

Curriculum Vitae

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Education

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| 2018-2022 | Post-doctoral fellow, Schulich Faculty of Chemistry, Technion. Mentor:
Dr. Graham de Ruiter |
| 2011-2017 | Ph.D. (in Organometallic Chemistry), IISER Bhopal, Thesis Supervisor:
Dr. Joyanta Choudhury

Thesis title: “ <i>Developing a Unique Reactivity of N-Heterocyclic Carbene (NHC)–Metal Template in C–H Activation-Annulation Catalysis: Synthetic and Mechanistic Studies</i> ” |
| 2008-2010 | Master of Science in Chemistry (First Class); Gandhigram Rural Institute, Tamilnadu, India. |
| 2005-2008 | Bachelor of Science in Chemistry (First Class Honors); Univ. of Calicut, Kerala, India. |

Technical Skills

- Syntheses, and characterization of inorganic, organic and organometallic compounds in milligram to gram scale.
- Experienced in manipulation of *air and moisture sensitive* organometallic compounds using standard *Schlenk line* techniques under inert atmosphere and by using *glove box*.
- Experienced in Isolation of organometallic intermediates
- Reaction monitoring, and kinetic study with the help of NMR.
- Single Crystal X-Ray data collection, and structure solution (**Bruker SMART APEX II CCD** diffractometer).
- Skilled in the interpretation of spectroscopic data (**NMR, HR-MS, UV-VIS**) for characterization of unknown compounds.
- Hands on experience in Cary 100 UV-VIS Spectrometer, CHI 620E Electrochemical Analyzer (Cyclic Voltammetry).

- Hands on experience in **AVANCE 200 MHz** and **AVANCE 300 MHz** NMR instruments.
- Experience in Flash Column Chromatography

Achievements & Extracurricular Activities

- Awarded **PBC Postdoctoral Fellowship** sponsored by *Israel Council for Higher education*, 2018-2021
- Poster entitled “*Developing a Unique Reactivity of N-Heterocyclic Carbene (NHC)–Metal Template in C–H Activation-Annulation Catalysis*” presented at the 20th *CRSI National Symposium in Chemistry, in Gauhati University, Assam, India.* during 2-5 February, 2017.
- Poster entitled “*N-Heterocyclic Carbene (NHC) Ligands in a New Action in C–H Activation-Annulation Catalysis*” presented at the Conference "Catalyst-2015: Advancements in Chemistry and Engineering", at Dr. Reddy's Laboratories in Hyderabad, India. during 3-4 July 2015. [**Best poster award** (1st prize)].
- Awarded National Fellowship from the *University Grants Commission (UGC-JRF and SRF)*, India to pursue Ph.D.
- University Grants Commission (UGC)-networking Summer Project Fellow-2010
- National Institute of Technology Karnataka (NITK), India-Summer Internship Fellow-2009
- National Service Scheme (NSS) volunteer during B.Sc.

Teaching Experience

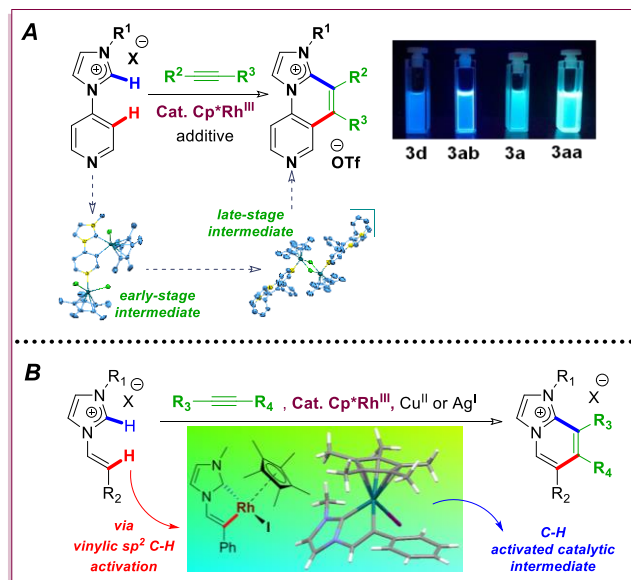
Teaching Assistantship for Inorganic Chemistry (Theory) in 1st year BS-MS. at IISER Bhopal (1 year).

Summary of PhD Research

The tremendous success of N-heterocyclic carbenes (NHCs) in homogeneous catalysis portrays a true reflection of their unique stereoelectronic properties, strong metal–C_(NHC) bonding, and excellent stability of the metal complexes toward heat, air and moisture. In fact, the robust and inert metal–C_(NHC) backbone is considered as a key factor to provide the opportunity for exploring catalytic reactions without any self-transformative unproductive side reaction.

