6 C_{10}H_{14}$ )Ru( $\kappa^2$ -NpyOH-L2)Cl]<sup>+</sup> also exhibited high stability in water , and a TON of 6050 was achieved over seven consecutive catalytic runs. The higher activity of  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-NpyOH-L2)Cl]^+$  could be associated with the involvement of the oxygen atom in a facile protonation – deprotonation step during the dehydrogenation process.

Extensive mass, NMR and kinetic investigations were employed to evidence the formation of important catalytic reaction intermediates such as the diruthenium species  $[\{(\eta^6-C_{10}H_{14})Ru(\kappa^2-N,O-\mu-O-L2\}_2]^{2+},$ the formate coordinated species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-NpyO-L2)(HCO_2)]$ and the Ru-hydride species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-NpyO-L2)(H)]$  formed during the catalytic dehydrogenation of formic acid over the active catalyst and hence, established the crucial role of these species in the catalytic dehydrogenation of formic acid. The diruthenium species [ $\{(\eta^6 C_{10}H_{14}$ )Ru( $\kappa^2$ -N,O- $\mu$ -O-L2 $_{2}$ <sup>2+</sup>, which is possibly the catalyst resting state was also isolated and its structure was determined by SCXRD. In addition, the active catalyst  $[(\eta^6 - C_{10}H_{14})Ru(\kappa^2 - NpyOH - L2)Cl]^+$  was also active for the hydrogen production from aqueous formaldehyde (37 wt. %) in water under additive and base free reaction conditions. GC-TCD and pH analysis of the course of the reaction support the two-step dehydrogenation pathway for formaldehyde over the active catalyst, where several of the reaction intermediates involved in formic acid dehydrogenation identified were also during formaldehyde dehydrogenation. Hence, the present catalytic system highlighted the integration of both formic acid dehydrogenation with formaldehyde dehydrogenation.





Based on the literature survey that imidazole ligated metal based catalysts are highly active in the dehydrogenation of formic acid in aqueous medium, we have synthesised a series of half sandwich arene-Ru(II) complexes based on bis-imidazole methane based ligands in this chapter and characterized them using various spectro analytical tools. The newly synthesised complexes were employed for the catalytic dehydrogenation of formic acid in water. Results inferred that the nature of the coordinating bis-imidazole methane ligands exerted a significant impact in tuning the catalytic performance of the studied complexes. The most active catalyst bearing the ligand {4,4'-((4methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1H-imidazole)}(L6) exhibited appreciably high initial TOF of 1545 h<sup>-1</sup>. Moreover, the active catalyst also exhibited robustness under the catalytic reaction conditions to achieve a turnover number of 8830 for hydrogen production from formic acid. Various catalytic and control experiments along with extensive mass and NMR investigations revealed all the crucial catalytic intermediates such  $[(\eta^{6}-p$ reaction as the Ru-aqua species cymene)Ru( $\kappa^2$ -L6–H<sup>+</sup>)(H<sub>2</sub>O)]<sup>+</sup>, the Ru-formate coordinated species  $[(\eta^6\text{-p-cymene})\text{Ru}(\kappa^2\text{-L6}-\text{H}^+)(\text{HCO}_2)]$  and the Ru-hydride species  $[(\eta^6\text{-}$ p-cymene)Ru( $\kappa^2$ -L6–H<sup>+</sup>)(H)] involved in the catalytic cycle. In addition, the temperature dependent gradual transformation of the Ru-formate coordinated species to the Ru-hydride species was demonstrated through mass investigation.





Inspired by our previous results on hydrogen production from formic acid with the bis-imidazole ligand based arene-ruthenium (II) complexes, we have employed them for additive free hydrogen production from formaldehyde-water system in this chapter. Among the screened complexes, the arene-Ru(II) complex  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-$ L7)(Cl)]<sup>+</sup> where L7 is {4,4'-((2-methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole)} outperformed over the others to achieve a TON of > 20000 (initial TOF  $> 4000 \text{ h}^{-1}$ ) in a long-term bulk reaction of aqueous paraformaldehyde dehydrogenation, which is to the best of our knowledge the second highest TON reported till date for hydrogen production from formaldehyde-water system. Extensive catalytic and controlled experiments along with mass and NMR analysis of the reaction aliquots revealed almost all the crucial reaction intermediates involved in the process such as the Ru-methanediol coordinated species  $[(\eta^{6}-p-\text{cymene})\text{Ru}(\kappa^{2}-\text{L7}-\text{H}^{+})(\text{CH}_{2}(\text{OH})_{2})]^{+},$ the Ru-formate coordinated species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{HCO}_2)]$  and the Ruhydride species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{H})]$ , thus providing detailed mechanistic insight into the catalytic cycle.

#### Chapter 6. Summary and future scope

We developed highly water-soluble arene-Ru(II) complexes with different N,N/N,O donor pyridine and imidazole based ligands for

hydrogen production from formic acid and formaldehyde under mild reaction conditions. First, we synthesized and employed several N,N bidentate donor ligand based arene-Ru(II) complexes for hydrogen production from formic acid in water wherein our studies revealed that the aminoquinoline based ligands attached to the Ru center had a higher activity than the ethylenediamine ligand. Moreover, electron rich 8-(Nmethylamino)quinoline ligand was found to be more effective than 8aminoquinoline in enhancing the catalytic activity. Furthermore, extensive mass investigations were carried out which evidenced the formation of several important catalytic reaction intermediates and most importantly, the plausible catalyst resting state was isolated and characterized as a dicationic diruthenium species [{ $(\eta^6$ -benzene)Ru( $\kappa^2$ -NpyNH-AmQ) $_{2}^{2+}$  by single crystal X-ray diffraction technique. Further, our experimental findings with pyridine-based N,O/N,N ligated arene-Ru(II) catalysts revealed that arene-Ru(II) complexes ligated with N,O donor pyridine based ligands outperform those containing N,N donor pyridine based ligands. In addition, extensive mass, NMR and kinetic investigations were employed to evidence the formation of important catalytic reaction intermediates formed during the catalytic dehydrogenation of formic acid over the active catalyst and hence, established the crucial role of these species in the catalytic dehydrogenation of formic acid. A diruthenium species, which is possibly the catalyst resting state was also isolated and its structure was determined by SCXRD. In addition, the active catalyst was also found to be efficient in the hydrogen production from aqueous formaldehyde (37 wt. %) in water under additive and base free reaction conditions. After the exploration of complexes with pyridine based donor ligands, we synthesised a new series of arene-Ru(II) complexes containing bisimidazole methane based donor ligands and employed them for hydrogen production from formic acid in aqueous medium. Results inferred that the nature of the substituent on the bridging methylene group had a pronounced effect in tuning the catalytic activities where the complex containing the electron rich 4-methoxy substituent outperformed over all the other explored catalysts. Further, detailed

mechanistic insights were provided by identifying/isolating the crucial reaction intermediates involved in the catalytic cycle. Further, the synthesised bis-imidazole ligand based arene-Ru(II) complexes were employed for the catalytic hydrogen production from formaldehydewater system under additive free reaction conditions. Highly efficient hydrogen production was achieved with the complex  $[(\eta^6-p)$ cymene)Ru( $\kappa^2$ -L7)(Cl)]<sup>+</sup> where L7 is {4,4'-((2methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole)} to obtain a TON of 20108 in a long-term bulk reaction of aqueous paraformaldehyde dehydrogenation. The crucial reaction intermediates involved in the catalytic cycle were identified by extensive mass and NMR analysis, thus, providing detailed mechanistic insight.

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 sustainable production of hydrogen from various LOHCs. C-1 based LOHCs are most popular among them due to the high atom efficiency and low carbon emission associated along with the production of hydrogen. Despite the extensive reports available in literature in this field, development of homogeneous catalytic systems for practical and industrial usage needs more attention. Moreover, the development of air stable and relatively inexpensive non-noble metal based catalytic systems also need special attention from the economic point of view. Attempts can be made to isolate and further crystallize the identified reaction intermediates for better understanding of their structure and the crucial role they play in the catalytic cycle which may further enhance the mechanistic understanding of these dehydrogenation reactions. Though attempts have been made in this thesis work to evaluate the catalyst recyclability and performance at the bulk-scale production of hydrogen gas, development of suitable technique to separate the CO<sub>2</sub> from the gas mixture so that pure H<sub>2</sub> can be utilized in the fuel cell can be further performed to evaluate the practical application of the developed catalytic systems.

#### **Publications included in thesis**

1. **Patra S**., Awasthi M. K., Rai R. K., Deka H., Mobin S. M., Singh S. K. (2019), Dehydrogenation of Formic Acid Catalyzed by Water-Soluble Ruthenium Complexes: X-ray Crystal Structure of a Diruthenium Complex, *Eur. J. Inorg. Chem.*, 1046–1053 (DOI: 10.1002/ejic.201801501) (Impact Factor: 2.524)

 Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water. *Inorg Chem.*, 59, 4234-4243 (DOI: 10.1021/acs.inorgchem.9b02882) (Impact Factor: 5.165)

3. **Patra S**., Deka H., Singh S. K. (2021), Bis-imidazole Methane ligated Ruthenium (II) Complexes: Synthesis, Characterization and Catalytic activity for Hydrogen Production from Formic acid in Water. *Inorg Chem.*, 60, 14275-14285 (DOI: 10.1021/acs.inorgchem.1c01784) (Impact Factor: 5.165)

4. **Patra S**., Kumar A., Singh S. K. (2021), Mechanistic Insights into Additive-Free Efficient Hydrogen Production from Formaldehyde-Water Solution Catalysed by Ru(II) Complexes, (*Manuscript Submitted*)

#### Publications other than included in thesis

Awasthi M. K., Tyagi D., Patra S., Rai R. K., Mobin S. M., Singh S. K. (2018), Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions. *Chem. Asian J.*, 13, 1424–1431 (DOI:10.1002/asia.201800315) (Impact Factor: 4.568)

2. Deka H., Kumar A., **Patra S**., Awasthi M. K., Singh, S. K. (2020), Synthesis, structure and catalytic activity of manganese(II) complexes derived from bis(imidazole)methane-based ligands. *Dalton Trans.*, 49, 757-763 (DOI: 10.1039/c9dt03886h) (Impact Factor: 4.390)

3. Panda D., **Patra S.**, Awasthi M.K., Singh, S. K. (2020), Lab Cooked MOF for CO<sub>2</sub> Capture: A Sustainable Solution to Waste Management.

*J. Chem. Edu.*, 97, 1101-1108 (DOI: 10.1021/acs.jchemed.9b00337) (Impact Factor: 2.979)

#### **Conferences and workshops**

 Attended GIAN Course: "Catalysis by metal complexes" (Course Instructor: Prof. Pierre H. Dixneuf, CNRS-Université de Rennes, France) at Indian Institute of Technology Indore, India (November 2016).

2. Attended **Industry Academia Conclave** (IAC-2017) at Indian Institute of Technology Indore, India (06-09-2017).

3. Attended **RSC-IIT Indore Symposium in Chemical Science** organized by Indian Institute of Technology (IIT) Indore & Royal Society of Chemistry, at Indian Institute of Technology (IIT) Indore (January 2018).

 Attended GIAN Course: "Metal-Ligand Interplay in Advanced Coordination Chemistry" (Course Instructor: Prof. Pierre Braunstein, CNRS-Université de Strasbourg, France) at IIT Indore, India (February 2018).

 5. Poster presentation at "National Conference on Recent Advances on Materials for Sustainable Energy-2018" (RAMSE-2018), IIT(ISM) Dhanbad (Dhanbad, Jharkhand), India (March 2018). Patra S., Awasthi M. K., Singh S. K., Ruthenium Catalyzed Dehydrogenation of Formic acid in water.

6. Attended "International Conference on Emerging Trends in Chemistry", IIT Indore (Indore, M. P.), India (July 2019).

 Poster presentation at "International Conference on Modern Trends in Inorganic Chemistry – XVIII" (MTIC-XVIII), IIT Guwahati (Guwahati, Assam), India (December 2019). Patra S., Singh S. K., Ruthenium Catalyzed Dehydrogenation Reactions in Water.

#### TABLE OF CONTENTS

1.	List of Figures	XVII
2.	List of Schemes	XXX
3.	List of Tables	XXXII
4.	Nomenclature	XXXV
5.	Acronyms	XXXVI
Chapter 1.	Introduction and Background	1-35
1.1	Introduction	1-3
1.2	Hydrogen Energy: Advantages and	3-4
	Challenges	
1.3	Hydrogen Storage	4-5
1.4	Formic acid as a liquid organic hydrogen	5-17
	carrier	
1.4.1	Noble metal-based catalysts	6-14
1.4.2	Non-noble metal-based catalysts	15-17
1.5	Formaldehyde-water as a potential LOHC	17-20
1.6	Half sandwich arene-Ru(II) complexes	20-22
1.7	Research gaps in transition metal catalyzed	22-23
	hydrogen production from formic acid and	
	formaldehyde-water	
1.8	Objectives of the thesis	23
1.9	Organization of the thesis	24
1.10	References	24-35
Chapter 2.	Hydrogen production from formic acid over	37-77
	water soluble arene ruthenium (II)	
	complexes based on bidentate N,N donor	
	ligands	
2.1	Introduction	37-39
2.2	Results and Discussion	39-57

2.3	Conclusions	57-58
2.4	Experimental section	58-65
2.4.1	Materials and instrumentation	58
2.4.2	Synthesis of the ligand 8-(N-	58-59
	methylamino)quinoline ( <i>L1</i> )	
2.4.3	Synthesis of the complex [Ru]-4	59
2.4.4	Controlled experiment for the synthesis of	59
	[Ru]-2A'	
2.4.5	Single-Crystal X-ray Diffraction Studies	59-60
2.4.6	The General process for formic acid	60
	dehydrogenation reactions	
2.4.7	The process for recycling experiments	60
2.4.8	The General process for the mechanistic	60-61
	studies	
2.4.9	GC-TCD Analysis	61
2.4.10	Characterization of metal complexes	61-65
2.5	References	65-77
Chapter 3.	Hydrogen production from formic acid and	79-129
	formaldehyde over N,O donor ligand based	
	arene-ruthenium (II) catalysts in water	
3.1	Introduction	79-82
3.2	<b>Results and Discussion</b>	82-100
3.2.1	Synthesis and characterization of catalysts	82-85
3.2.2	Ruthenium catalysed dehydrogenation of	85-90
	formic acid in water	
3.2.3	Mechanistic study	90-95
3.2.4	Catalytic dehydrogenation of formaldehyde in	95-100
	water	
3.3	Conclusions	101
3.4	Experimental Section	102-121
3.4.1	Materials and instrumentation	102
3.4.2	Synthesis of the ligand 1-(pyridine-2-	102
	yl)ethanol (L3)	

3.4.3	Synthesis of arene-ruthenium complexes	102-104		
	([Ru]-8-[Ru]-11)			
3.4.4	Single-Crystal X-ray Diffraction Studies	104		
3.4.5	General process for formic acid	105		
	dehydrogenation reaction			
3.4.6	Mechanistic investigations for formic acid	105		
	dehydrogenation over [Ru]-8 under catalytic			
	and controlled reaction condition			
3.4.7	Recycling experiments	105		
3.4.8	General process for formaldehyde	106		
	dehydrogenation reaction			
3.4.9	Mechanistic investigations for formaldehyde	106		
	dehydrogenation with [Ru]-8			
3.4.10	Gas Composition Analysis	106-108		
3.4.11	Characterization of ligands and metal	109-121		
	complexes			
3.5	References	122-129		
3.5 Chapter 4.	<b>References</b> <i>Hydrogen production from formic acid and</i>	122-129 131-190		
3.5 Chapter 4.	<b>References</b> <i>Hydrogen production from formic acid and</i> <i>formaldehyde over bis-imidazole methane</i>	122-129 131-190		
3.5 Chapter 4.	References Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water	122-129 131-190		
3.5 Chapter 4. 4.1	References Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water Introduction	122-129 131-190 131-134		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> </ul>	References Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water Introduction Results and Discussion	122-129 131-190 131-134 134-154		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands and	122-129 131-190 131-134 134-154 134-138		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> </ul>	References Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water Introduction Results and Discussion Synthesis and Characterization of ligands and metal complexes	122-129 131-190 131-134 134-154 134-138		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from Formic	122-129 131-190 131-134 134-134 134-138 138-145		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in Water	122-129 131-190 131-134 134-134 134-138 138-145		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> <li>4.2.3</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in WaterMechanistic study	122-129 131-190 131-134 134-134 134-138 138-145 145-154		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> <li>4.2.3</li> <li>4.3</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in WaterMechanistic studyConclusion	122-129 131-190 131-134 134-134 134-138 138-145 145-154 154-155		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> <li>4.2.3</li> <li>4.3</li> <li>4.4</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in WaterMechanistic studyConclusionExperimental Section	122-129 131-190 131-134 134-134 134-138 138-145 145-154 154-155 155-183		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> <li>4.2.3</li> <li>4.3</li> <li>4.4</li> <li>4.4.1</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in WaterMechanistic studyConclusionExperimental SectionMaterials and instrumentation	122-129 131-190 131-134 134-134 134-138 138-145 145-154 154-155 155-183 155		
<ul> <li>3.5</li> <li>Chapter 4.</li> <li>4.1</li> <li>4.2</li> <li>4.2.1</li> <li>4.2.2</li> <li>4.2.3</li> <li>4.3</li> <li>4.4</li> <li>4.4.1</li> <li>4.4.2</li> </ul>	ReferencesHydrogen production from formic acid andformaldehyde over bis-imidazole methaneligated ruthenium (II) complexes in waterIntroductionResults and DiscussionSynthesis and Characterization of ligands andmetal complexesCatalytic Hydrogen Production from FormicAcid in WaterMechanistic studyConclusionExperimental SectionMaterials and instrumentationGeneral procedure for the synthesis of ligands	122-129 131-190 131-134 134-134 134-138 138-145 145-154 154-155 155-183 155 155-156		

4.4.3	General Procedure for synthesis of the	156-158
	complexes ([ <b>Ru]-17</b> – [ <b>Ru]-26</b> )	
4.4.4	Single-Crystal X-ray Diffraction Studies	158-159
4.4.5	General process for formic acid	159
	dehydrogenation reaction	
4.4.6	Mechanistic investigations for formic acid	159-160
	dehydrogenation under catalytic and	
	controlled reaction condition	
4.4.7	Control Hg(0) poisoning experiment	160
4.4.8	Investigation of long-term stability of [Ru]-18	160-161
	for hydrogen production from formic acid with	
	batch-wise addition of formic acid	
4.4.9	Gas Composition Analysis	161-162
4.4.10	Characterization of ligands and metal	163-183
	complexes	
4.5	References	183-190
Chapter 5.	Efficient additive-free hydrogen production	191-224
	from formaldehyde-water over arene-	
	ruthenium (II) complexes	
5.1	Introduction	191-194
5.2	<b>Results and Discussion</b>	194-213
5.3	Conclusions	214
5.4	Experimental Section	214-221
5.4.1	Materials and instrumentation	214
5.4.2	General process for hydrogen production from	215
	HCHO-H <sub>2</sub> O system	
5.4.3	Mechanistic investigations for hydrogen	215-216
	production from formaldenyde in water under	
	catalytic and controlled reaction conditions.	
	catalytic and controlled reaction conditions. [ <b>Ru</b> ]-19	
5.4.4	<ul><li>production from formaldenyde in water under catalytic and controlled reaction conditions.</li><li>[Ru]-19</li><li>Gas Composition Analysis</li></ul>	216-217

5.5	References	222-224
Chapter 6.	Summary and Future Scope	225-229
6.1	Summary of this thesis	225-228
6.2	Future scope	228-229

#### **List of Figures**

#### Chapter 1. Introduction and Background

- Figure 1.1 Sector wise total energy consumption of the 2 world in 1971(a) and 2017(b). Total energy supply by the fuels globally of 1971(c) and 2017(d)
- **Figure 1.2** Hydrogen economy with formic acid as 5 storage medium and thermodynamics of the decomposition pathways of formic acid
- **Figure 1.3** Proposed mechanism and different rate- 12 determining steps for complexes with 4dihydroxy bipyridine and 6-dihydroxy bipyridine
- Figure 1.4Progressive development of some ligands for 14formic acid dehydrogenation in water
- Figure 1.5 Piano stool structure of half-sandwich arene- 21 Ru(II) complexes

#### Chapter 2. Hydrogen production from formic acid over water soluble arene ruthenium (II) complexes based on bidentate N,N donor ligands

- Figure 2.1 Catalytic formic acid dehydrogenation over 42 different Ru-arene complexes. Reaction conditions: formic acid (0.4 M, 2.5 mL), catalyst (1 mol%), HCOONa (0.05 mmol), 90 °C
- Figure 2.2 TOF (h<sup>-1</sup>) vs [HCO<sub>2</sub>Na] (mmol) plot for the 44 catalytic dehydrogenation of formic acid over complexes [Ru]-2 and [Ru]-4. Reaction conditions: formic acid (0.4 M, 2.5 mL),

catalyst (0.01 mmol), 90 °C. [a] formic acid (2.0 M, 2.5 mL)

- Figure 2.3 TON of the catalytic recyclability (1-5 44 catalytic runs) experiment for the catalytic dehydrogenation of formic acid over the complex [Ru]-4. Reaction conditions: formic acid (2.0 M, 2.5 mL), [Ru]-4 (0.01 mmol), [HCOONa]/[HCOOH] = 2:1, 90 °C. (5 mmol of formic acid was added to the reaction mixture after each run)
- Figure 2.4 (a) Temperature dependent formic acid 45 decomposition over [Ru]-4 (1 mol %), formic acid (2M, 2.5 mL), HCOONa/ HCOOH = 2:1, T = 60 - 90 °C. (b) Arrhenius plot of initial TOF values for formic acid (2 M, 2.5 mL) decomposition over [Ru]-4 (1 mol%), HCOONa/ HCOOH = 2:1.
- Figure 2.5Plot of ln [initial rate (mmol  $L^{-1} h^{-1}$ )]vs ln [cat]46(mmol  $L^{-1}$ ); Reaction conditions: catalyst(0.005 0.03 mmol), formic acid (2 M, 2.5mL), HCOONa (10 mmol), 90 °C
- Figure 2.6Plot of ln[initial rate (mmol  $L^{-1}h^{-1}$ )] vs ln[FA]47(mmol  $L^{-1}$ ); Reaction conditions: [Ru]-4 (0.01mmol), formic acid (0.4 2M, 2.5 mL), 90 °C
- Figure 2.7 Different species observed under mass 49 spectrometry after complex [Ru]-4 was stirred in water for 5 minutes at room temperature
- Figure 2.8 Various intermediate species observed during 50 mass investigation of an aqueous solution of complex [Ru]-2 under varying controlled reaction condition

Figure 2.9 Dehydrogenation of formic acid under varying 51 pH values, where pH values are altered by changing the [HCOONa]/[HCOOH] ratios. Reaction condition: catalyst [Ru]-2/[Ru]-4 (0.01 mmol), formic acid (0.4 M, 2.5 mL), T = 90 °C

Figure 2.10 Single crystal X-ray structure of the 54 diruthenium [Ru]-2A'

- Figure 2.11 Transformation of colour of the reaction 55 mixture from green to wine red brown during the initial minutes of the reaction and reverts back to green colour when treated with excess HCl
- Figure 2.12 Mass investigation of the green-colored 55 solutions obtained by the addition of an excess of dilute HCl to the brown solution after the catalytic reaction for [Ru]-2 and [Ru]-4
- Figure 2.13 Gas chromatogram (GC- TCD) of evolved (a) 61 H<sub>2</sub> gas and (b) CO<sub>2</sub> from the reaction mixture for the catalytic formic acid dehydrogenation reaction. Reaction conditions: [Ru]-4 (0.01 mmol), formic acid (0.4 M, 2.5 mL), HCOONa (0.05 mmol), 90 °C. (All analyses are performed using argon as the carrier gas)

# Chapter 3. Hydrogen production from formic acid and formaldehyde over N,O donor ligand based arene-ruthenium (II) catalysts in water

Figure 3.1	Single crystal X-ray molecular structure of	85
	[Ru]-9	
Figure 3.2	(a) Comparative catalytic activity of [Ru]-8 –	86
	[Ru]-16 for formic acid dehydrogenation.	
	Reaction conditions: formic acid (0.4 M, 2.5	

mL), catalyst (1 mol%), sodium formate (0.05 mmol), 90 °C. (b) pH dependent dehydrogenation of formic acid over [**Ru**]-8, where pH is altered by tuning n(formic acid)/n(sodium formate) ratio. Reaction condition: [**Ru**]-8 (1 mol%), formic acid (4.0 M, 2.5 mL), 90 °C

- (a) TOF (h<sup>-1</sup>) vs [HCOONa] (mmol) plot for 87 Figure 3.3 the catalytic dehydrogenation of formic acid over [Ru]-8. Reaction condition: formic acid (0.4 M, 2.5 mL), [Ru]-8 (0.01 mmol), 90 °C. <sup>a</sup>formic acid (2.0 M, 2.5 mL).<sup>b</sup>formic acid (4.0 M, 2.5 mL). (b) Gas produced (mmol) vs time (min) plot for the catalytic dehydrogenation of formic acid over [Ru]-8. Reaction condition: formic acid (4.0)M. 2.5 mL), [HCOONa]/[HCOOH] = 2:1, [Ru]-8 (0.01)mmol), 90 °C
- Figure 3.4 (a) Temperature dependent formic acid 89 dehydrogenation over [Ru]-8, and the corresponding (b) Arrhenius plot of the initial TOF values for formic acid (2M, 2.5 mL) dehydrogenation over [Ru]-8 (0.2 mol%), [HCOONa]/[HCOOH] = 2:1, 60°C 90 °C
- Figure 3.5 Recyclability experiment for the catalytic 90 dehydrogenation of formic acid over [Ru]-8. Reaction conditions: formic acid (4.0 M, 2.5 mL), [Ru]-8 (1 mol%), n(formic acid)/n(sodium formate) = 1:2, 90 °C. (10 mmol of formic acid is added to the reaction mixture after each run)
- **Figure 3.6** (a) Plot of  $\ln[initial rate(mmolL^{-1}h^{-1})]$  vs 90  $\ln[cat](mmol L^{-1})$ . Reaction conditions: **[Ru]**-

**8** (0.01 mmol – 0.04 mmol), formic acid (1.0 M, 2.5 mL), 90 °C. (**b**) Plot of ln[initial rate(mmolL<sup>-1</sup>h<sup>-1</sup>)] vs ln[HCOOH](mmol L<sup>-1</sup>). Reaction condition: [**Ru**]-8 (0.01 mmol), formic acid (0.2 - 0.8 M, 2.5 mL), 90 °C

- Figure 3.7 Transformation of colour of the reaction 91 mixture during the catalytic dehydrogenation of formic acid. Reaction Conditions: [Ru]-8 (0.01 mmol), formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol), T = 90 °C
- Figure 3.8Mass investigation of the reaction mixture for92catalytic dehydrogenation of formic acid over[Ru]-8 catalyst showing the colour changefrom the initial yellow to red-orange during theinitial minutes and reverts back to yellowcolour when treated with an excess of diluteHCl
- Figure 3.9 Various intermediate species observed during 92 the mass investigation for formic acid dehydrogenation reaction performed over [Ru]-8 under varying controlled reaction conditions, and X-ray molecular structure of the dimeric ruthenium species [Ru]-8A'
- Figure 3.10 <sup>1</sup>H NMR spectra showing the generation of 94 Ru-hydride species during the treatment of [Ru]-8 (0.01 mmol) with sodium formate (0.05 mmol) in D<sub>2</sub>O (0.6 mL) at 25 °C
- Figure 3.11 Time course plot for the catalytic 97 dehydrogenation of formaldehyde over the catalyst [Ru]-8. Reaction conditions: [Ru]-8 (0.01 mmol), formaldehyde (0.4 4.0 M, 2.5mL) in water at 90 °C

- Figure 3.12 Time-dependent pH plot for the catalytic 98 formaldehyde dehydrogenation reaction.
  Reaction conditions: [Ru]-8 (0.01 mmol), formaldehyde (0.4M, 2.5mL), 90 °C
- Figure 3.13 Transformation of colour of the reaction 99 mixture during the catalytic dehydrogenation of aqueous formaldehyde. Reaction conditions: [Ru]-8 (0.01 mmol), aq. formaldehyde (0.4 M, 2.5mL), 90 °C
- Figure 3.14 ESI-MS during the catalytic dehydrogenation 99 of aq. formaldehyde after 10 minutes. Reaction conditions: [Ru]-8 (0.01 mmol), formaldehyde (0.4 M, 2.5 mL), T = 90 °C
- Figure 3.15 GC-TCD analysis of evolved gas (H<sub>2</sub>:CO<sub>2</sub>≈ 107 1:1) gas after complete dehydrogenation of formic acid with [Ru]-8. Reaction conditions:
  [Ru]-8 (0.01 mmol), formic acid (0.4 M, 2.5 mL), sodium formate (0.05mmol), 90 °C. (Analysis is performed using Argon as the carrier gas).
- **Figure 3.16** Time-dependent GC-TCD analysis of the 108 evolved gas (H<sub>2</sub> and CO<sub>2</sub>) during the catalytic formaldehyde dehydrogenation reaction. (a) initial 10 minutes; H<sub>2</sub>:CO<sub>2</sub> $\approx$  6:1 (b) After 30 minutes; H<sub>2</sub>:CO<sub>2</sub> $\approx$  2.2:1. (c) After completion of reaction; H<sub>2</sub>:CO<sub>2</sub> $\approx$  2:1.Reaction conditions: [**Ru**]-8 (0.01 mmol), aq. formaldehyde (0.4 M, 2.5 mL), 90 °C. (Analysis is performed using Argon as the carrier gas)

# Chapter 4. Hydrogen production from formic acid and formaldehydeover bis-imidazole methane ligated ruthenium (II) complexes in waterFigure 4.1Single-crystal X-ray structure of [Ru]-19137
- Figure 4.2 Single-crystal X-ray structure of [Ru]-22 138
  Figure 4.3 Catalytic dehydrogenation of formic acid in 139 water over [Ru]-17 [Ru]-26 catalysts. Reaction conditions: formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol), catalyst (0.01 mmol), 90° C. TONs and TOFs are determined at the end of the reaction
- Figure 4.4 Controlled Hg(0) poisoning experiment. 140 Reaction conditions: Formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol) and [Ru]-18 (0.01 mmol) at 90° C with and without a large excess of elemental Hg(0)
- Figure 4.5 Temperature dependent formic acid 141 dehydrogenation over [Ru]-18, and the corresponding Arrhenius plot of the initial TOF values for formic acid. Reaction conditions: formic acid (2 M, 2.5 mL), [Ru]-18 (0.2 mol%), [HCOONa]/[HCOOH] = 1:1, 60 °C 90 °C
- Figure 4.6 TOF (h<sup>-1</sup>) vs [HCO<sub>2</sub>Na] (mmol) plot for the 142 catalytic dehydrogenation of formic acid over [Ru]-18. Reaction conditions: formic acid (2 M, 2.5 mL), [Ru]-18 (0.1 mol%), sodium formate (0-10) mmol, 90 °C
- Figure 4.7 pH dependent dehydrogenation of formic acid 143 over [Ru]-18, where pH is altered by tuning n(formic acid)/n(sodium formate) ratio. Reaction conditions: formic acid (2.0 M, 2.5 mL), sodium formate (0 30 mmol), [Ru]-18 (0.005 mmol), 90 °C
  Figure 4.8 (a) Plot of Infinitial ratal (mmol L<sup>-1</sup> h<sup>-1</sup>) va 144
- Figure 4.8(a) Plot of ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs 144ln[HCOOH] (mmol  $L^{-1}$ ). Reaction conditions:[Ru]-18 (0.01 mmol), formic acid (0.2 M 0.8

M, 2.5 mL), 90 °C. (b) Plot of ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs ln[cat](mmol  $L^{-1}$ ). Reaction conditions: **[Ru]-18** (0.005 mmol – 0.02 mmol), formic acid (0.6 M, 2.5 mL), 90 °C

- Figure 4.9 Long-term stability test of [Ru]-18 for the 145 catalytic dehydrogenation of formic acid. Reaction conditions: formic acid (4.0 M, 2.5 mL), sodium formate (10 mmol), [Ru]-18 (0.005 mmol) at 90 °C, and subsequent addition of formic acid (5 mmol) at 90, 180, 320 and 500 minutes during the reaction
- Figure 4.10 Colour transformation during the initial 146 minutes of dehydrogenation of formic acid with [Ru]-18
- Figure 4.11 Ru-aqua and Ru-formato species observed 146 during mass investigation of the catalytic reaction aliquots. Reaction conditions: formic acid (0.4 M, 2.5 mL) and [Ru]-18 (0.005 mmol) at 90 °C, with or without sodium formate (0.05 mmol)
- Figure 4.12 Ru-aqua species observed during mass 147 investigation of the reaction mixture of [Ru]-18 (0.005 mmol) dissolved in H<sub>2</sub>O (2.5 mL) and heated at 50 °C for 5 minutes
- Figure 4.13 ESI-MS showing the Ru-formate species for 147 the reaction of [Ru]-18 (0.005 mmol) with formic acid (0.5 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature
- Figure 4.14 Ru-formato and Ru-hydride species observed 148 during mass investigation for the reaction of [Ru]-18 (0.005 mmol) with sodium formate (0.05 mmol) in H<sub>2</sub>O (2 mL) at room

temperature (a) with and (b) without formic acid (0.5 mmol)

- Figure 4.15 (a) <sup>1</sup>H NMR spectrum of [Ru]-23 in D<sub>2</sub>O. (b) 149
  <sup>1</sup>H NMR spectrum of complex formed after
  [Ru]-23 (0.05 mmol) was heated in water (2 mL) at 50 °C for 1 hour. (c) <sup>1</sup>H NMR spectrum of complex formed after [Ru]-23 (0.05 mmol) was treated with formic acid (1 mmol) and sodium formate (0.05 mmol) in water (2 mL) at 0 °C for 1 hour showing the generation of Ru-formate species
- Figure 4.16 Temperature dependent (30 °C 90 °C) mass 150 study for the transformation of Ru-formate species to Ru-hydride species. Gas bubbles as observed in the vial during the heating of Ru-formate complex inferred the decarboxylation of Ru-formate to Ru-hydride
- Figure 4.17 <sup>1</sup>H NMR spectra showing the generation of 151 Ru-hydride species during the treatment of [Ru]-18 (0.01 mmol) with sodium formate (0.05 mmol) in D<sub>2</sub>O (0.6 mL) at 25 °C
- Figure 4.18 Mass investigation of the reaction mixture of 152
  [Ru]-18 (0.005 mmol) treated with sodium formate (0.05 mmol) in water showing the colour change from the initial yellow-green to pale-brown and reverts back to pale-brown colour when treated with an excess of dil. HCl
- Figure 4.19 GC-TCD analysis of the (a) evolved gas 162 (H<sub>2</sub>:CO<sub>2</sub>  $\approx$  1:1) gas for the catalytic dehydrogenation of formic acid over [**Ru**]-18 catalyst. Reaction condition: [**Ru**]-18 (0.01 mmol), formic acid (0.8 M, 2.5 mL), sodium

formate (0.05 mmol), 90 °C. (Analysis is performed using Argon as the carrier gas). (b) Pure H<sub>2</sub> gas. (c) Pure CO gas (detection limit 10 ppm). (d) Pure CO<sub>2</sub> gas

Chapter 5. Efficient additive-free hydrogen production from formaldehyde-water over arene-ruthenium (II) complexes

- Figure 5.1 Comparative catalytic activity (TOFs) of water 195 soluble [Ru]-17 [Ru]-26 catalysts explored for H<sub>2</sub> production from aqueous formaldehyde. Reaction conditions: aqueous formaldehyde (0.8 M, 2.5 mL), Ru-catalyst (0.01 mmol) at 90 °C
- Figure 5.2 Time course plot for (a) HCOOH yield (as 199 determined by <sup>1</sup>H NMR using sodium acetate as the internal standard), and (b) nH<sub>2</sub>/nCO<sub>2</sub> in the gas released (as analysed by GC-TCD) during the catalytic hydrogen production from paraformaldehyde in water over the [Ru]-19 catalyst. Reaction conditions: paraformaldehyde (2 mmol), [Ru]-19 (0.01 mmol) at 90 °C
- Figure 5.3 Time-dependent pH plot for the catalytic 199 paraformaldehyde dehydrogenation reaction. Reaction conditions: [Ru]-19 (0.01 mmol), paraformaldehyde (0.8 M, 2.5 mL), 90 °C
- Figure 5.4 (a) Initial stage of the dehydrogenation of 200 aqueous formaldehyde (1 M, 10 mL) (37 wt.% formaldehyde) with [Ru]-19 (0.01 mmol) at various temperatures. (b) Arrhenius plot of initial TOF values (initial 20 mins) for

dehydrogenation of aqueous formaldehyde (1 M, 10 mL) with **[Ru]-19** (0.01 mmol)

- Figure 5.5 (a) Dehydrogenation of different 201 concentrations of aqueous paraformaldehyde (10 mL) with [Ru]-19 (0.01 mmol) at 90 °C.
  (b) Hydrogen production from paraformaldehyde (10 M, 10 mL) with [Ru]-19 (0.01 mmol) at 90 °C
- Figure 5.6 Bulk scale reaction for hydrogen production 202 from large content of paraformaldehyde (5 M, 20 mL) in water with [Ru]-19 (0.004 mmol) at 90 °C
- Figure 5.7 Long-term stability and recyclability 203 experiment for catalytic hydrogen production from aqueous formaldehyde (37 wt.%) over catalyst [Ru]-19. Reaction conditions: aq. formaldehyde (0.8 M, 2.5 mL), [Ru]-19 (10 mmol) at 90 °C, 2 mmol of aq. formaldehyde added after each cycle
- Figure 5.8 Control Hg(0) poisoning experiment. Reaction 204 conditions: Aqueous formaldehyde (0.8 M, 2.5 mL) and [Ru]-19 (0.01 mmol) at 90 °C with and without a large excess of elemental Hg(0)
- **Figure 5.9** ESI-MS showing the Ru-aqua species for the 205 reaction of **[Ru]-19** (0.01 mmol) stirred in water (2.5 mL) for 5 minutes at 50 °C
- Figure 5.10ESI-MS showing the Ru-methanediol species205for the reaction of [Ru]-19 (0.01 mmol) andaq. formaldehyde (37 wt.%) (2 mmol) in water(2.5 mL) for 10 minutes at 60 °C
- Figure 5.11Different intermediate species of the [Ru]-19206catalyst observed during mass investigation of

the reaction mixture of aqueous formaldehyde (0.8 M, 2.5 mL), **[Ru]-19** (0.01 mmol) heated at 60  $^{\circ}$ C - 90  $^{\circ}$ C

- Figure 5.12 Transformation of colour of reaction solution 207 and ESI-MS analysis (in definite time intervals) of the reaction aliquots for catalytic dehydrogenation of aq. formaldehyde (37 wt.%). Reaction conditions: aq. formaldehyde (0.8 M, 2.5 mL), [Ru]-19 (0.01 mmol), 90 °C
- Figure 5.13 Temperature dependent (30  $^{\circ}$ C 70  $^{\circ}$ C) mass 208 study for the transformation of Ru-formate species to Ru-hydride species
- Figure 5.14 Mass investigation of the reaction mixture of 210
  [Ru]-19 (0.005 mmol) treated with sodium formate (0.05 mmol) in water showing the colour change from the initial yellow-green to red-orange and subsequently to blue colour when treated with a few drops of dil. H<sub>2</sub>SO<sub>4</sub>
- Figure 5.15 <sup>1</sup>H NMR spectra showing the generation of 211 Ru-hydride species during the treatment of [**Ru]-19** (0.01 mmol) with sodium formate (0.1 mmol) in  $D_2O$  (0.6 mL) at 25 °C and regeneration of the Ru-aqua species after subsequent treatment with a few drops of dil. H<sub>2</sub>SO<sub>4</sub>
- Figure 5.16 Ru–formato and Ru–formato-d (deuterated) 212 species observed during mass investigation of the catalytic reaction aliquots. Reaction conditions: (CH<sub>2</sub>O)<sub>n</sub> or (CD<sub>2</sub>O)<sub>n</sub> (2 mmol), D<sub>2</sub>O (2.5 mL) and [Ru]-19 (0.01 mmol) at 90 °C

Figure 5.17 Time-dependent GC-TCD analysis of the 217 evolved gas (H<sub>2</sub> and CO<sub>2</sub>) during the dehydrogenation of paraformaldehyde. (a) initial 10 minutes;  $H_2:CO_2 \approx 5:1$  (b) After 30 minutes;  $H_2:CO_2 \approx 1.62:1$ . (c) After 50 minutes;  $H_2:CO_2 \approx 1.35:1$ . (d) After 75 minutes;  $H_2:CO_2 \approx 1.33:1.$  (e) After 115 minutes;  $H_2:CO_2 \approx 1:1$ . Reaction condition: **[Ru]-19** (0.01 mmol), paraformaldehyde (0.8 M, 2.5 mL), 90 °C. (Analysis is performed using Argon as the carrier gas, ratios calculated by the area of the peaks in the chromatograms with the help of calibration curves for both the gases)

#### Chapter 6. Summary and Future Scope

Figure 6.1 Comparative turnover numbers for different 228 Ru(II)-based catalytic systems developed in this thesis work for hydrogen production from C-1 based LOHCs

### List of Schemes

### Chapter 1. Introduction and Background

Scheme 1.1	Different water-soluble sulfonated phosphine	7
	ligands explored by Laurenczy et. al	
Scheme 1.2	Oligocationic triarylphosphine based ligands	8
	with ammoniomethyl substitutions explored	
	for formic acid dehydrogenation	
Scheme 1.3	Aromatic phosphine based ligands bearing	9
	sulfonate groups explored for formic acid	
	dehydrogenation	
Scheme 1.4	Some precious metal- based catalysts explored	10
	for hydrogen production from formic acid	
Scheme 1.5	Two types of reaction pathways reported for	11
	formic acid dehydrogenation with C-3 by	
	Huang <i>et al</i> .	
Scheme 1.6	Some non-precious metal-based catalysts	15
	explored for hydrogen production from formic	
	acid	
Scheme 1.7	Plausible reaction pathway of formic acid	16
	dehydrogenation with C-20	
Scheme 1.8	Two-step pathway for hydrogen production	17
	from formaldehyde-water	
Scheme 1.9	Some metal-based catalysts explored for	18
	hydrogen production from formaldehyde-	
	water	
Scheme 1.10	Deprotonation equilibrium involved in the	19
	catalytic system reported by Suenobu et al.	
Scheme 1.11	Plausible mechanism of two-step	19
	dehydrogenation of paraformaldehyde to $\mathrm{H}_2$	
	and $CO_2$ with C-25	

Scheme 1.12 General procedure of synthesis of arene-Ru(II) 22 complexes based on various ligands

# Chapter 2. Hydrogen production from formic acid over water soluble arene ruthenium (II) complexes based on bidentate N,N donor ligands

Scheme 2.1	Complexes [Ru]-1 – [Ru]-7 explored for the	40		
	dehydrogenation of formic acid			
Scheme 2.2	Synthesis of N-methylquinolin-8-amine (L1)	40		
Scheme 2.3	Synthesis of complex [Ru]-4	40		
Scheme 2.4	Various intermediate species observed during	48		
	the mass investigation of an aqueous solution			
	of complex [Ru]-4 under varying controlled			
	reaction condition			
Scheme 2.5	A plausible route to the diruthenium species	52		
	([Ru]-2A'/[Ru]-4A'), the catalyst resting state,			
	via the coordinatively unsaturated species <b>[Ru]-2A/[Ru]-4A</b>			
Scheme 2.6	A plausible catalytic pathway for the base	57		
	assisted formic acid dehydrogenation over			
	complexes [Ru]-2 and [Ru]-4			

## Chapter 3. Hydrogen production from formic acid and formaldehyde over N,O donor ligand based arene-ruthenium (II) catalysts in water

Scheme 3.1	Literature available ruthenium-based catalysts	80
	for formic acid dehydrogenation in aqueous	
	medium	
Scheme 3.2	Complexes explored for the dehydrogenation	83
	of formic acid in water	
Scheme 3.3	Literature available ruthenium-based catalysts	96
	for hydrogen production from formaldehyde	
	in water	

Scheme 3.4 A plausible pathway for dehydrogenation of 100 aqueous formaldehyde and formic acid over [Ru]-8

### **Chapter 4.** Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water

Scheme 4.1	Literature known molecular catalysts for	132
	formic acid dehydrogenation	
Scheme 4.2	Synthesis of bis-imidazole methane ligated	135
	arene-ruthenium(II) complexes ([Ru]-17 –	
	[ <b>Ru]-26</b> )	
Scheme 4.3	A plausible pathway for the dehydrogenation	154
	of formic acid over bis-imidazole methane	

ligated arene-ruthenium(II) complexes

## Chapter 5. Efficient additive-free hydrogen production from formaldehyde-water over arene-ruthenium (II) complexes

Scheme 5.1	Literature known molecular catalysts for	193
	hydrogen generation from formaldehyde-	
	water system	
Scheme 5.2	A plausible pathway for hydrogen production	213
	from formaldehyde-water system over Ru(II)	

catalysts

#### **List of Tables**

## Chapter 2. Hydrogen production from formic acid over water soluble arene ruthenium (II) complexes based on bidentate N,N donor ligands

Table 2.1Catalytic dehydrogenation of formic acid over42various catalysts

Table 2.2	Optimization of reaction conditions for the	43
	dehydrogenation of formic acid over complex	
	[Ru]-2 and [Ru]-4 in water	
Table 2.3	KIE in the dehydrogenation of formic acid	56
	using complex [Ru]-4	
Table 2.4	Single crystal X-ray refinement data for	62
	complex [Ru]-2A'	
Table 2.5	Selected bond lengths (Å) for complex [Ru]-	63
	2A'	
Table 2.6	Selected bond angles (°) for complex [Ru]-2A'	63

## Chapter 3. Hydrogen production from formic acid and formaldehyde over N,O donor ligand based arene-ruthenium (II) catalysts in water

Table 3.1	Dehydrogenation of formic acid in water using 8	
	[Ru]-8 – [Ru]-16	
Table 3.2	KIE in the dehydrogenation of formic acid	95
	over [ <b>Ru]-8</b>	
Table 3.3	Catalytic dehydrogenation of formaldehyde	97
	over [Ru]-8 in water	
Table 3.4	Single crystal X-ray refinement data for	116
	complex [Ru]-9	
Table 3.5	Selected bond lengths (Å) for complex [Ru]-9	117
Table 3.6	Selected bond angles (°) for complex [Ru]-9	117
Table 3.7	Single crystal X-ray refinement data for [Ru]-	118
	8A'	

Table 3.8	Selected bond lengths (Å) for complex [Ru]-	
	8A'	
Table 3.9	Selected bond angles (°) for complex [Ru]-8A'	120

## **Chapter 4.** Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water

Table 4.1	Effect of formic acid/sodium formate ratio on	142
	the catalytic dehydrogenation of formic acid	
Table 4.2	KIE in the dehydrogenation of formic acid	153
	over <b>[Ru]-18</b>	
Table 4.3	Single crystal X-ray refinement data for [Ru]-	177
	19 and [Ru]-22	
Table 4.4	Selected bond lengths (Å) for complex [Ru]-	178
	19	
Table 4.5	Selected bond angles (°) for complex [Ru]-19	179
Table 4.6	Selected bond lengths (Å) for complex [Ru]-	181
	22	
Table 4.7	Selected bond angles (°) for complex [Ru]-22	182

### Chapter 5. Efficient additive-free hydrogen production from formaldehyde-water over arene-ruthenium (II) complexes

Table 5.1	Hydrogen generation from aqueous 1	97
	formaldehyde over [Ru]-17 – [Ru]-26	
	catalysts	
Table 5.2	Production of $H_2$ from different conc. of 2	01
	paraformaldehyde in water catalysed by [Ru]-	
	19	
Table 5.3	Kinetic Isotope Effects (KIE) results for the 2	11
	hydrogen production from paraformaldehyde	
	in water over the [Ru]-19 catalyst	

### 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
К	Kelvin
D	Density
V	Volume
Μ	Molar
mM	Milli Molar
cm	Centimeter
0	Degree
°C	Degree centigrade
mL	Millilitre
μL	Microlitre

### Acronyms

L1	8-(N-methylamino)quinoline
L2	pyridine-2-ylmethanol
L3	1-(pyridin-2-yl)ethanol
L4	pyridine-2ylmethanamine
L5	$\{4,4'-(phenylmethylene)bis(2-ethyl-5-methyl-1H$
	imidazole)}
L6	{4,4'-((4-methoxyphenyl)methylene)bis(2-ethyl-5-
	methyl-1 <i>H</i> - imidazole)}
L7	{4,4'-((2-methoxyphenyl)methylene)bis(2-ethyl-5-
	methyl-1 <i>H</i> -imidazole)}
L8	{4,4'-((4-chlorophenyl)methylene)bis(2-ethyl-5-methyl-
	1 <i>H</i> -imidazole)}
L9	{4,4'-((2-chlorophenyl)methylene)bis(2-ethyl-5-methyl-
	1 <i>H</i> -imidazole)}
[Ru]-1	$[(\eta 6-C_6H_6)Ru(\kappa^2-NH_2NH_2-ethylenediamine)Cl]^+$
[Ru]-2	$[(\eta 6-C_6H_6)Ru(\kappa^2-N_{py}NH_2-8-aminoquinoline)Cl]^+$
[Ru]-3	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2-N_{py}NH_2-8-aminoquinoline)Cl]^+$
[Ru]-4	$[(\eta 6\text{-}C_6\text{H}_6)\text{Ru}(\kappa^2\text{-}L1)\text{Cl}]^+$
[Ru]-5	$[(\eta 6-C_6H_6)Ru(\kappa^2-bipyridine)Cl]^+$
[Ru]-6	$[(\eta 6-\text{benzene})\text{RuCl}_2]_2]$
[Ru]-7	$[(\eta 6-p-cymene)RuCl_2]_2]$
[Ru]-8	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2-L_2)Cl]^+$
[Ru]-9	$[(\eta 6\text{-}C_6\text{H}_6)\text{Ru}(\kappa^2\text{-}L2)\text{Cl}]^+$
[Ru]-10	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2-L_3)Cl]^+$
[Ru]-11	$[(\eta 6\text{-}C_6\text{H}_6)\text{Ru}(\kappa^2\text{-}L3)\text{Cl}]^+$
[Ru]-12	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2-1-(pyridin-2-yl)ethan-1-one)Cl]^+$
[Ru]-13	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2 - N_{py}O-8-hydroxyquinoline)Cl]^+$
[Ru]-14	$[(\eta 6-C_6H_6)Ru(\kappa^2-N_{py}O-8-hydroxyquinoline)Cl]^+$
[Ru]-15	$[(\eta 6\text{-}C_{10}\text{H}_{14})\text{Ru}(\kappa^2\text{-}\text{N}_{py}\text{O-picolinic acid})\text{Cl}]^+$
[Ru]-16	$[(\eta 6-C_{10}H_{14})Ru(\kappa^2-L4)Cl]^+$

- $[Ru]-17 \qquad [(\eta 6-C_{10}H_{14})Ru(\kappa^2-L5)Cl]^+$
- [Ru]-18 [( $\eta$ 6-C<sub>10</sub>H<sub>14</sub>)Ru( $\kappa$ <sup>2</sup>-L6)Cl]<sup>+</sup>
- [Ru]-19 [( $\eta$ 6-C<sub>10</sub>H<sub>14</sub>)Ru( $\kappa^2$ -L7)Cl]<sup>+</sup>
- [Ru]-20  $[(\eta 6-C_{10}H_{14})Ru(\kappa^2-L8)Cl]^+$
- [Ru]-21 [( $\eta$ 6-C<sub>10</sub>H<sub>14</sub>)Ru( $\kappa$ <sup>2</sup>-L9)Cl]<sup>+</sup>
- [Ru]-22  $[(\eta 6-C_6H_6)Ru(\kappa^2-L5)Cl]^+$
- [Ru]-23 [( $\eta$ 6-C<sub>6</sub>H<sub>6</sub>)Ru( $\kappa$ <sup>2</sup>-L6)Cl]<sup>+</sup>
- [Ru]-24  $[(\eta 6-C_6H_6)Ru(\kappa^2-L7)Cl]^+$
- [Ru]-25  $[(\eta 6-C_6H_6)Ru(\kappa^2-L8)Cl]^+$
- [Ru]-26  $[(\eta 6-C_6H_6)Ru(\kappa^2-L9)Cl]^+$
- NMR Nuclear Magnetic Resonance
- UV-vis UV-visible Spectroscopy
- ESI-MS Electrospray Ionization- Mass Spectrometry
- GC-TCD Gas Chromatography-Thermal conductivity detector
- TLC Thin Layer Chromatography
- SCXRD Single crystal X-ray Diffraction
- GOF Goodness of fit
- CDCl<sub>3</sub> Chloroform-d
- D<sub>2</sub>O Deuterium oxide
- Ar Argon
- O<sub>2</sub> Oxygen
- H<sub>2</sub> Dihydrogen
- N<sub>2</sub> Nitrogen
- py 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. Room temperature

temp.	Temperature
TON	Turnover number
TOF	Turnover frequency
DMOA	Dimethyloctylamine
Me	Methyl
br	Broad
cat.	Catalyst
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)

### Chapter 1 Introduction and Background

#### **1.1. Introduction**

To achieve the goals set out in the Paris Agreement in 2015, renewable energy needs to be produced and utilized at six times faster rate than at present. The historic agreement seeks to limit the average rise in the global temperature to below 2 °C in the 21st century. The utilization of renewable forms of energy along with greater efficiency is the key to achieve this. The challenge associated with it lies in the rapid development and modernization of human society which triggers a tremendous increase in energy demand. According to the International Energy Agency (IEA) 2019 world energy balances overview, the total energy consumption across the globe increased 2.3 times from 4242 Mtoes (Million tonnes of oil equivalent) in 1971 to 9717 Mtoes in 2017. The most significant increase in the energy consumption contribution from 23% in 1971 to 29% in 2017 was observed in the transportation sector. During the same period, the total primary energy supply increased 2.5 times worldwide from 5519 Mtoes in 1971 to 13792 Mtoes in 2017.<sup>[1]</sup>(Figure 1.1)



*Figure 1.1.* Sector wise total energy consumption of the world in 1971(*a*) and 2017(*b*). Total energy supply by the fuels globally of 1971(*c*) and 2017(*d*). Source: IEA (2019) world energy balances overview.<sup>[1]</sup>

Although the growth rate of the energy supply has matched that of the energy consumption, more than 80% of the energy supply came from fossil fuels including coal, oil and natural gas.<sup>[2]</sup> The fossil fuel sources are continually depleting worldwide and with the ever-growing energy consumption, the present energy supply system will not be able to meet the needs in the near future. The extensive use of fossil fuels has led to excess  $CO_2$  emissions. The average annual increase of  $CO_2$  in the atmosphere was 1.28 ppm from 1970 to 1979 and increased to 2.40 ppm from 2010 to 2019.<sup>[3]</sup> High levels of  $CO_2$  in the atmosphere causes excess greenhouse effect<sup>[4]</sup> leading to an increase in the average global temperature and several other ecological problems associated with it.<sup>[5]</sup> At present, the global emission trends are not on track to meet the goal targeted in the Paris Agreement and immediate action is crucial. In view of this, researchers across the globe have started to focus on environment friendly renewable sources of energy.