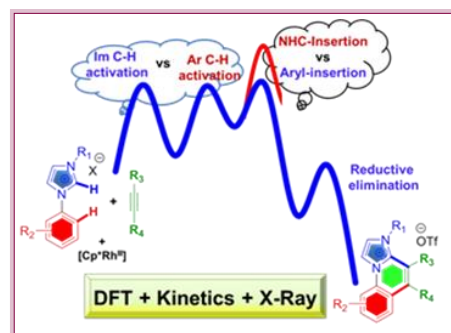
During my PhD, a unique reactivity of the metal–C_(NHC) motif has been developed and explored in the field of C–H activation/functionalization catalysis. Our research was started with a preliminary study towards the understanding of the directing group (DG) property of NHC ligand as well as the influence of pyridine-metal coordination during the C–H bond activation of pyridine backbone. As catalytic direct C–H functionalization of pyridine backbone is a challenging research area, the above understanding was further applied to develop a new rhodium(III)-catalyzed protocol for C–H activation and functionalization of poorly reactive pyridine backbones with the aid of in-built NHC ligand. This protocol highlights a novel conjugative action of NHC ligands as a DG as well as a *functionalizing* group (**Scheme I, A**). This chemistry was also demonstrated successfully for catalytic non-aromatic C–H activation and subsequent annulation of various vinylic-group substituted imidazolium substrates with internal alkynes (**Scheme I, B**). This newly developed catalytic protocol enables easy synthesis of imidazo[1,2-*a*]quinolinium, imidazo-[1,2-*a*][1,6]naphthyridinium, and imidazo[1,2-*a*]pyridinium architectures which might be useful in pharmaceutical industry, or as abnormal NHC ligands or as organic emitters (**Scheme I**).

Scheme I



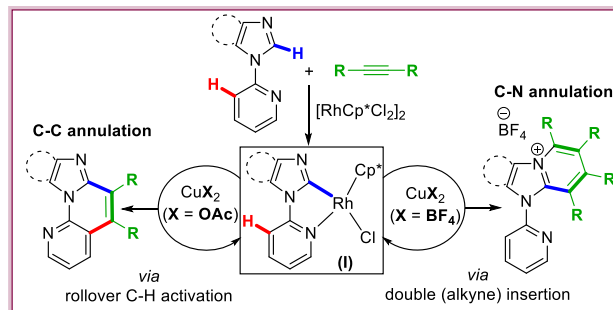
Mechanistic investigation of any newly discovered catalytic reaction is at the heart of its future development for potential application in diverse fields. Motivated by this philosophy, I explored the key mechanistic insights of this annulation reaction which unravel the crucial competition of two C–H bonds (imidazolium and aryl C–H) and two M–C bonds (M–C_{NHC} and M–C_{aryl}) in establishing the rate-limiting step and the alkyne-insertion regioselectivity in the reaction. Through careful isolation and X-ray structural characterization of the key seven-membered inserted intermediate along with a DFT rationale, the exclusive regioselectivity of the alkyne insertion to the M–C_{NHC} bond was established. Kinetics studies were used to evaluate the rate-determining step of the reaction, which was found to be the initial nondirected imidazolium C–H activation step (**Scheme II**). These mechanistic insights should be useful in understanding similar C–H activation processes in general which are topical in the area of catalysis.

Scheme II



In late stage of my PhD, the potential of the metal- $C_{(NHC)}$ template has been explored on chelating pyridyl-imidazole substrates to develop a novel switchable C-C annulation/C-N annulation protocol, via exquisite reactivity control of the metal-complex intermediates. With the basic and coordinating OAc anion, a rollover C-H activation pathway was favored resulting in C-C annulation products in non-polar solvent. In contrast, weakly basic and less/non-coordinating BF_4 anion triggered double alkyne insertion instead of C-H activation leading to C-N annulated cationic products in polar solvent (**Scheme III**). The key to the success of this switchable chemodivergent protocol is the control over the nature and reactivity of the organometallic rhodacyclic intermediates based on anion and solvent polarity.