Renewable sources of energy include solar, wind, tidal, hydropower, biomass and geothermal.<sup>[6]</sup> These are clean, waste-free, recyclable and hence have huge potential for further development. However, the intermittent nature of generation of renewable energy hinders its extensive use.<sup>[7,8]</sup> The challenges associated with a sustainable energy system include a proper energy storage program which would store the renewable energy when it is not being produced and a suitable energy carrier which can act as an alternative to gasoline. In this regard, hydrogen is considered as the most suitable energy storage system and the most promising energy carrier for the future.<sup>[9]</sup>

#### 1.2. Hydrogen Energy: Advantages and Challenges

Hydrogen energy generated from renewable resources can be an ultimate solution to the global energy and environmental problems if utilized to its full potential.<sup>[10-14]</sup> There are several advantages of hydrogen as an energy carrier. For example, it has a long storage period as well as it is environment friendly due to the generation of only water as the by-product when hydrogen reacts with oxygen in a fuel cell to produce electricity. Additionally, the mass energy density of hydrogen is quite high as compared to petrol.<sup>[15,16]</sup> In view of all these advantages, hydrogen can be effectively utilized in most of the sectors like transportation, household energy supply and industries.<sup>[17]</sup> Hydrogen can be effectively utilized through on-board hydrogen fuel cells which are highly efficient and offer environment friendly technology for energy utilization.<sup>[18-21]</sup> The efficiency of hydrogen fuel cell engines is much higher than the gasoline powered engines<sup>[22]</sup> which can be further increased by utilizing the heat generated by the hydrogen fuel cell in heat and power systems.<sup>[22]</sup> The adoption of hydrogen energy can be initially started with private vehicles and buses.<sup>[23]</sup> The greatest advantage of hydrogen fuel-cell vehicles is the low CO<sub>2</sub> emissions which can go a long way in solving the threat of global warming and other climate changes associated with it.<sup>[24]</sup>

There are several challenges associated with hydrogen energy despite its great advantages. Being gaseous in nature, hydrogen has low volumetric energy density and therefore suitable handling and storage techniques are essentially to be in place for successful implementation of hydrogen economy. An inexpensive storage system with sufficient volumetric and gravimetric H<sub>2</sub> capacities, as well as with good lifespan is desired. On-board hydrogen storage systems should contain enough gas to satisfy the requirement of the vehicle and in addition excess weight and volume should be minimized.<sup>[25]</sup> The gravimetric and volumetric targets for on-board vehicle H<sub>2</sub> storage as set by the U.S Department of Energy are 5.5 wt.% and 40 g/L respectively.<sup>[26]</sup>

#### **1.3. Hydrogen Storage**

At present, hydrogen is stored physically as compressed gaseous hydrogen or in the form of liquid hydrogen.<sup>[27]</sup> The disadvantages of compressing hydrogen gas to such high pressures include increased cost of the material of storage tanks and safety issues while handling and storing it. Liquefaction is a complicated multistep cooling procedure which is expensive and require the storage tanks to be perfectly insulated.<sup>[28]</sup> To overcome the limitations of these common hydrogen storage methods, techniques such as physisorption in porous materials and several other new chemical methods have been initiated.<sup>[29,30]</sup> There are several advantages and disadvantages associated with the physisorption process. Some of the advantages include fast kinetics, reversibility and good cyclability<sup>[31]</sup> while the main disadvantage is that low temperature and/or high pressure is generally required to attain satisfactory storage capacities. In chemical hydrogen storage methods, hydrogen is bound covalently in solid or liquid form that can be released on heating or with the intervention of a suitable catalyst. The solid borohydrides,<sup>[32]</sup> carriers include metal hydrides, metal imides/amides<sup>[33]</sup> and ammonia borane.<sup>[34]</sup> The liquid organic hydrogen carriers (LOHCs) include cyclohexane and heterocycles,<sup>[35]</sup> ammonia,<sup>[33]</sup> hydrazine,<sup>[36]</sup> formic acid,<sup>[37-40]</sup> formaldehyde<sup>[41-46]</sup> and alcohols.<sup>[40,47]</sup> Since this thesis comprises of work on catalytic dehydrogenation of formic acid and formaldehyde, the subsequent sections provide the overview of literature reports of the same.

#### 1.4. Formic acid as a liquid organic hydrogen carrier

Formic acid (HCOOH, FA) is a colourless liquid with a strong odour at room temperature.<sup>[48]</sup> It has low toxicity and being liquid in nature makes its storage, handling and transportation much more convenient than gaseous hydrogen. Formic acid has a hydrogen content of 53 g/L or 4.4 wt. % which can be released on demand with the help of suitable catalysts under mild reaction conditions. Dehydrogenation of formic acid to produce one equivalent each of H<sub>2</sub> and CO<sub>2</sub> is thermodynamically favourable ( $\Delta G^{\circ} = -32.9 \text{ kJ mol}^{-1}$ ) at room temperature but kinetically not favoured (Figure 1.2). The reaction kinetics can be speeded up by the addition of a base which facilitates the formation of corresponding formates. The main advantage of using formic acid is its atom efficiency as the stored hydrogen is available fully without any loss. Besides the dehydrogenation of formic acid to H<sub>2</sub> and CO<sub>2</sub>, the dehydration reaction forming water and the poisonous CO gas is also thermodynamically feasible<sup>[38]</sup> and hence the catalyst should be selective for the generation of hydrogen, so that the reaction does not proceed in the undesired pathway.



Figure 1.2. Hydrogen economy with formic acid as storage medium and thermodynamics of the decomposition pathways of formic acid. Reproduced with permission from ref. 38 of Royal Society of Chemistry.

#### 1.4.1. Noble metal-based catalysts

In 1967, the first report on homogeneously catalyzed formic acid dehydrogenation was established by Coffey. He screened several transition metal based complexes having phosphine ligands using acetic acid as the solvent at 118 °C. The maximum turnover frequency (TOF) was achieved with [IrH<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] complex, which was also found to be active in the transfer hydrogenation of n-butyraldehyde to n-butanol with good yield.<sup>[49]</sup> In 1998, Puddephatt *et al.* reported the ruthenium based complex Ru<sub>2</sub>( $\mu$ -CO)(CO)<sub>4</sub>( $\mu$ -DPPM)<sub>2</sub> in acetone (TOF = 500 h<sup>-1</sup>) without any base at room temperature (RT).<sup>[50,51]</sup> In 2008, the potential of formic acid as a LOHC was highlighted by the reports of Laurenczy and Beller<sup>[52,53]</sup> and subsequently there was a huge surge in research in this field and very efficient molecular catalysts were developed in the last decade by different researchers.

Beller et al. screened different metal precursors and amines in formic acid dehydrogenation. They found that [RhCl<sub>3</sub>.xH<sub>2</sub>O] and [RuCl<sub>3</sub>.xH<sub>2</sub>O] were not active, while the Ru-dimer precursor [ $(\eta^{6}$ - $C_{10}H_{14}$ )RuCl<sub>2</sub>]<sub>2</sub> showed some activity which was enhanced with the use of longer carbon chains of aliphatic dimethyl amines. The complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] gave the highest TOF of 2688 h<sup>-1</sup> in formic acid dehydrogenation with NEt<sub>3</sub> as the base at 40 °C.<sup>[53]</sup> Laurenczy et al. employed the complex  $[Ru(H_2O)_6]$  (tos) (tos = toluene-4-sulfonate) with meta trisulfonated triphenylphosphine for aqueous phase formic acid dehydrogenation at 100 °C in a solution of HCOOH/HCOONa (9:1, 4 M).<sup>[52]</sup> They also studied the effect of different ratios of phosphine based ligands to Ru precursor.<sup>[54]</sup> The complex  $[Ru(H_2O)_6]^{2+}$  with two equivalents of TPPTS was found to be efficient in continuous hydrogen generation from FA over a duration of one month. RuCl<sub>3</sub> with various water-soluble sulfonated phosphine ligands (1-9 in Scheme 1.1) were also explored for hydrogen production from FA by the research group of Laurenczy<sup>[55]</sup> (Scheme 1.1).



*Scheme 1.1.* Different water-soluble sulfonated phosphine ligands explored by Laurenczy et al.<sup>[55]</sup>

1-5 showed catalytic activity till 20 cycles. 6 and 7 were unstable. 9 displayed higher catalytic activity than 8. The solubility and steric effects were influenced by the position and number of sulfonato groups. High reaction rate was achieved with 1 and 2 which was attributed to their combined basicity, steric and solubility effects. After this work, Laurenczy *et al.* employed a series of ammoniomethyl-substituted triaryl phosphines (10-15) with Ru for formic acid dehydrogenation<sup>[56]</sup> (Scheme 1.2).



**Scheme 1.2.** Oligocationic triarylphosphine based ligands with ammoniomethyl substitutions explored for formic acid dehydrogenation (Reaction condition: catalysts formed in situ with RuCl<sub>3</sub>.xH<sub>2</sub>O and two equivalents of phosphine to Ru, 28mM; HCOOH/HCOONa 9:1, 10 M; at 90 °C; TOF was calculated for the fifth cycle of each catalyst).<sup>[56]</sup>

Experimental results indicated that strong  $\sigma$ -donating phosphines were influential in promoting the catalytic dehydrogenation reaction. A TOF of 1430 h<sup>-1</sup> was achieved with **13** which could be attributed to a combined  $\sigma$ -donating strength, steric properties, and high hydrophilicity. In 2014, Laurenczy and co-workers reported a catalytic system with RuCl<sub>3</sub>.xH<sub>2</sub>O and various aromatic phosphines containing sulfonate groups<sup>[57]</sup> (Scheme 1.3).



Scheme 1.3. Aromatic phosphine based ligands bearing sulfonate groups explored for formic acid dehydrogenation (Reaction conditions:  $RuCl_3.xH_2O$ , 0.056 mmol; Ru/L = 1:2; HCOOH/HCOONa 9:1;  $H_2O 2.5$  mL; 90 °C; 750 rpm).<sup>[57]</sup>

The highest final TOF of 1668 h<sup>-1</sup> was achieved with **17** with Ru:**17** ratio of 2 among all the monophosphines explored in this study. The catalytic systems with diphosphines (**23**) achieved higher TONs as compared to the monophosphines but the TOFs were lower. Beller and co-workers achieved a TON of 260000 in formic acid dehydrogenation with an insitu generated catalytic system comprising of the Ru-dimer precursor [( $\eta^{6}$ -C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub>, 6 equivalents of dppe (1,2-bis(diphenylphosphino)) butane and N,N'-dimethyl-n-hexylamine.<sup>[58]</sup> In 2018, Beller *et al.* 

reported base free hydrogen production from FA using the catalyst  $RuH_2(PPh_3)_4$  where a TOF of 36000 h<sup>-1</sup> was achieved at 60 °C and no significant loss in the catalytic activity was observed even after 4 months.<sup>[59]</sup>

A general trend observed in the phosphine based catalytic systems for formic acid dehydrogenation was that the activities were related to the basicity of the ligand. Ligands with higher basicity had strong  $\sigma$ -donating ability which was influential in achieving higher activities. The solubility of the ligand in the chosen solvent system as well as the steric effect had a role to play in achieving higher catalytic activities for the dehydrogenation reaction. Majority of the phosphines are poorly soluble in water; hence some organic solvent was required for most of the catalytic systems.



*Scheme 1.4.* Some precious metal-based catalysts explored for hydrogen production from formic acid.

Several nitrogen based ligands were also extensively explored in formic acid dehydrogenation (Scheme 1.4). For instance, Huang et al. reported the complex C-1 (Scheme 1.4) with a PNP-Pincer ligand which gave a TON of 95000 in DMSO at 50 °C. The presence of amines in the catalytic mixture further enhanced the catalytic robustness and a TON of 1000000 was achieved in 150 h.[60] Gonsalvi et al. developed the complex C-2 (Scheme 1.4) having a linear tetraphos ligand where the meso-isomer was more active than the rac-isomer. A TON of 220000 was achieved at 60 °C with this catalytic system in DMOA. Continuous H<sub>2</sub> generation made it possible for the fuel cell to generate electricity and drive electric fans.<sup>[61]</sup> Huang and co-workers recently reported an arene-Ru(II) complex C-3 (Scheme 1.4) bearing a bis-imidazoline ligand for hydrogen production from formic acid in aqueous medium. High catalytic TON of 350000 and TOF of 12000 h<sup>-1</sup> was achieved with this catalytic system. Two types of reaction pathways based on base free and base assisted reaction conditions was established by experimental and DFT studies (Scheme 1.5). More importantly, high pressure (24 MPa) gas generation was achieved through dehydrogenation of formic acid.<sup>[62]</sup>



Scheme 1.5. Two types of reaction pathways reported for formic acid dehydrogenation with C-3 by Huang et al. Reproduced with permission from ref. 62 of American Chemical Society.

Himeda et al. reported a series of Cp\*Ir catalysts for hydrogen production from formic acid in aqueous medium. The Cp\*Ir complex having OH substitution at the 4,4' position of the bipyridine ring (C-5) (Scheme 1.4) displayed 80 times higher activity than the Cp\*Ir complex with unsubstituted bipyridine (C-4) $^{[63]}$  (Scheme 1.4). The position of hydroxyl groups in bipyridine (C-6) (Scheme 1.4) was also found to affect the rate-determining step in the catalytic cycle.<sup>[64]</sup> Hydrogen production from formic acid generally proceeds through 3 steps : (i) generation of a formato complex by reaction of the active form of the catalyst and formate anion, (ii) decarboxylation of the formato complex to generate a metal-hydride species, and (iii) proton assisted hydrogen release from the metal-hydride complex. It was found that the ratedetermining step of C-5 was step (iii), whereas the rate-determining step of C-6 was step (ii). This was presumably due to the presence of pendant OH group near the metal center and was supported by DFT calculations<sup>[65]</sup> (Figure 1.3).



*Figure 1.3. Proposed mechanism and different rate-determining steps for complexes with 4-dihydroxy bipyridine and 6-dihydroxy bipyridine.*<sup>[65]</sup>

Subsequently, Himeda *et al.* developed a complex C-7 (Scheme 1.4) having an imidazoline based ligand combined with dihydroxy-pyrimidine to achieve a TON and TOF of 68000 and 322000  $h^{-1}$  respectively under reflux conditions.<sup>1661</sup> The pyridine analogue C-8 (Scheme 1.4) of C-7 was also effective and showed good catalytic

activity for formic acid dehydrogenation.<sup>[67]</sup> Li et al. reported a Cp\*Ir complex C-9 (Scheme 1.4) containing a bisimidazoline ligand to achieve the highest TOF of 4875000 h<sup>-1</sup> for formic acid dehydrogenation in water.<sup>[68]</sup> Himeda and co-workers also developed a Cp\*Ir pyridyl imidazoline complex C-10 (Scheme 1.4) with which highly robust hydrogen generation was achieved from formic acid.<sup>[69]</sup> The DHPT based catalyst C-11 (Scheme 1.4) was highly robust towards hydrogen generation from FA and a TON of 5000000 was reported with this catalytic system.<sup>[70]</sup> The Cp\*Ir complex bearing N-trifyl-1,2diphenylethylenediamine (C-12) (Scheme 1.4) was developed by Ikariya et al. for base free formic acid dehydrogenation. The Ir-H intermediate was isolated and a maximum TOF of above 6000 h<sup>-1</sup> could be achieved with this catalytic system. For protonation of metal hydrides, a proton relay mechanism with the involvement of the amine ligand and water was proposed.<sup>[71]</sup> Laurenczy et al. explored some Cp\*Ir complexes with non-aromatic diamine type ligands for formic acid dehydrogenation in aqueous medium among which the C-13 (Scheme 1.4) complex bearing 1,2-diaminocyclohexane ligand was found to be most efficient and achieved a TOF of 3300 h<sup>-1</sup> at 90 °C.<sup>[72]</sup> A water-soluble Ir-dihydride complex C-14 (Scheme 1.4) was reported by Joo and co-workers which exhibited excellent catalytic activity for formic acid dehydrogenation in water to achieve a TOF of 298000 h<sup>-1</sup> at 100 °C. The catalyst was highly soluble in water and 5 catalytic cycles could be achieved to obtain a TON of 674000 in 40 h.<sup>[73]</sup> The complex C-15 (Scheme 1.4) reported by Willams et al. catalyzed the dehydrogenation of neat FA with the addition of HCOONa (5 mol %) as the cocatalyst. A TON of 12530 could be achieved in 13 h at 90 °C.<sup>[74]</sup> Li et al. achieved a record turnover number of 5020000 in formic acid dehydrogenation in water by employing a Cp\*Ir-dioxime-based complex C-16 (Scheme 1.4). The high activity of the catalyst was attributed to the electron donating property of the amine substituent and the dioxime structure of the ligand.<sup>[75]</sup> Very recently, Himeda et al. have investigated some amine substituted bipyridine coordinated Cp\*Ir complexes C-17 (Scheme 1.4) for formic acid dehydrogenation which exhibited higher activity than the

hydroxy substituted bipyridine (C-5 and C-6). Interestingly, the Cp\*Ir complex with *p*-substituted amino groups displayed higher activity than *o*-substituted amine. Investigations revealed that the stability of the hydride intermediate had a significant role in the observed trend in activity.<sup>[76]</sup>

From the rich literature reports of formic acid dehydrogenation with Cp\*Ir catalysts bearing different ligand moieties, it was inferred that different substitutions in the ligand moiety alters the catalytic activity and more electron donating substituents resulted in higher catalytic activities. At few instances, steric hindrance also played an important role in tuning the catalytic activities. Pendant OH groups were found to have a significant effect on the catalytic activity by the formation of certain intermediates which lowered the overall activation barrier. When pyridine was replaced by other coordinating N atoms with high electron donating ability, the catalytic activities improved. So, ligand design played a vital role in the activity and durability of the catalyst towards hydrogen production from formic acid. Figure 1.4 depicts the progressive development of some ligands for formic acid dehydrogenation in water.



*Figure 1.4. Progressive development of some ligands for formic acid dehydrogenation in water.* 

#### 1.4.2. Non-noble metal-based catalysts



*Scheme 1.6.* Some non-precious metal-based catalysts explored for hydrogen production from formic acid.

Laurenczy et al. are the first to report formic acid dehydrogenation by an iron-based catalyst. They investigated Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O with phosphine based tetradentate ligand to achieve efficient hydrogen production from formic acid.<sup>[77]</sup> Subsequently, Laurenczy et al. studied the catalytic system comprising of Fe(BF<sub>4</sub>)<sub>2</sub> with water-soluble m-trisulfonated-tris[2-(diphenylphosphino)ethyl] phosphine sodium salt C-18 (Scheme 1.6) for formic acid dehydrogenation at 80 °C. This catalytic system was active in water, the green solvent as per excellence and an initial TOF of 200 h<sup>-1</sup> could be achieved.<sup>[78]</sup> Li et al. developed a Fe-H complex C-19 (Scheme 1.6) bearing a C,N cyclometalated ligand for hydrogen production from FA. A TON of 620 was achieved in 1,4-dioxane at 80 °C with the addition of NEt<sub>3</sub> and LiBF<sub>4</sub>.<sup>[79]</sup> Milstein and co-workers explored a Fe dihydride pincer complex trans-[Fe(tBuPNP)(H)<sub>2</sub>(CO)] for formic acid dehydrogenation under mild reaction conditions in 2013. A TON of 100000 could be achieved with this catalytic system in the presence of NEt<sub>3</sub>.<sup>[80]</sup> Subsequently Gonsalvi et al. developed a PNP-pincer type Fe complex with a 2,6-diaminopyridine moiety C-20 (Scheme 1.6) and explored it for hydrogen production from formic acid. TON and TOF values of 10000 and 2635 h<sup>-1</sup> respectively could be achieved with this

catalyst with NEt<sub>3</sub> as an additive at 80 °C. A plausible mechanism was proposed as shown in Scheme 1.7. The formato and the dihydride intermediate species (**C-20'** and **C-20''**) were detected by <sup>1</sup>H NMR studies. The presence of amines helped in activating the precatalyst **C-20** by elimination of bromide to creating a vacant coordination site at the metal center.<sup>[81]</sup>



Scheme 1.7. Plausible reaction pathway of formic acid dehydrogenation with C-20. Reproduced with permission from ref. 81 of American Chemical Society.

The same research group also investigated formic acid dehydrogenation using a tetraphos ligand. The catalytic activity of the *rac*-isomer was found to be higher than the *meso*-isomer. The metal to ligand ratio in the reaction also played a crucial role in tuning the catalytic activities. A TON of 6061 could be achieved with **C-21** (Scheme 1.6) for formic acid dehydrogenation at 60 °C.<sup>[82]</sup> Enthaler *et al.* investigated a Ni-H complex bearing a PCP-pincer ligand **C-22** (Scheme 1.6) in formic acid dehydrogenation usig nOctNMe<sub>2</sub> as an additive to achieve a TON of 481 in 2 h.<sup>[83]</sup> Very recently, Beller *et al.* reported a series of phosphine free manganese catalysts for the dehydrogenation of formic acid among which the complex Mn(pyridine-imidazoline)(CO)<sub>3</sub>Br (**C-23**) (Scheme 1.6) outperformed over the others to achieve a turnover number of 5763 in 45 h. Mechanistic insights were
provided with the help of various spectro analytical tools and kinetic isotope effect (KIE) experiments.<sup>[84]</sup>

#### 1.5. Formaldehyde-water system as a potential LOHC

The formaldehyde-water (HCHO-H<sub>2</sub>O) system is another potential LOHC, where water can act as a hydrogen storage material in combination with formaldehyde or paraformaldehyde to form methanediol which is subsequently dehydrogenated to release hydrogen and CO<sub>2</sub>. Hence, both molecules can act as hydrogen sources giving a weight efficiency of 8.4% assuming one equivalent each of water and formaldehyde. It is considerably higher than formic acid (4.4 wt.%) and the hydrogen efficiency is 5.0 wt.% if aqueous formaldehyde (37 wt.%) is used. In addition, the dehydrogenation reaction of formaldehyde/water is thermodynamically feasible ( $\Delta H_r = -35.8 \text{ kJ mol}^{-1}$ ) and hence it is possible to achieve hydrogen production from HCHO-H<sub>2</sub>O system with the help of suitably designed catalytic systems under mild reaction conditions. The dehydrogenation reaction generally proceeds through a two-step pathway, the first step being the dehydrogenation of methanediol (formed by hydration) to formic acid releasing one equivalent of H<sub>2</sub> and the second step being the dehydrogenation of formic acid to produce one equivalent each of H<sub>2</sub> and CO<sub>2</sub>.<sup>[45,46]</sup> (Scheme 1.8)



*Scheme 1.8. Two-step pathway for hydrogen production from formaldehyde-water.* 



*Scheme 1.9. Some metal-based catalysts explored for hydrogen production from formaldehyde-water.* 

The first report on homogeneously catalyzed hydrogen production from HCHO-H<sub>2</sub>O system was established by Prechtl *et al.* by employing the diruthenium complex [{Ru( $\eta^6$ -p-cymene)}<sub>2</sub>( $\mu$ -HCOO)( $\mu$ -Cl)( $\mu$ -H)]<sup>+</sup> (**C-24**) (Scheme 1.9) to achieve a turnover number of 700 at 95 °C. They first investigated the Ru-dimer precursor [( $\eta^6$ -C<sub>10</sub>H<sub>14</sub>)RuCl<sub>2</sub>]<sub>2</sub> for the dehydrogenation reaction and found that the complex **C-24** was the active component. Subsequently, they synthesized and isolated the active complex **C-24** and employed it for hydrogen production from HCHO-H<sub>2</sub>O.<sup>[45]</sup> Subsequently, Suenobu *et al.* reported the complex [Ir<sup>III</sup>(Cp\*)(4-(1H-pyrazol-1-yl)benzoic acid)-(H<sub>2</sub>O)]<sup>+</sup> (**C-25**) (Scheme 1.9) for hydrogen production from paraformaldehyde-water to achieve a TON of 51 at 60 °C under alkaline reaction conditions (pH = 11). A pH dependent deprotonation equilibrium was observed in the catalytic system (Scheme 1.10) and accordingly a catalytic cycle was proposed as shown in scheme 1.11.



Scheme 1.10. Deprotonation equilibrium involved in the catalytic system reported by Suenobu et al. Reproduced with permission from ref. 42 of Royal Society of Chemistry.



Scheme 1.11. Plausible mechanism of two-step dehydrogenation of paraformaldehyde to  $H_2$  and  $CO_2$  with C-25. Reproduced with permission from ref. 42 of Royal Society of Chemistry.

At a basic pH, C-25 is converted to the hydroxo complex (C-25A), which subsequently reacts with paraformaldehyde to generate the Irmethanediol intermediate (C-25B). Next, the Ir-hydride intermediate (C-25D) and formic acid is generated by  $\beta$ -hydrogen elimination from the Ir-methanediol species. Subsequently, water assisted hydrogen release occurs from the Ir-hydride intermediate (C-25D) to regenerate C-25A. (Scheme 1.11) The formation of the methanediol, formate and hydride intermediates were evidenced by UV-vis, ESI-MS and <sup>1</sup>H NMR studies.<sup>[42]</sup> Following this report, in the same year Fujita *et al.* investigated the complex [Ir<sup>III</sup>(Cp\*)(6,6'-dionato-2,2'-bipyridine)-(OH)]<sup>-</sup> (C-26) (Scheme 1.9) for hydrogen production from HCHO-H<sub>2</sub>O under basic reaction conditions to achieve a low TON of 178 under reflux conditions.<sup>[43]</sup> In 2017, Grutzmacher et al. reported the Ru-based complex C-27 (Scheme 1.9) for hydrogen production from aqueous formaldehyde with a high initial TOF of >20000  $h^{-1}$  at 60 °C albeit the reaction required a high concentration of base (KOH) and was carried out in THF. A TON of 1787 was achieved after six cycles.<sup>[44]</sup> Highly basic medium and the use of organic solvents are not compatible with the practical use of the catalytic process, hence in this direction Himeda et al. very recently investigated the complex  $[(\eta^6-C_6Me_6)Ru(2,2'$ diaminobiphenyl)( $H_2O$ )]<sub>2</sub><sup>+</sup> (C-28) (Scheme 1.9) for additive free hydrogen production from HCHO-H2O with high efficiency and selectivity. A record turnover number of 24000 with initial TOF of 8300  $h^{-1}$  was achieved with this catalytic system. Based on experimental studies and DFT calculations, a stepwise mechanism was proposed for the catalytic hydrogen production from HCHO-H<sub>2</sub>O.<sup>[46]</sup>

#### 1.6. Half sandwich arene-Ru(II) complexes

Half-sandwich ruthenium catalysts comprising of arene ligands are the most popular class of Ru-catalysts as they provide stability to the Ru(II) complexes. In general, arene-Ru complexes resemble a piano stool, with the arene ligand at the top and the other ligands represent the legs of the stool. The arene-ruthenium complexes are generally synthesized by using the arene-Ru dimer (arene =  $C_6H_6$  or  $C_{10}H_{14}$  *etc.*) with specific ligands. The  $\eta^6$ -arene ring coordinated to the Ru center stabilizes Ru in +2 oxidation state by preventing its oxidation to +3 state.<sup>[85-88]</sup> Three coordination sites of arene coordinated metal center are occupied by different monodentate, or polydentate ligands along with monodentate leaving groups stabilized by overall charge (n+) of the metal center. The arene ring is arranged in a planar fashion at the top of the metal center with the ligands and leaving groups behaving as three legs. Overall, a half sandwich "piano-stool" type structure is resembled with pseudo-octahedral geometry around the metal center. (Figure 1.5)



*Figure 1.5. Piano stool structure of half-sandwich arene-Ru(II) complexes.* 

There are several advantages of using the arene ring as a polyhapto ligand for instance the catalytic activity can be tuned with different substitutions on the arene ring, good water solubility of the half sandwich complexes and additionally it controls the thermodynamics and kinetics of these catalytic systems and significantly tune of the activities of the complexes for applications in various research fields. Furthermore, the choice of the arene ring together with the leaving group and mono, or bidentate ligands play a significant role in tuning the catalytic activity in terms of rate of hydrolysis of Ru-Cl bond and ease of dissociation of ligands during the catalytic cycle. The structure of the arene-Ru(II) complexes are substantiated by <sup>1</sup>H, <sup>13</sup>C NMR, infrared spectroscopy and single crystal X-ray analysis. The arene-Ru(II) complexes find wide applications in many organic transformations due to their versatile chemistry in mild reaction conditions. Based on

different type of ligands, neutral, moncationic or dicationic arene-Ru(II) complexes can be synthesized as depicted in Scheme 1.12.<sup>[88]</sup>



Scheme 1.12. General procedure of synthesis of arene-Ru(II) complexes based on various ligands. Reproduced with permission from ref. 88 of Royal Society of Chemistry.

# **1.7.** Research gaps in transition metal catalyzed hydrogen production from formic acid and formaldehyde-water

- For hydrogen production from formic acid, extensive literature reports revealed that Cp\* Ir based catalysts are very effective in aqueous-phase catalytic dehydrogenation reactions medium and exhibit fascinating chemistry but iridium is expensive and therefore cost effective, yet efficient catalytic systems are sought after.
- Most of the active catalysts reported are primarily phosphine based ligands which suffer from poor water solubility and hence some organic solvent/additive is required which in turn is not suitable for the sustainability of the process.

- The catalytic reaction intermediates involved are studied theoretically with the help of DFT calculations in many of the reports. Therefore, efforts need to be made to identify/isolate crucial reaction intermediates.
- For hydrogen production from formaldehyde-water, only a few reports are available and most of these catalytic systems required a high concentration of base and suffer from low catalytic turnovers.

## 1.8. Objective of this thesis

Design of efficient catalysts for hydrogen production from the LOHCs is in current demand from the viewpoint of hydrogen as an energy carrier for the future. Ruthenium based complexes are attractive candidates owing to their versatile activities and low cost as compared to the iridium-based complexes. Thus, by employing ruthenium-based metal catalysts, this thesis is targeted to achieve the following goals:

- To synthesize arene-Ru(II) based catalytic systems for efficient hydrogen production formic acid and formaldehyde in water under ambient reaction conditions.
- To explore ligand systems which can reveal the structure-activity relationship of the ligands attached to the metal center in the catalytic reaction.
- To characterize the synthesized ligands and complexes through various spectroscopic and other techniques.
- To study the different reaction parameters such as temperature and pH of the reaction medium which influence the kinetics of the catalytic reactions.
- For practical purposes, scaling up the catalytic activities of the developed catalysts by performing recyclability and bulk-scale reactions.
- To extensively investigate the reaction pathway by identifying and isolating different active catalytic reaction intermediates involved in the catalytic dehydrogenation process.

#### **1.9. Organization of thesis**

In *chapter 1*, the need for LOHCs in the current scenario and relevant literature survey for homogeneously catalyzed hydrogen production from formic acid and formaldehyde has been presented.

In *chapter 2*, synthesis, characterization and catalytic activities of watersoluble arene-Ru(II) complexes based on N,N bidentate donor ligands for hydrogen production from formic acid have been discussed.

In *chapter 3*, synthesis, characterization and catalytic activities of arene-Ru(II) complexes based on N,O bidentate donor ligands for catalytic hydrogen production formic acid and formaldehyde in water have been studied.

In *chapter 4*, synthesis, characterization and catalytic activities of watersoluble arene-Ru(II) complexes based on bis-imidazole methane based ligands for catalytic hydrogen production from formic acid has been extensively studied.

In *chapter* 5, efficient additive-free hydrogen production from formaldehyde-water over arene-Ru(II) complexes has been described.

In *chapter 6*, a summary of the present thesis work has been presented including the achievements and future scope of the current work is described.

#### 1.10. References

- 1. World Energy balances Overview, (2019), https://www.iea.org/reports/world-energy-balancesoverview/world.
- Züttel A. (2004), Hydrogen storage methods, *Naturwissenschaften.*, 91, 157–172 (10.1007/s00114-004-0516x).
- Earth's CO<sub>2</sub>, (2020). http://www.CO2.earth/. accessed Mar 25, 2020
- 4. Bolin B., Doos B. R., (1989), Greenhouse effect, web, John Wiley

and Sons Inc., New York, NY.

- Schneider S.H. (1988), Greenhouse Effect : Science and Policy, Science, 243, 771–779 (DOI: 10.1126/science.243.4892.771)
- Christopher K., Dimitrios R. (2012), A review on exergy comparison of hydrogen production methods from renewable energy sources, *Energy Environ. Sci.*, 5, 6640–6651 (DOI:10.1039/c2ee01098d)
- Moriarty P., Honnery D. (2017), Sustainable Energy Resources, *Clean Energy Sustain. Dev.*, 3–27 (DOI:10.1016/B978-0-12-805423-9.00001-6)
- Azarpour A., Suhaimi S., Zahedi G., Bahadori A. (2013), A Review on the Drawbacks of Renewable Energy as a Promising Energy Source of the Future, *Arab. J. Sci. Eng.*, 38, 317–328 (DOI:10.1007/s13369-012-0436-6)
- Turner J.A. (1999), A Realizable Renewable Energy Future, Science, 285, 687–689 (DOI:10.1126/science.285.5428.687)
- Momirlan M., Veziroglu T. (2002), Current status of hydrogen energy, Renew. Sustain. Energy Rev., 6, 141–179 (DOI:1016/S1364-0321(02)00004-7)
- Dunn S. (2002), Hydrogen futures: toward a sustainable energy system, *Int. J. Hydrogen Energy.*, 27, 235–264 (DOI:1016/S0360-3199(01)00131-8)
- Midilli A., Ay M., Dincer I., Rosen M.A. (2005), On hydrogen and hydrogen energy strategies, *Renew. Sustain. Energy Rev.*, 9, 255–271 (DOI:10.1016/j.rser.2004.05.003)
- Midilli A., Dincer I. (2007), Key strategies of hydrogen energy systems for sustainability, *Int. J. Hydrogen Energy.*, 32, 511–524 (DOI:1016/j.ijhydene.2006.06.050)
- 14. Honnery D., Moriarty P. (2009), Estimating global hydrogen production from wind, *Int. J. Hydrogen Energy.*, 34, 727–736

(DOI:10.1016/j.ijhydene.2008.11.001)

- Schlapbach L., Züttel A. (2001), Hydrogen-storage materials for mobile applications, *Nature.*, 414, 353–358 (DOI:10.1038/35104634)
- Kapdan I.K., Kargi F. (2006), Bio-hydrogen production from waste materials, *Enzyme Microb. Technol.*, 38, 569–582 (DOI:1016/j.enzmictec.2005.09.015)
- Midilli A., Ay M., Dincer I., Rosen M.A. (2005), On hydrogen and hydrogen energy strategies II: future projections affecting global stability and unrest, *Renew. Sustain. Energy Rev.*, 9, 273– 287 (DOI:1016/j.rser.2004.05.002)
- Leone P., Lanzini A., Squillari P., Asinari P., Santarelli M., Borchiellini R., Calì M. (2008), Experimental evaluation of the operating temperature impact on solid oxide anode-supported fuel cells, *Int. J. Hydrogen Energy.*, 33, 3167–3172 (DOI:10.1016/j.ijhydene.2008.03.042)
- Crabtree G.W., Dresselhaus M.S. (2008), The Hydrogen Fuel Alternative, *MRS Bull.*, 33, 421–428 (DOI:10.1557/mrs2008.84)
- Lucia U. (2014), Overview on fuel cells, *Renew. Sustain. Energy Rev.*, 30, 164–169 (DOI:10.1016/j.rser.2013.09.025)
- Haseli Y. (2018), Maximum conversion efficiency of hydrogen fuel cells, *Int. J. Hydrogen Energy.*, 43, 9015–9021 (DOI:10.1016/j.ijhydene.2018.03.076)
- 22. European Commission, Directorate-General for Energy and Transport, Directorate-General for Research and Innovation, (2003) *Hydrogen energy and fuel cells : a vision of our future : final report of the High Level Group*. Publications Office
- 23. Heid B., Linder M., Orthofer A., Wilthaner M. (2017),
  "Hydrogen: The next wave for electric 1348 vechicles?," https://www.mckinsey.com/industries/automotive-and-

assembly/our-insights/hydrogen-the-next-wave-for-1350 electric-vehicles#.html.

- Wang M. (2001), Well-to-wheel energy use and greenhouse gas emissions of advanced 1366 fuel/vehicle systems North American analysis, *1st ed., Argonne National Lab., IL (US), United States,.* (DOI:10.2172/781268)
- 25. Durbin D.J., Malardier-Jugroot C. (2013), Review of hydrogen storage techniques for on board vehicle applications, *Int. J. Hydrogen Energy.*, 38, 14595–14617 (DOI:1016/j.ijhydene.2013.07.058)
- Target Explanation Document: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles (2015), Washington, DC
- Leon A. (2008), Hydrogen Technology: mobile and portable applications, in: Hydrog. Technol. Mob. Portable Appl., 1st ed., Berlin,: pp. 81–128.
- Eberle U., Felderhoff M., Schüth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chemie Int. Ed.*, 48, 6608–6630 (DOI:10.1002/anie.200806293)
- Dalebrook A.F., Gan W., Grasemann M., Moret S., Laurenczy G. (2013), Hydrogen storage: beyond conventional methods, *Chem. Commun.*, 49, 8735 (DOI:10.1039/c3cc43836h)
- Broom D.P., (2011), Hydrogen Storage Materials: The Characterisation of Their Storage Properties, Springer Series in Green Energy and Technology;, London.
- Walker, G., (2008), Hydrogen Storage Technologies. In Solid-State Hydrogen Storage: Materials and Chemistry; Walker, G., Ed.; Woodhead Publishing Series in Electronic and Optical Materials; Woodhead Publishing: Cambridge, U.K., Chapter 1, pp 3–17.
- 32. Li H.-W., Yan Y., Orimo S., Züttel A., Jensen C.M. (2011),

Recent Progress in Metal Borohydrides for Hydrogen Storage, *Energies.*, 4, 185–214 (DOI:10.3390/en4010185)

- Gregory D.H. (2008), Imides and Amides as Hydrogen Storage Materials., in: Woodhead Publ. Ser. Electron. Opt. Mater., 2nd ed., Woodhead Publishing, Cambridge, U.K, pp. 450–477.
- Peng B., Chen J. (2008), Ammonia borane as an efficient and lightweight hydrogen storage medium, Energy Environ. Sci., 1, 479–483 (DOI:10.1039/b809243p)
- Zhu Q.-L., Xu Q. (2015), Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage, *Energy Environ*. *Sci.*, 8, 478–512 (DOI:10.1039/C4EE03690E)
- Moury R., Moussa G., Demirci U.B., Hannauer J., Bernard, Petit S. E., van der Lee A., Miele P. (2012), Hydrazine borane: synthesis, characterization, and application prospects in chemical hydrogen storage, *Phys. Chem. Chem. Phys.*, 14, 1768–1777 (DOI:10.1039/C2CP23403C)
- Grasemann M., Laurenczy G. (2012), Formic acid as a hydrogen source – recent developments and future trends, *Energy Environ*. *Sci.*, 5, 8171 (DOI:10.1039/c2ee21928j)
- Mellmann D., Sponholz P., Junge H., Beller M. (2016), Formic acid as a hydrogen storage material-development of homogeneous catalysts for selective hydrogen release, *Chem. Soc. Rev.*, 45, 3954–3988 (DOI:10.1039/c5cs00618j)
- Eppinger J., Huang K.-W. (2017), Formic Acid as a Hydrogen Energy Carrier, ACS Energy Lett., 2, 188–195 (DOI:10.1021/acsenergylett.6b00574)
- Sordakis K., Tang C., Vogt L.K., Junge H., Dyson P.J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*, 118, 372–433 (DOI:10.1021/acs.chemrev.7b00182)

- Fujita K.I., Kawahara R., Aikawa T., Yamaguchi R. (2015), Hydrogen Production from a Methanol-Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions, *Angew. Chemie - Int. Ed.*, 54, 9057–9060 (DOI:10.1002/anie.201502194)
- 42. Suenobu T., Isaka Y., Shibata S., Fukuzumi S. (2015), Catalytic hydrogen production from paraformaldehyde and water using an organoiridium complex, *Chem. Commun.*, 51, 1670–1672 (DOI:10.1039/c4cc06581f)
- 43. Heim L.E., Vallazza S., van der Waals D., Prechtl M.H.G. (2016), Water decontamination with hydrogen production using microwave-formed minute-made ruthenium catalysts, *Green Chem.*, 18, 1469–1474 (DOI:10.1039/C5GC01798J)
- 44. Trincado M., Sinha V., Rodriguez-Lugo R.E., Pribanic B., De Bruin B., Grützmacher H. (2017), Homogeneously catalysed conversion of aqueous formaldehyde to H<sub>2</sub> and carbonate, *Nat. Commun.*, 8, 1–11 (DOI:10.1038/ncomms14990)
- 45. Heim L.E., Schlörer N.E., Choi J.-H., Prechtl M.H.G., (2014), Selective and mild hydrogen production using water and formaldehyde, *Nat. Commun.*, 5, 3621 (DOI:10.1038/ncomms4621)
- 46. Wang L., Ertem M.Z., Kanega R., Murata K., Szalda D.J., Muckerman J.T., Fujita E., Himeda Y. (2018), Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity, *ACS Catal.*, 8, 8600–8605 (DOI:10.1021/acscatal.8b02088)
- Johnson T.C., Morris D.J., Wills M. (2010), Hydrogen generation from formic acid and alcohols using homogeneous catalysts, *Chem. Soc. Rev.*, 39, 81–88 (DOI:10.1039/B904495G)
- 48. Gibson H.W. (1969), Chemistry of formic acid and its simple derivatives, *Chem. Rev.*, 69, 673–692

(DOI:10.1021/cr60261a005)

- 49. Coffey R.S. (1967), The decomposition of formic acid catalysed by soluble metal complexes, *Chem. Commun.*, 923b-924 (DOI:10.1039/c1967000923b)
- Gao Y., Kuncheria J., Yap G.P.A., Puddephatt R.J. (1998), An efficient binuclear catalyst for decomposition of formic acid, *Chem. Commun.*, 2365–2366 (DOI:10.1039/a805789c)
- Gao Y., Kuncheria J.K., Jenkins H.A., Puddephatt R.J., Yap G.P.A. (2000), The interconversion of formic acid and hydrogen/carbon dioxide using a binuclear ruthenium complex catalyst, *J. Chem. Soc. Dalt. Trans.*, 2, 3212–3217 (DOI:10.1039/b004234j)
- Fellay C., Dyson P.J., Laurenczy G. (2008), A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst, *Angew. Chemie Int. Ed.*, 47, 3966– 3968 (DOI:10.1002/anie.200800320)
- Loges B., Boddien A., Junge H., Beller M. (2008), Controlled Generation of Hydrogen from Formic Acid Amine Adducts at Room Temperature and Application in H<sub>2</sub> /O<sub>2</sub> Fuel Cells, *Angew*. *Chemie Int. Ed.*, 47, 3962–3965 (DOI:10.1002/anie.200705972)
- Fellay C., Yan N., Dyson P.J., Laurenczy G. (2009) Selective Formic Acid Decomposition for High-Pressure Hydrogen Generation: A Mechanistic Study, *Chem. - A Eur. J.*, 15, 3752– 3760 (DOI:10.1002/chem.200801824)
- Gan W., Fellay C., Dyson P.J., Laurenczy G. (2010), Influence of water-soluble sulfonated phosphine ligands on ruthenium catalyzed generation of hydrogen from formic acid, *J. Coord. Chem.*, 63, 2685–2694 (DOI:10.1080/00958972.2010.492470)
- 56. Gan W., Snelders D.J.M., Dyson P.J., Laurenczy G. (2013), Ruthenium(II)-Catalyzed Hydrogen Generation from Formic

Acid using Cationic, Ammoniomethyl-Substituted Triarylphosphine Ligands, *ChemCatChem.*, 5, 1126–1132 (DOI:10.1002/cctc.201200782)

- 57. Guerriero, A. Bricout H., Sordakis K., Peruzzini M., Monflier E., Hapiot F., Laurenczy G., Gonsalvi L. (2014), Hydrogen Production by Selective Dehydrogenation of HCOOH Catalyzed by Ru-Biaryl Sulfonated Phosphines in Aqueous Solution, ACS Catal., 4, 3002–3012 (DOI:10.1021/cs500655x)
- Boddien A., Loges B., Junge H., Gärtner F., Noyes J.R., Beller M. (2009), Continuous Hydrogen Generation from Formic Acid: Highly Active and Stable Ruthenium Catalysts, *Adv. Synth. Catal.*, 351, 2517–2520 (DOI:10.1002/adsc.200900431)
- Prichatz C., Trincado M., Tan L., Casas F., Kammer A., Junge H., Beller M., Grützmacher H. (2018), Highly Efficient Base-Free Dehydrogenation of Formic Acid at Low Temperature, *ChemSusChem.*, 11, 3092–3095 (DOI:10.1002/cssc.201801072)
- 60. Pan Y., Pan C., Zhang Y., Li H., Min S., Guo X., Zheng B., Chen H., Anders A., Lai Z., Zheng J., Huang K. (2016), Selective Hydrogen Generation from Formic Acid with Well-Defined Complexes of Ruthenium and Phosphorus–Nitrogen PN 3 -Pincer Ligand, *Chem.–Asian J.*, 11, 1357–1360 (DOI:10.1002/asia.201600169)
- Mellone I., Bertini F., Peruzzini M., Gonsalvi L. (2016) An active, stable and recyclable Ru tetraphosphine-based catalytic system for hydrogen production by selective formic acid dehydrogenation, *Catal. Sci. Technol.*, 6, 6504–6512 (DOI:10.1039/C6CY01219A)
- 62. Guan C., Zhang D.-D., Pan Y., Iguchi M., Ajitha M.J., Hu J., Li H., Yao C., Huang M.-H., Min S., Zheng J., Himeda Y., Kawanami H., Huang K.-W. (2017), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N '-Diimine

Ligand, *Inorg. Chem.*, 56, 438–445 (DOI:10.1021/acs.inorgchem.6b02334)

- 63. Himeda Y. (2009), Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4'-dihydroxy-2,2'-bipyridine, *Green Chem.*, 11, 2018 (DOI:10.1039/b914442k)
- Wang W.-H., Xu S., Manaka Y., Suna Y., Kambayashi H., Muckerman J.T., Fujita E., Himeda Y. (2014), Formic Acid Dehydrogenation with Bioinspired Iridium Complexes: A Kinetic Isotope Effect Study and Mechanistic Insight, *ChemSusChem.*, 7, 1976–1983 (DOI:10.1002/cssc.201301414)
- Ertem M.Z., Himeda Y., Fujita E., Muckerman J.T. (2016), Interconversion of Formic Acid and Carbon Dioxide by Proton-Responsive, Half-Sandwich Cp\*Ir(III) Complexes: A Computational Mechanistic Investigation, ACS Catal., 6, 600– 609 (DOI:10.1021/acscatal.5b01663)
- 66. Wang W.-H., Ertem M.Z., Xu S., Onishi N., Manaka Y., Suna Y., Kambayashi H., Muckerman J.T., Fujita E., Himeda Y. (2015), Highly Robust Hydrogen Generation by Bioinspired Ir Complexes for Dehydrogenation of Formic Acid in Water: Experimental and Theoretical Mechanistic Investigations at Different pH, ACS Catal., 5, 5496–5504 (DOI:10.1021/acscatal.5b01090)
- Wang L., Onishi N., Murata K., Hirose T., Muckerman J.T., Fujita E., Himeda Y. (2017), Efficient Hydrogen Storage and Production Using a Catalyst with an Imidazoline-Based, Proton-Responsive Ligand, *ChemSusChem.*, 10, 1071–1075 (DOI:10.1002/cssc.201601437)
- 68. Wang Z., Lu S.-M., Li J., Wang J., Li C. (2015), Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an N, N '-Diimine Ligand in Water, *Chem. - A Eur.*

J., 21, 12592–12595 (DOI:10.1002/chem.201502086)

- Onishi N., Ertem M.Z., Xu S., Tsurusaki A., Manaka Y., Muckerman J.T., Fujita E., Himeda Y. (2016) Direction to practical production of hydrogen by formic acid dehydrogenation with Cp\*Ir complexes bearing imidazoline ligands, *Catal. Sci. Technol.*, 6, 988–992 (DOI:10.1039/C5CY01865J)
- Iguchi M., Himeda Y., Manaka Y., Kawanami H. (2016), Development of an Iridium-Based Catalyst for High-Pressure Evolution of Hydrogen from Formic Acid, *ChemSusChem.*, 9, 2749–2753 (DOI:10.1002/cssc.201600697)
- Matsunami A., Kayaki Y., Ikariya T. (2015) Enhanced Hydrogen Generation from Formic Acid by Half-Sandwich Iridium(III) Complexes with Metal/NH Bifunctionality: A Pronounced Switch from Transfer Hydrogenation, *Chem. - A Eur. J.*, 21, 13513–13517 (DOI:10.1002/chem.201502412)
- 72. Fink C., Laurenczy G. (2017), CO2 as a hydrogen vector transition metal diamine catalysts for selective HCOOH dehydrogenation, *Dalton. Trans.*, 46, 1670–1676 (DOI:10.1039/C6DT04638J)
- Papp G., Ölveti G., Horváth H., Kathó, Joó F. (2016), Highly efficient dehydrogenation of formic acid in aqueous solution catalysed by an easily available water-soluble iridium(III) dihydride, *Dalt. Trans.*, 45, 14516–14519 (DOI:10.1039/c6dt01695b)
- Celaje J.J.A., Lu Z., Kedzie E.A., Terrile N.J., Lo J.N., Williams T.J. (2016), A prolific catalyst for dehydrogenation of neat formic acid, *Nat. Commun.*, 7, 11308 (DOI:10.1038/ncomms11308)
- Lu S.-M., Wang Z., Wang J., Li J., Li C. (2018), Hydrogen generation from formic acid decomposition on a highly efficient iridium catalyst bearing a diaminoglyoxime ligand, *Green Chem.*, 20, 1835–1840 (DOI:10.1039/C8GC00495A)

- Kawanami H., Iguchi M., Himeda Y. (2020), Ligand Design for Catalytic Dehydrogenation of Formic Acid to Produce Highpressure Hydrogen Gas under Base-free Conditions, *Inorg. Chem.*, 59, 4191–4199 (DOI:10.1021/acs.inorgchem.9b01624)
- Boddien A., Mellmann D., Gärtner F., Jackstell R., Junge H., Dyson P.J., Laurenczy G., Ludwig R., Beller M. (2011), Efficient Dehydrogenation of Formic Acid Using an Iron Catalyst, *Science*, 333, 1733–1736 (DOI:10.1126/science.1206613)
- Montandon-Clerc M., Dalebrook A.F., Laurenczy G. (2016), Quantitative aqueous phase formic acid dehydrogenation using iron(II) based catalysts, *J. Catal.*, 343, 62–67 (DOI:10.1016/j.jcat.2015.11.012)
- Wang L., Sun H., Zuo Z., Li X., Xu W., Langer R., Fuhr O., Fenske D. (2016), Activation of CO<sub>2</sub>, CS<sub>2</sub> and Dehydrogenation of Formic Acid Catalyzed by Iron(II) Hydride Complexes, *Eur. J. Inorg. Chem.*, 5205–5214 (DOI:10.1002/ejic.201600642)
- Zell T., Butschke B., Ben-David Y., Milstein D. (2013), Efficient Hydrogen Liberation from Formic Acid Catalyzed by a Well-Defined Iron Pincer Complex under Mild Conditions, *Chem. - A Eur. J.*, 19, 8068–8072 (DOI:10.1002/chem.201301383)
- Mellone I., Gorgas N., Bertini F., Peruzzini M., Kirchner K., Gonsalvi L. (2016), Selective Formic Acid Dehydrogenation Catalyzed by Fe-PNP Pincer Complexes Based on the 2,6-Diaminopyridine Scaffold, *Organometallics.*, 35, 3344–3349 (DOI:10.1021/acs.organomet.6b00551)
- Bertini F., Mellone I., Ienco A., Peruzzini M., Gonsalvi L. (2015), Iron(II) Complexes of the Linear rac- Tetraphos-1 Ligand as Efficient Homogeneous Catalysts for Sodium Bicarbonate Hydrogenation and Formic Acid Dehydrogenation, ACS Catal., 5 1254–1265 (DOI:10.1021/cs501998t)
- 83. Enthaler S., Brück A., Kammer A., Junge H., Irran E., Gülak S.

(2015), Exploring the Reactivity of Nickel Pincer Complexes in the Decomposition of Formic Acid to  $CO_2$  /H<sub>2</sub> and the Hydrogenation of NaHCO<sub>3</sub> to HCOONa, *ChemCatChem.*, 7, 65–69 (DOI:10.1002/cctc.201402716)

- 84. Léval A., Agapova A., Steinlechner C., Alberico E., Junge H., Beller M. (2020), Hydrogen production from formic acid catalyzed by a phosphine free manganese complex: investigation and mechanistic insights, *Green Chem.*, 22, 913–920 (DOI:10.1039/C9GC02453K)
- Peacock A.F.A., Sadler P.J. (2008), Medicinal Organometallic Chemistry: Designing Metal Arene Complexes as Anticancer Agents, *Chem. - An Asian J.*, 3, 1890–1899 (DOI:10.1002/asia.200800149)
- Habtemariam A., Melchart M., Fernández R., Parsons S., Oswald I.D.H., Parkin A., Fabbiani F.P.A., Davidson J.E., Dawson A., Aird R.E., Jodrell D.I., Sadler P.J. (2006), Structure–Activity Relationships for Cytotoxic Ruthenium(II) Arene Complexes Containing N,N-, N,O-, and O,O-Chelating Ligands, *J. Med. Chem.*, 49, 6858–6868 (DOI:10.1021/jm060596m)
- 87. Pike R.D., Sweigart D.A. (1999), Electrophilic reactivity of coordinated cyclic π-hydrocarbons, *Coord. Chem. Rev.*, 187, 183–222 (DOI:10.1016/S0010-8545(98)00231-8)
- Kumar P., Gupta R.K., Pandey D.S. (2014), Half-sandwich arene ruthenium complexes: synthetic strategies and relevance in catalysis, *Chem. Soc. Rev.*, 43, 707–733 (DOI:10.1039/C3CS60189G)

# Chapter 2

Hydrogen production from formic acid over water soluble arene ruthenium (II) complexes based on bidentate N,N donor ligands

# 2.1. Introduction

In the modern era, there prevails a huge demand to supply gap concerning the energy resources and hence the quest for green and renewable energy sources to meet the global energy demand is one of the key challenges of the society. In this context, hydrogen (H<sub>2</sub>) is emerging as a clean alternative source of energy, as only H<sub>2</sub>O is produced by its reaction in fuel cells.<sup>[1,2]</sup> However, the extremely explosive nature of H<sub>2</sub> and the difficulty in its transportation lead to the search for suitable hydrogen storage compounds, which are safer to handle, can be transported easily and release H<sub>2</sub> under mild conditions.<sup>[3]</sup> In this regard, formic acid being a liquid under ambient conditions has attracted considerable interest, as it can be handled, stored and transported easily and safely.<sup>[4]</sup> In the presence of a suitable catalyst, formic acid generates H<sub>2</sub> and CO<sub>2</sub>, under relatively mild reaction condition.

After one of the first reports on formic acid dehydrogenation over Ir-phosphine complex in 1967 by Coffey,<sup>[5]</sup> this reaction has been investigated extensively only in the recent past. Several transition metal complexes based on iron,<sup>[6]</sup> rhodium,<sup>[7]</sup> ruthenium<sup>[8,9]</sup> and iridium<sup>[10-14]</sup> have been particularly proven to be active catalysts for formic acid dehydrogenation. Notably, ancillary ligands play an important role in tuning the catalytic activity of these metal catalysts for formic acid dehydrogenation. For instance, a strong  $\sigma$ -donor ligand enhances the electron density at the metal center, and such electron-rich metals are found to be the favorable site for efficient activation of formic acid to CO<sub>2</sub> and H<sub>2</sub>.<sup>[4j,10s]</sup> Moreover, the protic ligands are of particular

importance in formic acid dehydrogenation reactions, as these ligands enhance the dehydrogenation pathway by involving in hydrogen bond interactions with the solvent or formic acid.[4k,10c,10d,10g,10m-o] For example, iridium complexes bearing proton responsive ligands have been found to be particularly active for formic acid dehydrogenation in H<sub>2</sub>O.<sup>[11-13]</sup> Himeda *et al.* reported the catalyst [Cp\*Ir(4,4'-DHBP)(H<sub>2</sub>O)]SO<sub>4</sub> with the TOF of 14000  $h^{-1}$ .<sup>[13]</sup> The same group afterwards reported the catalyst [Cp\*Ir(TMBI)H<sub>2</sub>O]SO<sub>4</sub> with a TOF of 34000 h<sup>-1.[10e]</sup> In 2015, Himeda et al. further improved the results by developing the catalyst [Cp\*Ir(pyrimidylimidazoline)H<sub>2</sub>O]SO<sub>4</sub> which gave a TOF of 322000 h<sup>-1</sup> in HCOOH/HCOONa aqueous solution.<sup>[10q]</sup> Li *et al.* developed the catalyst  $[Ir(\eta^5-C_5Me_5)Cl(2,2'-bi-2-imidazole)]^+$ with the TOF of 487500 h<sup>-1.[11]</sup> Very recently, this group has reported a new iridium-based catalyst bearing a dioxime derived ligand which gave a record TON of 5020000 at 70 °C.<sup>[10]</sup> Joo et al. reported an iridium hydride complex which gave a TOF of 298000 h<sup>-1</sup> at 100 °C in formic acid dehydrogenation.<sup>[10t]</sup> Although iridium-based catalysts have been proven to be very active in formic acid dehydrogenation, its price prompts us to look for a more economical option. Literature reports revealed that ruthenium-based catalysts except a few such as  $[Ru(\eta^6 C_{10}H_{14}$ )Cl(2,2'-bi-2-imidazole)]<sup>+</sup> and [Ru(H<sub>2</sub>O)<sub>6</sub>](tos)<sub>2</sub>/TPPTS (tos = ptoluene sulfonate and TPPTS = m-trisulfonated triphenylphosphine) have all been tested in organic solvents for formic acid dehvdrogenation.<sup>[8a,8g-8j,9,15,16]</sup> Higher activities of the complexes [Ir( $\eta^5$ - $C_5Me_5$ )Cl(2,2'-bi-2-imidazole)]<sup>+</sup> and  $[Ru(\eta^{6}-C_{10}H_{14})Cl(2,2)-bi-2$ imidazole)]<sup>+</sup> for formic acid dehydrogenation suggest the importance of N-H moieties on the catalytic activity.<sup>[9,11]</sup>

In one of our recent findings, we observed that Ru-arene complexes containing ethylenediamine (en) and 8-aminoquinoline (AmQ) based chelating ligands efficiently catalyzed the furfural to levulinic acid (LA) transformation with the aid of formic acid. We demonstrated that the N-H moieties of en and AmQ ligands play a crucial role in the initial activation of formic acid to facilitate the transfer

hydrogenation of furfural to furfuryl alcohol, which eventually transformed to LA.<sup>[17,18]</sup> Very recently, Oro et al. reported Ir-NHC (NHC = N-heterocyclic carbene) based complexes for formic acid dehydrogenation in DMF and H<sub>2</sub>O.<sup>[14]</sup> Though these complexes exhibit only moderate activity in H<sub>2</sub>O, the initial TOF is highest (790  $h^{-1}$ ) for the Ir-NHC-AmQ complex. Moreover, a significant quenching of the catalytic activity of Ir-NHC complex was observed when AmQ was replaced with 8-(N, N-dimethylamino)quinoline (DMAmQ), suggesting the crucial role of NH moiety of AmQ in enhancing the catalytic activity for formic acid dehydrogenation in H<sub>2</sub>O. Envisioned by our previous observations, we investigated in detail the dehydrogenation of formic acid over Ru-arene complexes containing various nitrogen-donor chelating ligands and demonstrated the crucial role of these ligands on the formic acid dehydrogenation process. Moreover, mechanistic insights were elaborated by identifying several catalytic intermediates involved in various steps of the catalytic dehydrogenation of formic acid under the catalytic and controlled reaction conditions. Most importantly, the structure of a diruthenium species, possibly the catalyst resting state, was established by X-ray crystallography.

## 2.2. Results and Discussion

Complexes  $[(\eta^6-C_6H_6)Ru(\kappa^2-NH_2NH_2-en)Cl]^+$  (**[Ru]-1**),  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}NH_2-8-AmQ)Cl]^+$  (**[Ru]-2**) and  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{py}NH_2-8-AmQ)Cl]^+$  (**[Ru]-3**) shown in Scheme 2.1 were synthesized from the precursor  $[(\eta^6-arene)RuCl_2]_2$  (**[Ru]-6** and **[Ru]-7**) and the suitable ligands following our previously reported method.<sup>[17,18]</sup>



Scheme 2.1. Complexes [Ru]-1 - [Ru]-7 explored for the dehydrogenation of formic acid.

Complex  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}NHMe-8-AmQ)Cl]^+$  (**[Ru]-4**) was obtained at room temperature from the reaction of the precursor  $[(\eta^6-benzene)RuCl_2]_2$  (**[Ru]-6**) and the ligand 8-(N-methylamino)quinoline (MAmQ) (Scheme 2.2 and Scheme 2.3). Complex  $[(\eta^6-C_6H_6)Ru(\kappa^2-bpy)Cl]^+$  (**[Ru]-5**) was also synthesized from the reaction of  $[(\eta^6-benzene)RuCl_2]_2$  (**[Ru]-6**) and 2,2'-bipyridine (bpy), to evaluate the role of NH in formic acid dehydrogenation.



Scheme 2.2. Synthesis of N-methylquinolin-8-amine (L1).



Scheme 2.3. Synthesis of complex [Ru]-4.

For the initial screening of active catalysts, formic acid dehydrogenation over complexes [Ru]-1 – [Ru]-5 (1 mol%) and the precursor [Ru]-6 – [Ru]-7 (0.5 mol%) was investigated using 0.4 M formic acid (aq.) solution (2.5 mL) and sodium formate (5 mol%) at 90 °C (Table 2.1, entries 1-7). The amount of the evolved gases was measured by water displacement method, and the release of  $H_2$  and  $CO_2$ gas was confirmed by GC-TCD. Preliminary results inferred that the complexes **[Ru]-2** – **[Ru]-4** containing 8-aminoquinoline based ligands were much more efficient than the complex [Ru]-1 containing ethylenediamine ligand for formic acid dehydrogenation reaction (Table 2.1, entries 1-4 and Figure 2.1). The only marginal increment in the TOF of complex [Ru]-2 over [Ru]-3 suggests that the arene-ring offer no significant enhancement in formic acid dehydrogenation. Among the related complexes, the TOF for formic acid dehydrogenation over [Ru]-4 (TOF 364  $h^{-1}$ ) was found to be 4-fold higher than the complex [**Ru**]-2 (TOF 83 h<sup>-1</sup>) (Table 2.1, entries 2 and 4). On the other hand, the  $[(\eta^6 C_6H_6$   $Ru(\kappa^2$ -bpy)Cl]<sup>+</sup> (**[Ru]-5**) display only poor activity (Table 2.1, entry 5). Notably, the precursor complexes [Ru]-6 and [Ru]-7, lacking any nitrogen-based ligands, are also poorly active (Table 2.1, entries 6 and 7). These findings suggest the importance of protic ligands, availability of NH moiety and the stability of the catalyst for the catalytic formic acid dehydrogenation reaction.

	исоон	Ru-catalyst	TT I	CO					
$\frac{1}{1000} + \frac{1}{1000} + 1$									
Entry	Catalyst	Conv. $(\%)^b$	$\mathrm{TON}^d$	TOF $(h^{-1})^d$					
1	[Ru]-1	90	90	53					
2	[Ru]-2	91	91	83					
3	[Ru]-3	90	90	75					
4	[Ru]-4	97	97	364					
5	[Ru]-5	30	30	26					
6	[Ru]-6 <sup>c</sup>	39	39	18					
7	[Ru]-7 <sup>c</sup>	39	39	19					
<sup>a</sup> Reaction conditions: catalyst (0.01 mmol), formic acid (0.4 M, 2.5 mL),									
HCOONa (0.05 mmol), 90 °C. <sup>b</sup> Based on the total gas released. <sup>c</sup> Catalyst									
(0.005 mmol). <sup>d</sup> TOF/TON per Ru atom.									

Table 2.1. Catalytic dehydrogenation of formic acid over various catalysts<sup>a</sup>



**Figure 2.1.** Catalytic formic acid dehydrogenation over different Ruarene complexes. Reaction conditions: formic acid (0.4 M, 2.5 mL), catalyst (1 mol%), HCOONa (0.05 mmol), 90 °C.

Further, dehydrogenation of formic acid (0.4 M, 2.5mL) was performed over the active complexes **[Ru]-2** and **[Ru]-4**(1 mol%), using

a varying amount of sodium formate (0.05 to 3 equivalents) (Table 2.2, entries 1-14 and Figure 2.2). Results inferred that the TOF could be enhanced to 514 h<sup>-1</sup> for complex [**Ru**]-4 using [HCOONa]/[HCOOH] ratio of 2:1 (Table 2.2, entry 12). Further, a maximum initial TOF of 940 h<sup>-1</sup> was achieved with [**Ru**]-4 for formic acid (2.0 M, 2.5 mL) and [HCOONa]/[HCOOH] ratio of 2:1. Moreover, the complex [**Ru**]-4 was recycled for five consecutive catalytic runs for formic acid dehydrogenation reaction, with a TON of 2248, at 90 °C [HCOONa]/[HCOOH] ratio of 2:1 (Figure 2.3). These results suggest that the catalyst [**Ru**]-4 was quite stable and does not lose its catalytic reaction condition.

*Table 2.2. Optimization of reaction conditions for the dehydrogenation of formic acid over complex* **[Ru]-2** *and* **[Ru]-4** *in water.* 

Entry	Catalyst	HCOONa (mmol)	Formic acid (mmol)	Conv. (%)	TON <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup><i>a</i></sup>
1	[Ru]-2	1	0	-	-	-
2	[Ru]-2	0	1	88	88	30
3	[Ru]-2	0.05	1	91	91	83
4	[Ru]-2	0.5	1	91	91	152
5	[Ru]-2	1	1	91	91	182
6	[Ru]-2	2	1	91	91	212
7	[Ru]-2	10	5	97	485	296
8	[Ru]-4	1	0	-	-	-
9	[Ru]-4	0	1	88	88	73
10	[Ru]-4	0.05	1	97	97	364
11	[Ru]-4	1	1	94	94	460
12	[Ru]-4	2	1	94	94	514
13	[Ru]-4	10	5	99	495	875
14	[Ru]-4	20	10	95	950	325

Reaction conditions: All the reactions were performed at 90 °C. The amount of **[Ru]-2** and **[Ru]-4** used in all the cases was 0.01 mmol. All the initial volumes of reaction solutions are 2.5 mL. Each reaction was repeated at least twice with negligible errors. <sup>*a*</sup>Overall TON and TOF.



**Figure 2.2.** TOF (h<sup>-1</sup>) vs [HCO<sub>2</sub>Na] (mmol) plot for the catalytic dehydrogenation of formic acid over complexes [**Ru**]-2 and [**Ru**]-4. Reaction conditions: formic acid (0.4 M, 2.5 mL), catalyst (0.01 mmol), 90 °C. [a] formic acid (2.0 M, 2.5 mL).



Figure 2.3. TON of the catalytic recyclability (1-5 catalytic runs) experiment for the catalytic dehydrogenation of formic acid over the complex [Ru]-4. Reaction conditions: formic acid (2.0 M, 2.5 mL), [Ru]-4 (0.01 mmol), [HCOONa]/[HCOOH] = 2:1, 90 °C. (5 mmol of formic acid was added to the reaction mixture after each run).



Figure 2.4. (a) Temperature dependent formic acid decomposition over [Ru]-4 (1 mol %), formic acid (2M, 2.5 mL), HCOONa/HCOOH = 2:1, T = 60 - 90 °C. (b) Arrhenius plot of initial TOF values for formic acid (2 M, 2.5 mL) decomposition over [Ru]-4 (1 mol%), HCOONa/HCOOH = 2:1.

Further, the dependence of the rate of formic acid dehydrogenation on temperature, catalyst, and formic acid concentration was studied. The initial rates for the formic acid dehydrogenation over complex [Ru]-4 followed Arrhenius behavior in the temperature range of 60  $^{\circ}C - 90 ^{\circ}C$  (Figure 2.4). The obtained apparent activation energy of 87.9 kJ/mol is in line with the activation energies reported for formic acid dehydrogenation over the analogous system.<sup>[9]</sup> Subsequently, the dependence of the rate of formic acid dehydrogenation on the catalyst concentration was determined by varying the catalyst concentration between 0.005 mmol and 0.03 mmol, while keeping the formic acid concentration constant (2.0 M, 2.5 mL) at 90 °C. The double logarithmic plots of the initial reaction rates against the concentration of [Ru]-4 catalyst follows a linear dependence on catalyst concentration. The obtained order of 0.8 with respect to catalyst concentration (Figure 2.5) suggests that [Ru]-4 is converted into the active monomeric species during the induction period and presumably the monomeric species is only involved in the formic acid dehydrogenation reaction. Further, the

reaction order with respect to formic acid concentration, varied between 0.4 M and 2 M with a constant catalyst concentration of 0.01 mmol in 2.5 mL of aqueous solution at 90 °C, was found to be 0.31 (Figure 2.6). This result most probably indicates that only one formic acid or HCOO<sup>-</sup> is interacting with the Ru center to form an [HCOO-Ru] intermediate species.<sup>[11,19]</sup> Also, no change in formic acid dehydrogenation efficiency over complex **[Ru]-4** was observed in the presence of excess metallic mercury, suggesting that the reaction follows a homogeneous pathway.



Figure 2.5. Plot of ln [initial rate (mmol  $L^{-1} h^{-1}$ )]vs ln [cat] (mmol  $L^{-1}$ ); Reaction conditions: catalyst (0.005 – 0.03 mmol), formic acid (2 M, 2.5 mL), HCOONa (10 mmol), 90 °C.



Figure 2.6. Plot of  $ln[initial rate (mmol L^{-1}h^{-1})]$  vs  $ln[FA] (mmol L^{-1});$ Reaction conditions: [Ru]-4 (0.01 mmol), formic acid (0.4 – 2M, 2.5 mL), 90 °C.

Based on the observations of the kinetic studies, attempts were made to systematically investigate and identify various organometallic intermediates presumably involved in the catalytic dehydrogenation of formic acid over Ru-catalyst using mass spectrometry. Stirring catalyst [Ru]-4 in H<sub>2</sub>O at room temperature showed few prominent mass peaks at m/z = 169.0 and 178.0, which were assigned to [Ru]-4G and [Ru]-4E, respectively (Scheme 2.4 and Figure 2.7). The coordination of a  $H_2O$ molecule to the dicationic species,  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{pv})NHMe-$ MAmQ)]<sup>2+</sup> ([**Ru**]-4G; m/z = 169.0) gives a dicationic species [( $\eta^6$ - $C_{6}H_{6}$  $Ru(\kappa^{2}-N_{pv}NHMe-MAmQ)(H_{2}O)$ ]<sup>2+</sup> ([**Ru**]-4E; m/z = 178.0) in aqueous solution. Upon stirring an aqueous solution of [Ru]-4 in the presence of sodium formate at room temperature, prominent mass peak at m/z = 337.0 was observed, which was assigned to  $[(\eta^6 - C_6 H_6) Ru(\kappa^2 - M_6) Ru(\kappa^2 - M_6)$  $N_{py}NMe-MAmQ)$ ]<sup>+</sup> ([**Ru**]-4A) species (Figure 2.7). The analogous, mass profile was also observed for [Ru]-2 under identical reaction conditions (Figure 2.8). An H<sub>2</sub>O coordinated dicationic  $[(\eta^6 C_6H_6$  $Ru(\kappa^2-N_{py}NH_2-AmQ)$  (H<sub>2</sub>O)]<sup>2+</sup> ([**Ru**]-2**E**; m/z = 171.0) species was observed upon stirring the complex [Ru]-2 in H<sub>2</sub>O. Further, an intense peak corresponding to [**Ru**]-2A ([( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru( $\kappa^2$ -N<sub>py</sub>NH-AmQ)]<sup>+</sup>; m/z = 323.0), a species similar to [**Ru**]-4A, was also observed upon stirring the complex [**Ru**]-2 in the presence of sodium formate. Mass study of the dehydrogenation reaction with complex [**Ru**]-2 in the presence of sodium formate also revealed [**Ru**]-2A ([( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru( $\kappa^2$ -N<sub>py</sub>NH-AmQ)]<sup>+</sup> as the main metallic species formed in the reaction mixture (Figure 2.8). These observations, suggest that the presence of formate species facilitated the deprotonation of the N-H of the 8-aminoquinoline based ligands to form a coordinatively unsaturated [**Ru**]-2A/[**Ru**]-4A species.



Scheme 2.4. Various intermediate species observed during the mass investigation of an aqueous solution of complex [Ru]-4 under varying controlled reaction condition.



*Figure 2.7. Different species observed under mass spectrometry after complex* **[Ru]-4** *was stirred in water for 5 minutes at room temperature.* 



*Figure 2.8.* Various intermediate species observed during mass investigation of an aqueous solution of complex [*Ru*]-2 under varying controlled reaction condition.

The equilibria between the species [**Ru**]-4G and [**Ru**]-4A (for catalyst [**Ru**]-4) and [**Ru**]-2G and [**Ru**]-2A (for catalyst [**Ru**]-2) observed during the mass investigation (Scheme 2.4 and Figures 2.7 and 2.8) are pH sensitive and hence a pH-dependent study on the initial TOFs was conducted. The results showed that the highest TOF was achieved at pH = 4.0 (Figure 2.9), where the initial concentration of [HCOONa]/[HCOOH] was fixed at 2:1 and hence the concentration of such coordinatively unsaturated species [**Ru**]-4A/[**Ru**]-2A is expected to be high indicating that it may have a vital role in the catalytic cycle. The highest TOF obtained at moderately acidic condition indicates the importance of both H<sub>3</sub>O<sup>+</sup> ions as well as HCO<sub>2</sub><sup>-</sup> species in the dehydrogenation reaction.



**Figure 2.9.** Dehydrogenation of formic acid under varying pH values, where pH values are altered by changing the [HCOONa]/[HCOOH] ratios. Reaction conditions: catalyst [**Ru**]-2/[**Ru**]-4 (0.01 mmol), formic acid (0.4 M, 2.5 mL), T = 90 °C.

To further confirm, the formation of the unsaturated species **[Ru]-2A** and **[Ru]-4A** in the presence of HCOONa, controlled reactions were performed. Treating complex **[Ru]-2** with an excess of sodium formate in methanol under reflux condition also led us to obtain **[Ru]-**

2A. Further, orange colored block-shaped single crystals suitable for Xray diffraction analysis were obtained by slow diffusion of diethyl ether into the methanolic solution of [Ru]-2A. It is evident that the treatment of **[Ru]-2/[Ru]-4** with sodium formate led to the formation of the species [Ru]-2A/[Ru]-4A, which eventually dimerize to the stable diruthenium complex [Ru]-2A'/[Ru]-4A', plausibly the catalyst resting state (Scheme 2.5).<sup>[10g,21-23]</sup> Analogous unsaturated species [Ru( $\eta^6$ - $C_{10}H_{14}$ )(Imd-H)]<sup>+</sup> (Imd = 2,2'-bi-2-imidazole), generated in situ from  $[Ru(\eta^6-C_{10}H_{14})Cl(2,2'-bi-2-imidazole)]^+$  in the presence of sodium formate, was reported to play an important role in the formic acid dehydrogenation process.<sup>[9]</sup> Interesting to note here, that literature also revealed that such coordinatively unsaturated species are unstable and may undergo dimerization.<sup>[19-21]</sup> Similar dimeric species are also reported by Carmona et al., where treatment of acetone solution of the complex  $[(\eta^6 - C_{10}H_{14})Ru(\kappa^2 - N_{pv}OH)Cl]^+$  with Na<sub>2</sub>CO<sub>3</sub> afforded dimer  $[\{(\eta^6-C_{10}H_{14})Ru(\kappa^2 N, O-\mu-O-NO\}_2]^{2+}$ .<sup>[20]</sup> Valerga *et al.* also reported the crystal structure of a dinuclear Cp\* ruthenium (III) complex  $[{Cp*Ru(\kappa^2-N,S-\mu-S-SC_5H_4N)}_2]^{2+}$  while attempting to crystallize hydrido(alkoxo) derivative.<sup>[21]</sup> Nishibayashi et al. reported similar species which are particularly relevant in the context of catalytic propargylation reaction of ketones.<sup>[22]</sup>





The NMR spectra of [**Ru**]-2A' are consistent with the presence of deprotonated NH<sub>2</sub> ligand, and only one set of resonances was observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra indicating the chemical equivalence of the two halves of the molecule (see experimental section).
The single crystal X-ray structural determination showed that the asymmetric unit of **[Ru]-2A'** [{ $(\eta^6$ -benzene)Ru( $\kappa^2$ -N<sub>pv</sub>NH-AmQ)}<sub>2</sub>]<sup>2+</sup> is formed by two units of  $\{(\eta^6\text{-benzene})\text{Ru}(\kappa^2\text{-N}_{\text{pv}}\text{NH-AmQ})\}^+$  (**[Ru]-2A**), where two ( $\eta^6$ -benzene)Ru units are doubly bridged by -NH groups of two 8-AmQ ligands (Figure 2.10 and Tables 2.4 - 2.6). The ruthenium bound  $\eta^6$ -benzene ligands are placed at the mutually cisoid position. The center Ru-N-Ru-N core has a bent butterfly-like structure, with the dihedral angle of 151.44° between the two RuN<sub>2</sub> planes, presumably due to the steric crowding of the cisoid positioned  $\eta^6$ -benzene rings. Moreover, the Ru1-N2-Ru2 bond angle is 97.28°, which is slightly larger than the reported values, indicating a weak interaction between two Ru centers having a Ru- Ru distance of 3.2 Å. The Ru-N<sub>amido</sub> bond lengths of the two ruthenium units in the complex [Ru]-2A' are not same, suggesting the asymmetry in the coordination of N<sub>amido</sub> with the two ruthenium centers. In particular, the Ru1-N4 (2.157 Å) and Ru2-N2 (2.158 Å) bonds (distances between the ruthenium center and the bridging N<sub>amido</sub> from the other ruthenium unit) are significantly longer than the Ru1-N2 (2.106 Å) and Ru2-N4 (2.094 Å) bonds, further suggesting that two units of  $\{(\eta^6\text{-benzene})\text{Ru}(\kappa^2\text{-N}_{\text{pv}}\text{NH-AmQ})\}^+$  are weakly interacted via the two bridging Namido groups. Notably, the Ru-Npy bond lengths in [Ru]-2A' are analogous to that observed in the monometallic complex [Ru]-2, while the Ru-N<sub>amido</sub> bond lengths are quite short in comparison to Ru-Namine bond in the monometallic complex **[Ru]-2**.<sup>[20]</sup> Though the carbon atoms in the  $\eta^6$ -benzene rings show some distortion due to the occupancy factors, the overall structure of the diruthenium complex [Ru]-2A' is well in accordance with literature reported analogous dimeric complexes.<sup>[20-22]</sup>



Figure 2.10. Single crystal X-ray structure of the diruthenium [Ru]-2A'. Counter anions (Cl<sup>-</sup>) and all hydrogen atoms of [Ru]-2A', except those on nitrogen, are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-N4 2.157 (4), Ru2-N4 2.094(4), Ru1-N2 2.106(4), Ru2-N2 2.158(4), Ru1-N2-Ru2 97.28(16), Ru1-N4-Ru2 97.67(16), N2-Ru1-N4 77.94(15), N4-Ru2-N2 78.18(15).

Interesting to note that during the catalytic reaction, at first instance, a visible color change from a deep green solution of the catalysts **[Ru]-2/[Ru]-4** to a brown solution was observed during the initial minutes of the base-assisted catalytic dehydrogenation of formic acid (Figure 2.11). It should be noted that the observed brown color of the catalytic reaction was quite stable and we could not observe the initial green color of the solution even after the complete dehydrogenation of formic acid. Mass investigation of the brown solution showed the presence of **[Ru]-2A/[Ru]-4A** species. Further, the addition of an excess of dilute HCl in the obtained brown solution led to the regeneration of the initial green color. Mass spectral analysis of the obtained green solutions depicted the presence of prominent peaks at m/z 359.0 and m/z 373.0, corresponding to **[Ru]-2** and **[Ru]-4**, respectively (Figure 2.12).



*Figure 2.11. Transformation of colour of the reaction mixture from green to wine red brown during the initial minutes of the reaction and reverts to green colour when treated with excess HCl.* 



*Figure 2.12. Mass investigation of the green-colored solutions obtained by the addition of an excess of dilute HCl to the brown solution after the catalytic reaction for [Ru]-2 and [Ru]-4*.

The above findings inferred that, upon treatment with HCOONa, [**Ru**]-2/[**Ru**]-4 *in situ* transformed to the species [**Ru**]-2A/[**Ru**]-4A, which further reacted with formic acid/sodium formate to form formate coordinated Ru species ([**Ru**]-2B/[**Ru**]-4B).<sup>[23]</sup> A Ru-hydride species [**Ru**]-2C/[**Ru**]-4C is expected to be formed, upon extrusion of CO<sub>2</sub> from [**Ru**]-2B/[**Ru**]-4B. This step is most probably the rate determining step in the catalytic cycle as indicated by kinetic isotope effect studies, where the deuterated formic acid (DCOOD) substrate (KIE: 2.9, Table 2.3, entry 3) is more influential than deuterated H<sub>2</sub>O (D<sub>2</sub>O) (KIE: 1.9, Table 2.3, entry 2) on the reaction rate, indicating that C-H bond cleavage of formic acid is the rate determining step. <sup>[9,11]</sup>

Table 2.3. KIE in the dehydrogenation of formic acid using complex[Ru]-4<sup>a</sup>

Entry	Catalyst	Substrate	Solvent	TOF $(h^{-1})^b$	$KIE^{c}$
1	[Ru]-4	НСООН	H <sub>2</sub> O	75	-
2	[Ru]-4	НСООН	$D_2O$	40	1.9
3	[Ru]-4	DCOOD	$H_2O$	26	2.9
4	[Ru]-4	DCOOD	$D_2O$	22	3.4

<sup>*a*</sup>Reaction conditions: Catalyst (0.01 mmol), formic acid (0.4 M, 2.5 mL), 90 °C; <sup>*b*</sup>TOF was calculated in the initial 1 hour; <sup>*c*</sup>KIE = TOF (entry 1)/ TOF (entry n) (n = 2,3,4)

Further, upon the release of H<sub>2</sub> from the Ru-hydride species ([**Ru**]-2C/[**Ru**]-4C), the intermediate [Ru]-2A/[Ru]-4Awas regenerated (Scheme 2.6). All our attempts to detect and isolate these Ru-formate or Ru-hydride species were unsuccessful. The indirect evidence for the formation of Ru-hydride species was gathered by utilizing the Ru-hydride species (**[Ru]-2C**) in the transfer hydrogenation of *p*-anisaldehyde to obtain corresponding alcohol under identical reaction condition.<sup>[24]</sup> On the other hand, during base-free catalytic dehydrogenation of formic acid, a H<sub>2</sub>O coordinated dicationic ruthenium species ([Ru]-2E/[Ru]-4E) was possibly generated, as also evidenced by the appearance of a mass peak at m/z = 171.0 ([**Ru**]-2E) and m/z =178.0 ([Ru]-4E) (Figure 2.7 and Figure 2.8). Further, formate replaces H<sub>2</sub>O from **[Ru]-2E/[Ru]-4E** resulting in the formation of the species [Ru]-2F/[Ru]-4F. Hydride species [Ru]-2D/[Ru]-4D is formed after the decarboxylation of Ru-formate species ([Ru]-2F/[Ru]-4F). The H<sub>2</sub>O coordinated dicationic ruthenium species ([Ru]-2E/[Ru]-4E) will be regenerated, upon the proton-assisted release of H<sub>2</sub> from [Ru]-2D/[Ru]-4D. Based on the above mass studies and x-ray crystal structure, we propose a plausible pathway for both the base-free and base-assisted

dehydrogenation of formic acid over complexes [**Ru**]-2 and [**Ru**]-4 (Scheme 2.6).<sup>[4k,9]</sup>



-Me([Ru]-4)

Scheme 2.6. A plausible catalytic pathway for the base assisted formic acid dehydrogenation over complexes [Ru]-2 and [Ru]-4.

## **2.3.** Conclusions

In summary, we employed several Ru-arene complexes for the catalytic dehydrogenation of formic acid in  $H_2O$ , where the complex [**Ru**]-4 containing 8-(N-methylamino)quinoline ligand outperformed over others to achieve a TON of 2248. The high activity of [**Ru**]-4 can be attributed to the high aqueous stability of the catalyst and availability of -NH moiety. Further, we employed extensive mass and NMR investigations and kinetic studies to evidence the formation of several

important organometallic intermediate species, such as H<sub>2</sub>O coordinated dicationic ruthenium species  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}NHMe-MAmQ)(H_2O)]^{2+}$  ([**Ru**]-4**E**) and the active coordinatively unsaturated species  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}NMe-MAmQ)]^+$  ([**Ru**]-4A) during the catalytic dehydrogenation of formic acid over complex [**Ru**]-4, and hence, established their important role in the catalytic dehydrogenation of formic acid. Most importantly, we succeeded in isolating the plausible catalyst resting state and characterized it as a dicationic diruthenium species ([**Ru**]-2A'), by single crystal X-ray diffraction.

#### 2.4. Experimental Section

### 2.4.1. Materials and instrumentation

All reactions were performed in aerobic conditions using high- purity chemicals purchased from Sigma- Aldrich, and Alfa-Aesar. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C NMR (100 MHz) spectra were recorded at 298 K using D<sub>2</sub>O and CDCl<sub>3</sub> as solvents on a Bruker advance 400 spectrometer. ESI-mass spectra were recorded on a micrOTF-Q II mass spectrometer. The GC-TCD analysis was performed on a Shimadzu GC-2014 system using shin carbon-ST packed column.

## 2.4.2. Synthesis of the ligand 8-(N-methylamino)quinoline (L1)

To the freshly prepared solution of NaOMe (20 mmol) in MeOH (20 mL), 8-aminoquinoline (4 mmol) and paraformaldehyde (20 mmol) were added. The mixture was allowed to reflux for 4 hours, and NaBH<sub>4</sub> (6 mmol) was added portion wise at 0 °C and the mixture was refluxed for an additional 2 hours. The completion of the reaction analyzed by TLC, the mixture was cooled, and the solvent was evaporated on a vacuum pump to give a residue that was treated with an aqueous layer (20 mL). The compound was extracted with dichloromethane (2 × 15 mL). The organic residue was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed using vacuum pump and residue that was purified through silica gel column chromatography with hexane/ethyl acetate (9.5: 0.5 v/v) to obtain the pure product. Yellow color. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.70 (d, 1H, *J*= 4 Hz), 8.06 (d, 1H, *J*= 8 Hz),

7.42- 7.35 (m, 2H), 7.05 (d, 1H, *J*= 8 Hz), 6.65 (d, 1H, *J*= 8 Hz), 6.12 (br, 1H), 3.04 (d, 3H, *J*= 4Hz).

## 2.4.3. Synthesis of the complex [Ru]-4.

The ligand 8-(N-methylamino)quinoline (1.1 mmol) was dissolved in 30 mL MeOH taken in a 100 mL round-bottomed flask and  $[(\eta^{6}-$ benzene)RuCl<sub>2</sub>]<sub>2</sub> (0.5 mmol) was added to it. The mixture was stirred for 24 h at room temperature after which the volume of solvent was reduced on a vacuum pump. The complex was precipitated out with diethyl ether, washed several times to get rid of the excess ligand. It was then dried and collected. Colour: Deep green. Yield 68%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 9.38 (dd, *J* = 30.3, 5.1 Hz, 1H), 8.25 (t, *J* = 7.1 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.43 (dd, *J* = 10.4, 8.3 Hz, 2H), 5.96 – 5.75 (m, 6H), 3.06 (s, 3H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 129.34, 128.25, 127.75, 127.36, 126.51, 125.57, 124.27, 123.97, 123.71, 85.48, 85.35, 48.81. MS (ESI) *m*/*z* calculated for  $[(\eta^{6}-C_{6}H_{6})Ru(\kappa^{2}-N_{py})HMe-MAmQ)Cl]^{+}$ : 373.0 [M]<sup>+</sup>, found 373.0 [M]<sup>+</sup>

# 2.4.4. Controlled experiment for the synthesis of [Ru]-2A'.

Complex **[Ru]-2** (0.2 mmol) and HCOONa (0.4 mmol) in methanol (25 mL) were refluxed for 1 h till a visible color change from green to brown was observed. The resulting solution was filtered, and the solvent was removed under reduced pressure to obtain **[Ru]-2A'**. Colour: Brown. Yield 73%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 8.12 (d, 1H, *J* = 8 Hz), 7.82 (d, 2H, *J* = 8 Hz), 7.51 (t, 1H, *J* = 6 Hz), 7.16 (d, 1H, *J* = 8 Hz), 6.87-6.84 (m, 1H), 5.74 (s, 6H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta$  (ppm) = 155.32, 153.91, 144.06, 137.44, 128.06, 127.99, 122.96, 122.20, 120.75, 85.27.

### 2.4.5. Single-Crystal X-ray Diffraction Studies

A Single crystal was obtained by diffusion of diethyl ether into a methanol solution of **[Ru]-2A'**. X-ray structural studies of **[Ru]-2A'** were executed on a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. Using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å)-based diffraction, data were collected at

293(2) K by the standard "phi-omega" scan techniques and were scaled and reduced using CrysAlisPro RED software. The extracted data were evaluated using the CrysAlisPro CCD software. The structures were solved by direct methods using SHELXL-2018/1, and refined by fullmatrix least squares method, refining on  $F^{2, [25]}$  The positions of all of the atoms were determined by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions. The CCDC number 1810973 contains the supplementary crystallographic data for [Ru]-2A'. These data are freely available at www.ccdc. cam.ac.uk (or can be procured from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**2.4.6.** The General process for formic acid dehydrogenation reactions To an aqueous solution (2.5 mL) of complex [**Ru**]-4/[**Ru**]-2 (0.01 mmol) was added HCOONa (0.05 mmol) in a two-necked reaction tube fitted with a condenser and a gas burette. Further, HCOOH (1 mmol) was added to the reaction mixture and was heated at 90 °C. The release of gas was measured as the displacement of H<sub>2</sub>O in the burette. The release of H<sub>2</sub> gas was confirmed by GC-TCD.

## **2.4.7.** The process for recycling experiments

Formic acid (2.0 M, 2.5 mL), **[Ru]-4** (0.01 mmol), [HCOONa]/[HCOOH] = 2:1 was taken in a two-necked test tube and heated at 90 °C. The gas released was calculated by the water displacement method. After the release of gas stopped, 5 mmol of formic acid was added to the reaction mixture after each run, and the release of gas monitored.

# 2.4.8. The General process for the mechanistic studies

NMR and mass spectral studies were performed for the identification of various catalytic species involved in the catalytic dehydrogenation of formic acid over the complex [Ru]-2 and [Ru]-4. The species [Ru]-2A/[Ru]-4A and [Ru]-2E/[Ru]-4E was identified by mass spectrometry

from an aqueous solution of [Ru]-2/[Ru]-4 under varying reaction conditions.

## 2.4.9. GC-TCD Analysis.



*Figure 2.13.* Gas chromatogram (GC- TCD) of evolved (*a*) H<sub>2</sub> gas and (*b*) CO<sub>2</sub> from the reaction mixture for the catalytic formic acid dehydrogenation reaction. Reaction conditions: [*Ru*]-4 (0.01 mmol), formic acid (0.4 M, 2.5 mL), HCOONa (0.05 mmol), 90 °C. (All analyses are performed using argon as the carrier gas).

# 2.4.10. Characterization of metal complexes



<sup>1</sup>H NMR of [Ru]-2A'



<sup>13</sup>C NMR of **[Ru]-2A'** 

Table 2.4. Single crystal X-ray refinement data for complex [Ru]-2A'

[Ru]-2A'				
Formula	$C_{30}H_{24}Cl_2N_4Ru_2$			
Molecular weight	715.59			
Crystal system	Triclinic			
Space group	P-1			
Temperature/K	298			
Wavelength	0.71073			
a/Å	10.2327 (5)			
<i>b</i> /Å	10.8636 (4)			
$c/ m \AA$	13.1176 (4)			
a/°	82.743 (3)			
$\beta/^{\circ}$	82.409 (3)			
γ/°	78.325 (4)			
$V/Å^3$	1408.05 (10)			
Z	2			
Density/gcm <sup>-1</sup>	1.688			
Absorption Coefficient Absorption Correction	1.289 Multi-scan			

F(000)	712.0
Total no of reflections	4954
Reflections, $I > 2\sigma(I)$	4354
Max. 20/°	24.998
Ranges (h, k, l)	$-10 \le h \le 12$ $-12 \le k \le 12$ $-15 \le 1 \le 15$
Complete to $2\theta(\%)$	99.7
Refinement method	Full-matrix least-squares on $F^2$
Goof $(F^2)$	1.058
R indices $[I \ge 2\sigma(I)]$	0.0431
R Indices (all data)	0.0486

Table 2.5. Selected bond lengths (Å) for complex [Ru]-2A'

Ru1- N4	2.157 (4)
Ru2-N4	2.094 (4)
Ru1- N2	2.106 (4)
Ru2-N2	2.158 (4)
Ru1-N1	2.091 (4)
Ru2-N3	2.099 (4)
N2- C8	1.423 (6)
N4- C17	1.407 (6)

Table 2.6. Selected bond angles (°) for complex [Ru]-2A'

Ru1-N2-Ru2	97.28 (16)
Ru1-N4-Ru2	97.67 (16)
N1-Ru1-N2	79.20(15)
N1-Ru1-N4	88.61(15)
N2-Ru1-N4	77.94(15)
N4-Ru2-N3	78.83(16)
N4-Ru2-N2	78.18(15)
N3-Ru2-N2	88.52(15)



<sup>1</sup>H NMR of the ligand N-methylquinolin-8-amine in CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of complex [Ru]-4 in  $D_2O$ 



Mass of [Ru]-4

Note: The contents of this chapter is published as Patra et al., Eur. J. Inorg. Chem., 2019, 1046- 1053 (DOI: 10.1002/ejic.201801501) and reproduced with the permission from Wiley VCH with license number 5213580881346.

## 2.5. References

- Zhang H., Shen P. K. (2012), Recent Development of Polymer Electrolyte Membranes for Fuel Cell, *Chem. Rev.*, 112, 2780–2832 (DOI: 10.1021/cr200035s)
- Pourbaba M., Zirakkar S. (2011), Utilization of Renewable Energy to Produce Electrical Energy (Hydrogen Energy), *Procedia Eng.*, 21, 1088–1095 (DOI: 10.1016/j.proeng.2011.11.2115)
- a) Dalebrook A. F., Gan W., Grasemann M., Moret S., Laurenczy G. (2013), Hydrogen storage: Beyond Conventional Methods, *Chem. Commun.*, 8735-8751 (DOI: 10.1039/c3cc43836h)

b) Yadav M., Xu Q. (2012), Liquid-Phase Chemical Hydrogen
Storage, *Energy Environ. Sci.*, 5, 9698-9725 (DOI: 10.1039/c2ee22937d)

c) Jiang H. L., Singh S. K., Yan J. M., Zhang X. B., Xu Q. (2010),
Liquid-Phase Chemical hydrogen Storage: Catalytic Hydrogen
Storage under Ambient Conditions, *ChemSusChem.*, 3, 541-549
(DOI: 10.1002/cssc.201000023)

4. a) Mellman, D., Sponholz P., Junge H., Beller M. (2016), Formic Acid as a Hydrogen Storage Material- Development of Homogeneous Catalysts for Selective Hydrogen Storage, Chem. Soc. Rev. 45. 3954-3988 (DOI: 10.1039/c5cs00618j) b) Grasemann M., Laurenczy G. (2012), Formic acid as a hydrogen source – recent developments and future trends, *Energy Environ.* Sci., 5, 8171–8181 (DOI: 10.1039/c2ee21928j) c) Enthaler S., von Langermann J., Schmidt T. (2010), Carbon dioxide and formic acid-the couple for environmental-friendly hydrogen storage, Energy Environ. Sci., 3, 1207-1217 (DOI: 10.1039/b907569k) d) Johnson T. C., Morris D. J., Wills M. (2010), Hydrogen generation from formic acid and alcohols using homogeneous catalysts, Chem. Soc. Rev., 39, 81-88 (DOI: 10.1039/b904495g) e) Joó F. (2008), Breakthroughs in Hydrogen Storage-Formic Acid as a Sustainable Storage Material for Hydrogen, ChemSusChem., 1. 805-808 (DOI: 10.1002/cssc.200800133) f) Eppinger J., Huang K. W. (2017), Formic Acid as a Hydrogen Energy Carrier, ACS Energy Lett., 2,

188-195 (DOI:10.1021/acsenergylett.6b00574) g) Singh A. K., Singh S., Kumar A. (2016), Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system, Catal. Sci. 6. Technol., 12-40(DOI: 10.1039/c5cy01276g) h) Onishi N., Laurenczy G., Beller M., Himeda Y. (2018), Recent progress for reversible homogeneous catalytic hydrogen storage in formic acid and in methanol, Coordination Chemistry Reviews., 373, 317-332 (DOI: 10.1016/j.ccr.2017.11.021) i) Onishi N., Iguchi M., Yang X., Kanega R., Kawanami H, Xu Q., Himeda Y. (2018), Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid, Adv. Energy Mater., 1801275 (DOI: 10.1002/aenm.201801275) j) Sordakis K., Tang C., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, Chem. Rev., 118, 372-433 (DOI: 10.1021/acs.chemrev.7b00182) k) Iglesias M., Oro L. A. (2018), Mechanistic Considerations on Homogeneously Catalyzed Formic Acid Dehydrogenation, Eur. J. Inorg. Chem., 2125–2138 (DOI: 10.1002/ejic.201800159)

- Coffey R. S. (1967), The decomposition of formic acid catalysed by soluble metal complexes, *Chem. Commun.*, 923–924 (DOI: 1039/c1967000923b)
- a) Mellone I., Gorgas N., Bertini F., Peruzzini M., Kirchner K., Gonsalvi L. (2016), Selective Formic Acid Dehydrogenation Catalyzed by Fe-PNP Pincer Complexes Based on the 2,6-

Diaminopyridine Scaffold, *Organometallics*, 35, 3344–3349 (DOI: 10.1021/acs.organomet.6b00551) b) Bielinski E. A., Lagaditis P. O., Zhang Y., Mercado B. Q., Würtele C., Bernskoetter W. H., Hazari N., Schneider S. (2014), Lewis Acid-Assisted Formic Acid Dehydrogenation Using a Pincer-Supported Iron Catalyst, *J. Am. Chem. Soc.* 136, 10234–10237. (DOI: 10.1021/ja505241x) c) Zell T., Butschke B., Ben-David Y., Milstein D. (2013), Efficient Hydrogen Liberation from Formic Acid Catalyzed by a Well-Defined Iron Pincer Complex under Mild Conditions, *Chem. - Eur. J.*, 19, 8068–8072 (DOI: 10.1002/chem.201301383)

7. a) Fukuzumi S., Kobayashi T., Suenobu T. (2008), Efficient Catalytic Decomposition of Formic Acid for the Selective Generation of H<sub>2</sub> and H/D Exchange with a Water-Soluble Rhodium Complex in Aqueous Solution, ChemSusChem, 1, 827-834 (DOI: 10.1002/cssc.200800147) b) Himeda Y., Miyazawa S., Hirose T. (2011), Interconversion between Formic Acid and H<sub>2</sub>/CO<sub>2</sub> using Rhodium and Ruthenium Catalysts for CO<sub>2</sub> Fixation and H<sub>2</sub> Storage, *ChemSusChem*, 4, 487–493 (DOI: 10.1002/cssc.201000327) c) Jantke D., Pardatscher L., Dress M., Cokoja M., Herrmann W. A., Kuhn F. E. (2016) Hydrogen production and storage on a formic acid/Bicarbonate platform using water-soluble N-heterocyclic carbine complexes of late 9, 2849-2854 transition metals, ChemSusChem, (DOI: 10.1002/cssc.201600861) d) Wang Z., Lu S. M., Wu J., Li C., Xiao J. (2016), Iodide-Promoted Dehydrogenation of Formic Acid on a Rhodium Complex, *Eur. J. Inorg. Chem.*, 490-496 (DOI: 10.1002/ejic.201501061)

a) Pan Y., Pan C. L., Zhang Y., Li H., Min S., Guo X., Zheng B., 8. Chen H., Anders A., Lai Z., Zheng J., Huang K.-W. (2016), Selective Hydrogen Generation from Formic Acid with Well-Defined Complexes of Ruthenium and Phosphorus-Nitrogen PN3-Pincer Ligand, Chem. - Asian J., 11, 1357-1360 (DOI: 10.1002/asia.201600169) b) Czaun М., Goeppert A., Kothandaraman J., May R. B., Haiges R., Prakash G. K. S., Olah, G. A. (2013), Formic Acid As a Hydrogen Storage Medium: Ruthenium-Catalyzed Generation of Hydrogen from Formic Acid in Emulsions, ACS Catal., 4, 311–320 (DOI: 10.1021/cs4007974) c) Guerriero A., Bricout H., Sordakis K., Peruzzini M., Monflier E., Hapiot, F., Laurenczy G., Gonsalvi L. (2014), Hydrogen Production by Selective Dehydrogenation of HCOOH Catalyzed by Ru-Biaryl Sulfonated Phosphines in Aqueous Solution. ACS Catal., 4, 3002–3012 (DOI: 10.1021/cs500655x) d) Fukuzumi S., Kobayashi T., Suenobu T. (2010), Unusually Large Tunneling Effect on Highly Efficient Generation of Hydrogen and Hydrogen Isotopes in pH-Selective Decomposition of Formic Acid Catalyzed by a Heterodinuclear Iridium-Ruthenium Complex in Water, J. Am. Chem. Soc., 132. 1496-1497 (DOI: 10.1021/ja910349w) e) Boddien A., Loges B., Junge H., Gärtner F., Noyes J. R., Beller M. (2009), Continuous hydrogen generation

from formic acid: highly active and stable ruthenium catalysts, Adv. Synth. Catal.. 351. 2517-2520 (DOI: 10.1002/adsc.200900431) f) Fellay C., Dyson P. J., Laurenczy G. (2008), A Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst. Angew. Chem., Int. Ed., 47, 3966–3968 (DOI: 10.1002/anie.200800320) g) Loges B., Boddien A., Junge H., Beller M. (2008), Controlled Generation of Hydrogen from Formic Acid Amine Adducts at Room Temperature and Application in H<sub>2</sub>/O2 Fuel Cells, Angew. Chem., Int. Ed., 47, 3962–3965 (DOI: 10.1002/anie.200705972) h) Fellay C., Yan N., Dyson P. J., Laurenczy G. (2009), Selective Formic Acid Decomposition for High-Pressure Hydrogen Generation: A Mechanistic Study, Chem. - Eur. J., 15, 3752-3760 (DOI: 10.1002/chem.200801824) i) Boddien A., Federsel C., Sponholz P., Mellmann D., Jackstell R., Junge H., Laurenczy G., Beller M. (2012), Towards the development of a hydrogen battery, Energy Environ Sci., 5, 8907-8911 (DOI: 10.1039/c2ee22043a) j) Sponholz P., Mellmann D., Junge H., Beller M. (2013), Towards a Practical Setup for Hydrogen Production from Formic Acid, ChemSusChem., 6, 1172-1176 (DOI: 10.1002/cssc.201300186)

 Guan C., Zhang D., Pan Y., Iguchi M., Ajitha M.J., Hu J., Li H., Yao C., Huang M. H., Min S., Zheng J., Himeda Y., Kawanami H., Huang K. W. (2016), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N'-Diimine

70

Ligand, *Inorg Chem.*, 56, 438-445 (DOI: 10.1021/acs.inorgchem.6b02334)

10. a) Celaje J. J. A., Lu Z., Kedzie E. A., Terrile N. J., Lo J. N., Williams T. J. A. (2016), A prolific catalyst for dehydrogenation of neat formic acid, Nat. Commun., 7, 11308-11313 (DOI: 10.1038/ncomms11308) b) Czaun M., Kothandaraman J., Goeppert A., Yang B., Greenberg S., May R. B., Olah G. A., Prakash G. K. S. (2016), Iridium-Catalyzed Continuous Hydrogen Generation from Formic Acid and Its Subsequent Utilization in a Fuel Cell: Toward a Carbon Neutral Chemical Energy Storage, ACS Catal., 6, 7475–7484 (DOI: 10.1021/acscatal.6b01605) c) Matsunami A., Kayaki Y., Ikariya T. (2015), Enhanced Hydrogen Generation from Formic Acid by Half-Sandwich Iridium(III) Complexes with Metal/NH Bifunctionality: A Pronounced Switch from Transfer Hydrogenation., Chem. Eur. J., 21, 13513-13517 (DOI: 10.1002/chem.201502412) d) Oldenhof S., Lutz M., de Bruin B., van der Vlugt J. Ι Reek. J. N. H. (2015), Dehydrogenation Formic of Acid by IrbisMETAMORPhos Complexes: Experimental and Computational Insight into the Role of a Cooperative Ligand, Chem. Sci., 6, 1027-1034 (DOI: 10.1039/c4sc02555e) e) Manaka Y., Wang W.-H., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2014), Efficient H<sub>2</sub> generation from formic acid using azole complexes in water, Catal. Sci. Technol., 4, 34-37 (DOI: 10.1039/c3cy00830d) f) Fujita E., Muckerman J. T.,

Himeda Y. (2013), Interconversion of CO2 and formic acid by bioinspired Ir complexes with pendent bases, Biochim. Biophys. Acta, *Bioenerg.*, 1827, 1031-1038 (DOI: 10.1016/j.bbabio.2012.11.004) g) Barnard J. H., Wang C., Berry N. G., Xiao J. L. (2013), Longrange metal-ligand bifunctional catalysis: cyclometallated iridium catalysts for the mild and rapid dehydrogenation of formic acid, *Chem. Sci.*, 4, 1234–1244 (DOI: 10.1039/c2sc21923a) h) Oldenhof S., de Bruin B., Lutz M., Siegler M. A., Patureau F. W., van der Vlugt J. I., Reek J. N. H. (2013), Base-Free Production of H<sub>2</sub> by Dehydrogenation of Formic Acid Using An IridiumbisMETAMORPhos Complex, Chem. - Eur. J., 19, 11507-11511 (DOI:10.1002/chem.201302230) i) Tanaka R., Yamashita M., Chung L. W., Morokuma K., Nozaki K. (2011), Mechanistic Studies on the Reversible Hydrogenation of Carbon Dioxide Catalyzed by an Ir-PNP Complex, Organometallics, 30, 6742-6750 (DOI: 10.1021/om2010172) j) Fink C., Laurenczy G. (2017), CO<sub>2</sub> as a hydrogen vector – transition metal diamine catalysts for selective HCOOH dehydrogenation, Dalton trans., 46, 1670- 1676 (DOI: 10.1039/c6dt04638j) k) Iguchi M., Zhong H., Himeda Y., Kawanami H. (2017), Kinetic Studies on Formic acid Dehydrogenation Catalyzed by an Iridium Complex towards Insights into the Catalytic Mechanism of High-Pressure Hydrogen Gas Production, *Eur. J.*, 1-6 Chem. -23. (DOI: 10.1002/chem.201702969) l) Lu S. M., Wang Z., Wang J., Li J., Li C. (2018), Hydrogen Generation from Formic Acid Decomposition on a Highly Efficient Iridium Catalyst Bearing a Diaminoglyoxime Ligand, Green Chem., 20, 1835-1840 (DOI: 10.1039/c8gc00495a) m) Matsunami A., Kuwata S., Kayaki Y. (2017), A Bifunctional Iridium Catalyst Modified for Persistent Hydrogen Generation from Formic Acid: Understanding Deactivation via Cyclometalation of а 1.2-Diphenylethylenediamine Motif, ACS Catal., 7, 4479-4484 (DOI: 10.1021/acscatal.7b01068) n) Wang W.-H., Xu S., Manaka Y., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2014), Formic Acid Dehydrogenation with Bioinspired Iridium Complexes: A Kinetic Isotope Effect Study and Mechanistic Insight, ChemSusChem., 7, 1976–1983 (DOI: 10.1002/cssc.201301414) o) Li J., Li J., Zhang D, Liu C. (2016), DFT Study on the Mechanism of Formic Acid Decomposition by a Well-Defined Bifunctional Cyclometalated Iridium(III) Catalyst: Self-Assisted Concerted Dehydrogenation via Long-Range Intermolecular Hydrogen Migration, ACS Catal., 6, 4746-4754 (DOI: 10.1021/acscatal.6b00564) p) Hull J. F., Himeda Y., Wang W. H., Hashiguchi B., Periana R., Szalda D. J., Muckerman J. T., Fujita E. (2012), Reversible Hydrogen Storage using CO<sub>2</sub> and a Proton-Switchable Iridium Catalyst in Aqueous Media under Mild Temperatures and Pressures, Nat. Chem., 4, 383-388 (DOI: 10.1038/nchem.1295) q) Wang W. H., Ertem M. Z., Xu S., Onishi N., Manaka Y., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2015), Highly Robust Hydrogen Generation by Bioinspired Ir Complexes for Dehydrogenation of Formic Acid in Water: Experimental and Theoretical Mechanistic Investigations at Different pH, ACS Catal., 5, 5496-5504 (DOI: 10.1021/acscatal.5b01090) r) Iguchi M., Himeda Y., Manaka Y., Kawanami H. (2016), Development of an Iridium-Based Catalyst for High-Pressure Evolution of Hydrogen from Formic Acid, ChemSusChem., 9, 2749-2753 (DOI: 10.1002/cssc.201600697) s) Kanega R., Onishi N., Wang L., Murata K., Muckerman J., Fujita E., Himeda Y. (2018), Picolinamide-Based Iridium Catalysts for Dehydrogenation of Formic Acid in Water: Effect of Amide N-Substituent on Activity and Stability, Chem. - Eur. J., 24, 1-5 (DOI: 10.1002/chem.201805174) t) Papp G., Olveti G., Horvath H., Katho A., Joo F. (2016), Highly efficient dehydrogenation of formic acid in aqueous solution catalysed by an easily available water-soluble iridium(iii) dihydride, Dalton trans., 45, 14516-14519 (DOI: 10.1039/c6dt01695b)

- Wang Z., Lu S.-M., Li J., Wang J., Li C. (2015), Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an N,N'-Diimine Ligand in Water, *Chem. - Eur. J.*, 21, 12592–12595 (DOI: 10.1002/chem.201502086)
- Hull J. F., Himeda Y., Wang W.-H., Hashiguchi B., Periana R., Szalda D. J., James T., Muckerman J. T., Fujita E. (2012), Reversible hydrogen storage using CO<sub>2</sub> and a proton-switchable

iridium catalyst in aqueous media under mild temperatures and pressures, *Nat. Chem.*, 4, 383-388 (DOI: 10.1038/nchem.1295)

- Himeda Y. (2009), Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4'-dihydroxy-2,2'-bipyridine, *Green Chem.*, 11, 2018-2022 (DOI: 10.1039/b914442k)
- Iturmendi A., R- Perez L., Perez- Torrente J. J., Iglesias M., Oro
   L. A. (2018), Impact of Protic Ligands in the Ir-Catalyzed
   Dehydrogenation of Formic Acid in Water, *Organometallics*, 20, 3611–3618 (DOI: 10.1021/acs.organomet.8b00289)
- Filonenko G. A., van Putten R., Schulpen E. N. Hensen E. J, Pidko
   E. A. (2014), Highly Efficient Reversible Hydrogenation of Carbon Dioxide to Formates Using a Ruthenium PNP-Pincer
   Catalyst, *ChemCatChem*, 6, 1526–1530 (DOI: 10.1002/cctc.201402119)
- Rodrguez- Lugo R. E., Trincado M., Vogt M., Tewes F., Santiso-Quinones G., Gritzmacher H. (2013), A homogeneous transition metal complex for clean hydrogen production from methanolwater mixtures, *Nat. Chem.*, 5, 342- 347 (DOI: 10.1038/nchem.1595)
- Gupta K., Tyagi D., Dwivedi A. D., Mobin S. M., Singh S. K. (2015), Catalytic transformation of bio-derived furans to valuable ketoacids and diketones by water-soluble ruthenium catalysts, *Green Chem.*,17, 4618-4627 (DOI: 10.1039/c5gc01376c)

- Dwivedi A. D., Gupta K., Tyagi D., Rai R. K., Mobin S. M., Singh S. K. (2015), Ruthenium and Formic Acid Based Tandem Catalytic Transformation of Bioderived Furans to Levulinic Acid and Diketones in Water, *ChemCatChem*, 7, 4050- 4058 (DOI: 10.1002/cctc.201501021)
- Boddien A., Mellmann D., Gärtner F., Jackstell R., Junge H., Dyson P. J., Laurenczy G., Ludwig R., Beller M. (2011), Efficient Dehydrogenation of Formic Acid Using an Iron Catalyst, *Science*, 333, 1733-1736 (DOI: 10.1126/science.1206613)
- Carmona D., Lamata P., Sanchez A., Pardo P., Rodriguez R., Ramirez P., Lahoz F. J., Garcia-orduna P., Oro L. A. (2014), Chiral bronsted acid catalysts. Activation of methyl 3, 3, 3triflouropyruvate by hydroxymethylpyridine-containing halfsandwich complexes, *Organometallics*, 33, 4016-4026 (DOI: 10.1021/om5005463)
- 21. Tenorio M. J., Puerta M. C., Valerga P. (2011), Facile O–H Bond Activation in Alcohols by [Cp\*RuCl(iPr2PSX)] (X = Pyridyl, Quinolyl): a Route to Ruthenium (IV) Hydrido(alkoxo) Derivatives, *Inorg. Chem.*, 50, 12399-12401 (DOI: 10.1021/ic201912b)
- 22. Nishibayashi Y., Imajima H., Onodera G., Inada Y., Hidai M., Uemura S. (2004), Preparation of Alkanechalcogenolate- and Benzenechalcogenolate-Bridged Diruthenium Complexes and Their Catalytic Activity toward Propargylation of Acetone with

Propargylic Alcohol, *Organometallics*, 23, 5100– 5103 (DOI: 10.1021/om049475f)

- 23. Mellone I., Peruzzini M., Rosi L., Mellmann D., Junge H., Beller M., Gonsalvi L. (2013), Formic Acid Dehydrogenation Catalysed by Ruthenium Complexes Bearing the Tripodal Ligands Triphos and NP3, *Dalton trans.*, 42, 2495-2501 (DOI: 10.1039/c2dt32043f)
- Yang Z., Zhu Z., Luo R., Qiu X., Liu J. T., Yang J. K., Tang W. (2017), Iridium-Catalyzed Highly Efficient Chemoselective Reduction of Aldehydes in Water using Formic Acid as the Hydrogen Source, *Green Chem.*, 19, 3296- 3301 (DOI: 10.1039/c7gc01289f)
- Sheldrick G. M. (2008), A short history of SHELX, Acta crystallogr, Sect. A: Found. Crystallogr. 64, 112-122 (DOI: 10.1107/s0108767307043930)

# Chapter 3

Hydrogen production from formic acid and formaldehyde over N,O donor ligand based areneruthenium (II) catalysts in water

# **3.1. Introduction**

Sustainable development of our society requires the use of renewable energy and reduce the global dependency over the depleting fossil fuel resources. Hydrogen gas is one of the most promising alternative sources of energy for the next generation,<sup>[1]</sup> but its explosive nature limits the safe storage and transportation of hydrogen.<sup>[2-4]</sup> In this context, worldwide scientific efforts are concentrated on the liquid organic hydrogen carriers (LOHCs)<sup>[5,6]</sup> such as formic acid (4.4 wt%  $H_2$ ,<sup>[7-12]</sup> formaldehyde (8.4 wt%  $H_2$  HCHO- $H_2O$ ),<sup>[13-18]</sup> and methanol (12.5 wt% H<sub>2</sub>),<sup>[11]</sup> which are not only stable, safe to handle and transport but also release hydrogen under relatively mild conditions in the presence of a suitable catalyst. Moreover, formic acid can be produced either from biomass or directly by the catalytic hydrogenation of CO<sub>2</sub>.<sup>[19,20]</sup> Most importantly, hydrogen generation from formic acid has a low reaction enthalpy and is thermodynamically favourable allowing the dehydrogenation reaction to occur at mild reaction conditions.<sup>[9]</sup> However, the dehydration of formic acid to CO gas is also thermodynamically favourable<sup>[11]</sup> and hence the development of effective catalyst is essentially required for the selective production of  $H_2$  from formic acid by suppressing this side reaction. Beller *et al.*<sup>[21]</sup> and Laurenczy et al.<sup>[22]</sup> independently reported efficient and selective ruthenium catalysts for the production of hydrogen gas from formic acid (Scheme 3.1). Laurenczy et al. performed formic acid (HCOOH/HCOONa = 9:1) dehydrogenation in aqueous solution using [Ru(H<sub>2</sub>O)<sub>6</sub>](tos)<sub>2</sub>/ TPPTS (tos is *p*-toluene sulfonate and TPPTS is *m*trisulfonated triphenylphosphine) (C-29 in Scheme 3.1), to achieve a

turnover frequency of 460 h<sup>-1</sup> at a temperature of 120 °C.<sup>[22]</sup> Since then, many efficient homogeneous catalysts for formic acid dehydrogenation have been reported,<sup>[7-11,23-25]</sup> but most of the catalysts explored so far either requires organic additives (*e.g.* amines) or are active in organic solvents.<sup>[26-31]</sup>



*Scheme 3.1. Literature available ruthenium-based catalysts for formic acid dehydrogenation in aqueous medium.* 

Notably the use of organic additives or solvents are not suitable for PEM fuel cells, and hence the development of aqueous catalytic systems are highly sought after.<sup>[32]</sup> Until now, only a limited number of catalysts, mostly iridium-based complexes are found to be very effective for formic acid dehydrogenation in water in the absence of any organic additives.<sup>[7-11,33-39]</sup> Himeda *et al.* reported a family of  $(\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(III) complexes bearing N,N-donor bidentate ligands as active catalysts for formic acid dehydrogenation in aqueous medium, where the electrondonating ability of the ligands to the metal centre is found to be a crucial parameter to achieve higher catalytic activity.<sup>[40-46]</sup> Although ( $\eta^5$ -C5Me5)Ir(III) based catalysts have shown very promising results for hydrogen production from formic acid, development of other less expensive alternative catalysts such as Ru based complexes are also gaining attention. For instance, Huang et al. investigated formic acid dehydrogenation over  $[(\eta^6-C_{10}H_{14})RuCl(2,2'-bi-2-imidazolin)]^{+2}$  (C-3 in Scheme 3.1) at 90 °C in water.<sup>[24]</sup> On the other hand, Gonsalvi et al. investigated RuCl<sub>3</sub>.3H<sub>2</sub>O, in presence of different water-soluble phosphines bearing sulphonated groups as ligands (C-30 in Scheme 3.1),

for formic acid dehydrogenation in water at 90 °C.<sup>[47]</sup> Recently, we have also investigated arene-ruthenium catalyst  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}NHMe-MAmQ)Cl]^+$  (MAmQ is 8-(N-methylamino)quinoline) ([**Ru**]-4 in Scheme 3.1) for formic acid dehydrogenation in water at 90 °C. Our findings including detailed mechanistic investigations inferred that the 8-aminoquinoline ligands played a crucial role in the observed enhanced catalytic activity.<sup>[48]</sup>

Analogous to formic acid, formaldehyde is also emerging as an attractive liquid organic hydrogen carrier (LOHC), as formaldehyde exhibits long-term stability (as methanediol in water), non-flammable and a hydrogen weight efficiency of 8.4 wt % (HCHO-H<sub>2</sub>O).<sup>[13]</sup> In addition to this, the dehydrogenation of formaldehyde/water system is exothermic ( $\Delta H_r = -35.8 \text{ kJ mol}^{-1}$ ) in nature, and hence is thermodynamically favourable.<sup>[13]</sup> The catalytic dehydrogenation of formaldehyde involves a two-step dehydrogenation pathway: (i) the first being water-assisted dehydrogenation of formaldehyde to formic acid and one equivalent of  $H_2$  and (ii) finally dehydrogenation of formic acid to release the second equivalent of  $H_2$  and one equivalent of  $CO_2$ .<sup>[13-18]</sup> In this direction, Prechtl et al. first reported hydrogen production from formaldehyde using the diruthenium catalysts  $[(\eta^6-p-\text{cymene})\text{RuCl}_2]_2$ and  $[(\text{Ru}(p\text{-cymene}))_2(\mu\text{-H})(\mu\text{-HCO}_2)(\mu\text{-Cl})]^+$  (C-24 in Scheme 3.3) in water at 95 °C.<sup>[13,14]</sup> Later, several ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(III) and Ru(II) based catalysts were explored for formaldehyde dehydrogenation in water.<sup>[15-</sup> <sup>17]</sup> For instance, Grutzmacher *et al.* investigated ruthenium catalyst for formaldehyde dehydrogenation and achieved a turnover number of 1787 and initial TOF >20000  $h^{-1}$ , albeit reaction required strongly alkaline condition in H<sub>2</sub>O/THF solution.<sup>[17]</sup> Very recently, Himeda et al. reported a water-soluble arene-ruthenium complex (C-28 in Scheme 3.3) for an efficient additive-free dehydrogenation of aqueous formaldehyde with a turnover number of 24000.<sup>[49]</sup> Hence, it is evident that dehydrogenation of formic acid and formaldehyde in water can be achieved over a suitably designed catalytic system.

Herein, we report water soluble arene-ruthenium complexes  $[(\eta^{6} - arene)Ru(\kappa^{2}-L)]^{n+}$  (n = 0,1) (**[Ru]-8 – [Ru]-16**) bearing pyridine-based ligands as active catalysts for hydrogen production from formic acid in water. Molecular structure of a representative complex **[Ru]-9** is authenticated by X-ray crystallography. In addition, the role of reaction temperature, pH, formic acid and catalyst concentration on the reaction kinetics are investigated in detail. Moreover, mechanistic insights are elaborated by identifying several catalytic intermediates involved in various steps of the catalytic dehydrogenation of formic acid under the catalytic and controlled reaction conditions. The structure of a diruthenium species, possibly the catalyst resting state, is also established by X-ray crystallography. Encouraged by the results obtained in formic acid dehydrogenation, we also employed the most active catalyst **[Ru]-8** for the base-free hydrogen production from formic formic formic formic acid under moderate reaction conditions.

#### 3.2. Results and Discussion

#### **3.2.1.** Synthesis and characterization of catalysts

Monocationic water-soluble arene-ruthenium complexes [**Ru**]-8 – [**Ru**]-11 bearing pyridine-2-ylmethanol (**L2**) and 1-(pyridin-2-yl)ethanol (**L3**) are synthesized in good yields by treating the respective ligands with the arene-ruthenium precursors  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene = C<sub>6</sub>H<sub>6</sub> and C<sub>10</sub>H<sub>14</sub>) in methanol under refluxing condition (Scheme 3.2). The complexes [**Ru**]-12 – [**Ru**]-15 are synthesized in accordance with the previously reported procedures, and the characterization data of these complexes corroborate well with their established molecular structures.<sup>[50,51]</sup> Analogous monocationic arene-ruthenium complex [**Ru**]-16 is also synthesised by treating pyridine-2ylmethanamine (**L4**) with [( $\eta^6$ -C<sub>10</sub>H<sub>14</sub>)RuCl<sub>2</sub>]<sub>2</sub> in methanol under refluxing condition.<sup>[52]</sup> The obtained yellow to brown coloured complexes are characterized using various spectro-analytical techniques, which corroborated well with the proposed structures. ESI-mass spectra of the obtained complexes showed prominent mass peaks corresponding to the cationic mononuclear arene-ruthenium complexes with general formula  $[(\eta^6 - C_6H_6)RuCl(\kappa^2-L)]^+$  (L = L2 – L3) for the complexes [Ru]-8 – [Ru]-11.



*Scheme 3.2. Complexes explored for the dehydrogenation of formic acid in water.* 

<sup>1</sup>H NMR spectra of the complexes [**Ru**]-8 – [**Ru**]-11 displayed the downfield shift in the chemical shift for the protons of the ligands as compared to that of respective free ligands, which is consistent with the coordination of these ligands with the ( $\eta^6$ -arene)Ru(II) moiety. In [**Ru**]-**8**, pyridine protons of **L2** resonated in the range of 7.39–9.17 ppm as compared to that observed in the free ligand **L2** (7.36–8.54 ppm). Analogously for [**Ru**]-9, pyridine protons of **L2** resonated in the downfield region of 7.38-9.22 ppm. Pyridine protons of **L3** in [**Ru**]-10 also resonated in the downfield region of 7.36-9.21 ppm as compared to that observed for the free ligand **L3** (7.19-8.36 ppm). In addition, the CH<sub>3</sub> protons of **L3** appeared as a doublet at 1.52 ppm for [**Ru**]-10. Similar trend in the aromatic and methyl protons of ligand **L3** is also observed for [**Ru**]-11. In addition, methylene (-CH<sub>2</sub>-) protons of **L2** in complexes [**Ru**]-8 and [**Ru**]-9 resonated in its usual chemical shift value.<sup>[53]</sup> The <sup>1</sup>H NMR resonances for the protons corresponding to  $\eta^6$ -

C<sub>10</sub>H<sub>14</sub> ring coordinated to ruthenium in [Ru]-8 and [Ru]-10 are observed in the expected region.<sup>[51]</sup> Moreover, the ruthenium bound  $\eta^6$ - $C_6H_6$  ring protons resonated as a singlet in the range of 5.92 and 5.95 ppm respectively for [Ru]-9 and [Ru]-11, suggesting the equivalence of ruthenium coordinated benzene ring in [Ru]-9 and [Ru]-11. Further, the molecular structure of the representative complex [Ru]-9 is also confirmed by X-ray crystallography using X-ray suitable crystals of [Ru]-9 grown by slow diffusion of diethyl ether in methanol solution of [Ru]-9 at room temperature (Figure 3.1 and Tables 3.4 - 3.6). [Ru]-9 crystallized in triclinic crystal system with the P-1 space group. The geometry around the ruthenium metal centre is pseudo-octahedral with piano-stool geometry of [**Ru**]-9, where the  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ring occupied the top of the piano stool and the legs of the stool are occupied by the  $\kappa^2$ -L2 and chloro ligands. The bond angle from the  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> ring centroid (C<sub>t</sub>) to each of the legs are more than 120°, (Ct-Ru-Npy, Ct-Ru-O and Ct-Ru-Cl are 133.23°, 130.94° and 128.15°, respectively), which is consistent with the piano stool geometry of [Ru]-9.<sup>[6,50,51]</sup> Centroid (C<sub>t</sub>) to Ru distance (1.422 Å) and Ru-Cl bond length (2.406 Å) are also consistent with analogous ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru(II) complexes.<sup>[51]</sup> The ligand pyridine-2ylmethanol (L2) is coordinated with the ruthenium metal in a bidentate fashion, involving the nitrogen atom  $(N_{py})$  of the pyridine ring and the oxygen atom of the hydroxyl group. The Ru-N<sub>py</sub> and Ru-O bond lengths are 2.104 Å and 2.131 Å respectively, which is consistent with the sp<sup>2</sup> hybridized  $N_{py}$  as observed for analogous arene-ruthenium complexes.<sup>[51]</sup> The important crystallographic details and selected bond parameters are summarized in Tables 3.4 - 3.6 (in experimental section).



*Figure 3.1.* Single crystal X-ray molecular structure of [*Ru*]-9. Selected bond lengths (Å) and angles (°): *Ru*(1)-*N*(1) 2.1035(16), *Ru*(1)-*O*(1) 2.1307(14), *Ru*(1)-*Cl*(1) 2.4060(5), *N*(1)-*Ru*(1)-*O*(1) 76.08(6), *N*(1)-*Ru*(1)-*C*(11) 123.45(11), *O*(1)-*Ru*(1)-*C*(11) 159.86(11).

3.2.2. Ruthenium catalysed dehydrogenation of formic acid in water. Preliminary investigation for screening the most active catalyst among the complexes [Ru]-8 – [Ru]-16 (1 mol%), inferred that the complexes [Ru]-8 – [Ru]-15 bearing pyridine-based N,O donor ligands outperformed over [Ru]-16 containing pyridine-2yl-methanamine (L4) for hydrogen generation from formic acid (0.4 M, 2.5 mL) in the presence of sodium formate (5 mol%) at 90 °C in water (Table 3.1 and Figure 3.2). Moreover, the  $\eta^6$ -arene ring exerted significant effect on the catalytic activity, where the electron rich  $(\eta^6-C_{10}H_{14})Ru(II)$  complexes ([Ru]-8, [Ru]-10, [Ru]-12, [Ru]-13 and [Ru]-15) exhibited higher activity than the  $(\eta^6 - C_6H_6)Ru(II)$  complexes ([Ru]-9, [Ru]-11 and [Ru]-14). Among these catalysts, [Ru]-8 displayed the highest turnover frequency (TOF) of 660 h<sup>-1</sup> under the optimized reaction conditions (Table 1, entry 1). Analogous to [Ru]-8, the 1-(pyridin-2-yl)ethanol ligated  $(\eta^6-C_{10}H_{14})Ru(II)$  complex **[Ru]-10** also exhibited similar activity (TOF 653 h<sup>-1</sup>). Interesting to note that the cationic ( $\eta^6$ -C<sub>10</sub>H<sub>14</sub>)Ru(II)-pyridyl-ethanone complex [Ru]-12 also displayed

appreciably good activity (TOF 535 h<sup>-1</sup>). On the other hand, **[Ru]-13** bearing a strongly chelating  $\kappa^2$ -hydroxyquinoline ligand exhibited lower activity (TOF 475 h<sup>-1</sup>). Moreover, ruthenium-picolinate complex **[Ru]-15** exhibited the lowest activity (TOF 237 h<sup>-1</sup>). The observed trend in the catalytic activities are associated with the involvement of oxygen atom in facile de/protonation pathway during the dehydrogenation reaction and the coordination behaviour of the ligands in the complexes **[Ru]-8** – **[Ru]-16** (Table 3.1 and Figure 3.2).



**Figure 3.2**. (a) Comparative catalytic activity of [**Ru**]-8 – [**Ru**]-16 for formic acid dehydrogenation. Reaction conditions: formic acid (0.4 M, 2.5 mL), catalyst (1 mol%), sodium formate (0.05 mmol), 90 °C. (b) pH dependent dehydrogenation of formic acid over [**Ru**]-8, where pH is altered by tuning n(formic acid)/n(sodium formate) ratio. Reaction condition: [**Ru**]-8 (1 mol%), formic acid (4.0 M, 2.5 mL), 90 °C.

Sodium formate concentration exerted a crucial role in enhancing the rate of formic acid dehydrogenation over **[Ru]-8**. Results inferred that TOF gradually increased with the increase in sodium formate content from 0.02 to 0.5 equiv with respect to formic acid. An initial TOF of 1548 h<sup>-1</sup> is achieved for the dehydrogenation of formic acid (4 M, 2.5 mL) with 2 equiv. of sodium formate over **[Ru]-8**, under the optimized reaction condition (Table 3.1, and Figure 3.3).



**Figure 3.3.** (a) TOF  $(h^{-1})$  vs [HCOONa] (mmol) plot for the catalytic dehydrogenation of formic acid over [**Ru**]-8. Reaction condition: formic acid (0.4 M, 2.5 mL), [**Ru**]-8 (0.01 mmol), 90 °C. <sup>a</sup>formic acid (2.0 M, 2.5 mL).<sup>b</sup>formic acid (4.0 M, 2.5 mL). (b) Gas produced (mmol) vs time (min) plot for the catalytic dehydrogenation of formic acid over [**Ru**]-8. Reaction condition: formic acid (4.0 M, 2.5 mL), [HCOONa]/[HCOOH] = 2:1, [**Ru**]-8 (0.01 mmol), 90 °C.

The produced gas is analysed as a mixture of H<sub>2</sub> and CO<sub>2</sub> (H<sub>2</sub>:CO<sub>2</sub> = 1:1) using GC-TCD, which is consistent with the expected H<sub>2</sub>/CO<sub>2</sub> ratio for formic acid dehydrogenation. Figure 3.2b displayed the pH dependent TOF for [**Ru**]-**8** catalysed formic acid dehydrogenation. As inferred from the graph, TOF increased with the decrease in pH from 7.5 to 4.0, and a highest TOF of 1548 h<sup>-1</sup> is achieved at pH  $\approx$  4.0. Moreover, with further decrease in pH < 4.0, TOF also decreases. These observations suggesting the important role of hydronium (H<sub>3</sub>O<sup>+</sup>) and formate (HCO<sub>2</sub><sup>-</sup>) ions in formic acid dehydrogenation. At 60 °C, dehydrogenation of formic acid is found to be sluggish, while with the increase in the reaction temperature TOF also increased (Figure 3.4a). The apparent activation energy (E<sub>a</sub>) of 25.4 kcal mol<sup>-1</sup> (Figure 3.4b) revealed that the catalyst [**Ru**]-**8** is inherently active for formic acid dehydrogenation in water.<sup>[24,37,48]</sup>

entry	catalyst	T(°C)	<i>n</i> (formic acid)/ <i>n</i> (sodium formate)	TON <sup>b</sup>	$TOF(h^{-1})^b$
1	[Ru]-8	90	1/0.05	99	660
2	[Ru]-9	90	1/0.05	95	380
3	[ <b>R</b> u]-10	90	1/0.05	98	653
4	[Ru]-11	90	1/0.05	95	380
5	[Ru]-12	90	1/0.05	98	535
6	[Ru]-13	90	1/0.05	95	475
7	[Ru]-14	90	1/0.05	91	366
8	[Ru]-15	90	1/0.05	91	237
9	[Ru]-16	90	1/0.05	95	95
10	[Ru]-8	90	1/-	95	146
11	[Ru]-8	90	-/1	-	-
12	[Ru]-8	90	1/0.02	95	228
13	[Ru]-8	90	1/0.04	98	490
14	[Ru]-8	90	1/0.5	95	1141
15	[Ru]-8	90	5/5	450	1241 <sup>c</sup>
16	[Ru]-8	90	5/10	450	1446 <sup><i>c</i></sup>
17	[Ru]-8	90	5/15	450	1262 <sup><i>c</i></sup>
18	[Ru]-8	90	10/20	880	$1548^{c}$
<sup>a</sup> Reaction	on conditions:	formic	acid (0.4 - 4.0 M, 2	2.5 mL), ca	atalyst (0.01
mmol)	00 °C Each	roantia	n is repeated twice	bTONG on	d TOEs are

 Table 3.1. Dehydrogenation of formic acid in water using [Ru]-8 – [Ru] 

 16<sup>a</sup>

"Reaction conditions: formic acid (0.4 - 4.0 M, 2.5 mL), catalyst (0.01 mmol), 90 °C. Each reaction is repeated twice. <sup>*b*</sup>TONs and TOFs are determined after completion of the reaction unless specified otherwise. <sup>*c*</sup>Initial TOFs (15 min)


**Figure 3.4.** (a) Temperature dependent formic acid dehydrogenation over [**Ru**]-8, and the corresponding (b) Arrhenius plot of the initial TOF values for formic acid (2M, 2.5 mL) dehydrogenation over [**Ru**]-8 (0.2 mol%), [HCOONa]/[HCOOH] = 2:1, 60°C – 90 °C.

[Ru]-8 also exhibited appreciably good stability in water and in the presence of higher concentration of formic acid ([HCOOH]/[cat] up to 7000) (Figure 3.5). The double logarithmic plots of the initial reaction rates of formic acid dehydrogenation (1.0 M, 2.5 mL) with the concentration of [Ru]-8 (0.01 mmol - 0.04 mmol) followed a linear dependence (Figure 3.6a). The obtained order of 0.97 with respect to the catalyst concentration suggesting that presumably the monomeric species of [Ru]-8 catalyst generated during the initial period of the catalytic reaction, is the most active species involved in formic acid dehydrogenation reaction. Noteworthy to mention, that a turnover number up to 6050 is achieved for the dehydrogenation of formic acid using [Ru]-8 catalyst for seven consecutive catalytic runs at 90 °C, evidenced the higher stability of [Ru]-8 in water (Figure 3.5). Further, the reaction order of 0.43 for the dehydrogenation of varying concentration of formic acid (0.2 M - 0.8 M) over 0.01 mmol of [Ru]-8 catalyst at 90 °C, evidenced the equimolar interaction of formic acid or formate ion with Ru center to form [HCOO-Ru] species during the catalytic dehydrogenation of formic acid (Figure 3.6b).<sup>[24,37,48]</sup>



**Figure 3.5.** Recyclability experiment for the catalytic dehydrogenation of formic acid over **[Ru]-8**. Reaction condition: formic acid (4.0 M, 2.5 mL), **[Ru]-8** (1 mol%), n(formic acid)/n(sodium formate) = 1:2, 90 °C. (10 mmol of formic acid is added to the reaction mixture after each run).



**Figure 3.6.** (a) Plot of  $ln[initial rate(mmolL^{-1}h^{-1})]$  vs  $ln[cat](mmol L^{-1})$ . Reaction condition: **[Ru]-8** (0.01 mmol – 0.04 mmol), formic acid (1.0 M, 2.5 mL), 90 °C. (b) Plot of  $ln[initial rate(mmolL^{-1}h^{-1})]$  vs  $ln[HCOOH](mmol L^{-1})$ . Reaction condition: **[Ru]-8** (0.01 mmol), formic acid (0.2 – 0.8 M, 2.5 mL), 90 °C.

### 3.2.3. Mechanistic study

Mass investigations of formic acid dehydrogenation reaction under catalytic and controlled reaction conditions evidenced the presence of several important ruthenium species. At first instance, a visible colour change from the initial yellow solution of the catalyst **[Ru]-8** to a redorange solution is observed during the initial minutes of the catalytic dehydrogenation of formic acid, and this colour remains stable even after the completion of the catalytic reaction (Figure 3.7).



**Figure 3.7.** Transformation of colour of the reaction mixture during the catalytic dehydrogenation of formic acid. Reaction Conditions: **[Ru]-8** (0.01 mmol), formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol), T = 90 °C.

A prominent mass peak at m/z 344 corresponding to  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{py}O-L2)]^+$  [**Ru**]-8A is observed in the reaction aliquot obtained after the catalytic dehydrogenation of formic acid (0.4 M, 2.5 mL) over [**Ru**]-8 (1 mol %) in the presence of sodium formate (0.05 mmol) at 90 °C. (Figure 3.8). Further, the addition of an excess of dilute HCl in the redorange solution obtained after the catalytic reaction resulted in the regeneration of the yellow colour. Mass analysis of this solution exhibited the presence of a prominent mass peak at m/z 380.0, suggesting the regeneration of [**Ru**]-8 (Figure 3.8).



Figure 3.8. Mass investigation of the reaction mixture for catalytic dehydrogenation of formic acid over [Ru]-8 catalyst showing the colour change from the initial yellow to red-orange during the initial minutes and reverts back to yellow colour when treated with an excess of dilute HCl.

Mass analysis of the reaction aliquot obtained from the reaction of [Ru]-8 with formic acid (in the absence of sodium formate) in water at room temperature also inferred the presence of several ruthenium species including  $[(\eta^6 - C_{10}H_{14})Ru(\kappa^2 - N_{py}OH - L2)(H_2O)]^{2+}([Ru] - 8D, m/z)$ 181),  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{py}OH-L2)]^{2+}$  ([**Ru**]-8E, m/z 172) and  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{py}OH-L2)]^{2+}$  $_{10}H_{14}$ )Ru( $\kappa^2$ -N<sub>py</sub>O-L2)]<sup>+</sup> ([Ru]-8A, m/z 344) (pH of the solution was 2.1) (Figure 3.9). Further, a weak mass peak at m/z = 412 ([**Ru**]-8B + Na<sup>+</sup>, Figure 3.9) corresponding to formate coordinated ruthenium species [Ru]-8B is also observed when formic acid-sodium formate (10:1) was added to [Ru]-8 in water at room temperature (pH of the solution was 2.6). However, **[Ru]-8B** is not observed during the mass investigation of the sodium formate assisted dehydrogenation of formic acid over [Ru]-8 at 90 °C. It has been observed that in the presence of sodium formate, an intense mass peak at m/z 344 corresponding to [Ru]-8A appeared as the only most populated species in the reaction aliquot, while the species [Ru]-8D, [Ru]-8E or [Ru]-8B are not observed (Figure 3.9). Further, in an attempt to isolate [Ru]-8A via crystallization, we eventually obtained a dimeric form of [**Ru**]-8A,  $[\{(\eta^6-C_{10}H_{14})Ru(\kappa^2 N, O-\mu-O-L1\}_2]^{2+1}$ 

designated as [**Ru**]-**8A**' (Figure 3.9). X-ray molecular structure of [**Ru**]-**8A**' is displayed in Figure 3.9. While the crystallographic refinement data for [**Ru**]-**8A**' is not satisfactory for reporting, the obtained molecular structure is consistent with the proposed structure of [**Ru**]-**8A**' (Figure 3.9 and Tables 3.7 – 3.9). It is evident that coordinatively unsaturated [**Ru**]-**8A** species dimerized to form [**Ru**]-**8A**', where oxygen atom of pyridine-2-ylmethanol (**L2**) bridged two units of [**Ru**]-**8A** to form a stable dicationic [**Ru**]-**8A**'. Similar dimerization of analogous unsaturated metallic species is also available in literature.<sup>[48,54]</sup> Further, we noted that the mass spectra of the isolated dimeric species [**Ru**]-**8A**' also shows intense peak at m/z = 344. Therefore, it might be possible that the signals in the mass spectra for [**Ru**]-**8A** is a fragment of [**Ru**]-**8A**' formed by dissociation in the gas phase, and in solution [**Ru**]-**8A**'.



*Figure 3.9.* Various intermediate species observed during the mass investigation for formic acid dehydrogenation reaction performed over *[Ru]-8* under varying controlled reaction conditions, and X-ray molecular structure of the dimeric ruthenium species *[Ru]-8A'*.

Further, indication for the involvement of Ru-hydride species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{py}O-L1)(H)]$  ([**Ru**]-8C) in formic acid dehydrogenation reaction is obtained by the presence of the corresponding <sup>1</sup>H NMR signals at  $\delta = -10.56 \sim -10.98$  ppm during the reaction of [**Ru**]-8 (0.01 mmol) with HCOONa (0.05 mmol) in D<sub>2</sub>O (0.6 mL) at room temperature (Figure 3.10).



**Figure 3.10.** (a) <sup>1</sup>H NMR spectra showing the generation of Ru-hydride species during the treatment of [**Ru**]-8 (0.01 mmol) with sodium formate (0.05 mmol) in  $D_2O$  (0.6 mL) at 25 °C (b) <sup>1</sup>H NMR of [**Ru**]-8 in  $D_2O$  at 25 °C.

g	p	С	l	
C	)			

entry	catalyst	substrate	solvent	$\begin{array}{l} \text{TOF} \\ (\text{h}^{-1})^b \end{array}$	KIE <sup>c</sup>
1	[Ru]-8	НСООН	$H_2O$	146	
2	[Ru]-8	НСООН	$D_2O$	80	1.8
3	[Ru]-8	DCOOD	$H_2O$	51	2.9
4	[Ru]-8	DCOOD	$D_2O$	42	3.5
<sup>a</sup> Reaction conditions: [Ru]-8 (0.01 mmol), formic					
acid (0.4 M, 2.5 mL), 90 °C. $^{b}$ Initial TOF at 30 min.					
<sup><i>c</i></sup> KIE = TOF (entry 1)/ TOF (entry n) (n = 2, 3, 4)					

Moreover, kinetic isotope effect (KIE) studies indicated that decarboxylation is the rate determining step and not the proton assisted release of hydrogen gas in the catalytic cycle of formic acid dehydrogenation (Table 3.2). Results inferred that the deuterated formic acid (DCOOD) is more influential than D<sub>2</sub>O (Table 3.2, entries 2,3) in the reaction rate for the catalytic reaction performed over [**Ru**]-**8** with HCOOH in D<sub>2</sub>O or DCOOD in H<sub>2</sub>O under the optimized reaction condition. Therefore, these findings inferred the crucial role of [**Ru**]-**8A**' in sodium formate assisted formic acid dehydrogenation reaction, where initially the coordination of formate to [**Ru**]-**8A**' generated [**Ru**]-**8B**, which further undergoes decarboxylation to form [**Ru**]-**8C** and finally [**Ru**]-**8A**' is regenerated after the proton assisted hydrogen gas release from [**Ru**]-**8C**.

**3.2.4.** Catalytic dehydrogenation of formaldehyde in water. Dehydrogenation pathway for complete conversion of formaldehyde to  $H_2$  also involves *in situ* generation of formate ions, which subsequently dehydrogenate to yield two equivalents of  $H_2$  per molecule of formaldehyde in water. Therefore, it is evident that most of the active catalytic species involved in formic acid dehydrogenation may also be active for formaldehyde dehydrogenation.



*Scheme* 3.3. *Literature available ruthenium-based catalysts for hydrogen production from formaldehyde in water.* 

The time course plot for **[Ru]-8** catalysed gas generation from varying concentration of aqueous formaldehyde (0.4, 2.0 and 4.0 M) is displayed in Figure 3.11. The release of H<sub>2</sub> and CO<sub>2</sub> gas from [Ru]-8 catalysed dehydrogenation of formaldehyde is confirmed by GC-TCD analysis. To our delight, **[Ru]-8** is also active for the catalytic hydrogen production from formaldehyde (aq.) at 90 °C in the absence of any additive or base. [Ru]-8 catalyst performed well even with higher concentration of formaldehyde (4.0 M, 2.5 mL), to achieve a turnover number of 1838 with an initial turnover frequency of 1072 h<sup>-1</sup> (Table 3.3). Though the catalyst reported by Himeda et al. (C-28 in Scheme 3.3) displayed the highest activity for formaldehyde dehydrogenation under base-free condition in water,<sup>[49]</sup> the observed catalytic performance of [Ru]-8 is promising. Notably, the activity of [Ru]-8 is still several folds higher than the earlier reported Cp\*Ir(III) catalysts active under alkaline condition.<sup>[15,16]</sup> Moreover, the turnover number of [**Ru**]-8 is higher than the diruthenium complex (C-24 in Scheme 3.3) reported by Prechtl et al. for formaldehyde dehydrogenation, however, we could achieve a turnover frequency of 1072 h<sup>-1</sup> only using [**Ru**]-8 catalyst.[13,14]



**Figure 3.11.** Time course plot for the catalytic dehydrogenation of formaldehyde over the catalyst **[Ru]-8**. Reaction conditions: **[Ru]-8** (0.01 mmol), formaldehyde (0.4 – 4.0 M, 2.5mL) in water at 90 °C.

**Table 3.3.** Catalytic dehydrogenation of formaldehyde over [Ru]-8 inwater<sup>a</sup>

entry	[ <b>Ru]-8</b> (mmol)	aq. formaldehyde (mmol)	$\mathrm{TON}^b$	TOF $(h^{-1})^c$
1	0.01	1	82(246)	131(247)
2	0.01	5	317(961)	328(807)
3	0.01	10	618(1838)	327(1072)

<sup>*a*</sup>Reaction conditions: All the reactions are performed at 90 °C. All the initial volume of the reaction is 2.5 mL. <sup>*b*</sup>TON is determined at the completion of the reaction (values given in parenthesis are determined by  $n(H_2 + CO_2)/n(\text{catalyst})$ ). <sup>*c*</sup>Initial TOF (10 mins), values given in parenthesis are determined by  $\{n(H_2 + CO_2)/n(\text{catalyst})\}/t$ .

In order to gain further insights into the reaction pathway of formaldehyde dehydrogenation in water, composition of the gas released

was analysed by GC-TCD and the pH of the reaction medium was monitored at different time intervals of the reaction progress (Figure 3.12). By measuring the composition of the gas released (showing a gradual increase in CO<sub>2</sub>:H<sub>2</sub> ratio) and the pH values, we could confirm that the reaction follows the same pathway as described by Prechtl *et*  $al.^{[13]}$ 



*Figure 3.12. Time-dependent pH plot for the catalytic formaldehyde dehydrogenation reaction. Reaction conditions:* [*Ru*]-8 (0.01 mmol), *formaldehyde* (0.4M, 2.5mL), 90 °C.

Notably, mass investigation of the catalytic reaction aliquots inferred the presence of several ruthenium species (**[Ru]-8A'**, **[Ru]-8D**, **[Ru]-8E**) (Figure 3.13 and Figure 3.14). Moreover, the mass investigations also revealed the presence of m/z peak at 551.6 corresponding to the formate bridged diruthenium species [{Ru( $\eta^6$ -p-cymene)}<sub>2</sub>( $\mu$ -HCOO)( $\mu$ -Cl)( $\mu$ -H)]<sup>+</sup>, as earlier reported by Prechtl *et al.*<sup>[13,14]</sup> The time dependent mass study for formaldehyde dehydrogenation reaction also inferred the presence of this diruthenium species which is presumably formed due to ligand dissociation. Noticeably, mass investigation inferred that the mass peak m/z 344 corresponding to **[Ru]-8A'** always remains the most

intense peak during the formaldehyde dehydrogenation reaction (Figure 3.14).



*Figure 3.13. Transformation of colour of the reaction mixture during the catalytic dehydrogenation of aqueous formaldehyde. Reaction condition: [Ru]-8* (0.01 mmol), aq. formaldehyde (0.4 M, 2.5mL), 90 °C.



*Figure 3.14.* ESI-MS during the catalytic dehydrogenation of aq. formaldehyde after 10 minutes. Reaction conditions: [*Ru*]-8 (0.01 mmol), formaldehyde (0.4 M, 2.5 mL), T = 90 °C.

Further, we also investigated the catalytic activity of **[Ru]-8** for formaldehyde dehydrogenation under the reaction condition as reported by Prechtl *et al.* (0.026 mmol (0.2 mol %) **[Ru]-8**, 13.55 mmol, formaldehyde (37 wt% aq. formaldehyde), 95 °C). Results inferred the

release of 246 mL of gas (H<sub>2</sub> and CO<sub>2</sub>) in 200 minutes for [Ru]-8 catalysed dehydrogenation of formaldehyde in comparison to the release of 180 mL of gas released in 200 minutes using [{Ru( $\eta^6$ -p-cymene)}<sub>2</sub>( $\mu$ - $HCOO(\mu-Cl)(\mu-H)$ <sup>+</sup> under analogous base-free condition as reported by Prechtl et al.<sup>[13]</sup> Based on our findings, we can conclude that during dehydrogenation, initially the formaldehyde coordination of methanediol to [Ru]-8A' resulted in the formation of Ru-methanediol species ([Ru]-8F), which subsequently upon dehydrogenation to an equivalent of H<sub>2</sub> (via a Ru-H intermediate) form a ruthenium-formate species ([Ru]-8B). Consequently, the Ru-formate species ([Ru]-8B) undergoes decarboxylation to generate a Ru-H species ([Ru]-8C). Further, an equivalent of H<sub>2</sub> molecule is released from Ru-H species via a proton assisted dehydrogenation to regenerate the active catalytic species [Ru]-8A'. A plausible reaction pathway for the catalytic dehydrogenation of formaldehyde over [Ru]-8 is displayed in Scheme 3.4.



*Scheme 3.4.* A plausible pathway for dehydrogenation of aqueous formaldehyde and formic acid over [*Ru*]-8.

### 3.3. Conclusions

In summary, we employed several arene-ruthenium complexes [Ru]-8 -[Ru]-16 containing N,O/N,N donor ligands for the catalytic dehydrogenation of formic acid in water. Results inferred that the complex  $[(\eta^6 - C_{10}H_{14})Ru(\kappa^2 - N_{py}OH - L2)Cl]^+$  [**Ru**]-8 outperformed over other complexes with a turnover frequency of 1548 h<sup>-1</sup>. The catalyst [Ru]-8 also exhibited high stability in water and a total turnover number of 6050 is achieved while using the catalyst [Ru]-8 for seven consecutive catalytic runs. The higher activity of [Ru]-8 can be associated with the involvement of oxygen atom in a facile protonation deprotonation step during the dehydrogenation process. To gain mechanistic insights, we probed extensive mass, NMR and kinetic investigations to evidence the formation of several important organometallic intermediate species, such as the diruthenium species  $[\{(\eta^6-C_{10}H_{14})Ru(\kappa^2 N,O-\mu-O-L2\}_2]^{2+}$ ([**Ru**]-8A'), the formate coordinated species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-N_{pv}O-$ L1)(HCO<sub>2</sub>)] ([**Ru**]-8B), and the ruthenium hydride species [( $\eta^{6}$ - $C_{10}H_{14}$ )Ru( $\kappa^2$ -N<sub>pv</sub>O-L2)(H)] ([Ru]-8C)during the catalytic dehydrogenation of formic acid over [Ru]-8, and hence, established the crucial role of these species in the catalytic dehydrogenation of formic acid. We also isolated and determined the X-ray molecular structure of the dicationic diruthenium species [Ru]-8A', the plausible catalyst resting state. In addition, [Ru]-8 is also active for the hydrogen production from formaldehyde in water under additive-free and basefree condition. Mass and GC-TCD investigation support the two-step dehydrogenation pathway for formaldehyde over [Ru]-8 catalyst, where several of the reaction intermediates involved in formic acid dehydrogenation also identified during formaldehyde are dehydrogenation. Hence, the present catalytic system highlighting the integration of formic acid dehydrogenation with formaldehyde dehydrogenation over a same catalyst, may seek broad scientific attention for the development of other active catalysts for analogous dehydrogenation reactions in water.

### **3.4. Experimental Section**

### 3.4.1. Materials and instrumentation

All reactions are performed without any inert gas protection using highpurity chemicals purchased from Sigma-Aldrich (Merck) and Alfa-Aesar. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra are recorded at 298 K using MeOH- $d_4$  and D<sub>2</sub>O as solvents on a Bruker advance 400 spectrometer. The pH values were measured on a Eutech pH meter, Model Eco Testr pH2. 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 shin carbon-ST packed column.

### **3.4.2.** Synthesis of the ligand 1-(pyridine-2-yl)ethanol (L3)

In a 100 mL round bottom reaction vessel, 1-(pyridine-2-yl)ethenone (10 mmol) is dissolved in 25 mL methanol and an excess of NaBH<sub>4</sub> (12 mmol) is added to it, and the reaction mixture is stirred at room temperature for 4 h. After completion of the reaction, all volatiles are removed under reduced pressure. The obtained solid residue is dispersed in water (20 mL), and the organic product is extracted with dichloromethane (3 × 15 mL). Further, the combined organic fractions are dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the volatiles are removed under reduced pressure to obtain the purified product as a colourless liquid. Yield: 86 % (1.06 g) <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) = 8.36 (d, *J* = 4 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 1.37 (d, *J* = 8 Hz, 3H).

### 3.4.3. Synthesis of arene-ruthenium complexes ([Ru]-8-[Ru]-11)

[ $(\eta^6$ -C<sub>10</sub>H<sub>14</sub>)Ru( $\kappa^2$ -N<sub>py</sub>OH-L2)Cl]<sup>+</sup>([Ru]-8). [ $(\eta^6$ -C<sub>10</sub>H<sub>14</sub>)RuCl<sub>2</sub>]<sub>2</sub> (0.306 g, 0.5 mmol) is dissolved in 30 mL HPLC methanol, and pyridine-2-ylmethanol (101 µL, 1.1 mmol) is added to it. The reaction mixture is refluxed for 12 h, and then volume of the reaction mixture is reduced to 3 mL under reduced pressure. An excess of diethyl ether is poured in to the above methanolic solution to precipitate a yellow solid. Yield: 73 % (0.305 g). <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) = 9.16 (d, J = 8.0 Hz, 1H), 7.92 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 5.89 (d, J = 4.0 Hz, 1H), 5.81 (d, J = 4.0 Hz, 1H), 5.66 (d, J = 8.0 Hz, 1H), 5.60 (d, J = 8.0 Hz, 1H), 4.83 – 4.94 (m, 2H), 2.83 – 2.80 (m, 1H), 2.17 (s, 3H), 1.20 (d, J = 8.0 Hz, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm) =160.51, 154.90, 141.04, 126.80, 121.92, 104.52, 100.42, 84.28, 82.98, 82.73, 81.01, 69.68, 32.32, 22.50, 22.22, 18.67. ESI-MS: calcd. for [M]<sup>+</sup> [C<sub>16</sub>H<sub>21</sub>ClNRuO] 380.0; found 380.0.

Synthesis of  $[(\eta^6 - C_6H_6)Ru(\kappa^2 - N_{py}OH-L2)Cl]^+$  ([Ru]-9):  $[\{(\eta^6 - C_6H_6)RuCl_2\}_2]$  (0.250 g, 0.5 mmol) is suspended in 30 mL HPLC methanol and stirred for 30 minutes at room temperature . Subsequently, pyridine-2-ylmethanol (101µL, 1.1 mmol) is added to it. The reaction mixture is refluxed for 12h, and then the volume of the reaction mixture is reduced to 3 mL under reduced pressure. An excess of diethyl ether is poured in to the above methanolic solution to precipitate a yellow solid. Yield: 72 % (0.258 g). <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) = 9.22 (d, *J* = 4.0 Hz, 1H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) = 160.68, 155.27, 141.17, 126.77, 121.94, 85.07, 70.28. ESI-MS: calcd. for [M]<sup>+</sup> [C<sub>12</sub>H<sub>13</sub>ClNRuO] 324.0; found 324.0

**Synthesis of**  $[(η^6-C_{10}H_{14})Ru(κ^2-N_{py}OH-L3)Cl]^+$  ([**Ru**]-10):  $[{(η^6-C_{10}H_{14})RuCl_2}_2]$  (0.306 g, 0.5 mmol) is dissolved in 30 mL HPLC methanol, and 1-(pyridin-2-yl)ethanol (135 mg, 1.1 mmol) is added to it. The reaction mixture is refluxed for 12h, and then the volume of the reaction mixture is reduced to 3 mL under reduced pressure. An excess of diethyl ether is poured in to the above methanolic solution to precipitate a brown solid. Yield: 80 % (0.343 g). <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>): δ (ppm) = 9.21 (d, *J* = 4.0 Hz, 1H), 7.96 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 8.0 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 4.0 Hz, 1H), 4.93 (d, *J* = 8.0 Hz, 1H), 2.78-2.81 (m, 1H), 2.18 (s, 3H), 1.52 (d, *J*= 4.0 Hz, 3H), 1.19-122 (m, 6H). <sup>13</sup>C NMR (100 MHz, MeOH-*d*<sub>4</sub>): δ = 163.32, 154.84, 141.24, 126.71, 122.90, 104.16, 100.30, 84.39, 83.09,

82.77, 80.98, 75.66, 32.21, 22.46, 22.17, 18.65. ESI-MS: calcd. for [M]<sup>+</sup> [C<sub>17</sub>H<sub>23</sub>ClNRuO] 394.1; found 394.4.

Synthesis of  $[(\eta^6-C_6H_6)Ru(\kappa^2-N_{py}OH-L3)Cl]^+$  ([Ru]-11):  $[\{(\eta^6-C_6H_6)RuCl_2\}_2]$  (0.250 g, 0.5 mmol) is suspended in 30 mL HPLC methanol and stirred for 30 minutes at room temperature. Subsequently,1-(pyridin-2-yl)ethanol (135 mg, 1.1 mmol) is added to it. The reaction mixture is refluxed for 12h, and then the volume of the reaction mixture is reduced to 3 mL under reduced pressure. An excess of diethyl ether is poured in to the above methanolic solution to precipitate a brown solid. Yield: 68 % (0.254 g). <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>): 9.26 (d, *J* = 4.0 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.48 (t, 8.0 Hz 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 6H), 4.98 (m, 1H), 1.53 (d, *J* = 8.0 Hz, 3H).<sup>13</sup>C NMR (100 MHz, MeOH-*d*<sub>4</sub>):  $\delta$  (ppm) = 163.75, 155.14, 141.29, 126.61, 122.69, 85.01, 76.54, 21.84. ESI-MS: calcd. for [M]<sup>+</sup> [C<sub>13</sub>H<sub>15</sub>CINRuO] 338.0; found 338.0.

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

Single crystals are obtained by slow diffusion of diethyl ether into a methanolic solution of [**Ru**]-9 and [**Ru**]-8A'. X-ray structural studies of [**Ru**]-9 and [**Ru**]-8A' are executed on a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. Using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å)-based diffraction, data are collected at 293(2) K by the standard "phi-omega" scan techniques and are scaled and reduced using CrysAlisPro RED software. The extracted data are evaluated using the CrysAlisPro CCD software. The structures are solved by direct methods using SHELXL-2018/1, and refined by full-matrix least squares method, refining on F<sup>2</sup>.<sup>[55]</sup> The positions of all of the atoms are determined by direct methods. All nonhydrogen atoms are refined anisotropically. The remaining hydrogen atoms are placed in geometrically constrained positions. The CCDC number 1564211 contain the supplementary crystallographic data for [**Ru**]-9.

### 3.4.5. General process for formic acid dehydrogenation reaction

An aqueous solution (2.5 mL) containing the catalyst (as specified), HCOONa (as specified), and formic acid (as specified) in a two-necked 10 mL reaction tube, fitted with a condenser and a gas burette, is stirred at 90 °C over a preheated oil bath. The volume of gas produced is measured as the displacement of water in the burette with respect to time. Identity of the produced gas is confirmed by GC-TCD. The turnover number (TON) was calculated by the formula [(substrate/catalyst) × (conversion/100)].<sup>[48]</sup> The turnover frequency (TOF) was calculated as TON/time.

## **3.4.6.** Mechanistic investigations for formic acid dehydrogenation over [Ru]-8 under catalytic and controlled reaction condition

Formic acid (1 mmol) and [**Ru**]-8 (0.01 mmol) were dissolved in 2.5 mL water and stirred at room temperature for 10 minutes. The resulting solution was analysed by mass spectrometry to identify several areneruthenium species (such as [**Ru**]-8A, [**Ru**]-8E and [**Ru**]-8G). Formic acid (1 mmol), sodium formate (0.05 mmol), [**Ru**]-8 (0.01 mmol) were dissolved in 2.5 mL water and heated at 90 °C. Reaction aliquot was collected from the reaction mixture after 5 minutes and end of the reaction and analysed by ESI-MS. A controlled reaction is also performed to identify a formate coordinated arene-ruthenium species ([**Ru**]-8B) by stirring [**Ru**]-8 (0.01 mmol), formic acid (0.5 mmol) and HCOONa (0.05 mmol) for 10 min in water (2.5 mL) at room temperature. To identify the ruthenium-hydride species, [**Ru**]-8 (0.01 mmol) is dissolved in 0.6 mL D<sub>2</sub>O in an NMR tube and HCOONa (0.05 mmol) is added and analysed by <sup>1</sup>H NMR.

### **3.4.7.** *Recycling experiments*

Formic acid (4.0 M, 2.5 mL) with n(sodium formate)/n(formic acid) = 2:1 is stirred at 90 °C in the presence of [**Ru**]-8 (0.01 mmol) in a twonecked 10 mL reaction tube fitted with a condenser and a gas burette. The volume of gas produced is measured as the displacement of water in the burette with respect to time. After completion of each catalytic run, 10 mmol of formic acid is added to the reaction mixture, and the release of gas is monitored.

### 3.4.8. General process for formaldehyde dehydrogenation reaction

An aqueous formaldehyde (0.4-4.0 M, 2.5 mL) solution is stirred at 90 °C in the presence of **[Ru]-8** (0.01 mmol) in a two-necked 10 mL reaction tube fitted with a condenser and a gas burette. The volume of gas produced is measured as the displacement of water in the burette with respect to time. Further, the identity of the produced gas is confirmed by GC-TCD. The turnover number (TON) was calculated by the formula  $[n(H_2 + CO_2)/n(catalyst)]$ .<sup>[13]</sup> The turnover frequency (TOF) was calculated as TON/time.

# **3.4.9.** Mechanistic investigations for formaldehyde dehydrogenation over [Ru]-8

Formaldehyde (0.4 M, 2.5 mL) is stirred with **[Ru]-8** (0.01 mmol) in water at 90 °C. Reaction aliquots are collected at every 5 minutes from the reaction mixture and analysed by ESI-MS.

### **3.4.10.** Gas Composition Analysis

The identification of gaseous products during the decomposition of formic acid and aq. formaldehyde was confirmed as H<sub>2</sub> and CO<sub>2</sub> with no detectable level of CO using a Shimadzu GC-2014 system. The chromatograph was equipped with a shin carbon-ST packed column with thermal conductivity detector (TCD) using argon as a carrier gas. Parameters set for the program to detect H<sub>2</sub> and CO<sub>2</sub> (Detector temperature: 200 °C, oven temperature: 90 °C; program: 90 °C (hold time: 1 min), 90 °C - 200 °C (rate: 15 °C per minute) The H<sub>2</sub>:CO<sub>2</sub> molar ratio during formic acid and aq. formaldehyde dehydrogenation was found to be approximately 1:1 and 2:1, respectively based on the calibration curve using standard H<sub>2</sub> and CO<sub>2</sub> gas.



Figure 3.15. GC-TCD analysis of evolved gas  $(H_2:CO_2 \approx 1:1)$  gas after complete dehydrogenation of formic acid with **[Ru]-8**. Reaction condition: **[Ru]-8** (0.01 mmol), formic acid (0.4 M, 2.5 mL), sodium formate (0.05mmol), 90 °C. (Analysis is performed using Argon as the carrier gas).



**Figure 3.16.** Time-dependent GC-TCD analysis of the evolved gas ( $H_2$  and  $CO_2$ ) during the catalytic formaldehyde dehydrogenation reaction. (a) initial 10 minutes;  $H_2:CO_2 \approx 6:1$  (b) After 30 minutes;  $H_2:CO_2 \approx 2.2:1$ . (c) After completion of reaction;  $H_2:CO_2 \approx 2:1$ .Reaction condition: [**Ru**]-8 (0.01 mmol), aq. formaldehyde (0.4M, 2.5mL), 90 °C. (Analysis is performed using Argon as the carrier gas).

### 3.4.11. Characterization of ligands and metal complexes



<sup>1</sup>H NMR of **L2** in MeOH- $d_4$ 



<sup>1</sup>H NMR of **[Ru]-8** in MeOH-d<sub>4</sub>



<sup>13</sup>C NMR of **[Ru]-8** in MeOH-d<sub>4</sub>



Mass of [Ru]-8



<sup>13</sup>C NMR of **[Ru]-9** in MeOH-d<sub>4</sub>









<sup>1</sup>H NMR of **L3** in MeOH- $d_4$ 



<sup>13</sup>C NMR of **[Ru]-10** in MeOH-*d*<sub>4</sub>





<sup>1</sup>H NMR of **[Ru]-11** in MeOH-d<sub>4</sub>



<sup>13</sup>C NMR of [Ru]-11 in MeOH-d<sub>4</sub>



[Ru]-9			
Formula	C <sub>12</sub> H <sub>17</sub> Cl <sub>2</sub> NO <sub>3</sub> Ru		
Molecular weight	395.23		
Crystal system	Triclinic		
Space group	P-1		
Temperature/K	293		
Wavelength	0.71073		
a/Å	6.7939 (3)		
b/Å	9.0656 (5)		
$c/\text{\AA}$	13.3758 (7)		
α/°	98.946 (5)		
$\beta/^{\circ}$	103.638 (4)		
$\gamma/^{\circ}$	105.280 (4)		
$V/ Å^3$	751.19		
Z	2		
Density/gcm <sup>-1</sup>	1.747		
Absorption Coefficient	1.401		
Absorption Correction	Semi empirical from equivalents		
F(000)	396.0		
Total no of reflections	5945		
Reflections, $I > 2\sigma(I)$	3396		
Max. $2\theta/^{\circ}$	28.807		
Ranges (h, k, l)	$-9 \le h \le 8$		
	-9≤ k ≤12 -16<1<16		
Complete to $2\theta(\%)$	99.9		
Refinement method	Full-matrix least-		
Goof $(F^2)$	squares on $F^2$ 1.027		
R indices $[I > 2\sigma(I)]$	0.0238		
R Indices (all data)	0.0250		

Table 3.4. Single crystal X-ray refinement data for complex [Ru]-9

Ru(1)-N(1)	2.1035(16)
Ru(1)-O(1)	2.1307(14)
Ru(1)-C(11)	2.153(2)
Ru(1)-C(12)	2.159(2)
Ru(1)-C(7)	2.177(2)
Ru(1)-C(10)	2.177(2)
Ru(1)-C(8)	2.179(2)
Ru(1)-C(9)	2.184(2)
Ru(1)-Cl(1)	2.4060(5)
O(1)-C(6)	1.434(3)
N(1)-C(1)	1.347(3)
N(1)-C(5)	1.351(3)

Table 3.5. Selected bond lengths (Å) for complex [Ru]-9

Table 3.6. Selected bond angles (°) for complex [Ru]-9

N(1)-Ru(1)-O(1)	76.08(6)
N(1)-Ru(1)-C(11)	123.45(11)
O(1)-Ru(1)-C(11)	159.86(11)
N(1)-Ru(1)-C(12)	97.43(9)
O(1)-Ru(1)-C(12)	155.02(9)
C(11)-Ru(1)-C(12)	38.01(12)
N(1)-Ru(1)-C(7)	96.14(8)
O(1)-Ru(1)-C(7)	117.96(8)
C(11)-Ru(1)-C(7)	68.36(10)
C(12)-Ru(1)-C(7)	37.84(10)
N(1)-Ru(1)-C(10)	161.61(11)
O(1)-Ru(1)-C(10)	121.62(10)
C(11)-Ru(1)-C(10)	38.48(12)
C(12)-Ru(1)-C(10)	68.61(11)
C(7)-Ru(1)-C(10)	80.24(9)
N(1)-Ru(1)-C(8)	119.12(8)
O(1)-Ru(1)-C(8)	94.12(7)
C(11)-Ru(1)-C(8)	80.74(9)

67.62(9)
36.74(9)
67.84(10)
155.81(9)
95.90(8)
68.15(10)
80.14(10)
67.12(9)
37.12(10)
37.70(9)
84.07(5)
85.76(4)
91.19(7)
117.94(8)
155.72(7)
91.91(7)
156.14(7)
118.52(7)

Table 3.7. Single crystal X-ray refinement data for [Ru]-8A'

Formula	$C_{32}H_{40}F_{12}N_2O_2P_2Ru_2\\$
Molecular weight	976.74
Crystal system	Triclinic
Space group	P-1
Temperature/K	293
Wavelength	0.71073
a/Å	11.3876 (13)
$b/ m \AA$	12.6247(18)
c/Å	14.534 (2)
α/°	82.822 (6)
$eta/^{\circ}$	83.484 (5)
γ/°	75.943 (5)

$V/ Å^3$	2003.5 (5)
Z	2
Density/gcm <sup>-1</sup>	1.619
Absorption Coefficient	0.920
F(000)	976
Total no of reflections	7234
Reflections, $I > 2\sigma(I)$	6189
Max. 20/°	25.25
Ranges (h, k, l)	-13≤ h ≤13
	$-15 \le k \le 15$
Complete to $2\theta(\%)$	-1/≤1≤1/ 99.5 %
Refinement method	Full-matrix least-
Refinement method	squares on $F^2$
Goof $(F^2)$	1.071
R indices $[I > 2\sigma(I)]$	0.0541
R Indices (all data)	0.0636

 Table 3.8. Selected bond lengths (Å) for complex [Ru]-8A'

Ru(2)-N(2)	2.080(5)
Ru(2)-O(2)	2.082(4)
Ru(2)-O(1)	2.120(4)
Ru(2)-C(25)	2.172(6)
Ru(2)-C(28)	2.178(7)
Ru(2)-C(24)	2.181(6)
Ru(2)-C(26)	2.187(7)
Ru(2)-C(29)	2.187(7)
Ru(2)-C(27)	2.192(7)
Ru(1)-N(1)	2.084(5)
Ru(1)-O(1)	2.093(4)
Ru(1)-O(2)	2.103(4)
Ru(1)-C(15)	2.169(6)
Ru(1)-C(19)	2.171(6)

Ru(1)-C(18)	2.178(6)
Ru(1)-C(16)	2.188(6)
Ru(1)-C(14)	2.191(7)
Ru(1)-C(17)	2.205(6)
O(2)-C(7)	1.419(7)
O(1)-C(1)	1.417(8)
N(1)-C(6)	1.323(9)
N(1)-C(2)	1.362(9)
N(2)-C(12)	1.325(9)
N(2)-C(8)	1.340(9)
-	

Table 3.9. Selected bond angles (°) for complex [Ru]-8A'

\_

77.83(19)
90.20(2)
76.91(15)
147.9(3)
93.8(2)
118.4(2)
100.2(3)
165.1(3)
118.0(3)
111.6(3)
98.1(2)
156.4(2)
166.9(3)
115.3(3)
92.1(3)
92.1(3)
127.0(2)
155.9(2)
129.5(3)
150.7(3)

O(1)-Ru(2)-C(27)	90.9(3)
N(1)-Ru(1)-O(1)	78.5(2)
N(1)-Ru(1)-O(2)	89.8(19)
O(1)-Ru(1)-O(2)	77.03(16)
N(1)-Ru(1)-C(15)	150.0(3)
O(1)-Ru(1)-C(15)	95.4(2)
O(2)-Ru(1)-C(15)	117.7(2)
N(1)-Ru(1)-C(19)	93.7(2)
O(1)-Ru(1)-C(19)	128.5(2)
O(2)-Ru(1)-C(19)	154.4(2)
N(1)-Ru(1)-C(18)	99.6(3)
O(1)-Ru(1)-C(18)	166.0(2)
O(2)-Ru(1)-C(18)	116.9(2)
N(1)-Ru(1)-C(16)	165.4(3)
O(1)-Ru(1)-C(16)	115.5(2)
O(2)-Ru(1)-C(16)	90.7(2)
N(1)-Ru(1)-C(14)	113.8(3)
O(1)-Ru(1)-C(14)	99.5(2)
O(2)-Ru(1)-C(14)	155.2(2)
N(1)-Ru(1)-C(17)	127.7(3)
O(1)-Ru(1)-C(17)	151.2(2)
O(2)-Ru(1)-C(17)	90.0(2)

Note: The contents of this chapter is published as Patra et al., Inorg. Chem., 2020, 59, 4234-4243 (DOI: 10.1021/acs.inorgchem.9b02882) and reproduced with the permission from American Chemical Society.

### **3.5. References**

- Schlapbach L., Zuttel A. (2001), Hydrogen-storage materials for mobile applications. *Nature*, 414, 353-358 (DOI: 10.1038/35104634)
- Eberle U., Felderhoff M., Schüth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chem., Int. Ed.*, 48, 6608-6630 (DOI: 10.1002/anie.200806293)
- 3. Armaroli N. Balzani V. (2011), The Hydrogen Issue, *ChemSusChem*, 4, 21-36 (DOI: 10.1002/cssc.201000182)
- Dalebrook A. F., Gan W., Grasemann M., Moret S., Laurenczy G. (2013), Hydrogen storage: beyond conventional methods, *Chem. Commun.*, 49, 8735-8751 (DOI: 10.1039/c3cc43836h)
- Jiang H. L., Singh S. K., Yan J. M., Zhang, X. B., Xu, Q. (2010), Liquid- Phase Chemical Hydrogen Storage: Catalytic Hydrogen generation under Ambient Conditions, *ChemSusChem.*, 3, 541-549 (DOI: 10.1002/cssc.201000023)
- Awasthi M. K., Tyagi D., Patra S., Rai, R. K., Mobin S. M., Singh S. K. (2018), Ruthenium Complexes for Catalytic Dehydrogenation of Hydrazine and Transfer Hydrogenation Reactions, *Chem. Asian J.*, 13, 1424–1431 (DOI:10.1002/asia.201800315)
- Grasemann M., Laurenczy G. (2012), Formic acid as a hydrogen source – recent developments and future trends, *Energy Environ*. *Sci.*, 5, 8171-8181 (DOI:1039/c2ee21928j)
- Singh A. K., Singh S., Kumar A. (2016), Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system, *Catal. Sci. Technol.*, *6*, 12-40 (DOI: 10.1039/c5cy01276g)
- Mellmann D., Sponholz P., Junge H., Beller M. (2016), Formic acid as a hydrogen storage material – development of homogeneous catalysts for selective hydrogen release, *Chem.Soc. Rev.*, 45, 3954-3988 (DOI: 10.1039/c5cs00618j)

- Eppinger J., Huang K.-W. (2017), Formic Acid as a Hydrogen Energy Carrier, ACS Energy Lett., 2, 188-195 (DOI: 10.1021/acsenergylett.6b00574)
- Sordakis K., Tang C., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*,118, 372-433 (DOI: 10.1021/acs.chemrev.7b00182)
- Zhong H., Iguchi M., Chatterjee M., Himeda Y., Xu Q., Kawanami H. (2018), Formic Acid-Based Liquid Organic Hydrogen Carrier System with Heterogeneous Catalysts, *Adv. Sustainable Syst.*, 2, 1700161 (DOI: 10.1002/adsu.201700161)
- Heim L. E., Schlörer N. E., Choi J.-H., Prechtl M. H. G. (2014), Selective and Mild Hydrogen Production Using Water and Formaldehyde, *Nat. Commun.*, 5, 3621 (DOI: 10.1038/ncomms4621)
- Heim L. E., Vallazza S., van der Waals D., Prechtl M. H. G. (2016), Water Decontamination with Hydrogen Production Using Microwave-formed Minute-made Ruthenium Catalysts, *Green Chem.*, 18, 1469–1474 (DOI: 10.1039/c5gc01798j)
- Suenobu T., Isaka Y., Shibata S., Fukuzumi S. (2015), Catalytic Hydrogen Production from Paraformaldehyde and Water Using an Organoiridium Complex, *Chem. Commun.*, 51, 1670–1672 (DOI: 10.1039/c4cc06581f)
- 16. Fujita K.-I., Kawahara R., Aikawa T., Yamaguchi R. (2015), Hydrogen Production from a Methanol–Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions, *Angew. Chem., Int. Ed.*, 54, 9057–9060 (DOI: 10.1002/anie.201502194)
- Trincado M., Sinha V., Rodriguez-Lugo R. E., Pribanic B., de Bruin B., Grutzmacher H. (2017), Homogeneously catalysed Conversion of Aqueous Formaldehyde to H<sub>2</sub> and Carbonate, *Nat. Commun.*, 8, 14990 (DOI: 10.1038/ncomms14990)

- Li R. H., Zhu X. H., Yan X. Q., Kobayashi H., Yoshida S., Chen W. X., Du L. L., Qian K. C., Wu B., Zou S., Lu L., Yi W., Zhou Y., Fan J. (2017), Oxygen-Controlled Hydrogen Evolution Reaction: Molecular Oxygen Promotes Hydrogen Production from Formaldehyde Solution Using Ag/MgO Nanocatalyst, *ACS Catal.*, 7, 1478–1484 (DOI: 10.1021/acscatal.6b03370)
- Wang W.-H., Himeda Y., Muckerman J. T., Manbeck G. F., Fujita E. (2015), CO<sub>2</sub> Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO<sub>2</sub> Reduction, *Chem. Rev.*, 115, 12936-12973 (DOI: 10.1021/acs.chemrev.5b00197)
- Klankermayer J., Wesselbaum S., Beydoun K., Leitner W. (2016), Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry, *Angew. Chem., Int. Ed.*, 55, 7296-7343 (DOI: 10.1002/anie.201507458)
- Loges B., Boddien A., Junge H., Beller M. (2008), Controlled generation of hydrogen from formic acid amine adducts at room temperature and application in H<sub>2</sub>/O<sub>2</sub> fuel cells, *Angew. Chem., Int. Ed.*, 47, 3962-3965 (DOI: 10.1002/anie.200705972)
- Fellay, C., Dyson, P. J., Laurenczy, G. (2008), A viable hydrogenstorage system based on selective formic acid decomposition with a ruthenium catalyst, *Angew. Chem., Int. Ed.*, 47, 3966-3968 (DOI: 10.1002/anie.200800320)
- Iguchi M., Himeda Y., Manaka Y., Matsuoka K., Kawanami H. (2016), Simple Continuous High-Pressure Hydrogen Production and Separation System from Formic Acid under Mild Temperatures, *ChemCatChem*, 8, 886-890 (DOI: 10.1002/cctc.201501296)
- Guan C., Zhang D., Pan Y., Iguchi M., Ajitha M. J., Hu J., Li H., Yao C., Huang M. H., Min S., Zheng J., Himeda Y., Kawanami H., Huang K. W. (2017), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N'-Diimine Ligand, *Inorg. Chem.*, 56, 438-445. (DOI: 10.1021/acs.inorgchem.6b02334)
- Iguchi M., Chatterjee M., Onishi N., Himeda Y., Kawanami H. (2018), Sequential hydrogen production system from formic acid and H<sub>2</sub>/CO<sub>2</sub> separation under high-pressure conditions. *Sustainable Energy Fuels*, 2, 1719–1725 (DOI: 10.1039/c8se00087e)
- Pan Y., Pan C. L., Zhang Y., Li H., Min S., Guo X., Zheng B., Chen H., Anders A., Lai Z., Zheng J., Huang K.-W. (2016), Selective Hydrogen Generation from Formic Acid with Well-Defined Complexes of Ruthenium and Phosphorus–Nitrogen PN3-Pincer Ligand, *Chem. Asian J.*, 11, 1357–1360 (DOI: 10.1002/asia.201600169)
- Boddien A., Federsel C., Sponholz P., Mellmann D., Jackstell R., Junge H., Laurenczy G. Beller M. (2012), Towards the development of a hydrogen battery, *Energy Environ Sci.*, 5, 8907-8911 (DOI: 10.1039/c2ee22043a)
- Sponholz P., Mellmann D., Junge H., Beller M. (2013), Towards a Practical Setup for Hydrogen Production from Formic Acid, *ChemSusChem*, 6, 1172-1176 (DOI: 10.1002/cssc.201300186)
- Filonenko G. A., Putten, R., Van Schulpen E. N., Hensen E. J., Pidko E. A. (2014), Highly Efficient Reversible Hydrogenation of Carbon Dioxide to Formates Using a Ruthenium PNP-Pincer Catalyst. *ChemCatChem*, 6, 1526–1530 (DOI: 10.1002/cctc.201402119)
- Rodrguez- Lugo R. E., Trincado M., Vogt M., Tewes F., Santiso-Quinones G., Gritzmacher H. (2013), A homogeneous transition metal complex for clean hydrogen production from methanol–water mixtures, *Nat. Chem.*, 5, 342-347 (DOI:10.1038/nchem.1595)
- Boddien A., Loges B., Junge H., Gartner F., Noyes J. R., Beller M. (2009), Continuous Hydrogen Generation from Formic Acid: Highly Active and Stable Ruthenium Catalysts, *Adv. Synth. Catal.*, 351, 2517 2520 (DOI: 10.1002/adsc.200900431)

- Muller K., Brook, K., Autrey T. (2017), Hydrogen Storage in Formic Acid: A Comparison of Process Options, *Energy Fuels*, 31, 12603-12611 (DOI: 10.1021/acs.energyfuels.7b02997)
- 33. Fukuzumi S., Kobayashi T., Suenobu T. (2008), Efficient catalytic decomposition of formic acid for the selective generation of H<sub>2</sub> and H/D exchange with a water-soluble rhodium complex in aqueous solution, *ChemSusChem*, 1, 827-834 (DOI: 10.1002/cssc.200800147)
- Fukuzumi S., Kobayashi T., Suenobu T. (2010), Unusually Large Tunneling Effect on Highly Efficient Generation of Hydrogen and Hydrogen Isotopes in pH-Selective Decomposition of Formic Acid Catalyzed by a Heterodinuclear Iridium–Ruthenium Complex in Water, J. Am. Chem. Soc., 132, 1496-1497 (DOI: 10.1021/ja910349w)
- 35. Maenaka Y., Suenobu T., Fukuzumi S. (2012), Catalytic interconversion between hydrogen and formic acid at ambient temperature and pressure, *Energy Environ. Sci.*, 5, 7360-7367 (DOI: 10.1039/c2ee03315a)
- Horvath H., Papp G., Szabolcsi R., Katho A., Joo F. (2015), Water-Soluble Iridium-NHC-Phosphine Complexes as Catalysts for Chemical Hydrogen Batteries Based on Formate, *ChemSusChem*, 8, 3036-3038 (DOI: 10.1002/cssc.201500808)
- 37. Wang Z. J., Lu S. M., Li J., Wang J. J., Li C. (2015), Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an N,N'- Diimine Ligand in Water, *Chem. Eur. J.*, 21, 12592-12595 (DOI: 10.1002/chem.201502086)
- Montandon-Clerc M., Dalebrook A. F., Laurenczy G. (2016), Quantitative Aqueous Phase Formic Acid Dehydrogenation Using Iron(II) Based Catalysts, *J. Catal.*, 343, 62-67 (DOI: 10.1016/j.jcat.2015.11.012)

- Fink C., Laurenczy G. (2017), CO<sub>2</sub> as a hydrogen vector transition metal diamine catalysts for selective HCOOH dehydrogenation, *Dalton Trans.*, 46, 1670-1676 (DOI: 10.1039/c6dt04638j)
- Himeda Y. (2009), Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4'dihydroxy-2,2'-bipyridine, *Green Chem.*, 11, 2018-2022 (DOI: 10.1039/b914442k)
- Wang W.-H., Xu S., Manaka Y., Suna Y., Kambayashi H., Muckerman, J. T., Fujita, E. Himeda Y. (2014), Formic Acid Dehydrogenation with Bioinspired Iridium Complexes: A Kinetic Isotope Effect Study and Mechanistic Insight, *ChemSusChem*, 7, 1976-1983 (DOI: 10.1002/cssc.201301414)
- 42. Hull J. F., Himeda Y., Wang W.-H., Hashiguchi B., Periana R., Szalda D. J., Muckerman J. T., Fujita E. (2012), Reversible hydrogen storage using CO<sub>2</sub> and a proton-switchable iridium catalyst in aqueous media under mild temperatures and pressures, *Nat. Chem.*, 4, 383-388 (DOI: 10.1038/nchem.1295)
- 43. Manaka Y., Wang W.-H., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda, Y. (2014), Efficient H<sub>2</sub> generation from formic acid using azole complexes in water, *Catal. Sci. Technol.*, 4, 34-37 (DOI: 10.1039/c3cy00830d)
- 44. Onishi N., Ertem M. Z., Xu S., Tsurusaki A., Manaka Y., Muckerman J. T., Fujita E., Himeda Y. (2016), Direction to practical production of hydrogen by formic acid dehydrogenation with Cp\*Ir complexes bearing imidazoline ligands, *Catal. Sci. Technol.*, 6, 988-992 (DOI: 10.1039/c5cy01865j)
- 45. Wang L., Onishi N., Murata K., Hirose T., Muckerman J. T., Fujita E., Himeda Y. (2017), Efficient Hydrogen Storage and Production Using a Catalyst with an Imidazoline-Based, Proton-Responsive Ligand, *ChemSusChem*, 10, 1071-1075 (DOI: 10.1002/cssc.201601437)

- Lu S. M., Wang Z., Wang J., Li J., Li C. (2018), Hydrogen generation from formic acid decomposition on a highly efficient iridium catalyst bearing a diaminoglyoxime ligand, *Green Chem.*, 20, 1835-1840 (DOI: 10.1039/c8gc00495a)
- 47. Guerriero A., Bricout H., Sodarkis K., Peruzzini M., Monflier E., Hapiot F., Laurenczy G., Gonsalvi L. (2014), Hydrogen Production by Selective Dehydrogenation of HCOOH Catalyzed by Ru-Biaryl Sulfonated Phosphines in Aqueous Solution, *ACS Catal.*, 4, 3002–3012 (DOI: 10.1021/cs500655x)
- Patra S., Awasthi M. K., Rai R. K., Deka H., Mobin S. M., Singh S. K. (2019), Dehydrogenation of Formic Acid Catalyzed by Water-Soluble Ruthenium Complexes: X-ray Crystal Structure of a Diruthenium Complex, *Eur. J. Inorg. Chem.*, 1046–1053 (DOI: 10.1002/ejic.201801501)
- Wang L., Ertem M. Z., Kanega R., Murata K., Szalda D. J., Muckerman J. T., Fujita E., Himeda Y. (2018), Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity, *ACS Catal.*, 8, 8600–8605 (DOI: 10.1021/acscatal.8b02088)
- Gemel C., John R., Slugovc C., Mereiter K., Schmid R., Kirchner K. (2000), Synthesis and characterization of ruthenium quinolin-8-olate complexes. Unexpected formation of a κ<sup>1</sup>-hydrotris(pyrazolyl)borate complex, *J. Chem. Soc., Dalton Trans.*, 2607–2612 (DOI: 10.1039/b002490m)
- Binnani C., Rai R. K., Tyagi D., Mobin S. M., Singh S. K. (2018), Ligand-Tuned C–H Bond Activation/Arylation of 2-Arylpyridines over Pyridine-Based N,O/N,N Ligated Ruthenium–Arene Complexes, *Eur. J. Inorg. Chem.*, 2018, 1435-1445 (DOI: 10.1002/ejic.201701446)
- 52. Gunnaz S., Ozdemir N., Dayan S., Dayan O., Cetinkayn B. (2011), Synthesis of Ruthenium(II) Complexes Containing Tridentate Triamine (NNN) and Bidentate Diamine Ligands (NN): as Catalysts

for Transfer Hydrogenation of Ketones, *Organometallics*, 30, 4165–4173 (DOI: 10.1021/om200470p)

- 53. Dwivedi A. D., Sahu V. K., Mobin S. M., Singh S. K. (2018), Cyclopentadienyl-Ru(II)- Pyridylamine Complexes: Synthesis, Xray Structure and Application in Catalytic Transformation of Bio-Derived Furans to Levulinic Acid and Diketones in Water, *Inorg. Chem.*, 57, 4777-4787 (DOI: 10.1021/acs.inorgchem.8b00536)
- 54. Carmona D., Lamata P., Sanchez A., Pardo P., Rodriguez R., Ramirez P., Lahoz F. J., Orduna P. G., Oro, L. A. (2014), Chiral Brønsted Acid Catalysts. Activation of Methyl 3,3,3-Trifluoropyruvate by Hydroxymethylpyridine-Containing Half-Sandwich Complexes, *Organometallics*, 33, 4016–4026 (DOI: 10.1021/om5005463)
- Sheldrick G. M. (2008), A short history of SHELX, Acta Crystallogr., Sect. A: Found. Crystallogr. 64, 112–122 (DOI: 10.1107/s0108767307043930)

### **Chapter 4**

### Hydrogen production from formic acid and formaldehyde over bis-imidazole methane ligated ruthenium (II) complexes in water

#### 4.1. Introduction

Hydrogen is a promising and potential source of clean energy to meet the global energy demand in a more sustainable way.<sup>[1-6]</sup> Advantageously, hydrogen has high gravimetric energy density and produce water as the only by-product when subjected to a fuel cell. However, due to some of its physical properties, the safe storage and transportation of hydrogen gas is still a great challenge.<sup>[6-8]</sup> Therefore, technological advances in the production and delivery of hydrogen is required to materialize hydrogen economy.<sup>[6]</sup> In this direction, liquid hydrogen carriers (LOHCs)<sup>[9-10]</sup> such as methanol. organic formaldehyde, formic acid and others containing appreciably high gravimetric content of hydrogen and being liquids ensure the safe storage and transportation of hydrogen. Among these LOHCs, formic acid having a high hydrogen content (53 g H<sub>2</sub>/L), can release hydrogen gas with the intervention of a suitable catalyst under mild conditions.<sup>[11-</sup> <sup>18]</sup> Advantageously, formic acid is a liquid at ambient conditions and can be transported and stored safely. Several interesting reports in the past few decades showed that a wide range of molecular catalysts based on Ir,<sup>[19]</sup> Ru,<sup>[20]</sup> Rh,<sup>[21]</sup> Fe<sup>[22]</sup> and Mn<sup>[23]</sup> have been extensively explored for formic acid dehydrogenation. Interestingly, great deal of efforts has also

been devoted towards the development of catalytic systems for aqueousphase formic acid dehydrogenation.<sup>[11,12, 19a, 19e-f, 19i-k, 20g]</sup>



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

Literature studies revealed that the coordinating ligands in the studied molecular catalysts can significantly influence the catalytic performance towards the production of hydrogen from formic acid. For instance, Himeda et al. explored several Cp\*-Ir based molecular catalysts, where the role of bipyridine ligands was found to be crucial in improving the catalytic activity for hydrogen production from formic acid. Cp\*-Ir complex having 4,4'-OH substituted bipyridine exhibited 80-fold higher activity as compared to Cp\*-Ir complex with unsubstituted bipyridine (C-4 in Scheme 4.1).<sup>[19a]</sup> Further, the position of hydroxyl groups in bipyridine (C-5 and C-6 in Scheme 4.1) also greatly influenced the catalytic activity by tuning the rate-determining steps.<sup>[19c]</sup> The bipyrimidine bridged bis-Cp\*Ir catalyst (C-31 in Scheme 4.1) with four OH groups on bipyrimidine ligand showed even higher activity (TOF: 31600 h<sup>-1</sup>) attributed to a combined electronic and pendant base effect.<sup>[19d]</sup> Interestingly, amine-substituted bipyridine coordinated Cp\*Ir catalyst (C-17 in Scheme 4.1) exhibited higher activity and durability for formic acid dehydrogenation as compared to

those with hydroxy-substituted bipyridine (C-5 in Scheme 4.1). Notably, Cp\*Ir-bipyridine with *p*-substituted amino groups displayed higher activity than o-substituted amine. The observed trend was attributed to the stability of the hydride intermediate.<sup>[19e]</sup> Compared to bipyridine ligands, complexes with imidazole-based ligands also exhibited superior performance for formic acid dehydrogenation. For instance, Cp\*Ir bisimidazole aqua complex (C-32 in Scheme 4.1) displayed a TOF of 3980  $h^{-1}$ , while the analogous complex with bis-imidazole dihydrogen ligand (C-33 in Scheme 4.1) yielded a TOF of 54700 h<sup>-1</sup>.<sup>[19f,g]</sup> Analogous Cp\*Ir-bis-imidazoline complex (C-9 in Scheme 4.1) displayed a very high TOF of 257000 h<sup>-1.[19j]</sup> In this direction, Huang et al. reported the complex  $[(\eta^6-C_{10}H_{14})RuCl(2,2'-bi-2-imidazoline)]^+$  (C-3 in Scheme 4.1) to achieve a TOF of 12000  $h^{-1}$  for formic acid dehydrogenation in water at 90 °C.<sup>[20g]</sup> Further, Cp\*Ir-dioxime based complex (C-16 in Scheme 4.1) also displayed a very high TON of 5020000, attributed to the electron rich amine substituents and the dioxime structure of the ligand.<sup>[19k]</sup> Pyridyl-imidazoline bound Cp\*Ir complexes (C-10 and C-8 in Scheme 4.1) are also explored for formic acid dehydrogenation to achieve enhanced catalytic activity.<sup>[19g,i]</sup> Analogous Mn complex Mn(pyridine-imidazoline)(CO)<sub>3</sub>Br (C-23 in Scheme 4.1) as reported by Beller and co-workers, also displayed high activity for hydrogen production from formic acid.<sup>[23c]</sup> From the extensive literature reports, it is evident that complexes based on iridium are very active towards hydrogen production from formic acid in aqueous medium. However, iridium is a very expensive metal, and therefore researchers are also exploring to design more inexpensive yet active catalysts for formic acid dehydrogenation. In this direction, several Ru based complexes are also explored, but exempting those reported by Huang's<sup>[20g]</sup> and Laurenczy's<sup>[20i]</sup>, other complexes require the addition of some organic base such as triethylamine (Et<sub>3</sub>N) or the dehydrogenation reaction is performed in organic solvents (e.g., DMF, DMSO or Me<sub>2</sub>NHex). Previously, we have also explored a range of arene-Ru(II) complexes with 8-amino-quinoline ([Ru]-4 in Scheme 4.1) and pyridine methanol

(**[Ru]-8** in Scheme 4.1) based ligands to achieve appreciably good catalytic activity for formic acid dehydrogenation in water.<sup>[11,12]</sup>

These findings demonstrated the crucial role of ligands in tuning the catalytic activity of the studied molecular catalysts for formic acid dehydrogenation. In particular, ligands stabilize important reaction intermediates such as metal-hydride under varying pH conditions, and hence facilitated the dehydrogenation pathway to achieve high efficiency and durability for these molecular catalysts. Moreover, molecular catalysts those having imidazole-based ligands showed interesting activities in catalytic formic acid dehydrogenation.<sup>[19f,g,j]</sup> Further, exploring active homogeneous catalysts for formic acid dehydrogenation in water is also of prime importance in terms of sustainability of the process. In this direction, we have long-term interest in exploring catalytic dehydrogenation reactions in water<sup>[11,12,24,25]</sup> and therefore herein, we report a series of newly synthesized water soluble arene-ruthenium(II) complexes containing bis-imidazole methane based ligands for hydrogen production from formic acid in water. All the synthesized complexes are well characterized and the molecular structures of the representative complexes [Ru]-19 and [Ru]-22 are authenticated by X-ray crystallography. Kinetic investigations and extensive NMR and mass studies are performed to identify the active reaction intermediates and elucidate the reaction pathway for formic acid dehydrogenation.

#### 4.2. Results and Discussion

# 4.2.1. Synthesis and Characterization of ligands and metal complexes.

At an outset, two new bis-imidazole methane-based ligands {4,4'-((4methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole)} (**L6**) and {4,4'-((4-chlorophenyl)methylene)bis(2-ethyl-5-methyl-1*H*imidazole)} (**L8**) are synthesized by refluxing 2-ethyl-4-methyl imidazole with 4-methoxybenzaldehyde and 4-chlorobenzaldehyde respectively in the presence of KOH in methanol-water mixture (Scheme

The ligands  $\{4,4'-(phenylmethylene)bis(2-ethyl-5-methyl-1H-$ 2). imidazole)} (L5), {4,4'-((2-methoxyphenyl) methylene)bis(2-ethyl-5methyl-1*H*-imidazole)  $\{L7\}$ , and  $\{4,4'-((2-chlorophenyl)methylene)$ bis(2-ethyl-5-methyl-1*H*-imidazole)} (L9) are synthesized in a similar manner as reported earlier by us.<sup>[26]</sup> The ligands (L5 – L9) are characterized by various spectro-analytical techniques (see experimental section). The synthesised bis-imidazole methane-based ligands (L5 -L9) have substituted or unsubstituted phenyl group at the methylene carbon, where L5 has phenyl group, while L6, L7, L8 and L9 have 4methoxy phenyl, 2-methoxy phenyl, 4-chloro phenyl and 2-chloro phenyl substituents, respectively. Further, mono-cationic water soluble arene-Ru(II) complexes ([Ru]-17 – [Ru]-26) are synthesized in good yields by treating the respective ligands (L5 - L9) with the arene-Ru(II) precursors  $[(\eta^6\text{-arene})\text{RuCl}_2]_2$  (arene = C<sub>6</sub>H<sub>6</sub> and C<sub>10</sub>H<sub>14</sub>) in methanol under reflux condition (Scheme 4.2).



Scheme 4.2. Synthesis of bis-imidazole methane ligated areneruthenium(II) complexes ([Ru]-17 – [Ru]-26).

The obtained yellow to brown coloured complexes are characterized by various spectro-analytical techniques. HRMS of the obtained complexes corroborates well with the proposed molecular structures, where the mass peak corresponding to the cationic mononuclear arene-Ru(II) complexes with the general formula  $[(\eta^6\text{-arene})\text{RuCl}(\kappa^2\text{-L})]^+$  (L = L5 –

L9) for the complexes [Ru]-17 – [Ru]-26 (see the experimental section) are observed. In the <sup>1</sup>H NMR spectra of the complexes [Ru]-17 – [Ru]-26, the methylene proton of the metal coordinated bis-imidazole methane ligands resonated at a slightly shifted position as compared to the free ligands. For instance, the methylene proton in [Ru]-17 and [Ru]-22 appeared at a slightly upfielded region of 5.01 ppm and 5.31 ppm, respectively, as compared to the free ligand L5 (5.39 ppm). Analogous shifting in peaks position corresponding to the methylene carbon in the <sup>13</sup>C NMR spectra of all synthesised complexes is also observed as compared to that in the free ligand. The three equivalent protons of the methoxy group appeared at 3.84 and 3.78 ppm respectively in [Ru]-18 and [Ru]-23, which is shifted slightly downfield as compared to the free ligand L6 (3.75 ppm). Analogously, the three equivalent protons of the methoxy group appeared at 3.92 and 3.75 ppm respectively for [Ru]-19 and [Ru]-24 as compared to that in the free ligand L7 (3.77 ppm). The <sup>1</sup>H NMR resonances for the protons corresponding to the  $\eta^6$ -p-cymene and  $\eta^6$ -benzene ring coordinated to the Ru(II) centre in all the complexes are observed in the expected region.<sup>[27-29]</sup> Therefore, the observed trend in the NMR and HRMS analysis is consistent with the coordination of bis-imidazole methane based ligands with the arene-Ru(II) in the proposed manner.

Further, molecular structures of the representative complexes [**Ru**]-19 (Figure 4.1) and [**Ru**]-22 (Figure 4.2) have also been authenticated by single crystal X-ray diffraction studies by growing single crystals suitable for X-ray diffraction by the diffusion of diethyl ether into the methanolic solution of these complexes at room temperature. [**Ru**]-19 crystallizes in the monoclinic crystal system with the P2<sub>1</sub>/n space group, whereas [**Ru**]-22 crystallizes in the orthorhombic crystal system with the Pbam space group. In both the complexes, the geometry around the ruthenium metal centre is pseudo-octahedral, where the  $\eta^6$ -arene ring occupies the top of the piano-stool, while the three legs are represented by the bidentate bis(imidazole)methane ligand and one chloro ligand. The  $\eta^6$ -arene ring centroid (C<sub>1</sub>) is displaced from

the Ru<sup>II</sup> centre by 1.691 and 1.681 Å for the complexes [Ru]-19 and [Ru]-22 respectively, which is in line with similar arene-Ru(II) complexes previously reported.<sup>[27-29]</sup> For both the complexes [Ru]-19 and [Ru]-22, the respective ligands L7 and L5 are coordinated with the arene-Ru(II) moiety in a bidentate fashion, involving the two nitrogen atoms of the imidazole group. The Ru-N distances in [Ru]-19 are 2.106 Å (Ru-N2) and 2.105 Å (Ru-N3) respectively, the those in [Ru]-22 is 2.101 Å (Ru-N2), which is within the permissible ranges for analogous arene ruthenium complexes.<sup>[27,28]</sup> The Ru-Cl bond distances in [Ru]-19 and **[Ru]-22** are 2.432 Å and 2.385 Å respectively. The bond angles from the  $\eta^6$ -arene ring centroid (C<sub>t</sub>) to each of the legs in [**Ru**]-19 and [**Ru**]-22 are more than 120° ([Ru]-19: Ct-Ru-N3 129.46°, Ct-Ru-N2 129.06° and Ct-Ru-Cl 124.99°; [Ru]-22: Ct-Ru-N2 129.58° and Ct-Ru-Cl 126.75°), while those between the legs of the complexes are less than 90° ([Ru]-19: N3-Ru-Cl 88.21° and N2-Ru-Cl 88.26°; [Ru]-22: N2-Ru-Cl 85.57°), which is consistent with the piano stool geometry of these complexes. Further, the N3-Ru-N2 bite angle is 82.56° and 84.28° for the complex [Ru]-19 and [Ru]-22. The important crystallographic details and selected bond parameters are summarized in (Tables 4.3 -4.7 in experimental section)



Figure 4.1. Single-crystal X-ray structure of [Ru]-19. Counterion Cl<sup>-</sup> and all hydrogen atoms (except those on N1 and N4) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–N3 2.105(16), Ru– N2 2.106(16), Ru–Cl1 2.431(7), Ru–Ct 1.691, N3–Ru–Cl1 88.21(5), N2– Ru–Cl1 88.26(5), N3–Ru–N2 82.56(6).



*Figure 4.2.* Single-crystal X-ray structure of [*Ru*]-22. Counterion Cl<sup>−</sup> and all hydrogen atoms (except those on N1) are omitted for clarity. Selected bond lengths (Å) and angles (°): *Ru1–N2* 2.101(7), *Ru1–Cl1* 2.385(3), *Ru–Ct* 1.681, *N2–Ru1–Cl1* 85.57(18), *N2–Ru–N2* 84.28(4).

4.2.2. Catalytic Hydrogen Production from Formic Acid in Water Initially, we screened the complexes [Ru]-17 – [Ru]-26 (1 mol%) for the dehydrogenation of formic acid (0.4 M, 2.5 mL) in the presence of sodium formate (0.05 mmol) in water at 90 °C (Figure 4.3). Results inferred that the molecular catalysts based on  $(\eta^6-p-\text{cymene})\text{Ru}(\text{II})$ complexes ([Ru]-17 - [Ru]-21) exhibited higher activity for the dehydrogenation of formic acid as compared to the ( $\eta^6$ -benzene)Ru(II) based complexes ([Ru]-22 – [Ru]-26) under the optimized reaction conditions (Figure 4.3). Further, the nature of substituents on the bridging methylene group in the Ru-coordinated bis-imidazole methane ligand also played a crucial role in tuning the catalytic efficiency of the studied molecular catalysts.  $[(\eta^6 - p - cymene)RuCl(\kappa^2 - L6)]^+$  [Ru]-18 complex having an electron rich 4-methoxy phenyl substitution at the methylene group outperformed (TOF 793 h<sup>-1</sup>) over **[Ru]-17** (with phenyl substituted methylene group) (TOF 573 h<sup>-1</sup>) and [Ru]-20 (with 4-chloro phenyl substituted methylene group) (TOF 503 h<sup>-1</sup>). The position of -OMe or -Cl group on the phenyl substitution of methylene group also influenced the catalytic activity, where catalysts those having 4-OMe phenyl substituted methylene group exhibited slightly higher activity than those with 2-OMe phenyl substituted methylene group [Ru]-19.

Nevertheless, catalysts having methoxy–phenyl substituted methylene group [**Ru**]-18 and [**Ru**]-19 showed higher activity than those having chloro–phenyl substituted methylene group ([**Ru**]-20 and [**Ru**]-21) (Figure 4.3). Therefore, the trend in the catalytic performance of ( $\eta^6$ -*p*cymene)Ru(II) complexes for aqueous phase formic acid dehydrogenation is found to be [**Ru**]-18 > [**Ru**]-19 > [**Ru**]-17 > [**Ru**]-20 > [**Ru**]-21. Analogous trend is also observed for ( $\eta^6$ -benzene)Ru(II) based molecular catalysts: [**Ru**]-23 > [**Ru**]-24 > [**Ru**]-22 > [**Ru**]-25 > [**Ru**]-26.



*Figure 4.3.* Catalytic dehydrogenation of formic acid in water over [*Ru*]-17 – [*Ru*]-26 catalysts. Reaction conditions: formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol), catalyst (0.01 mmol), 90° C. TONs and TOFs are determined at the end of the reaction.

Therefore, further optimization of the reaction conditions for formic acid dehydrogenation is performed over [**Ru**]-18. Notably, GC-TCD analysis of the gas produced form the catalytic reaction confirmed the presence of a mixture of H<sub>2</sub> and CO<sub>2</sub> (in 1:1 molar ratio), which is in line with the expected H<sub>2</sub> to CO<sub>2</sub> ratio for formic acid dehydrogenation with no traces of CO (detection limit = 10 ppm). Further to eliminate the role of any colloidal catalytic species in the observed activity for formic acid dehydrogenation over the [**Ru**]-18 catalyst, we performed controlled Hg(0) poisoning experiment by stirring the [**Ru**]-18 (1 mol%) catalyst with an excess of elemental Hg(0) during the dehydrogenation of formic acid (0.4 M, 2.5 mL) in the presence of sodium formate (0.05 mmol) in water at 90 °C (Figure 4.4). Results inferred no significant change in the gas release for the reactions performed with or with elemental Hg(0), which clearly suggests the involvement of homogeneous catalytic species in the formic acid dehydrogenation, and eliminates any contribution by water-soluble Ru colloids under our optimized reaction conditions.



*Figure 4.4.* Controlled Hg(0) poisoning experiment. Reaction conditions: Formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol) and *[Ru]-18* (0.01 mmol) at 90 °C with and without a large excess of elemental Hg(0).

Further, the catalytic dehydrogenation of formic acid is also greatly influenced by the reaction temperature (60 - 90 °C), where high TOF is achieved for the reaction performed at 90 °C. The estimated activation energy (E<sub>a</sub>) of 91.3 kJ/mol obtained from the Arrhenius plot is found to be in good agreement with those reported for analogous systems (Figure 4.5).<sup>[12,20g]</sup>



Figure 4.5. (a) Temperature dependent formic acid dehydrogenation over [Ru]-18, and the corresponding (b) Arrhenius plot of the initial TOF values for formic acid. Reaction condition: formic acid (2 M, 2.5 mL), [Ru]-18 (0.2 mol%), [HCOONa]/[HCOOH] = 1:1, 60°C - 90 °C.

While performing the formic acid (2 M, 2.5 mL) dehydrogenation using different concentrations of sodium formate (0 – 4M), we observed that the TOF for **[Ru]-18** (0.1 mol %) catalysed dehydrogenation of formic acid is increasing up to the formic acid/sodium formate ratio of 1:1 and thereafter with high formate concentration, a decline in the TOF is observed (Table 4.1, and Figure 4.6).



**Figure 4.6.** TOF (h<sup>-1</sup>) vs [HCO<sub>2</sub>Na] (mmol) plot for the catalytic dehydrogenation of formic acid over [**Ru**]-18. Reaction condition: formic acid (2 M, 2.5 mL), [**Ru**]-18 (0.1 mol %), sodium formate (0-10) mmol, 90 °C.

The formic acid dehydrogenation rate is observed to be highly dependent on the pH of the reaction. As inferred from the graph shown in Figure 4.7, TOF increased with the decrease in pH from 6.2 to 3.5 and a highest TOF of ~1400 h<sup>-1</sup> is achieved at pH 3.5. However, with lower pH < 3.5, TOF also decreased. This observation suggests that the reaction can be expressed as a function of the formate and hydronium ion concentrations. Notably, the highest TOF of 1545 h<sup>-1</sup> is achieved for formic acid (4M, 2.5mL), formic acid/sodium formate ratio of 1:1 with [**Ru**]-18 (0.05 mol %) (Table 4.1).

 Table 4.1. Effect of formic acid/sodium formate ratio on the catalytic

 dehydrogenation of formic acid<sup>a</sup>

Entry	Catalyst	<i>n</i> (formic acid)/ <i>n</i> (sodium formate)	TON <sup>b</sup>	Initial TOF <sup>c</sup> (h <sup>-1</sup> )				
1	[Ru]-18	5/-	840	198				
2	[Ru]-18	5/0.25	860	268				
3	[Ru]-18	5/1	870	416				
4	[Ru]-18	5/5	870	1364				
5	[Ru]-18	5/10	800	485				
6	[Ru]-18	10/10	1830	1545				
7	[Ru]-19	10/10	1800	1509				
8	[Ru]-17	10/10	1762	1052				
9	[Ru]-20	10/10	1740	989				
<sup><i>a</i></sup> Reaction conditions: formic acid $(2 - 4 \text{ M}, 2.5 \text{ mL})$ , sodium formate								
(0 - 10  mmol), catalyst (0.005 mmol), 90 °C. <sup>b</sup> TONs are calculated at								

the completion of the reaction. <sup>c</sup>TOFs (initial 20 minutes).



*Figure 4.7.* pH dependent dehydrogenation of formic acid over [*Ru*]-18, where pH is altered by tuning n(formic acid)/n(sodium formate) ratio. Reaction condition: formic acid (2.0 M, 2.5 mL), sodium formate (0 - 30 mmol), [*Ru*]-18 (0.005 mmol), 90 °C.

Further the kinetic studies inferred that the initial rate of dehydrogenation of formic acid increased with the increase in formic acid concentration in the low concentration range. The reaction order of 0.48 for the dehydrogenation of varying concentrations of formic acid (0.2 M - 0.8 M) over 0.01mmol of [**Ru**]-18 at 90 °C evidenced that only one HCO<sub>2</sub><sup>-</sup> or (HCO<sub>2</sub>H) coordinates to the Ru centre to form [HCOO<sup>-</sup>-Ru] species during the catalytic dehydrogenation of formic acid (Figure 4.8a).<sup>[11-12,19j]</sup> Further, the double logarithmic plot of the initial rates of formic acid dehydrogenation (0.6 M, 2.5 mL) with the concentration of [**Ru**]-18 (0.005 mmol – 0.02 mmol) indicated a first order reaction with respect to the catalyst concentration (Figure 4.8b). This suggest that presumably the monomeric active species is involved in the catalytic reaction.<sup>[11-12,19j]</sup>



**Figure. 4.8.** (a) Plot of ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs ln[HCOOH] (mmol  $L^{-1}$ ). Reaction condition: **[Ru]-18** (0.01 mmol), formic acid (0.2 M - 0.8 M, 2.5 mL), 90 °C. (b) Plot of ln[initial rate] (mmol  $L^{-1} h^{-1}$ ) vs ln[cat](mmol  $L^{-1}$ ). Reaction condition: **[Ru]-18** (0.005 mmol - 0.02 mmol), formic acid (0.6 M, 2.5 mL), 90 °C.

The long-term stability of the high performing [Ru]-18 catalyst is further evaluated by performing the formic acid dehydrogenation with batch-wise addition of formic acid at regular intervals of time during the reaction. Results inferred that the high performing [Ru]-18 catalyst exhibited appreciably long-term stability over 12 to 17 h producing over 2 L of gas  $(H_2+CO_2)$  mixture during formic acid dehydrogenation (Figure 4.9). The observed catalytic performance of [Ru]-18 catalyst, with an initial TOF of 1424 h<sup>-1</sup> to achieve a turnover of 8830, is higher than our previously reported arene-Ru(II) catalysts<sup>[11,12]</sup> and is next to Huang's<sup>[20g]</sup>  $[(\eta^{6}-C_{10}H_{14})RuCl(2,2'-bi-2-imidazoline)]^{+2}$ and Laurenczy's<sup>[20i]</sup> catalysts [Ru(H<sub>2</sub>O)<sub>6</sub>](tos)<sub>2</sub>/ TPPTS (tos is *p*-toluene sulfonate and TPPTS is *m*-trisulfonated triphenylphosphine) for formic acid dehydrogenation in aqueous medium. It is also worthy to mention that Laurenczy's catalyst works best at 120 °C to give a turnover frequency (TOF) of 460 h<sup>-1</sup>, while we observed that **[Ru]-18** catalyst works well even at 90 °C giving a significantly higher TOF.



*Figure 4.9.* Long-term stability test of *[Ru]-18* for the catalytic dehydrogenation of formic acid. Reaction conditions: formic acid (4.0 M, 2.5 mL), sodium formate (10 mmol), *[Ru]-18* (0.005 mmol) at 90 °C, and subsequent addition of formic acid (5 mmol) at 90, 180, 320 and 500 minutes during the reaction.

### 4.2.3. Mechanistic study

Mass spectrometry, NMR analyses and KIE measurements are performed to elucidate the possible pathway for formic acid dehydrogenation over the studied arene-Ru(II) catalyst. A noticeable colour change from the initial pale-brown solution of the catalyst **[Ru]-18** to a red-orange solution is observed during the initial minutes of both the base-free and sodium formate assisted dehydrogenation of formic acid. Mass analysis of the aliquots taken at different time intervals of the catalytic reaction revealed the presence of prominent mass peaks at m/z591.2 and 619.2 corresponding to the Ru-aqua species  $[(\eta^6-p$ cymene)Ru( $\kappa^2$ -L6–H<sup>+</sup>)(H<sub>2</sub>O)]<sup>+</sup> (**[Ru]-18A**) and Ru-formato species  $[(\eta^6-p-cymene)Ru(\kappa^2$ -L6–H<sup>+</sup>)(HCO<sub>2</sub>)] (**[Ru]-18B+H**<sup>+)</sup> respectively (Figure 4.10 and Figure 4.11).



*Figure.* 4.10. Colour transformation during the initial minutes of dehydrogenation of formic acid with [*Ru*]-18.



*Figure 4.11.* Ru-aqua and Ru-formato species observed during mass investigation of the catalytic reaction aliquots. Reaction conditions: formic acid (0.4 M, 2.5 mL) and [*Ru*]-18 (0.005 mmol) at 90 °C, with or without sodium formate (0.05 mmol).

Further, the mass peak at m/z 591.2 corresponding to the Ru-aqua species remains the most prominent peak throughout the progress of the catalytic dehydrogenation reaction, suggesting that the aqua coordinated Ru species [**Ru**]-18A is presumably the active form of the catalyst. Several controlled experiments are also performed to gain more insights into the active catalytic species involved in the dehydrogenation of formic acid over [**Ru**]-18. At first, [**Ru**]-18 is stirred in water for 5 minutes at 50 °C and the reaction aliquot showed a prominent mass peak

at m/z 591.2, corresponding to the Ru-aqua species  $[(\eta^6-p-cymene)Ru(\kappa^2-L6-H^+)(H_2O)]^+$  (**[Ru]-18A**) (Figure 4.12) Notably, this observation is in contrast to the mass analysis of **[Ru]-18** in MeOH, where the peak at m/z 609.2 corresponding to the molecular ion peak of **[Ru]-18** is present as the only dominant species.



Figure 4.12. Ru-aqua species observed during mass investigation of the reaction mixture of [Ru]-18 (0.005 mmol) dissolved in  $H_2O(2.5 \text{ mL})$  and heated at 50 °C for 5 minutes.

In another controlled experiment, **[Ru]-18** (0.005 mmol) is treated with formic acid (0.5 mmol) in water at room temperature and mass analysis is performed. Mass peak at m/z 619.2 corresponding to the formate coordinated Ru species  $[(\eta^6-p\text{-cymene})\text{Ru}(\kappa^2\text{-L6}-\text{H}^+)(\text{HCO}_2)]$ (**[Ru]-18B+H**<sup>+</sup>) is observed, suggesting that the addition of formic acid may lead to the formation of the formate coordinated Ru intermediate **[Ru]-18B** (Figure 4.13).



*Figure 4.13. ESI-MS* showing the *Ru-formate species for the reaction of [Ru]-18* (0.005 mmol) with formic acid (0.5 mmol) stirred in water (2.5 mL) for 15 minutes at room temperature.

Upon addition of sodium formate in the above reaction mixture, intensity of the mass peak at m/z 619.2 (Ru-formato species **[Ru]-18B**) also increased, inferred that more formate ions in the solution facilitated the formation of **[Ru]-18B** species, which is in line with our experimental findings (Figure 4.14).



Figure 4.14. Ru-formato and Ru-hydride species observed during mass investigation for the reaction of [Ru]-18 (0.005 mmol) with sodium formate (0.05 mmol) in  $H_2O$  (2 mL) at room temperature (a) with and (b) without formic acid (0.5 mmol).

The formation of Ru-formato species is further confirmed by the observation of a peak at  $\delta = 7.15$  in the <sup>1</sup>H NMR spectrum of the product obtained from the reaction of the analogous [( $\eta^6$ -benzene)Ru( $\kappa^2$ -L6)Cl] ([**Ru**]-23) complex with formic acid and sodium formate at 0 °C (Figure 4.15).



Figure 4.15. (a) <sup>1</sup>H NMR spectrum of [Ru]-23 in  $D_2O$ . (b) <sup>1</sup>H NMR spectrum of complex formed after [Ru]-23 (0.05 mmol) was heated in water (2 mL) at 50 °C for 1 hour. (c) <sup>1</sup>H NMR spectrum of complex formed after [Ru]-23 (0.05 mmol) was treated with formic acid (1 mmol) and sodium formate (0.05 mmol) in water (2 mL) at 0 °C for 1 hour showing the generation of Ru-formate species.

To further decipher the role of the Ru-formato species in the catalytic cycle, the Ru-formato species  $[(\eta^6\text{-benzene})\text{Ru}(\kappa^2\text{-L6}-\text{H}^+)(\text{HCO}_2)]$  (m/z =564.1) is synthesized and isolated from [**Ru**]-23, and further the transformation of the synthesized Ru-formato species under temperature treatment (60 – 90 °C) is investigated by mass studies (Figure 4.16). Results inferred with the increase in reaction temperature, the intensity of the mass peak corresponding to the Ru-hydride intermediate [( $\eta^6$ -benzene)Ru( $\kappa^2$ -L6-H<sup>+</sup>)(H)] at m/z =519.1 gradually increases and appeared as the most prominent peak in the mass spectra after the reaction mixture is heated for 10 minutes at 90 °C. Notably, some bubbles of gas is also observed in the vial during the heat treatment, corresponding to the release of CO<sub>2</sub> during the decarboxylation of Ruformato species, as evident by the observed intense mass peak for the Ru-hydride species in the reaction aliquot obtained after heat treatment.



**Figure 4.16.** Temperature dependent (30 °C – 90 °C) mass study for the transformation of Ru-formate species to Ru-hydride species. Gas bubbles as observed in the vial during the heating of Ru-formate complex inferred the decarboxylation of Ru-formate to Ru-hydride.

Earlier, Huang *et al.* performed DFT studies to propose the involvement of Ru-formato in formic acid dehydrogenation, where in decarboxylation of Ru-formato species led to the formation of Ruhydride species.<sup>[20g]</sup> However, they could only identify the Ru-hydride species. In a subsequent controlled experiment, we treated [**Ru**]-18 (0.005 mmol) with sodium formate (0.05 mmol) in H<sub>2</sub>O at room temperature, where a prominent mass peak at m/z 575.2 corresponding

the Ru-hydride species  $[(\eta^6 - C_{10}H_{14})Ru(\kappa^2 - L6 - H^+)(H)]$  (**[Ru]**to **18C**+ $H^+$ ) is observed in the mass spectra (Figure 4.14) The formation of Ru-hydride species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-L6-H^+)(H)]$  ([**Ru**]-18C) in formic acid dehydrogenation reaction is also evidenced by the presence of the corresponding <sup>1</sup>H NMR signal at  $\delta = -7.35$  ppm in a time dependent NMR study during the reaction of [Ru]-18 (0.01 mmol) with HCO<sub>2</sub>Na (0.05 mmol) in D<sub>2</sub>O (0.6 mL) at room temperature (Figure 4.17). As the Ru hydride intermediate is not observed in the presence of formic acid (acidic condition) (Figure 4.13) and under catalytic reaction conditions at 90 °C, we envisioned that reaction between the Ru-hydride intermediate [Ru]-18C and formic acid (H<sup>+</sup>) generates H<sub>2</sub>, leading to the regeneration of the aqua coordinated species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L6}-\text{L6})$  $H^+$ )( $H_2O$ )]<sup>+</sup> ([**Ru**]-18A). Interestingly, the addition of an excess of dilute HCl in the red-orange solution of [Ru]-18, obtained in the presence of sodium formate, resulted in the regeneration of the original pale-brown color of **[Ru]-18**. Further, mass analysis of the aliquot of this pale-brown solution showed the presence of a prominent mass peak at m/z 609.2 which is corresponding to the molecular ion peak of [Ru]-18 (Figure 4.18).



**Figure 4.17.** <sup>1</sup>*H* NMR spectra showing the generation of Ru-hydride species during the treatment of **[Ru]-18** (0.01 mmol) with sodium formate (0.05 mmol) in  $D_2O$  (0.6 mL) at 25 °C.



Figure 4.18. Mass investigation of the reaction mixture of [Ru]-18 (0.005 mmol) treated with sodium formate (0.05 mmol) in water showing the colour change from the initial yellow-green to pale-brown and reverts back to pale-brown colour when treated with an excess of dil. HCl.

Moreover, the observed trend in KIE studies indicated that decarboxylation is the rate determining step in the catalytic cycle of formic acid dehydrogenation and not the proton assisted release of hydrogen gas. Our experimental findings inferred that the deuterated formic acid (DCOOD) is more influential than  $D_2O$  in the reaction rate for the catalytic reaction performed over [**Ru**]-18 with HCOOH in  $D_2O$  or DCOOD in H<sub>2</sub>O under the optimized reaction conditions (Table 4.2).

entry	catalyst	substrate	solvent	$\begin{array}{c} \text{TOF} \\ (h^{-1})^b \end{array}$	KIE <sup>c</sup>
1	[Ru]-18	НСООН	$H_2O$	300	
2	[Ru]-18	НСООН	$D_2O$	156	1.9
3	[Ru]-18	DCOOD	H <sub>2</sub> O	96	3.1
4	[Ru]-18	DCOOD	$D_2O$	76	3.9

Table 4.2. KIE in the dehydrogenation of formic acid over [Ru]-18<sup>a</sup>

<sup>*a*</sup>Reaction conditions: **[Ru]-18** (0.01 mmol), formic acid (0.4 M, 2.5 mL), 90 °C. <sup>*b*</sup>Initial TOF at 20 min. <sup>*c*</sup>KIE = TOF (entry 1)/ TOF (entry n) (n = 2, 3, 4)

On the basis of the experimental findings, and the identification of several important catalytic intermediate species as identified during NMR and mass investigations, we propose a plausible reaction pathway as shown in scheme 4.3. At first, **[Ru]** catalyst is dechlorinated to form a Ru-aqua species, which subsequently form  $[(\eta^6-p-cymene)Ru(\kappa^2-L H^+)(H_2O)]^+$  (**[Ru]-A**) with deprotonated **L** in the aqueous medium. Further, formate replaced the aqua ligand to generate a formate coordinated Ru species  $[(\eta^6-p-cymene)Ru(\kappa^2-L-H^+)(HCO_2)]$  (**[Ru]-B**). Subsequent release of CO<sub>2</sub> *via* decarboxylation generated the Ruhydride species  $[(\eta^6-p-cymene)Ru(\kappa^2-L-H^+)(H)]$  (**[Ru]-C**). Finally, proton assisted hydrogen (H<sub>2</sub>) release from the Ru-hydride species (**[Ru]-C**) regenerated the active aqua coordinated species **[Ru]-A** to complete the catalytic cycle (Scheme 4.3).



*Scheme 4.3.* A plausible pathway for the dehydrogenation of formic acid over bis-imidazole methane ligated arene-ruthenium(II) complexes.

#### 4.3. Conclusion

In summary, we reported the synthesis of a series of arene-Ru(II) complexes having bis-imidazole methane-based ligands, and employed these complexes for the catalytic dehydrogenation of formic acid in water. Results inferred that the nature of the coordinating bis-imidazole methane ligands exerted significant impact in tuning the catalytic performance of the studied complexes. Consequently, the complex [**Ru**]-**18** containing **L6** outperformed over the analogous complexes for formic acid dehydrogenation, where the high performing [**Ru**]-**18** catalyst exhibited appreciably high TOF 1545 h<sup>-1</sup>. Moreover, [**Ru**]-**18** catalyst also displayed appreciably high long-term stability for formic acid dehydrogenation to achieve a turnover of 8830. Various catalytic and control experiments along with the extensive mass and NMR

investigations of revealed the identification of all the crucial catalytic intermediate species, Ru-aqua species  $[(\eta^6-p\text{-cymene})\text{Ru}(\kappa^2\text{-}\text{L6}-\text{H}^+)(\text{H}_2\text{O})]^+$  ([**Ru**]-18A), the Ru-formato species  $[(\eta^6-p\text{-cymene})\text{Ru}(\kappa^2\text{-}\text{L6}-\text{H}^+)(\text{HCO}_2)]$  ([**Ru**]-18B) and the Ru-hydride species  $[(\eta^6-p\text{-cymene})\text{Ru}(\kappa^2\text{-}\text{L6}-\text{H}^+)(\text{H})]$  ([**Ru**]-18C). Noteworthily, our experimental findings with temperature dependednt gradual transformation of the Ru-formato species to the Ru-hydride species evidenced the determining role of Ru-formato species as a crucial component in formic acid dehydrogenation reaction. We hope that our present study will pave the way for the development of high performing catalysts for water-based dehydrogenation reactions.

#### 4.4. Experimental Section

#### 4.4.1. Materials and instrumentation

All reactions are performed without any inert gas protection using highpurity chemicals purchased from Sigma-Aldrich (Merck) and Alfa-Aesar. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra are recorded at 298 K using CD<sub>3</sub>OD and D<sub>2</sub>O as solvents on a Bruker advance 400 spectrometer. The pH values are measured on a Eutech pH meter, Model Eco Testr pH2. HRMS and 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 shin carbon-ST packed column.

#### **4.4.2.** General procedure for the synthesis of ligands L6 and L8

To a solution of 2-ethyl-4-methyl imidazole (2.2 g, 20 mmol) in methanol (5 mL), corresponding substituted benzaldehyde (10 mmol) and an aqueous solution of potassium hydroxide (3.36 g, 60 mmol) are added. The reaction mixture is stirred for 3 days at 80 °C to obtain the solid product, which is filtered and washed several times with water and finally with diethyl ether. The obtained solid is dried in an oven overnight to obtain yellow-coloured solids.

**L6**. Yellow powder; (71% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.00 (s, 2H), 6.83 (s, 2H), 5.35 (s, 1H), 3.75 (s, 3H), 2.62 (s, 4H),

1.90 (s, 6H), 1.23 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 160.06, 149.51, 135.30, 130.61, 114.95, 114.03, 55.85, 40.24, 22.34, 13.50, 10.75.

**L8**. Pale yellow powder, (76% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.25 (s, 2H), 7.08 (s, 2H), 5.37 (s, 1H), 2.62 (s, 4H), 1.92 (s, 6H), 1.22 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 149.58, 142.54, 133.17, 131.12, 129.76, 129.33, 127.86, 40.51, 22.32, 13.41, 10.63.

## **4.4.3.** General Procedure for synthesis of the complexes ([Ru]-17 – [Ru]-26)

 $[(\eta^{6}\text{-arene})\text{RuCl}_{2}]_{2}$  (0.5 mmol) is dissolved in 30 mL HPLC grade methanol, and the corresponding ligand (L5 – L9) (1.1 mmol) is added to it. The reaction mixture is refluxed for 20 h, and then volume of the reaction mixture is reduced to 3 mL under reduced pressure. An excess of diethyl ether is poured in to the above methanolic solution to precipitate yellow to light-brown solids.

[**Ru**]-17. Yellow powder, (72% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.44 – 7.40 (m, 5H), 5.64 (s, 2H), 5.57 (s, 2H), 5.01 (s, 1H), 5.04 (s, 1H), 3.39 (s, 2H), 3.03 (s, 2H), 2.33 (s, 1H), 2.20 (s, 3H), 1.31 (s, 6H), 1.26 (s, 6H), 1.14 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$ (ppm): 153.36, 139.76, 132.82, 130.07, 129.53, 128.74, 125.46, 106.45, 101.35, 86.01, 83.56, 45.99, 33.13, 24.18, 22.79, 18.44, 13.58, 11.69, 9.42. HRMS (*m*/*z*): calcd, 579.1827; found, 579.1841

[**Ru**]-18. Yellow powder; (70% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.29 (s, 2H), 7.01 (s, 2H), 5.63 (s, 2H), 5.56 (s, 2H), 4.96 (s, 1H), 3.84 (s, 3H), 2.32 (s, 2H), 2.20 (s, 2H), (s, 2H), 1.99 (s, 1H), 1.13 (s, 6H), 0.78 (s, 3H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 161.42, 153.29, 133.72, 133.27, 129.75, 125.41, 115.34, 106.41, 101.32, 86.01, 83.55, 55.83, 45.13, 33.13, 24.17, 22.78, 18.43, 13.57, 11.77, 9.40. HRMS (m/z): calcd, 609.1933; found, 609.1937.

[**Ru**]-19. Yellow powder; (78% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.42 (t, J = 8 Hz, 1H), 7.26 (d, J = 8 Hz, 1H), 7.15 (d, J = 12Hz, 1H), 7.01 (t, J = 8 Hz, 1H), 5.70 (s, 1H), 5.59 (d, J = 8 Hz, 2H), 5.53 (d, J = 8 Hz, 2H), 3.92 (s, 3H), 3.02 (q, J = 8 Hz, 4H), 2.71 (m, 1H), 2.25 (s, 3H), 1.32 (t, J = 8 Hz, 12H), 1.13 (d, J = 8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 159.00, 153.28, 134.92, 132.90, 130.86, 126.96, 124.71, 122.10, 112.60, 106.12, 101.67, 86.01, 83.58, 56.44, 35.95, 32.97, 24.13, 22.76, 18.56, 13.55, 11.70. HRMS (m/z): calcd, 609.1933; found, 609.1935

[**Ru**]-20. Yellow powder; (76% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.47 – 7.41 (m, 4H), 5.64 – 5.57 (m, 4H), 5.05 (s, 1H), 3.38 (br, 2H), 3.03 (br, 2H), 2.73 (br, 1H), 2.19 (s, 3H), 1.32 (s, 12H), 1.14 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 153.52, 134.40, 132.55, 131.63, 130.21, 126.05, 125.35, 106.53, 101.32, 86.00, 83.57, 45.27, 37.12, 33.10, 24.18, 22.79, 13.56, 11.88. HRMS (m/z): calcd, 613.1435; found, 613.1445.

**[Ru]-21**. Yellow powder; (70% yield); <sup>1</sup>H NMR (400 MHz, MeOH-*d*<sub>4</sub>)  $\delta$  (ppm): 7.58 (d, J = 4 Hz, 1H), 7.44 (d, J = 4 Hz, 1H), 7.38 (d, J = 4 Hz, 2H), 5.62 (d, J = 4 Hz, 2H), 5.55 (d, J = 4 Hz, 2H), 5.33 (s, 1H), 3.07 – 3.00 (m, 1H), 2.26 (s, 6H), 2.09 (s, 3H), 1.36 – 1.32 (m, 4H), 1.13 (d, J = 4 Hz, 6H), 0.82 (d, J = 4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, MeOH-*d*<sub>4</sub>)  $\delta$  (ppm): 153.65, 137.64, 136.08, 135.54, 132.01, 131.18, 130.80, 129.03, 125.26, 106.20, 101.70, 86.02, 83.71, 40.99, 33.16, 24.19, 22.79, 18.62, 13.55, 11.44. HRMS (*m*/*z*): calcd, 613.1435; found, 613.1437.

[**Ru**]-22. Light brown powder; (80% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.40 (br, 2H), 7.31 (br, 1H), 7.00 (d, J = 4 Hz, 2H), 5.31 (s, 1H), 5.23 (s, 6H), 3.47 (d, J = 8 Hz, 2H), 3.04 (br, 2H), 2.35 (s, 6H), 1.35 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 154.27, 143.02, 132.07, 130.15, 128.29, 128.27, 125.76, 86.45, 37.49, 24.22, 13.04, 9.17. HRMS (m/z): calcd, 523.1200; found, 523.1200.

[**Ru**]-23. Yellow powder; (77% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 6.95 (d, J = 8 Hz, 2H), 6.88 (d, J = 8 Hz, 2H), 5.27 (s, 6H), 5.24 (s, 1H), 3.78 (s, 3H), 3.04 (q, J = 8 Hz, 4H), 2.33 (s, 6H), 1.33 (t, J = 8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 160.43, 154.19,

134.62, 132.60, 129.26, 125.53, 115.48, 86.46, 55.88, 36.80, 24.22, 13.04, 9.17. HRMS (*m*/*z*): calcd, 553.1306; found, 553.1307.

**[Ru]-24**. Yellow powder; (74% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.32 (t, J = 8 Hz, 1H), 7.01 (d, J = 8 Hz, 1H), 6.96 (t, J = 8 Hz, 1H), 6.74 (d, J = 8 Hz, 1H), 5.42 (s, 6H), 5.32 (s, 1H), 3.74 (s, 3H), 3.05 (q, J = 4 Hz, 4H), 2.27 (s, 6H), 1.33 (t, J = 8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 159.66, 153.41, 132.29, 131.04, 130.20, 125.12, 121.07, 113.02, 86.54, 56.19, 35.23, 24.45, 12.96, 9.56. HRMS (m/z): calcd, 553.1306; found, 553.1306.

[**Ru**]-25. Yellow powder; (68% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.42 (s, 2H), 7.00 (s, 2H), 5.28 (s, 6H), 4.91 (s, 1H), 3.05 (br, 4H), 2.34 (s, 6H), 1.35 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 154.41, 141.89, 134.14, 131.66, 130.18, 129.97, 125.95, 86.49, 37.10, 24.26, 13.02, 9.18. HRMS (m/z): calcd, 557.0808; found, 557.0822.

[**Ru**]-26. Yellow powder; (66% yield); <sup>1</sup>H NMR (400 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 7.45 (s, 1H), 7.34 (s, 2H), 7.01 (s, 1H), 5.82 (s, 1H), 5.38 (s, 6H), 3.07 (br, 4H), 2.29 (s, 6H), 1.35 – 1.28 (m, 6H), 1.31 (s, 6H). <sup>13</sup>C NMR (100 MHz, MeOH- $d_4$ )  $\delta$  (ppm): 154.31, 139.24, 134.57, 133.19, 132.82, 132.04, 130.32, 128.24, 125.90, 86.39, 37.25, 24.48, 12.98, 9.70. HRMS (m/z): calcd, 557.0808; found, 557.0829.

#### 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**]-19 and [**Ru**]-22. X-ray structural studies are executed on a CCD Agilent Technologies (Oxford Diffraction) SUPERNOVA diffractometer. Using graphite-monochromated Cu Ka radiation ( $\lambda = 1.54184$  Å)-based diffraction, data are collected at 293(2) K by the standard "phi-omega" scan techniques and are scaled and reduced using CrysAlisPro RED software. The extracted data are evaluated using the CrysAlisPro CCD software. The structures are solved by direct methods using SHELXL-2018/1, and refined by full-matrix least squares method, refining on F<sup>2</sup>.<sup>[30]</sup> 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 numbers 2069897 and 2069898 contain the supplementary crystallographic data for [**Ru**]-22 and [**Ru**]-19 respectively.

#### 4.4.5. General process for formic acid dehydrogenation reaction

An aqueous solution (2.5 mL) containing the catalyst (as specified), HCOONa (as specified), and formic acid (as specified) in a two-necked 5 mL reaction tube, fitted with a condenser and a gas burette, is stirred at 90 °C over a preheated oil bath. The volume of gas produced is measured as the displacement of water in the burette with respect to time. 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.

# **4.4.6.** Mechanistic investigations for formic acid dehydrogenation under catalytic and controlled reaction condition

Formic acid (0.4 M, 2.5mL) and [Ru]-18 (0.005 mmol) are taken in a 5mL two-necked test tube and heated at 90 °C. Reaction aliquots are taken out from the reaction in every 5 min. and analysed by mass spectrometry to identify the catalytic species involved in base-free dehydrogenation of formic acid. Formic acid (0.4 M, 2.5mL), [Ru]-18 (0.005 mmol) and sodium formate (0.05 mmol) are taken in a 5 mL twonecked test tube and heated at 90 °C. Reaction aliquots are taken out from the reaction mixture in every 5 minutes for mass analysis to identify the catalytic species involved in the sodium formate assisted dehydrogenation of formic acid over [Ru]-18. [Ru]-18 (0.005 mmol) is dissolved in 2.5 mL water by heated at 50 °C, and the reaction aliquot is analysed by mass spectrometry to detect the Ru-aqua species. [Ru]-18 (0.005 mmol) is dissolved in 2 mL H<sub>2</sub>O and formic acid (0.5 mmol) is added to it, and the reaction aliquot is analysed by mass spectrometry to detect the Ru-formato coordinated species. To the above solution, sodium formate (0.05 mmol) is added and analysed by mass

spectrometry to gain the insights into the effect of higher concentration of formate ions over the formation of Ru-formato species. [Ru]-18 (0.005 mmol) is dissolved in 2 mL water and sodium formate (0.05 mmol) is added to it at room temperature, and the reaction aliquot is analysed by mass spectrometry to detect the Ru-hydride species. [Ru]-18 (0.01 mmol) is dissolved in  $D_2O$  (0.6 mL) and sodium formate (0.05 mmol) is added to it in an NMR tube and analysed by <sup>1</sup>H NMR spectroscopy at different time intervals to confirm the formation of Ruhydride species. In an aqueous solution of [Ru]-23 (0.04 mmol), formic acid (1 mmol) and sodium formate (0.1 mmol) are added, and the reaction mixture is stirred at 0 °C for 2h after which, the solvent is removed under vacuum to obtain a solid product, which is analysed by <sup>1</sup>H NMR spectroscopy to confirm the formation of Ru-formato species. A pinch of the purified and isolated Ru-formato complex was dissolved in HPLC water in a mass vial and subjected to temperature treatment from 30 - 90 °C to investigate the role of Ru-formato species in the catalytic cycle of formic acid dehydrogenation.

#### **4.4.7.** Controlled Hg(0) poisoning experiment

Formic acid (0.4 M, 2.5 mL), sodium formate (0.05 mmol), **[Ru]-18** (0.01 mmol) are taken in a two-necked 5 mL reaction tube. Hg(0) (10 mmol) is added in the reaction tube and stirred for sometime to mix it. The reaction mixture is then stirred at 90 °C. The condenser is fitted with a gas burette. The amount of gas generated is measured by the water displacement method.

**4.4.8.** Investigation of long-term stability of [Ru]-18 for hydrogen production from formic acid with batch-wise addition of formic acid Formic acid (4.0 M, 2.5 mL) and sodium formate (10 mmol) are stirred at 90 °C in the presence of [Ru]-18 (0.005 mmol) catalyst in a two-necked 5 mL reaction tube fitted with a condenser and a gas burette. 10 mmol of formic acid is added to the reaction mixture after 90, 180, 320 and 500 minutes, and the volume of gas produced is measured as the displacement of water in the burette with respect to time. In another reaction, 5 mmol of formic acid is added at different intervals of time
(55, 107, 203, 316, 482, 595, 750 and 900 minutes) to the reaction vessel (10 mL flask) containing initially formic acid (4.0 M, 5 mL), sodium formate (20mmol) and **[Ru]-18** (0.005 mmol). The volume of gas produced is measured as the displacement of water in the burette with respect to time, and the respective plot of  $(H_2+CO_2)$  mL *vs*. time suggest that **[Ru]-18** catalyst exhibits appreciably long-term stability for 12 to 17 hours producing almost 2 L of the gas mixture.

#### 4.4.9. Gas Composition Analysis

The identification of gaseous products during the decomposition of formic acid was confirmed as H<sub>2</sub> and CO<sub>2</sub> with no detectable level of CO using a Shimadzu GC-2014 system. The chromatograph was equipped with a shin carbon-ST packed column with thermal conductivity detector (TCD) using argon as a carrier gas. Parameters set for the program to detect H<sub>2</sub> and CO<sub>2</sub> (Detector temperature: 200 °C, oven temperature: 90 °C; program: 90 °C (hold time: 1 min), 90 °C - 200 °C (rate: 15 °C per minute) The H<sub>2</sub>:CO<sub>2</sub> molar ratio during formic acid dehydrogenation was found to be approximately 1:1 and 2:1 based on the calibration curve using standard H<sub>2</sub> and CO<sub>2</sub> gas.



Figure 4.19. 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]-18 catalyst. Reaction condition: [Ru]-18 (0.01 mmol), formic acid (0.8 M, 2.5 mL), sodium formate (0.05 mmol), 90 °C. (Analysis is performed using Argon as the carrier gas). (b) Pure H<sub>2</sub> gas. (c) Pure CO gas (detection limit 10 ppm). (d) Pure CO<sub>2</sub> gas.

# 4.4.10. Characterization of ligands and metal complexes





<sup>13</sup>C NMR of L5



<sup>13</sup>C NMR of L6



<sup>1</sup>H NMR of L7

Methanol-d4



<sup>13</sup>C NMR of L7





HRMS of [Ru]-17









HRMS of [Ru]-19





HRMS of [Ru]-20



HRMS of [Ru]-21



HRMS of [Ru]-22



HRMS of [Ru]-23











HRMS of [Ru]-25



# <sup>13</sup>C NMR of [Ru]-26



HRMS of [Ru]-26

	[Ru]-19	[Ru]-22
Formula	$C_{30}H_{42}N_4O_2Cl_2Ru$	$C_{25}H_{30}N_4Cl_2Ru$
Molecular weight	662.64	558.50
Crystal system	monoclinic	orthorhombic
Space group	P21/n	Pbam
Temperature/K	273.15	273.15
Wavelength	0.71073	0.71073
a/Å	10.957(3)	12.5273(19)
<i>b</i> /Å	12.714(5)	22.320(3)
$c/\text{\AA}$	22.775(5)	11.4301(17)
<i>α</i> /°	90	90
$\beta/^{\circ}$	98.903(7)	90
γ/°	90	90
$V/Å^3$	3134.6(17)	3195.9(8)
Z	4	4
Density/gcm <sup>-1</sup>	1.4	1.161
Absorption Coefficient	0.703	0.673
Absorption Correction	Semi empirical from equivalents	Semi empirical from equivalents
F(000)	1376	1144
Total no of reflections	5597	4119
Reflections, $I > 2\sigma(I)$	5098	1984
Max. $2\theta/^{\circ}$	25.249	28.455
Ranges (h, k, l)	-13≤ h ≤13	$-13 \le h \le 16$
	$-15 \le k \le 15$	$-29 \le k \le 28$

*Table 4.3.* Single crystal X-ray refinement data for [*Ru*]-19 and [*Ru*]-22.

	-23≤1 <i>≤</i> 27	$-15 \le 1 \le 14$
Complete to $2\theta(\%)$	98.6	98.2
Refinement method	'SHELXL 2014/7 (Sheldrick, 2015)'	'SHELXL 2014/7 (Sheldrick, 2015)'
Goof $(F^2)$	1.044	1.002
R indices $[I > 2\sigma(I)]$	0.0241	0.0939
R Indices (all data)	0.0279	0.1673

Table 4.4. Selected bond lengths (Å) for complex [Ru]-19.

Ru-N3	2.1050(16)
Ru-N2	2.1060(16)
N3-C9	1.403(2)
N3-C8	1.326(3)
C8-N4	1.336(3)
N4-C10	1.383(3)
C10-C11	1.504(3)
C8-C12	1.499(3)
C12-C13	1.517(4)
N2-C1	1.335(2)
N2-C3	1.404(2)
C1-N1	1.344(2)
C2-N1	1.377(2)
C1-C5	1.495(3)
C5-C6	1.519(3)
Ru-Cl1	2.4315(7)
C9-C7	1.526(3)
C7-C3	1.519(3)

C7-C14	1.529(3)
C15-O1	1.359(2)
O1-C20	1.436(3)
Ru-C25	2.1821(19)
Ru-C23	2.193(2)
Ru-C22	2.1931(19)
Ru-C26	2.210(2)
Ru-C24	2.228(2)
Ru-C21	2.239(2)

**Table 4.5**. Selected bond angles (°) for complex [Ru]-19.

N3-Ru-N2	82.55(6)
N3-Ru-C25	123.92(7)
N2-Ru-C25	153.04(7)
N3-Ru-C23	151.55(7)
N2-Ru-C23	91.89(7)
C25-Ru-C23	67.31(8)
N3-Ru-C22	114.34(7)
N2-Ru-C22	94.46(6)
C25-Ru-C22	79.78(7)
N3-Ru-C26	95.87(7)
N2-Ru-C26	159.33(7)
N3-Ru-C24	161.75(7)
N2-Ru-C24	115.62(7)
C25-Ru-C24	37.83(8)
C23-Ru-C24	37.16(8)

C22-Ru-C24	68.01(7)
C26-Ru-C24	67.80(8)
N3-Ru-C21	91.49(7)
N2-Ru-C21	121.67(7)
C25-Ru-C21	67.61(7)
C23-Ru-C21	67.74(7)
C22-Ru-C21	37.08(7)
C26-Ru-C21	37.67(7)
C24-Ru-C21	80.46(7)
N3-Ru-Cl1	88.21(5)
N2-Ru-Cl1	88.26(5)
C25-Ru-Cl1	87.67(6)
C23-Ru-Cl1	119.62(6)
C22-Ru-Cl1	157.45(5)
C26-Ru-Cl1	112.33(6)
C24-Ru-Cl1	90.63(6)
C21-Ru-Cl1	149.78(5)
C15-O1-C20	117.59(17)
C1-N1-C2	109.82(16)
C1-N2-C3	107.20(15)
C1-N2-Ru	128.12(12)
C3-N2-Ru	124.35(12)
C8-N3-C9	107.25(16)
C8-N3-Ru	127.34(13)
C9-N3-Ru	124.80(12)
C8-N4-C10	109.65(18)
N2-C1-N1	109.07(16)

N2-C1-C5	121.90(17)
C3-C2-N1	105.69(16)
C3-C2-C4	136.67(18)
N1-C2-C4	117.63(17)
C2-C3-N2	108.19(16)
C2-C3-C7	131.05(17)
N2-C3-C7	120.74(15)
C1-C5-C6	112.48(17)
N3-C8-N4	109.36(17)
N3-C8-C12	128.12(19)
N4-C8-C12	122.49(19)

**Table 4.6**. Selected bond lengths (Å) for complex [Ru]-22.

Ru1-Cl1	2.385(3)
Ru1-N2	2.101(7)
Ru1-C12	2.207(8)
Ru1-C13	2.202(8)
Ru1-C14	2.159(8)
N1-C1	1.386(13)
N1-C2	1.392(14)
N2-C1	1.297(13)
N2-C3	1.422(9)
C1-C5	1.481(15)
C2-C3	1.371(15)
C2-C4	1.497(13)
C3-C7	1.428(12)

C5-C6	1.513(16)
C7-C3	1.428(12)
C7-C8	1.540(17)
C8-C9	1.322(17)
C9-C10	1.416(16)
C10-C11	1.390(2)
C12-C13	1.4298(10)
C13-C14	1.4299(10)

 Table 4.7. Selected bond angles (°) for complex [Ru]-22.

N2-Ru1-Cl1	85.54(18)
N2-Ru1-N2	84.30(4)
N2-Ru1-C12	156.3(3)
N2-Ru1-C13	156.5(3)
N2-Ru1-C14	118.7(3)
C12-Ru1-Cl1	90.9(2)
C13-Ru1-Cl1	117.5(3)
C13-Ru1-C12	68.2(4)
C14-Ru1-Cl1	155.8(3)
C14-Ru1-C12	67.62(19)
C14-Ru1-C13	38.27(11)
C1-N1-C2	108.0(10)
C1-N2-Ru1	128.7(6)
C1-N2-C3	109.0(8)
C3-N2-Ru1	122.2(7)
N1-C1-C5	119.6(11)
N2-C1-N1	109.2(10)

N2-C1-C5	131.1(10)
N1-C2-C4	122.6(12)
C3-C2-N1	106.8(8)
N2-C3-C7	124.4(9)
C2-C3-N2	106.9(10)
C1-C5-C6	117.1(10)
C3-C7-C8	113.7(6)
C9-C8-C7	121.6(8)
C8-C9-C10	125.8(17)
C12-C12-Ru1	71.1(13)
C12-C12-C13	119.9(4)
C13-C12-Ru1	70.9(4)
C12-C13-Ru1	71.3(4)
C12-C13-C14	116.37(12)
C14-C13-Ru1	69.3(4)

Note: The contents of this chapter is published as Patra et al., Inorg.Chem.,2021,60,14275-14285(DOI:10.1021/acs.inorgchem.1c01784) and reproduced with the permissionfrom American Chemical Society.

### 4.5. References

- Turner J. A. (2004), Sustainable hydrogen production, *Science*, 305,972–974 (DOI: 10.1126/science.1103197)
- Whitesides G. M., Crabtree G. W. (2007), Don't forget long-term fundamental research in energy, *Science*, 315, 796–798 (DOI: 10.1126/science.1140362)

- Moriarty P., Honnery D. (2009), Hydrogen's role in an uncertain energy future, *Int. J. Hydrogen Energy*, 34, 31–39 (DOI: 10.1016/j.ijhydene.2008.10.060)
- Moriarty P., Honnery D. (2010), A hydrogen standard for future energy accounting? *Int. J. Hydrogen Energy*, 35, 12374–12380 (DOI: 10.1016/j.ijhydene.2010.08.060)
- Lewis N. S., Nocera D. G. (2006), Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci. U. S. A.*, 103, 15729–15735 (DOI: 10.1073/pnas.0603395103)
- Armaroli N., Balzani V. (2011), The hydrogen issue, *ChemSusChem*, 4, 21–36 (DOI: 10.1002/cssc.201000182)
- Eberle U., Felderhoff M., Schüth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chem., Int. Ed.*, 48, 6608–6630 (DOI: 10.1002/anie.200806293)
- Dalebrook A. F., Gan W., Grasemann M., Moret S., Laurenczy G. (2013), Hydrogen storage: beyond conventional methods, *Chem. Commun.*, 49, 8735–8751 (DOI: 10.1039/c3cc43836h)
- Jiang H. L., Singh S. K., Yan J. M., Zhang X. B., Xu Q. (2010), Liquid-Phase Chemical Hydrogen Storage: Catalytic Hydrogen generation under Ambient Conditions, *ChemSusChem*, 3, 541–549 (DOI: 10.1002/cssc.201000023)
- Sordakis K., Tang C., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*,118, 372–433 (DOI: 10.1021/acs.chemrev.7b00182)
- Patra S., Awasthi M. K., Rai R. K., Deka H., Mobin S. M., Singh S. K. (2019), Dehydrogenation of Formic Acid Catalyzed by Water-Soluble Ruthenium Complexes: X-ray Crystal Structure of a Diruthenium Complex, *Eur. J. Inorg. Chem.*, 1046–1053 (DOI: 10.1002/ejic.201801501)

- Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water, *Inorg Chem.*, 59, 4234-4243 (DOI: 10.1021/acs.inorgchem.9b02882)
- Grasemann M., Laurenczy G. (2012), Formic acid as a hydrogen source– recent developments and future trends, *Energy Environ*. *Sci*, 5, 8171–8181 (DOI: 10.1039/c2ee21928j)
- Singh A. K., Singh S., Kumar A. (2016), Hydrogen energy future with formic acid: a renewable chemical hydrogen storage system, *Catal. Sci. Technol.*, 6, 12–40 (DOI: 10.1039/c5cy01276g)
- Mellmann D., Sponholz P., Junge H., Beller M. (2016), Formic acid as a hydrogen storage material – development of homogeneous catalysts for selective hydrogen release, *Chem. Soc. Rev.*, 45, 3954–3988 (DOI: 10.1039/c5cs00618j)
- Eppinger J., Huang K.-W. (2017), Formic Acid as a Hydrogen Energy Carrier, ACS Energy Lett., 2, 188–195, (DOI: 10.1021/acsenergylett.6b00574)
- Zhong H., Iguchi M., Chatterjee M., Himeda Y., Xu Q., Kawanami H. (2018), Formic Acid-Based Liquid Organic Hydrogen Carrier System with Heterogeneous Catalysts, *Adv. Sustainable Syst.*, 2, 1700161 (DOI: 10.1002/adsu.201700161)
- Guan C., Pan Y., Zhang T., Ajitha M. J., Huang K.-W. (2020), An update on Formic Acid Dehydrogenation by Homogeneous Catalysis, *Chem. -Asian J.*, 15, 937–946 (DOI: 10.1002/asia.201901676)
- 19. (a) Himeda Y. (2009), Highly efficient hydrogen evolution by decomposition of formic acid using an iridium catalyst with 4,4'-dihydroxy-2,2'-bipyridine, *Green Chem.*, 11, 2018–2022 (DOI: 10.1039/b914442k) (b) Wang W.-H., Hull J. F., Muckerman J. T., Fujita E., Hirose T., Himeda Y. (2012), Highly Efficient D<sub>2</sub> Generation by Dehydrogenation of Formic Acid in D<sub>2</sub>O through H+/D+ Exchange on an Iridium Catalyst: Application to the

Synthesis of Deuterated Compounds by Transfer Deuterogenation, *Chem. Eur. J.*, 18, 9397-9404 (DOI: 10.1002/chem.201200576) (c) Wang W.-H.; Xu S., Manaka Y., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2014), Formic Acid Dehydrogenation with Bioinspired Iridium Complexes: A Kinetic Isotope Effect Study and Mechanistic Insight, ChemSusChem, 7, 1976-1983 (DOI: 10.1002/cssc.201301414) (d) Hull J. F., Himeda Y., Wang W.-H., Hashiguchi B., Periana, R., Szalda D. J., James T., Muckerman J.T., Fujita E. (2012), Reversible hydrogen storage using CO<sub>2</sub> and a proton switchable iridium catalyst in aqueous media under mild temperatures and pressures, Nat. Chem., 4, 383-388 (DOI: 10.1038/nchem.1295) (e) Kawanami H., Iguchi M., Himeda Y. (2020), Ligand Design for Catalytic Dehydrogenation of Formic Acid to Produce High-pressure Hydrogen Gas under Basefree Conditions, Inorg. Chem., 59, 7, 4191-419 (DOI: 10.1021/acs.inorgchem.9b01624) (f) Manaka Y., Wang W.-H., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2014), Efficient H<sub>2</sub> generation from formic acid using azole complexes in water, Catal. Sci. Technol., 4, 34-37 (DOI: 10.1039/c3cy00830d) (g) Onishi N., Ertem, M. Z., Xu S., Tsurusaki A., Manaka Y., Muckerman J. T., Fujita E., Himeda Y. (2016), Direction to practical production of hydrogen by formic acid dehydrogenation with Cp\*Ir complexes bearing imidazoline ligands, Catal. Sci. Technol., 6. 988-992 (DOI: 10.1039/c5cy01865j) (h) Wang W.-H., Ertem M. Z., Xu, S., Onishi N., Manaka Y., Suna Y., Kambayashi H., Muckerman J. T., Fujita E., Himeda Y. (2015), Highly Robust Hydrogen Generation by Bioinspired Ir Complexes for Dehydrogenation of Formic Acid in Water: Experimental and Theoretical Mechanistic Investigations at Different ACS Catal., 5. 5496-5504 pH, (DOI: 10.1021/acscatal.5b01090) (i) Wang L., Onishi N., Murata K., Hirose T., Muckerman J. T., Fujita E., Himeda Y. (2017), Efficient Hydrogen Storage and Production Using a Catalyst with an Imidazoline-Based, Proton-Responsive Ligand, ChemSusChem.,

10, 1071–1075 (DOI: 10.1002/cssc.201601437) (j) Wang Z. J., Lu S. M., Li J., Wang J. J., Li C. (2015), Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an N,N'- Diimine Ligand in Water, Chem. Eur. J., 21, 12592-12595 (DOI: 10.1002/chem.201502086) (k) Lu S. M., Wang Z. Wang J., Li J.; Li C. (2018), Hydrogen generation from formic acid decomposition on a highly efficient iridium catalyst bearing a diaminoglyoxime ligand, Green Chem., 20, 1835-1840 (DOI: 10.1039/c8gc00495a) (l) Matsunami A., Kayaki Y., Ikariya T. (2015), Enhanced Hydrogen Generation from Formic Acid by Half-Sandwich Iridium(III) Complexes with Metal/NH Bifunctionality: A Pronounced Switch from Transfer Hydrogenation, Chem. - Eur. J., 21, 13513–13517 (DOI: 10.1002/chem.201502412) (m) Oldenhof S., Lutz M., de Bruin B., van der Vlugt J. I., Reek J. N. H. (2015), Dehydrogenation of formic acid by Ir-bisMETAMORPhos complexes: experimental and computational insight into the role of a cooperative ligand, Chem. Sci., 6, 1027-1034 (DOI: 10.1039/c4sc02555e) (n) Celaje J. J. A., Lu, Z., Kedzie E. A., Terrile N. J., Lo J. N., Williams T. J. (2016), A prolific catalyst for dehydrogenation of neat formic acid, Nat. Commun., 7, 11308-11313 (DOI: 10.1038/ncomms11308) (o) Iguchi M., Himeda Y., Manaka Y., Kawanami H. (2016), Development of an Iridium-Based Catalyst for High-Pressure Evolution of Hydrogen from Formic Acid, ChemSusChem., 9, 2749-2753 (DOI: 10.1002/cssc.201600697) (p) Iturmendi A., Perez L. R., Perez-Torrente J. J., Iglesias M., Oro L. A. (2018), Impact of Protic Ligands in the Ir-Catalyzed Dehydrogenation of Formic Acid in Water, Organometallics, 37, 20, 3611-3618 (DOI: 10.1021/acs.organomet.8b00289)

 (a) Fellay C., Dyson P. J., Laurenczy G. (2008), Viable Hydrogen-Storage System Based On Selective Formic Acid Decomposition with a Ruthenium Catalyst, *Angew. Chem., Int. Ed.*, 47, 3966–3968 (DOI: 10.1002/anie.200800320) (b) Loges B., Boddien A., Junge H., Beller M. (2008), Controlled generation of hydrogen from formic acid amine adducts at room temperature and application in H<sub>2</sub>/O<sub>2</sub> fuel cells, Angew. Chem., Int. Ed., 47, 3962–3965 (DOI: 10.1002/anie.200705972) (c) Boddien A., Loges B., Junge, H., Gärtner F., Noyes J. R., Beller M. (2009), Continuous Hydrogen Generation from Formic Acid: Highly Active and Stable Ruthenium Catal., 351. 2517-2520 Catalysts, Adv. Synth. (DOI: 10.1002/adsc.200900431) (d) Filonenko G. A., van Putten R., Schulpen E. N., Hensen E. J., Pidko E. A. (2014), Highly Efficient Reversible Hydrogenation of Carbon Dioxide to Formates Using a Ruthenium PNP-Pincer Catalyst, ChemCatChem., 6, 1526-1530 (DOI: 10.1002/cctc.201402119) (e) Czaun M., Goeppert A., Kothandaraman J., May R.B., Haiges R., Prakash G. K. S., Olah G. A. (2014), Formic Acid As a Hydrogen Storage Medium: Ruthenium - Catalyzed Generation of Hydrogen from Formic Acid in Emulsions, ACS Catal., 4, 311–320 (DOI: 10.1021/cs4007974) (f) Pan Y., Pan C. L., Zhang Y., Li H., Min S., Guo X., Zheng B., Chen H., Anders A., Lai Z., Zheng J., Huang K.-W. (2016), Selective Hydrogen Generation from Formic Acid with Well-Defined Complexes of Ruthenium and Phosphorus - Nitrogen PN<sup>3</sup>--Asian J., 11, 1357–1360 (DOI: Pincer Ligand, Chem. 10.1002/asia.201600169) (g) Guan C., Zhang D.-D., Pan Y., Iguchi M., Ajitha, M. J.; Hu, J.; Li, H.; Yao, C.; Huang, M.-H.; Min, S.; Zheng, J.; Himeda, Y.; Kawanami H., Huang K.-W. (2017), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N'-Diimine Ligand, Inorg. Chem., 56, 438–445 (DOI: 10.1021/acs.inorgchem.6b02334) (h) Guerriero A., Bricout H., Sordakis K., Peruzzini M., Monflier E., Hapiot F., Laurenczy G., Gonsalvi L. (2014), Hydrogen Production by Selective Dehydrogenation of HCOOH Catalyzed by Ru-Biaryl Sulfonated Phosphines in Aqueous Solution, ACS Catal., 4, 3002–3012 (DOI: 10.1021/cs500655x) (i) Fellay C., Yan N., Dyson P. J., Laurenczy G. (2009), Selective Formic Acid Decomposition for High-Pressure Hydrogen Generation: A Mechanistic Study, Chem. -Eur. J., 15,

3752-3760 (DOI: 10.1002/chem.200801824) (j) Boddien A., Federsel C., Sponholz P., Mellmann D., Jackstell R., Junge H., Laurenczy G., Beller M. (2012), Towards the development of a hydrogen battery, *Energy Environ. Sci.*, 5, 8907-8911 (DOI: 10.1039/c2ee22043a) (k) Sponholz P., Mellmann D., Junge H., Beller M. (2013), Towards a Practical Setup for Hydrogen Production from Formic Acid, *ChemSusChem*, 6, 1172-1176 (DOI: 10.1002/cssc.201300186)

- Wang Z., Lu S.-M., Wu J., Li C., Xiao J. (2016), Iodide-Promoted Dehydrogenation of Formic Acid on a Rhodium Complex, *Eur. J. Inorg. Chem.*, 4, 490–496 (DOI: 10.1002/ejic.201501061)
- (a) Boddien A., Loges B., Gärtner F., Torborg C., Fumino K., Junge H., Ludwig R., Beller M. (2010), Iron-Catalyzed Hydrogen Production from Formic Acid, *J. Am. Chem. Soc.* 132, 8924–8934 (DOI: 10.1021/ja100925n) (b) Mellone I., Gorgas N., Bertini F., Peruzzini M., Kirchner K., Gonsalvi L. (2016), Selective Formic Acid Dehydrogenation Catalyzed by Fe PNP Pincer Complexes Based on the 2,6-DiaminopyridineScaffold, *Organometallics*, 35, 3344–3349 (DOI: 10.1021/acs.organomet.6b00551)
- 23. (a) Tondreau A. M., Boncella J. M. (2016), 1, 2-Addition of Formic Acid to  $-N\{CH_2CH_2(PiPr_2)\}_2$ -Supported Mn(I) or Oxalic Dicarbonyl Complexes and the Manganese-Mediated Decomposition of Formic Acid, Organometallics, 35, 2049-2052 (DOI: 10.1021/acs.organomet.6b00274) (b) Anderson N., Boncella J., Tondreau A. N. (2019), Manganese-Mediated Formic Acid Dehydrogenation, Chem. 1 - 5\_ Eur. J., 25, (DOI: 10.1002/chem.201901177) (c) Leval A., Agapova A., Steinlechner C. Alberico E. Junge H. Beller M. (2020), Hydrogen production from formic acid catalyzed by a phosphine free manganese complex: investigation and mechanistic insights, Green Chem., 22, 913-920 (DOI: 10.1039/c9gc02453k)

- Awasthi M. K., Rai R. K., Behrens S., Singh S. K. (2021), Lowtemperature hydrogen production from methanol over a ruthenium catalyst in water, *Catal. Sci. Technol.*, 11, 136-142 (DOI: 10.1039/d0cy01470b)
- Awasthi M. K., Singh S. K. (2021), Ruthenium catalyzed hydrogen production from formaldehyde- water solution, *Sustainable Energy Fuels*, 5, 549-555 (DOI: 10.1039/d0se01330g)
- 26. Deka H., Kumar A., Patra S., Awasthi M. K., Singh S. K. (2020), Synthesis, structure and catalytic activity of manganese(ii) complexes derived from bis(imidazole)methane-based ligands, *Dalton Trans.*, 49, 757-763 (DOI: 10.1039/c9dt03886h)
- Tyagi D., Binnani C., Rai R. K., Dwivedi A. D., Gupta K., Li P. Z., Zhao Y., Singh S. K. (2016), Ruthenium-Catalyzed Oxidative Homocoupling of Arylboronic Acids in Water: Ligand Tuned Reactivity and Mechanistic Study, *Inorg Chem.*, 55, 6332-6343 (DOI; 10.1021/acs.inorgchem.6b01115)
- Awasthi M. K., Singh S. K. (2019), Ruthenium Catalyzed Dehydrogenation of Alcohols and Mechanistic Study, *Inorg Chem.*, 58, 14912-14923 (DOI: 10.1021/acs.inorgchem.9b02691)
- Binnani C., Rai R. K., Tyagi D., Mobin S. M., Singh S. K. (2018), Ligand-Tuned C–H Bond Activation/Arylation of 2-Arylpyridines over Pyridine-Based N,O/N,N Ligated Ruthenium–Arene Complexes, *Eur. J. Inorg. Chem.*, 1435-1445 (DOI: 10.1002/ejic.201701446)
- Sheldrick G. M. (2008), A short history of SHELX. Acta Crystallogr, Sect. A: Found. Crystallogr., 64, 112–122 (DOI: 10.1107/s0108767307043930)

## Chapter 5

Efficient additive-free hydrogen production from formaldehyde-water over arene-ruthenium (II) complexes

### **5.1. Introduction**

The fossil fuel reserves are rapidly declining globally and the threat of global warming associated with it leads the scientific community to explore alternative, sustainable and renewable energy sources to cope with the ever-increasing global energy demand. Hydrogen  $(H_2)$  gas is regarded as one of the most promising energy sources owing to its high energy density by weight.<sup>[1–6]</sup> In addition, the release of water vapour as the only by-product when hydrogen is combined with oxygen in a fuel cell or in combustion engine further highlights the suitability of hydrogen gas as a clean fuel. However, there are few technical challenges and safety concerns associated with the handling, storage and transportation of gaseous hydrogen due to its low energy density which needs to be addressed.<sup>[6–8]</sup> In view of this, liquid organic hydrogen carriers (LOHCs) such as methanol, formaldehyde and formic acid have gained considerable attention of the researchers as these are liquids in nature and hence much safer and convenient to handle and transport as compared to the gaseous hydrogen.<sup>[9–11]</sup> Among these, formaldehyde-water (HCHO-H<sub>2</sub>O) system contain 8.4 wt.% of hydrogen, that can be released on demand using suitable catalysts under mild reaction conditions.<sup>[12–17]</sup> In addition, formaldehyde is an important platform C-1 chemical which is produced in bulk scale in the industry. The low cost, ready availability of formaldehyde and the favourable thermodynamics ( $\Delta H_r = -35.8 \text{ kJ mol}^{-1}$ ) of the dehydrogenation of aqueous formaldehyde make it an ideal candidate for on demand production of hydrogen gas using a suitable catalyst under ambient reaction conditions (Scheme 5.1).<sup>[12]</sup> It is known that formaldehyde is

primarily present as stable methanediol in aqueous solution and the catalytic dehydrogenation reaction occurs in two steps to ideally produce 2 equivalents of  $H_2$  gas and 1 equivalent of  $CO_2$  gas per equivalent of formaldehyde (Scheme 5.1).<sup>[12,16]</sup>

The first homogeneous catalytic system was established by Prechtl *et al.* using the diruthenium complex [{ $Ru(\eta^6-p-cymene)$ }<sub>2</sub>(µ- $HCOO)(\mu$ -Cl $)(\mu$ -H)]<sup>+</sup> (C-24 in Scheme 5.1) to obtain a turnover number (TON) of 700 at 95 °C.<sup>[12]</sup> Subsequently, several homogeneous metal catalysts have been explored for the production of hydrogen from HCHO-H<sub>2</sub>O solution (Scheme 5.1).<sup>[12–17]</sup> For instance, Suenobu et al. studied the complex [Ir<sup>III</sup>(Cp\*)(4-(1H-pyrazol-1-yl)benzoic acid)- $(H_2O)$ ]<sup>+</sup> for catalytic hydrogen generation from paraformaldehyde-water to obtain a TON of 51 at 60 °C in an alkaline medium (pH 11) using NaOH as the base (C-25 in Scheme 5.1).<sup>[13]</sup> Fujita *et al.* also explored a  $(\eta^5-C_5Me_5)$ Ir(III) catalyst bearing the (6,6'-dionato-2,2'-bipyridine)ligand under alkaline reaction conditions to obtain a TON of 178 (C-26 in Scheme 5.1).<sup>[14]</sup> In 2017, Grutzmacher et al. reported a Ru(II) hydrido complex with very high initial TOF (>20000 h<sup>-1</sup>) but moderate TON of 1787 for hydrogen generation from aqueous formaldehyde at 60 °C under a highly alkaline condition (KOH) in H<sub>2</sub>O/THF mixed solvent (C-**27** in Scheme 5.1).<sup>[15]</sup>



*Scheme 5.1. Literature known molecular catalysts for hydrogen generation from formaldehyde-water system.* 

The need for an organic solvent is not ideal for the sustainability of the process, and hence, a catalytic system which can efficiently dehydrogenate aqueous formaldehyde under additive-free and organic solvent free conditions is highly desirable. In 2018, Himeda *et al.* employed the complex  $[(\eta^6-C_6Me_6)Ru(2,2'-diaminobiphenyl)(H_2O)]^{2+}$ to achieve a record TON of 24000 for dehydrogenation of paraformaldehyde-water solution at 95 °C under additive-free reaction condition (**C-28** in Scheme 5.1).<sup>[16]</sup> High efficiency and selectivity for hydrogen production from HCHO-H<sub>2</sub>O solution achieved with this catalytic system was also studied by the extensive DFT studies, which helped in elucidating the reaction mechanism in details.<sup>[16]</sup> Recently, we have also reported the arene-Ru(II) complexes  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2$ pyridine-2-ylmethanol)(Cl)]<sup>+</sup> ([**Ru]-8** in Scheme 5.1) and  $[(\eta^6 C_{10}H_{14})Ru(imidazole)(Cl)_2]^{2+}$  (**C-34** in Scheme 5.1) for additive-free hydrogen production from HCHO-H<sub>2</sub>O solution with an impressive TON of 12905 (initial TOF = 5175 h<sup>-1</sup>) achieved with the later complex (7 in Scheme 5.1).<sup>[17,18]</sup> In view of the available reports, it is evident that hydrogen production from HCHO-H<sub>2</sub>O system is not as extensively explored as the other two C-1 based LOHCs (MeOH and HCOOH).<sup>[10]</sup> Moreover, the structure-activity relationship of the complexes in the catalytic behaviour and experimental mechanistic insights into the reaction pathway also needs to be further explored.

Recently, we have reported a series of bis-imidazole methane based arene-Ru(II) complexes for hydrogen production from formic acid in aqueous medium and provided detailed mechanistic insights into the reaction pathway.<sup>[19]</sup> Encouraged by these results and the rich literature reports regarding the high activity of imidazole based complexes in aqueous formic acid dehydrogenation,<sup>[19–23]</sup> herein we have employed the arene-Ru(II) complexes based on bis-imidazole methane ligands for hydrogen production from HCHO-H<sub>2</sub>O solution under base-free and additive-free reaction conditions to achieve an impressive TON of >20000 in 30 hours at 90 °C. Moreover, extensive mechanistic studies led us to identify most of the crucial reaction intermediates by mass, NMR and KIE experiments under catalytic and controlled reaction conditions, and accordingly a plausible reaction pathway is proposed.

#### 5.2. Results and Discussion

A series of bis-imidazole methane based arene-Ru(II) complexes were explored for the catalytic hydrogen generation from formaldehyde in water. The complexes **[Ru]-17** – **[Ru]-26** were synthesized according to the previously reported method of our laboratory (Figure 5.1). At an outset, the arene-Ru(II) complexes (0.5 mol%) were examined for the catalytic hydrogen generation from aqueous formaldehyde (37 wt.%) (0.8 M, 2.5 mL) without any additives at 90 °C. Results inferred that the ( $\eta^6$ -p-cymene) based Ru(II) complexes (**[Ru]-17** – **[Ru]-21**) exhibited superior catalytic activity over the ( $\eta^6$ -benzene) based Ru(II) complexes (**[Ru]-22** – **[Ru]-26**) for the production of hydrogen gas from aqueous formaldehyde under the optimized reaction conditions (Figure 5.1 and Table 5.1).



Figure 5.1. Comparative catalytic activity (TOFs) of water soluble [Ru]-17 – [Ru]-26 catalysts explored for  $H_2$  production from aqueous formaldehyde. Reaction conditions: aqueous formaldehyde (0.8 M, 2.5 mL), Ru-catalyst (0.01 mmol) at 90 °C.

Further the initial screening of these catalysts inferred that the nature of the substituents on the bridging methylene group in the Ru(II) catalysts had a pronounced effect in tuning the catalytic efficacy for hydrogen production from aqueous formaldehyde. It was found that the catalysts having electron rich 4-methoxy and 2-methoxy phenyl substitutions at the bridging methylene group (**[Ru]-18** and **[Ru]-19**) outperformed (initial TOFs = 633 h<sup>-1</sup> and 753 h<sup>-1</sup>) over **[Ru]-17** (with

unsubstituted phenyl group attached to the methylene carbon) (initial  $TOF = 575 h^{-1}$ ) (Table 5.1, entries 1, 2 and 3). Further, the catalysts having electron withdrawing 4-chloro and 2-chloro phenyl substitutions at the bridging methylene group ([Ru]-20 and [Ru]-21) was found to have a detrimental effect on the catalytic activity (initial TOFs =  $377 \text{ h}^{-1}$ and 476 h<sup>-1</sup>) as compared to [**Ru**]-17 (Table 5.1, entries 4 and 5). The position of the substituents (-OMe or -Cl) on the phenyl group of the methylene carbon was also found to be influential, as the catalysts having substitutions at the 2-position on the phenyl group ([Ru]-19 and [Ru]-21) was found to have a slightly higher catalytic activity (initial TOFs = 753  $h^{-1}$  and 476  $h^{-1}$ ) than those having similar substitutions at the 4-position on the phenyl group ( [Ru]-18 and [Ru]-20) (initial TOFs  $= 633 \text{ h}^{-1}$  and  $377 \text{ h}^{-1}$ ) (Table 5.1, entries 2, 4, 3 and 5). Hence, the overall trend of the catalytic activity of  $(\eta^6 - p$ -cymene)Ru(II) complexes was found to be **[Ru]-19** > **[Ru]-18** > **[Ru]-17** > **[Ru]-21** > **[Ru]-20** (Figure 5.1). A similar trend was also observed for the ( $\eta^6$ -benzene)Ru(II) based complexes with the catalytic activities being in the order of [Ru]-24 > [Ru]-23 > [Ru]-22 > [Ru]-26 > [Ru]-25 (Table 5.1, entries 6 – 10, and Figure 5.1). Notably among all the catalysts screened in this study, the release of 445 moles of gas per mole of the catalyst with an initial TOF of 753 h<sup>-1</sup> was achieved over the **[Ru]-19** catalyst, and therefore further screening of reaction conditions for hydrogen generation from formaldehyde in water was performed over [Ru]-19.
Table 5.1. Hydrogen generation from aqueous formaldehyde over [Ru]-17 – [Ru]-26 catalysts<sup>a</sup>

	псп0 + п <sub>2</sub> 0	90 °	°C	• 2H <sub>2</sub> + CC	J <sub>2</sub>
Entry	Catalyst	Gas (H <sub>2</sub> released	2 + CO <sub>2</sub> )	$\mathbf{TON}^b$	<b>TOF</b> ( <b>h</b> <sup>-1</sup> ) <sup><i>c</i></sup>
		(mL)	(mmol)		
1	[Ru]-17	110	4.5	451	575
2	[Ru]-18	110	4.5	451	633
3	[Ru]-19	109	4.45	445	753
4	[Ru]-20	102	4.2	418	377
5	[Ru]-21	101	4.1	411	476
6	[Ru]-22	106	4.3	433	377
7	[Ru]-23	104	4.3	425	450
8	[Ru]-24	107	4.4	437	476
9	[Ru]-25	93	3.8	380	198
10	[Ru]-26	96	3.9	392	218

HCHO + H<sub>2</sub>O  $\frac{[Ru] \text{ cat. (0.5 mol \%)}}{90 \degree C} \ge 2H_2 + CO_2$ 

<sup>*a*</sup>Reaction conditions: aqueous formaldehyde (0.8 M, 2.5 mL), Rucatalyst (0.01 mmol) at 90 °C. <sup>*b*</sup>TONs are calculated at the completion of the reaction. <sup>*c*</sup>TOFs (initial 20 minutes).

Literature reports suggest that in aqueous solution formaldehyde can be released from paraformaldehyde and hydrogen production from methanediol (formed by hydration) proceeds through a two-step pathway, the first step being the transformation of methanediol to formic acid with the release of one equivalent of H<sub>2</sub> and the subsequent step being the dehydrogenation of formic acid releasing one equivalent each of H<sub>2</sub> and CO<sub>2</sub>.<sup>*[16]*</sup> To acquire better knowledge of the reaction pathway with our present catalytic system, the yield of formic acid throughout the initial hour of the catalytic reaction for hydrogen production from paraformaldehyde (0.8 M, 2.5 mL) over [Ru]-19 (0.5 mol%) in H<sub>2</sub>O at 90 °C, was monitored by <sup>1</sup>H NMR spectroscopy using sodium acetate as an internal standard. Results inferred that the yield of formic acid rapidly increased initially to reach the highest yield within initial 10 minutes and then gradually decreased afterwards, suggesting the involvement of formic acid dehydrogenation to  $H_2$  and  $CO_2$  (Figure 5.2a). In order to further support the two-step dehydrogenation pathway, the composition of the gas released from the catalytic reaction was monitored by GC-TCD. Results inferred that indeed at the initial stage (initial 10 minutes), the ratio of  $H_2/CO_2$  was high (approx. 5:1), suggesting that in the initial hours of the reaction hydrogen production from methanediol was dominating over the dehydrogenation of formic acid. Analysis of the gas mixture at subsequent time intervals from the reaction revealed a gradual decrease in the  $H_2/CO_2$  ratio to reach finally the 1:1  $H_2/CO_2$  gas composition, which is in line with the dehydrogenation of formic acid to H<sub>2</sub> and CO<sub>2</sub> (Figure 5.2b). Notably, no traces of CO were detected (detection limit = 10 ppm) in the GC-TCD analysis at any point throughout the course of the reaction. pH analysis of the reaction aliquot during the catalytic reaction indicated a sharp decrease in pH from pH 7 to below 2 during the initial 15 minutes then gradually increasing to around pH 5, further supporting the two-step dehydrogenation pathway of formaldehyde in water with our present catalytic system (Figure 5.3).



**Figure 5.2.** Time course plot for (a) HCOOH yield (as determined by <sup>1</sup>H NMR using sodium acetate as the internal standard), and (b)  $nH_2/nCO_2$  in the gas released (as analysed by GC-TCD) during the catalytic hydrogen production from paraformaldehyde in water over the **[Ru]-19** catalyst. Reaction conditions: paraformaldehyde (2 mmol), **[Ru]-19** (0.01 mmol) at 90 °C.



*Figure 5.3. Time-dependent pH plot for the catalytic paraformaldehyde dehydrogenation reaction. Reaction conditions: [Ru]-19 (0.01 mmol), paraformaldehyde (0.8M, 2.5mL), 90 °C.* 

Reaction temperature was also found to be influential in tuning the catalyst efficacy, where highest catalytic turnover frequency (TOF) was achieved at 90 °C for the catalytic hydrogen production from aqueous formaldehyde (1 M, 10 mL) over **[Ru]-19** (0.01 mmol). The calculated activation energy of 77.6 kJ/mol from the Arrhenius plot was found to be in good agreement with similar systems reported previously (Figure 5.4).<sup>[16,17]</sup>



**Figure 5.4.** (a) Initial stage of the dehydrogenation of aqueous formaldehyde (1 M, 10 mL) (37 wt.% formaldehyde) with **[Ru]-19** (0.01 mmol) at various temperatures. (b) Arrhenius plot of initial TOF values (initial 20 mins) for dehydrogenation of aqueous formaldehyde (1 M, 10 mL) with **[Ru]-19** (0.01 mmol).

To further evaluate the catalytic performance of the high-performing catalyst **[Ru]-19**, we investigated the substrate concentration dependence of the hydrogen production process from paraformaldehyde (1 M, 3 M, 5 M and 10 M) in 10 mL water over **[Ru]-19** (0.01 mmol) catalyst (Figure 5.5 and Table 5.2). Results inferred that the initial TOF (first 20 minutes) increased significantly from 218 h<sup>-1</sup> to 708 h<sup>-1</sup> with an increase in the concentration of paraformaldehyde from 1 M to 5 M but was low for the highly concentrated (10 M) solution (Figure 5.5b). Nevertheless, a steady gas release was observed for the reaction with 10 M paraformaldehyde over **[Ru]-19** to achieve a turnover of >12400 in 72 hours at 90 °C (Table 5.2).

**Table 5.2.** Production of  $H_2$  from different conc. of paraformaldehyde in water catalysed by **[Ru]-19**<sup>a</sup>

Entr	y (CH <sub>2</sub> O) <sub>n</sub>	Time	Gas	нсоон	MeOH	TON	$\mathbf{p}\mathbf{H}^{d}$
		$(\mathbf{h})^b$	(H <sub>2</sub> + CO <sub>2</sub> )	yield (%)	yield <sup>c</sup> (%)		
			released				
			(mmol)				
1	1 M	6	16.0	-	40.9	1600	6.53
2	3 M	10	51.5	_	26.4	5155	6.24
2	0.111	10	51.5		20.1	5155	0.21
3	5 M	14	77.7	-	19.6	7771	5.93
4	10 M	72	124.3	15.4	14	12434	1.78
5 <sup>e</sup>	5 M	30	80.4	21	8.5	20108	1.62

<sup>*a*</sup>Reaction conditions: **[Ru]-19** (0.01 mmol), H<sub>2</sub>O (10 mL), 90 °C. HCOOH and CH<sub>3</sub>OH yields were determined by <sup>1</sup>H NMR spectroscopy using CH<sub>3</sub>COONa (0.25 mmol) as the internal standard. <sup>*b*</sup>Time at which reaction stopped and no further increase in gas release was observed. <sup>c</sup>Normalized maximum yield considering 66.6 % as the maximum limit. <sup>*d*</sup>The pH values are measured after reaction. <sup>*e*</sup>**[Ru]-19** (0.004 mmol), H<sub>2</sub>O (20 mL).



Figure 5.5. (a) Dehydrogenation of different concentrations of aqueous paraformaldehyde (10 mL) with **[Ru]-19** (0.01 mmol) at 90 °C. (b) Hydrogen production from paraformaldehyde (10 M, 10 mL) with **[Ru]-19** (0.01 mmol) at 90 °C.

Notably the presence of a base favours the disproportionation of formaldehyde (via Cannizzaro reaction) and hence most of the catalytic systems reported earlier to Himeda's work used a low concentration of formaldehyde which may limit practical application of the system.<sup>[13,15]</sup> It is therefore expected that an efficient catalytic system should be able to produce hydrogen gas from varying concentration of formaldehyde without significant loss in the catalytic performance, hence enabling to achieve high energy density and thus rendering its application at industrial scale.



*Figure 5.6.* Bulk scale reaction for hydrogen production from large content of paraformaldehyde (5 M, 20 mL) in water with [*Ru*]-19 (0.004 mmol) at 90 °C.

Further, efficacy of the **[Ru]-19** catalyst was evaluated for the production of hydrogen gas from a bulk-scale reaction having paraformaldehyde-water (5 M, 20 mL) with **[Ru]-19** (0.004 mmol) at 90 °C (Figure 5.6). Notably the catalyst **[Ru]-19** was proved to be highly robust under the additive-free reaction conditions to achieve a turnover of 20108 after 30 h with an initial high turnover frequency of 4045 h<sup>-1</sup> (initial 5 minutes) (Figure 5.6 and Table 5.2). Furthermore, recyclability experiments were performed using aqueous formaldehyde (37 wt.%)

(0.8 M, 2.5 mL), where the catalyst **[Ru]-19** exhibited appreciably good activity over 7 consecutive cycle runs without any significant loss in the catalytic activity (Figure 5.7).



**Figure 5.7.** Long-term stability and recyclability experiment for catalytic hydrogen production from aqueous formaldehyde (37 wt. %) over catalyst **[Ru]-19**. Reaction conditions: aq. formaldehyde (0.8 M, 2.5 mL), **[Ru]-19** (10 mmol) at 90 °C, 2 mmol of aq. formaldehyde added after each cycle.

Moreover, to investigate the homogeneity of the reaction and to rule out any role of colloidal ruthenium species in the catalytic activity of **[Ru]-19** for hydrogen production from aqueous formaldehyde, a Hg(0) poisoning experiment was performed by adding an excess of elemental mercury during the catalytic reaction. Results inferred no loss in the catalytic activity in the presence of elemental mercury which evidenced that the homogenous nature of the active catalytic species involved in the hydrogen production from formaldehyde in water (Figure 5.8).



Figure 5.8. Controlled Hg(0) poisoning experiment. Reaction conditions: Aqueous formaldehyde (0.8 M, 2.5 mL) and [Ru]-19 (0.01 mmol) at 90 °C with and without a large excess of elemental Hg(0).

Further to investigate the role of various possible catalytic species in the hydrogen production from formaldehyde, extensive mass spectrometry, NMR spectroscopy and KIE experiments were employed under varying reaction conditions. Initially, two controlled experiments were performed in which [**Ru**]-19 (0.01 mmol) was stirred in water (2.5 mL) for 5 minutes at 50 °C, where the reaction aliquot showed an intense mass peak at m/z 591.2, possibly corresponding to the Ru-aqua species [ $(\eta^6$ -p-cymene)Ru( $\kappa^2$ -L7–H<sup>+</sup>)(H<sub>2</sub>O)]<sup>+</sup> ([**Ru**]-19A) (Figure 5.9).



*Figure 5.9. ESI-MS* showing the Ru-aqua species for the reaction of *[Ru]-19* (0.01 mmol) stirred in water (2.5 mL) for 5 minutes at 50 °C.

Next, the reaction mixture was allowed to cool to room temperature and subsequently aqueous formaldehyde (2 mmol) was added to it, and the reaction mixture was again stirred for 10 minutes at 60 °C. Analysis of the reaction aliquot by mass spectrometry revealed a small peak at m/z 621.2 possibly corresponding to the Ru-methanediol coordinated species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{CH}_2(\text{OH})_2)]^+$  (**[Ru]-19B**) (Figure 5.10).



*Figure 5.10. ESI-MS* showing the Ru-methanediol species for the reaction of [*Ru*]-19 (0.01 mmol) and aq. formaldehyde (37 wt. %) (2 mmol) in water (2.5 mL) for 10 minutes at 60 °C.



Figure 5.11. Different intermediate species of the [Ru]-19 catalyst observed during mass investigation of the reaction mixture of aqueous formaldehyde (0.8 M, 2.5 mL), [Ru]-19 (0.01 mmol) heated at 60 °C – 90 °C.

During the catalytic reaction condition, a visible colour change from the original pale brown solution of the catalyst [Ru]-19 to a redorange solution was observed. Mass analysis of the reaction mixture at different time intervals revealed mass peaks at m/z 591.2 and m/z 619.2 corresponding to the Ru-aqua species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{L7}-\text{L7})]$  $H^+$ )(H<sub>2</sub>O)]<sup>+</sup> ([**Ru**]-19A) and Ru-formato species [( $\eta^6$ -p-cymene)Ru( $\kappa^2$ - $L-H^+$ )(HCO<sub>2</sub>)] ([**Ru**]-19C+H<sup>+</sup>) respectively present in the mass spectra (Figure 5.11 and Figure 5.12). Notably, the mass peak at m/z 621.2 corresponding to the Ru-methanediol coordinated species ([Ru]-19B) was not present in the mass analysis of the aliquot from the reaction performed under the optimized reaction condition at 90 °C, suggesting the facile transformation of Ru-methanediol to Ru-formato with the release of an equivalent of H<sub>2</sub>. These observations are in line with the <sup>1</sup>H NMR, GC-TCD and pH analysis of the reaction mixture. It is worthy to note that the formate bridged diruthenium species [{ $Ru(\eta^6-p)$ cymene) $_{2}(\mu$ -HCOO)( $\mu$ -Cl)( $\mu$ -H)]<sup>+</sup> was not observed at any stage of the time dependent mass analysis of the reaction aliquot, inferred that presumably ligand dissociation does not takes place in our present catalytic system (Figure 5.12).



**Figure 5.12.** Transformation of colour of reaction solution and ESI-MS analysis (in definite time intervals) of the reaction aliquots for catalytic dehydrogenation of aq. formaldehyde (37 wt. %). Reaction condition: aq. formaldehyde (0.8 M, 2.5 mL), **[Ru]-19** (0.01 mmol), 90 °C.

Subsequently, experiments were performed for a temperature dependent (30 °C – 70 °C) mass investigation to identify the intermediate species which may be formed during the said reaction to decipher the role of these species in the catalytic cycle. Starting with the Ru-formato complex, mass analysis inferred that as reaction temperature increases, the mass peak at m/z 575.2 corresponding to the Ru-hydride intermediate  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{H})]$  ([**Ru**]-19D+H<sup>+</sup>) intensifies and it remains as the most prominent peak in the mass spectra after the reaction mixture is heated for 10 minutes at 70 °C (Figure 5.13).



*Figure 5.13. Temperature dependent* (30 °C - 70 °C) *mass study for the transformation of Ru-formate species to Ru-hydride species.* 

Notably, earlier studies also proposed the involvement of Rumethanediol and Ru-formato species in catalytic hydrogen production from aqueous formaldehyde with the help of DFT.<sup>[16]</sup> We also identified the presence of Ru-methanediol species in our previous studies by mass spectrometry.<sup>[17]</sup> Further, we performed a controlled experiment where **[Ru]-19** (0.005 mmol) was treated with sodium formate (0.05 mmol) in water at room temperature. Mass analysis of the reaction aliquot revealed the presence of a prominent mass peak at m/z 575.2 corresponding to the Ru-hydride species  $[(\eta^6-p-cymene)Ru(\kappa^2-L7-H^+)(H)]$  (**[Ru]-19D+H**<sup>+</sup>). Subsequently, addition of a few drops of dilute 0.2 M solution of H<sub>2</sub>SO<sub>4</sub> to the reaction mixture and analysis of the reaction aliquot by mass spectrometry revealed the presence of a mass peak at m/z 591.2 corresponding to the Ru-aqua species  $[(\eta^6-p-cymene)Ru(\kappa^2-L7-H^+)(H_2O)]^+$  (**[Ru]-19A**) and absence of the mass peak at m/z 575.2, suggesting that the Ru-hydride species reverts back to the Ru-aqua species in the presence of H<sup>+</sup> by liberating H<sub>2</sub> in the catalytic cycle (Figure 5.14).



*Figure 5.14.* Mass investigation of the reaction mixture of [Ru]-19 (0.005 mmol) treated with sodium formate (0.05 mmol) in water showing the colour change from the initial yellow-green to red-orange and subsequently to blue colour when treated with a few drops of dil. H<sub>2</sub>SO<sub>4</sub>.

This observation was further confirmed by <sup>1</sup>H NMR study, where a signal at  $\delta = -7.62$  ppm was observed during the reaction of **[Ru]-19** (0.01 mmol) with sodium formate (0.1 mmol) in D<sub>2</sub>O (0.6 mL) performed in a NMR tube at room temperature. Addition of a few drops of dilute 0.2 M H<sub>2</sub>SO<sub>4</sub> solution in the tube, resulted in the disappearance of the signal corresponding to the Ru-hydride in <sup>1</sup>H NMR (Figure 5.15).



**Figure 5.15.** <sup>1</sup>H NMR spectra showing the generation of Ru-hydride species during the treatment of **[Ru]-19** (0.01 mmol) with sodium formate (0.1 mmol) in D<sub>2</sub>O (0.6 mL) at 25 °C and regeneration of the Ru-aqua species after subsequent treatment with a few drops of dil.  $H_2SO_4$ .

**Table 5.3.** Kinetic Isotope Effects (KIE) results for the hydrogen production from paraformaldehyde in water over the **[Ru]-19** catalyst<sup>a</sup>

Entry	Substrate	Solvent	Initial TOF (h <sup>-1</sup> ) <sup>b</sup>	<b>KIE</b> <sup>c</sup>			
1	$(CH_2O)_n$	H <sub>2</sub> O	397	-			
2	$(CH_2O)_n$	$D_2O$	218	1.82			
3	$(CD_2O)_n$	H <sub>2</sub> O	139	2.86			
4	$(CD_2O)_n$	$D_2O$	104	3.82			
<sup>a</sup> Reaction conditions. Substrate (0.8 M, 2.5 mL), catalyst (0.01							
mmol), 90 °C. <sup><i>b</i></sup> TOF calculated for initial 20 minutes. <sup><i>c</i></sup> KIE = TOF							
(entry 1)/TOF (entry n) (n = 2, 3, 4)							

Initial TOF values from the KIE experiments indicated that the deuterated formaldehyde (KIE: 2.86, Table 5.3, entry 3) was more influential than  $D_2O$  (KIE: 1.82, Table 5.3, entry 2), suggesting the involvement of  $(CD_2O)_n$  in the rate-determining step of the catalytic

cycle and ruling out the possibility of the proton assisted hydrogen release step being the rate determining step in the catalytic cycle. Further to confirm the source of the hydride and the proton between paraformaldehyde and water, we performed mass studies of the reaction aliquot of paraformaldehyde (0.8 M, 2.5 mL D<sub>2</sub>O) with [Ru]-19 (0.01 mmol) at different time intervals under the catalytic reaction conditions. Mass studies revealed the presence of a mass peak at m/z 619.2 corresponding to the Ru-formato species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{L7}-\text{L7})]$  $H^+$ )(HCO<sub>2</sub>)] ([**Ru**]-19C+H<sup>+</sup>) which gradually transformed to the Ruhvdride species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{H})]$  (not observed under catalytic reaction condition), further evidenced that paraformaldehyde might serve as the hydride donor (Figure 5.16). Analogously, mass peak at m/z 620.3 corresponding to the Ru-formato-d species was also observed in the mass analysis of the reaction aliquot of deuterated paraformaldehyde (0.8 M, 2.5 mL  $D_2O$ ) with [Ru]-19 (0.01 mmol) at 90 °C (Figure 5.16).



*Figure 5.16.* Ru-formato and Ru-formato-d (deuterated) species observed during mass investigation of the catalytic reaction aliquots. Reaction conditions:  $(CH_2O)_n$  or  $(CD_2O)_n(2 \text{ mmol})$ ,  $D_2O$  (2.5 mL) and [*Ru*]-19 (0.01 mmol) at 90 °C.

Based on these experimental findings and extensive mass and NMR studies revealing several important catalytic intermediate species,

a plausible catalytic cycle is proposed as shown in Scheme 5.2, for hydrogen production from formaldehyde in water over the studied Ru(II) catalyst. At first, the Ru-aqua species [**Ru**]-**A** was formed by a loss of a chloro ligand from the [**Ru**] catalyst and the subsequent deprotonation of the ligand. Further, with the reaction of methanediol, the Rumethanediol species ([**Ru**]-**B**) was formed from the Ru-aqua [**Ru**]-**A** species. Subsequently, with the release of one equivalent of H<sub>2</sub>, the Ruformato species ([**Ru**]-**C**) was generated, which further undergoes decarboxylation to generate the Ru-hydride species ([**Ru**]-**D**). Finally, with the proton assisted hydrogen release from [**Ru**]-**D**, the active catalytic Ru-aqua species [**Ru**]-**A** was regenerated to complete the catalytic cycle.



Scheme 5.2. A plausible pathway for hydrogen production from formaldehyde-water system over Ru(II) catalysts.

## **5.3.** Conclusions

In conclusion, we report an efficient catalytic system for additive free hydrogen production from formaldehyde-water under ambient reaction condition to achieve an impressive turnover of 20108 (with initial TOF 4045 h<sup>-1</sup>), where the role of the ligand was found to be crucial in achieving enhanced catalytic performance. Time dependent GC-TCD analysis of the gaseous products suggest the two-step dihydrogen process for hydrogen production from formaldehyde-water system. Experimental findings were well supported by the extensive mass and NMR studies under varying reaction conditions, which led us to identify most of the crucial reaction intermediates, such as Ru-aqua, Rumethandiol, Ru-formato and Ru-hydride species, involved in the process of formaldehyde dehydrogenation and hence provided a detailed mechanistic insight for hydrogen production from formaldehyde in water. We hope that our present study provided detailed mechanistic insights of the catalytic formaldehyde dehydrogenation which may pave the way for the development of more active homogeneous catalysts for hydrogen production from formaldehyde-water system in the near future.

#### **5.4. Experimental Section**

# 5.4.1. Materials and instrumentation

All reactions are performed without any inert gas protection using highpurity chemicals purchased from Sigma-Aldrich (Merck) and Alfa-Aesar. <sup>1</sup>H NMR (400 and 500 MHz) spectra are recorded on Bruker Avance III 400 MHz and Bruker Ascend 500 spectrometers. The pH values are measured on a Eutech pH meter, Model Eco Testr pH2. ESImass spectra are recorded on a micrOTF-Q II mass spectrometer. The GC-TCD analyses are performed on a Shimadzu GC-2014 system using shin carbon-ST packed column.

# **5.4.2.** General process for hydrogen production from HCHO-H<sub>2</sub>O system

An aqueous solution (as specified) containing the catalyst (as specified), and formaldehyde solution (37 wt. %)/paraformaldehyde (as specified) in water (as specified) were taken in an appropriate reaction vessel, fitted with a condenser and a gas burette and stirred at 90 °C over a preheated oil bath. The volume of gas produced was measured as the displacement of water in the burette with respect to time. Composition of the produced gas was confirmed by GC-TCD. The turnover number (TON) was calculated by the formula  $n(H_2 + CO_2)/n(catalyst)$ . The turnover frequency (TOF) was calculated as TON/time.

# 5.4.3. Mechanistic investigations for hydrogen production from formaldehyde in water under catalytic and controlled reaction conditions

[Ru]-19 (0.01 mmol) was dissolved in 2.5 mL water and heated at 50 °C, where the analysis of the reaction aliquot by mass spectrometry revealed the formation of the Ru-aqua species [Ru]-19A. Further, formaldehyde solution (37 wt. %) (0.8 M, 2.5 mL) and [Ru]-19 (0.01 mmol) were taken in a 5 mL two-necked test tube and heated at 60 °C and subsequent analysis of the reaction aliquot by mass spectrometry inferred the presence of the Ru-methanediol coordinated species ([Ru]-19B). Formaldehyde solution (37 wt. %) (0.8 M, 2.5mL) and [Ru]-19 (0.01 mmol) were taken in a 5 mL two-necked test tube and heated at 90 °C and reaction aliquots were taken out at definite time intervals and analysed by mass spectrometry to detect the active catalytic species involved during the dehydrogenation reaction. [Ru]-19 (0.005 mmol) was dissolved in 2 mL water and sodium formate (0.05 mmol) was added at room temperature, where mass spectrometry analysis of the reaction aliquot revealed the formation of Ru-hydrido species ([Ru]-19D). <sup>1</sup>H NMR analysis of the reaction mixture containing [Ru]-19 (0.01 mmol) and sodium formate (0.01 mmol) dissolved in D<sub>2</sub>O (0.6 mL) at room temperature, also revealed the presence of Ru-hydride signals. Further addition of 3 drops of 0.2 M H<sub>2</sub>SO<sub>4</sub> to the above NMR tube, resulted in the disappearance of the Ru-hydride peak in the <sup>1</sup>H NMR spectra. Ruformato species was synthesised by treating a methanolic solution of [**Ru**]-19 (0.05 mmol) with sodium formate (0.052 mmol). Initially, methanolic solution of [**Ru**]-19 (0.05 mmol) was stirred with AgNO<sub>3</sub> (0.2 mmol) for 6 h at room temperature. Further, the reaction mixture was filtered through celite, and the resulting solvent was added HCO<sub>2</sub>Na (0.052 mmol) and further stirred for 4 h at room temperature. The resulting reaction mixture was concentrated to  $1/4^{\text{th}}$  volume, and upon addition of diethyl ether, a solid precipitate was obtained which was analysed as Ru-formato species ([**Ru**]-19C) by mass analysis (*m/z* 619.2). The isolated Ru-formato species was subjected to a temperature dependent mass study to observe its transformation to the Ru-hydride species ([**Ru**]-19D). Deuterated paraformaldehyde (2 mmol), D<sub>2</sub>O (2.5 mL) and [**Ru**]-19 (0.01 mmol) were taken in a 5 mL two-necked test tube and heated at 90 °C to detect the Ru-DCO<sub>2</sub> species.

#### 5.4.4. Gas Composition Analysis

The identification of gaseous products during the decomposition of paraformaldehyde was confirmed as  $H_2$  and  $CO_2$  with no detectable level of CO using a Shimadzu GC-2014 system. The chromatograph was equipped with a shin carbon-ST packed column with thermal conductivity detector (TCD) using argon as a carrier gas. Parameters set for the program to detect  $H_2$  and  $CO_2$  (Detector temperature: 200 °C, oven temperature: 90 °C; program: 90 °C (hold time: 1 min), 90 °C - 200 °C (rate: 15 °C per minute)



Figure 5.17. Time-dependent GC-TCD analysis of the evolved gas ( $H_2$  and  $CO_2$ ) during the dehydrogenation of paraformaldehyde. (a) initial 10 minutes;  $H_2:CO_2 \approx 5:1$  (b) After 30 minutes;  $H_2:CO_2 \approx 1.62:1$ . (c) After 50 minutes;  $H_2:CO_2 \approx 1.35:1$ . (d) After 75 minutes;  $H_2:CO_2 \approx 1.33:1$ . (e) After 115 minutes;  $H_2:CO_2 \approx 1:1$ . Reaction condition: [Ru]-19 (0.01 mmol), paraformaldehyde (0.8M, 2.5mL), 90 °C. (Analysis is performed using Argon as the carrier gas, ratios calculated by the area of the peaks in the chromatograms with the help of calibration curves for both the gases).

# 5.4.5. <sup>1</sup>H NMR of different catalytic reactions



**Figure 5.18.** <sup>1</sup>H NMR of reaction aliquot after initial 10 minutes. Reaction condition: paraformaldehyde (0.8 M, 2.5 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



**Figure 5.19.** <sup>1</sup>H NMR of reaction aliquot after initial 20 minutes. Reaction condition: paraformaldehyde (0.8 M, 2.5 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



**Figure 5.20.** <sup>1</sup>H NMR of reaction aliquot after initial 35 minutes. Reaction condition: paraformaldehyde (0.8 M, 2.5 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



**Figure 5.21.** <sup>1</sup>H NMR of reaction aliquot after 1 hour. Reaction condition: paraformaldehyde (0.8 M, 2.5 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



*Figure 5.22.* <sup>1</sup>*H NMR* of reaction aliquot after the end of reaction. *Reaction condition: paraformaldehyde (1 M, 10 mL) and [Ru]-19 (0.01 mmol) at 90 °C.* 



**Figure 5.23.** <sup>1</sup>*H* NMR of reaction aliquot after the end of reaction. Reaction condition: paraformaldehyde (3 M, 10 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



**Figure 5.24.** <sup>1</sup>*H* NMR of reaction aliquot after the end of reaction. Reaction condition: paraformaldehyde (5 M, 10 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.



**Figure 5.25.** <sup>1</sup>H NMR of reaction aliquot after the end of reaction. Reaction condition: paraformaldehyde (10 M, 10 mL) and **[Ru]-19** (0.01 mmol) at 90 °C.

## **5.5. References**

- Turner J. A. (2004), Sustainable hydrogen production, *Science*, 305, 972–974 (DOI: 10.1126/science.1103197)
- Whitesides G. M., Crabtree G. W. (2007), Don't forget long-term fundamental research in energy, *Science*, 315, 796–798 (DOI: 10.1126/science.1140362)
- Moriarty P., Honnery, D. (2009), Hydrogen's role in an uncertain energy future, *Int. J. Hydrogen Energy*, 34, 31–39 (DOI: 10.1016/j.ijhydene.2008.10.060)
- Moriarty P., Honnery D. (2010), A hydrogen standard for future energy accounting? *Int. J. Hydrogen Energy*, 35, 12374–12380 (DOI: 10.1016/j.ijhydene.2010.08.060)
- Lewis N. S., Nocera D. G. (2006), Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci. U. S.* A., 103, 15729–15735 (DOI: 10.1073/pnas.0603395103)
- Armaroli N., Balzani V. (2011), The hydrogen issue, *ChemSusChem*, 4, 21–36 (DOI: 10.1002/cssc.201000182)
- Eberle U., Felderhoff M., Schüth F. (2009), Chemical and Physical Solutions for Hydrogen Storage, *Angew. Chem., Int. Ed.*, 48, 6608–6630 (DOI: 10.1002/anie.200806293)
- Dalebrook A. F., Gan W., Grasemann M., Moret S., Laurenczy G. (2013), Hydrogen storage: beyond conventional methods, *Chem. Commun.*, 49, 8735–8751 (DOI: 10.1039/c3cc43836h)
- Jiang H. L., Singh S. K., Yan J. M., Zhang X. B., Xu Q. (2010), Liquid-Phase Chemical Hydrogen Storage: Catalytic Hydrogen generation under Ambient Conditions, *ChemSusChem.*, 3, 541–549 (DOI: 10.1002/cssc.201000023)
- Sordakis K., Tang C., Vogt L. K., Junge H., Dyson P. J., Beller M., Laurenczy, G. (2018), Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols, *Chem. Rev.*, 118, 372–433 (DOI: 10.1021/acs.chemrev.7b00182)

- Preuster P., Papp C. Wasserscheid P. (2017), Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy, Acc. Chem. Res., 50(1), 74–85 (DOI: 10.1021/acs.accounts.6b00474)
- Heim L. E., Schlörer N. E., Choi J.-H., Prechtl M. H. G. (2014), Selective and Mild Hydrogen Production Using Water and Formaldehyde, *Nat. Commun.*, 5, 3621 (DOI: 10.1038/ncomms4621)
- Suenobu T., Isaka Y., Shibata S., Fukuzumi S. (2015), Catalytic Hydrogen Production from Paraformaldehyde and Water Using an Organoiridium Complex, *Chem. Commun.*, 51, 1670–1672 (DOI: 10.1039/c4cc06581f)
- 14. Fujita K., Kawahara R., Aikawa T., Yamaguchi R. (2015), Hydrogen Production from a Methanol-Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions, *Angew. Chem. Int. Ed.*, 54(31), 9057–9060 (DOI: 10.1002/anie.201502194)
- Trincado M., Sinha V., Rodriguez-Lugo R. E., Pribanic B., de Bruin B., Grutzmacher, H. (2017), Homogeneously catalysed Conversion of Aqueous Formaldehyde to H<sub>2</sub> and Carbonate, *Nat. Commun.*, 8, 14990 (DOI: 10.1038/ncomms14990)
- Wang L., Ertem M. Z., Kanega R., Murata K., Szalda D. J., Muckerman J. T., Fujita E., Himeda Y. (2018), Additive-Free Ruthenium-Catalyzed Hydrogen Production from Aqueous Formaldehyde with High Efficiency and Selectivity, *ACS Catal.*, 8, 8600–8605 (DOI: 10.1021/acscatal.8b02088)
- Awasthi M. K., Singh S. K. (2021), Ruthenium Catalyzed Hydrogen Production from Formaldehyde–Water Solution, Sustain. Energy Fuels, 5, 549–555 (DOI:10.1039/d0se01330g)

- Patra S., Singh S. K. (2020), Hydrogen Production from Formic Acid and Formaldehyde over Ruthenium Catalysts in Water, *Inorg Chem.*, 59, 4234-4243 (DOI: 10.1021/acs.inorgchem.9b02882)
- Patra S., Deka H., Singh S. K. (2021), Bis-Imidazole Methane Ligated Ruthenium(II) Complexes: Synthesis, Characterization, and Catalytic Activity for Hydrogen Production from Formic Acid in Water, *Inorg. Chem.*, 60, 14275-14285 (DOI: 10.1021/acs.inorgchem.1c01784)
- Onishi N., Ertem M. Z., Xu S., Tsurusaki A., Manaka Y., Muckerman J. T., Fujita E.; Himeda Y. (2016), Direction to practical production of hydrogen by formic acid dehydrogenation with Cp\*Ir complexes bearing imidazoline ligands, *Catal. Sci. Technol.*, 6, 988–992 (DOI: 10.1039/c5cy01865j)
- Manaka Y., Wang W.-H., Suna Y., Kambayashi H.; Muckerman, J. T., Fujita E., Himeda Y. (2014), Efficient H<sub>2</sub> Generation from Formic Acid Using Azole Complexes in Water, *Catal. Sci. Technol.*, 4, 34–37 (DOI: 10.1039/c3cy00830d)
- Wang Z.; Lu S.-M.; Li J.; Wang, J.; Li C. (2015), Unprecedentedly High Formic Acid Dehydrogenation Activity on an Iridium Complex with an N,N'-Diimine Ligand in Water, *Chem. -Eur. J.*, 21, 12592–12595 (DOI: 10.1002/chem.201502086)
- Guan C., Zhang D.-D., Pan Y., Iguchi M., Ajitha M. J., Hu J., Li H., Yao C., Huang M.-H., Min S., Zheng, J., Himeda Y.; Kawanami H.; Huang K.-W. (2017), Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an N,N'-Diimine Ligand, *Inorg. Chem.*, 56, 438–445 (DOI: 10.1021/acs.inorgchem.6b02334)

# Chapter 6 Summary and Future Scope

## 6.1. Summary of this thesis

In summary, during my thesis work, I aimed to design and develop new arene-Ru(II) complexes with bidentate N,N/N,O donor ligands and explore them for catalytic hydrogen production from formic acid and formaldehyde in water. A structure-activity relationship of the coordinated ligands to the Ru center on the catalytic activities was established and different parameters which affect the reaction kinetics of these dehydrogenation reactions were studied in detail. Extensive mass and NMR studies were performed to gain insights into the catalytic pathway of the reactions.

In *chapter 1*, the need of liquid organic hydrogen carriers (LOHCs) in the current scenario, history of transition metal catalyzed hydrogen production from formic acid and formaldehyde and a general introduction of arene-Ru(II) complexes have been discussed.

In *chapter 2*, several N,N bidentate donor ligand based arene-Ru(II) complexes were employed for catalytic hydrogen production from formic acid in water wherein our studies revealed that the arene-Ru(II) complexes containing aminoquinoline based ligands ([**Ru**]-2 – [**Ru**]-4) outperformed over the complex bearing ethylene diamine ligand ([**Ru**]-1) under our optimized reaction conditions. Further, the arene-Ru(II) complex having electron rich 8-(N-methylamino)quinoline ligand ([**Ru**]-4) was found to be more effective than the complex containing 8aminoquinoline ([**Ru**]-2) in enhancing the catalytic activity. Maximum TON and TOF of 2248 and 940 h<sup>-1</sup> respectively were achieved with the complex [**Ru**]-4. In addition, extensive mass investigations were carried out which evidenced the formation of several important catalytic reaction intermediates during the course of the reaction and most importantly, the plausible catalyst resting state was isolated and characterized as a dicationic diruthenium species  $[{(\eta^6-\text{benzene})\text{Ru}(\kappa^2-\text{NpyNH-AmQ})}_2]^{2+}$  (**[Ru]-2A'**) by single crystal x-ray diffraction technique.

In chapter 3, several pyridine-based N,O/N,N ligated arene-Ru(II) catalysts were explored for hydrogen production from formic acid and formaldehyde in water. A systematic study of all the catalysts revealed that the arene-Ru(II) complex ligated with N,O donor bidentate ligand outperformed over the arene-Ru(II) complex bearing the N,N donor analogous ligand. The high activity of the complex  $[(\eta^6-p$ cymene)RuCl( $\kappa^2$ -L2)]<sup>+</sup> ([Ru]-8) (L2 = pyridine-2yl-methanol) in formic acid dehydrogenation was attributed to the acidic nature of the N,O donor ligand, thus ability to undergo de-protonation readily. In addition, extensive mass, NMR and kinetic investigations were employed to evidence the formation of important catalytic reaction intermediates formed during the catalytic dehydrogenation of formic acid over [Ru]-8 and hence established the crucial role of these species in the dehydrogenation reaction. A diruthenium species [{ $(\eta^6$ - $C_{10}H_{14}$ )Ru( $\kappa^2$  N,O- $\mu$ -O-L2 $_{2}^{2+}$  ([Ru]-8A') possibly the catalyst resting state was isolated and its structure was determined by single crystal xray diffraction. Further, [Ru]-8 was also found to be efficient in the hydrogen production from aqueous formaldehyde (37 wt. %) in water under additive-free reaction conditions.

In *chapter 4*, a new series of arene-Ru(II) complexes containing electron rich bis-imidazole methane based ligands were synthesized and fully characterized through various techniques. Different substitutions were present at the methylene carbon atom to tune the catalytic activities. The synthesized complexes were employed for hydrogen production from formic acid in water where results inferred that the arene-Ru(II) complex  $[(\eta^6-p-\text{cymene})\text{RuCl}(\kappa^2-\text{L6})]^+$  (L6 = {4,4'-((4methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole)}) (**IBul-18**) containing the electron rich 4-methoxy substituent at the

(**[Ru]-18**) containing the electron rich 4-methoxy substituent at the bridging methylene group outperformed over the others. A maximum

TON and initial TOF of 8830 and 1545 h<sup>-1</sup> respectively could be achieved with **[Ru]-18**. Further, detailed mechanistic insights were provided by identifying/isolating almost all the crucial reaction intermediates such as the Ru-aqua coordinated species  $[(\eta^6-p$ cymene)Ru( $\kappa^2$ -L6–H<sup>+</sup>)(H<sub>2</sub>O)]<sup>+</sup> (**[Ru]-18A**), Ru-formate coordinated species  $[(\eta^6-p-$ cymene)Ru( $\kappa^2$ -L6–H<sup>+</sup>)(HCO<sub>2</sub>)] (**[Ru]-18B**) and Ruhydride species  $[(\eta^6-C_{10}H_{14})Ru(\kappa^2-L6-H^+)(H)]$  (**[Ru]-18C**) involved in the catalytic cycle.

Chapter 5 deals with the application of the synthesized arene-Ru(II) complexes based on bis-imidazole methane based ligands in hydrogen production from formaldehyde-water under additive and basefree reaction conditions. Highly efficient hydrogen production was achieved with the complex  $[(\eta^6 - p - \text{cymene})\text{RuCl}(\mathbf{L7})]^+\text{Cl}^-$  ( $\mathbf{L7} = \{4, 4' - 4'\}$ ((2-methoxyphenyl)methylene)bis(2-ethyl-5-methyl-1*H*-imidazole)}) ([Ru]-19) to obtain a maximum TON and initial TOF of 20108 and 4045 h<sup>-1</sup> respectively. A two step dehydrogenation pathway of formaldehydewater system was supported by <sup>1</sup>H NMR, pH and GC-TCD analysis. Almost all the crucial reaction intermediates such as the Ru-methanediol coordinated species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{H}^+)(\text{CH}_2(\text{OH})_2)]^+$  ([**Ru**]-**19B**), Ru-formate coordinated species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{L7})]$ H<sup>+</sup>)(HCO<sub>2</sub>)] ([**Ru**]-19C), Ru-hydride species  $[(\eta^6-p-\text{cymene})\text{Ru}(\kappa^2-\text{L7}-\text{L7}-\text{L7})]$ H<sup>+</sup>)(H)] (**[Ru]-19D**) involved in the catalytic cycle were identified by extensive mass and NMR analysis, thus, providing detailed mechanistic insight.



**Figure 6.1.** Comparative turnover numbers for different Ru(II)-based catalytic systems developed in this thesis work for hydrogen production from C-1 based LOHCs.

# 6.2. Future Scope

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 sustainable production of hydrogen from various LOHCs. C-1 based LOHCs are the most promising candidates due to the high atom efficiency and low carbon emission associated along with the production of hydrogen from them. Despite the extensive reports available in literature in this field, development of homogeneous catalytic systems for practical and industrial usage needs more attention. Moreover, the development of air stable and relatively inexpensive non-noble metal based catalytic systems also need special attention from the economic point of view. Attempts can be made to isolate and further crystallize the identified reaction intermediates for better understanding of their structure and the crucial role they play in the catalytic cycle which may further enhance the mechanistic understanding of these dehydrogenation reactions. Though attempts have been made in this thesis work to evaluate the catalyst recyclability and performance at the bulk-scale production of hydrogen gas, the development of suitable technique to separate  $CO_2$  from the gas mixture so that pure H<sub>2</sub> can be utilized directly in the fuel cell is desirable to evaluate the practical application of the developed catalytic systems.

# **APPENDIX-I**

(Rights and Permissions)



- Permission is granted for your request in both print and electronic formats, and translations.

- If figures and/or tables were requested, they may be adapted or used in part.

Please print this page for your records and send a copy of it to your publisher/graduate school.

- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

One-time permission is granted only for the use specified in your RightsLink request. No additional uses are
granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com


- Permission is granted for your request in both print and electronic formats, and translations.

If figures and/or tables were requested, they may be adapted or used in part.

- Please print this page for your records and send a copy of it to your publisher/graduate school.

- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society," Insert appropriate information in place of the capitalized words.

- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

CC Riał	<b>C</b> htsLink		A Home	<b>?</b> Help ~	<b>R</b> Live Chat	Soumyadip Pat
Eur	Compl Author: Publicat Date: Jai	rogenation of Formic A lexes: X-ray Crystal Stru Sanjay K. Singh, Shaikh M. Mol ion: European Journal of Inorg er: John Wiley and Sons n 18, 2019 //LEY-VCH Verlag GmbH & Co. KGaA	cid Cataly, Icture of a Din, Hemanta anic Chemistr Weinheim	<b>zed by Wa</b> <b>Diruthen</b> Deka, et al y	ater-Solub ium Comp	le Rutheniun lex
Ord	der Completed					
T T y C	hank you for your orde his Agreement betwee our license details and enter.	er. n Mr. Soumyadip Patra ("You") ar the terms and conditions provid	nd John Wiley a ed by John Wile	nd Sons ("Joh ey and Sons a	n Wiley and Sc nd Copyright C	ons") consists of learance
Lice	nse Number	5213580881346	r for fucure re	serence.	6	Printable Details
Lice	nse date	Dec 21, 2021				
	Licensed Content		菌 Order	Details		
Lice Pub Lice Pub Lice Title	nsed Content lisher nsed Content lication nsed Content	John Wiley and Sons European Journal of Inorganic Chemistry Dehydrogenation of Formic Acid Catalyzed by Water- Soluble Ruthenium Complexes: X-ray Crystal Structure of a Diruthenium	Type of use Requestor f Format Portion Will you be translating	type ?	Dissertatio Author of Print and e Full article No	on/Thesis this Wiley article electronic
Lice	nsed Content hor	Complex Sanjay K. Singh, Shaikh M. Mobin, Hemanta Deka, et al				
Lice	nsed Content e	Jan 18, 2019				
Lice	nsed Content Ime	2019				
Lice	nsed Content e	7				
Lice Pag	nsed Content es	8				
	About Your Work		🖕 Additi	onal Data		
Title	2	Development of Efficient Molecular Catalysts for Hydrogen Production from C- 1 based LOHCs				
Inst	itution name	IIT INDORE				
pre	sentation date	Dec 2021				

# 12/21/21, 5:07 PM

Requestor Loc	ation	Tax Details	
	Mr. Soumyadip Patra Unit 605 , HJB Hall of Residence, IITI Khandwa road. Indore.	Publisher Tax ID	EU826007151
Requestor Location			
	INDORE, MADHYA PRADESH		
	India		
	Attn: IIT INDORE		
\$ Price			
Total	0.00 USD		
Would you like	to purchase the full text of this article	e? If so, please continue	on to the content ordering
system located If you click on t system.	he buttons below or close this window	w, you will not be able to	return to the content ordering
lf you click on t system.	he buttons below or close this window	w, you will not be able to	Total: 0.00 US

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com



- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

# 12/21/21, 5:18 PM

# Rightslink® by Copyright Clearance Center

Prove Pr	lopment of Effective Cata g Formic Acid r: Yuichiro Himeda, Qiang Xu, Ha ation: Advanced Energy Material: her: John Wiley and Sons Sep 3, 2018 WILEY-VCH Verlag GmbH & Co. KGaA,	il <b>ysts for Hydrog</b> jime Kawanami, et al s Weinheim	gen Storage Technol	ogy
Order Completed				
Thank you for your or This Agreement betwy your license details ar Center.	der. een Mr. Soumyadip Patra ("You") an d the terms and conditions provide	d John Wiley and Sons i ed by John Wiley and So	"John Wiley and Sons") cons ns and Copyright Clearance	ists of
Your confirmation ema	il will contain your order number	r for future reference.	屇 Printable	e Details
License date	Dec 21, 2021			
Licensed Content		Order Details		
Licensed Content Publisher Licensed Content Publication Licensed Content Title Licensed Content Author Licensed Content Date Licensed Content Volume Licensed Content Issue Licensed Content Pages	John Wiley and Sons Advanced Energy Materials Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid Yuichiro Himeda, Qiang Xu, Hajime Kawanami, et al Sep 3, 2018 9 23	Type of use Requestor type Format Portion Number of figures/tables Will you be translating?	Dissertation/Thesis University/Academic Print and electronic Figure/table 1 No	c
About Your Work		Additional Da	ta	
Title Institution name Expected presentation date	Development of Efficient Molecular Catalysts for Hydrogen Production from C- 1 based LOHCs IIT INDORE Dec 2021	Portions	Figure 5	

#### 12/21/21, 5:18 PM

## Rightslink® by Copyright Clearance Center

	cation	📕 Tax Details	
	Mr. Soumyadip Patra Unit 605 , HJB Hall of Residence, IITI Khandwa road, Indore.	Publisher Tax ID	EU826007151
Requestor Location	INDORE, MADHYA PRADESH 452020 India Attn: IIT INDORE		
\$ Price			
Total	0.00 USD		
Would you like system located If you click on system.	e to purchase the full text of this articl d here: Purchase PDF the buttons below or close this windo	e? If so, please continue w, you will not be able to	on to the content ordering return to the content ordering
Would you like system locatee If you click on system.	e to purchase the full text of this articl d here: Purchase PDF the buttons below or close this windo	e? If so, please continue w, you will not be able to	on to the content ordering oreturn to the content ordering Total: 0.00 USI

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

## Rightslink® by Copyright Clearance Center

12/21/21, 5:21 PW	12/21/2	1.5:21	PM
-------------------	---------	--------	----

55	0	Home	Help ∨	Live Chat	Soumyadip
ghtsLinl	Č				A
CHENSUSCIEN Au Pu	ormic Acid as a Potential On evelopment of Homogeneou ehydrogenation Reactions thor: Jian Guo, Chengkai K. Yin, Dulir blication: ChemSusChem blisher: John Wiley and Sons	-Board Hyd us Noble M n L. Zhong, et a	drogen S letal Cat	torage Me alysts for	thod:
Da	te: Jun 7, 2021				
©.	2021 Wiley-VCH GmbH				
Order Complete	d				
Thank you for you	ır order.				
This Agreement b your license detai Center.	etween Mr. Soumyadip Patra ("You") ar Is and the terms and conditions provide	id John Wiley a ed by John Wile	nd Sons ("Jol ey and Sons a	nn Wiley and So and Copyright (	ons") consists c Clearance
License Number	5213590292003	r for future re	ference.	Ģ	Printable Der
License date	Dec 21 2021				
Licensed Cont	ent	🗊 Order I	Details		
Licensed Content		Type of use	Jetans	Dissertatio	on/Thesis
Publisher	John Wiley and Sons	Requestor t	ype	University	/Academic
Licensed Content Publication	ChemSusChem	Format		Print and	electronic
	Formic Acid as a Potential	Portion Number of	es	Figure/tab 3	le
Licensed Content Title	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Author	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Author Licensed Content Date	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Author Licensed Content Date Licensed Content Volume	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021 14	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Author Licensed Content Date Licensed Content Usume Licensed Content Issue	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021 14	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Author Licensed Content Date Licensed Content Volume Licensed Content Issue Licensed Content Pages	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021 14 13 27	figures/tabl Will you be translating?		No	
Licensed Content Title Licensed Content Date Licensed Content Volume Licensed Content Issue Licensed Content Pages	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021 14 13 27	figures/tabl Will you be translating?	onal Data	No	
Licensed Content Title Licensed Content Date Licensed Content Volume Licensed Content Issue Licensed Content Pages About Your W Title	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K, Yin, Dulin L. Zhong, et al Jun 7, 2021 14 13 27 Development of Efficient Molecular Catalysts for Hydrogen Production from C- 1 based LOHCs	figures/tabl Will you be translating? Additi Portions	onal Data	No Figures 2,3	3,4
Licensed Content Title Licensed Content Date Licensed Content Usensed Content Usensed Content Usensed Content Usensed Content Pages About Your W Title	Method: Development of Homogeneous Noble Metal Catalysts for Dehydrogenation Reactions Jian Guo, Chengkai K. Yin, Dulin L. Zhong, et al Jun 7, 2021 14 13 27 ork Development of Efficient Molecular Catalysts for Hydrogen Production from C- 1 based LOHCs IIT INDORE	figures/tabl Will you be translating? Additi Portions	onal Data	No Figures 2,:	3,4

# 12/21/21, 5:21 PM

<ul> <li>Requestor Loc</li> </ul>	ation	Tax Details	
	Mr. Soumyadip Patra Unit 605 , HJB Hall of Residence, IITI Khandwa road Indore	Publisher Tax ID	EU826007151
Requestor Location	interferte rota, interfer		
	INDORE, MADHYA PRADESH		
	India		
	Attn: IIT INDORE		
\$ Price			
Total	0.00 USD		
Would you like	to purchase the full text of this article here: Purchase PDF	e? If so, please continue	on to the content ordering
system located If you click on t system.	he buttons below or close this window	w, you will not be able to	return to the content ordening
system located If you click on t system.	he buttons below or close this windo	w, you will not be able to	Total: 0.00 USI

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com

5:24 PM	Rightslink® by Copyright Clearance Center				
CCC RightsLink	Ame Home	<b>?</b> Help ~	<b>R</b> Live Chat	Soumyadip Patra	
	Selective Formic Acid Dehydro Pincer Complexes Based on th	genation ne 2,6-Dia	Catalyzed minopyrid	by Fe-PNP ine Scaffold	
ACS Publications	Author: Irene Mellone, Nikolaus Gorgas, Publication: Organometallics Publicher: American Chemical Society	, Federica Be	ertini, et al		
	Date: Oct 1, 2016				
	Copyright © 2016, American Chemical Society				
This type of permission/licen charged for your order. Pleas - Permission is granted for yy - If figures and/or tables werd - Please print this page for yc - Appropriate credit for the rr from {COMPLETE REFERENCE information in place of the cr - One-time permission is gran granted (such as derivative w	se, instead of the standard Terms and Cor ie note the following: our request in both print and electronic for requested, they may be adapted or used our records and send a copy of it to your p equested material should be given as follo 5 CITATION}. Copyright {YEAR} American Cl apitalized words. Ited only for the use specified in your Righ vorks or other editions). For any uses, plea	nditions, is s rmats, and t l in part. ublisher/gra ws: "Reprint hemical Soc ntsLink requ se submit a n RightsLink,	ent to you bed ranslations. (duate school. (adapted) iety." Insert ap est. No additionew request. permission m	ause no fee is being with permission propriate onal uses are ust be obtained	
If credit is given to another se	ource for the material your equested from				

© 2021 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com