Scheme III

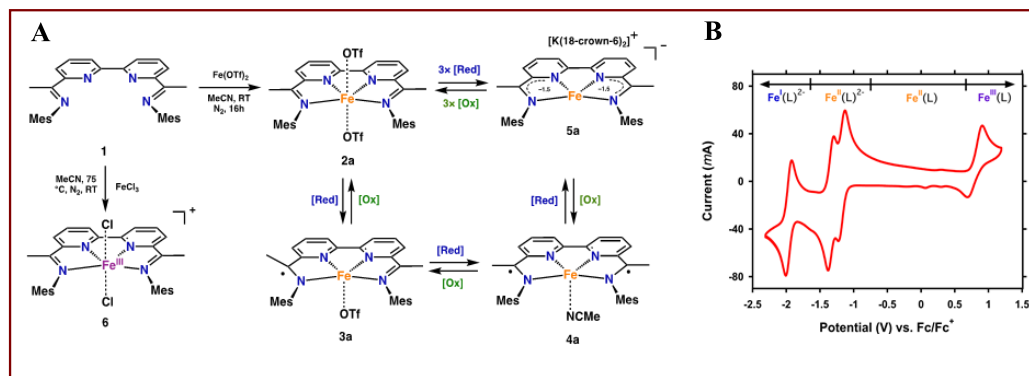


Summary of Postdoctoral Research

Homogeneous catalysis is increasingly important in both academia and industry. Till date, this field is mainly dominated by second and third row transition metals. During my PhD research, I was also worked only with noble metal complexes. But, due to their toxicity, high price and limited abundance, scientists are trying to replace noble metals by the more abundant, first row transition metals. However, the reactivity of those metal complexes is difficult to control due to their different electronic structure, orbital overlap, and bonding character. To make use of first row transition metals, bespoke ligand design is highly desirable. Our research evaluates the synthesis of metal complexes with two different types of ligand systems able to work using (i) metal ligand cooperativity and (ii) or by providing a strong-field ligand environment.

Besides their importance in biology, the application of redox non-innocent ligands in catalysis has recently shifted the paradigm that mainly noble metals can participate in reversible two-electronchemistry.

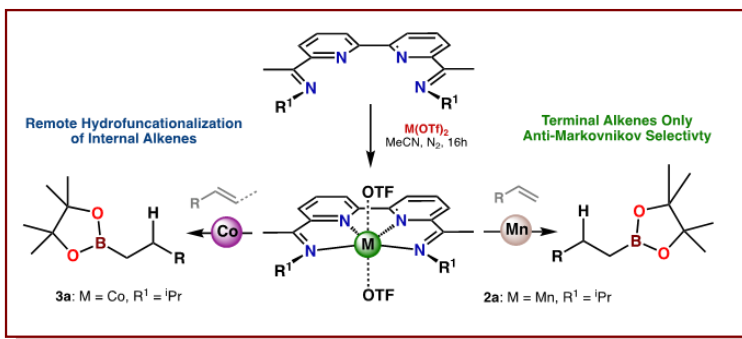
Scheme IV



Here, we synthesised iron bipyridine (BDI) complexes exhibit an extensive electron-transfer series that spans a total of five oxidation states, ranging from the trication $[\text{Fe}(\text{BDI})]^{3+}$ to the monoanion $[\text{Fe}(\text{BDI})]^{-1}$. Structural characterization by X-ray crystallography revealed the multifaceted redox non-innocence of the the BDI ligand, while spectroscopic (e.g., ^{57}Fe Mössbauer and EPR spectroscopy) and computational studies were employed to elucidate the electronic structure of the isolated complexes.

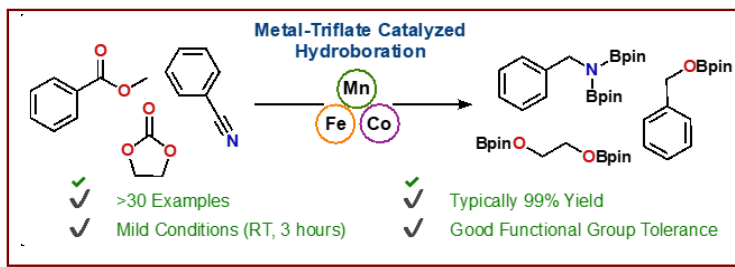
Afterwards, we developed well-defined manganese complex, $[\text{Mn}(\text{}^{iPr}\text{BDI})(\text{OTf})_2]$ (**2a**; BDI = bipyridinediimine), that is an active precatalyst in the hydroboration of a variety of electronically differentiated alkenes (>20 examples). The hydroboration is specifically selective for terminal alkenes and occurs with exclusive anti-Markovnikov selectivity. In contrast, when using the analogous cobalt complex $[\text{Co}(\text{}^{iPr}\text{BDI})(\text{OTf})_2]$ (**3a**), internal alkenes hydroborated efficiently, where a sequence of isomerization steps ultimately leads to their hydroboration. The contrasting terminal versus internal alkene selectivity for manganese and cobalt was investigated computationally and is further discussed in the study.

Scheme V



During this study I discovered an effective methodology for the hydroboration of challenging $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ bonds that is simple and applicable to a wide set of substrates. The methodology is based on using a simple manganese(II) triflate salt that, in

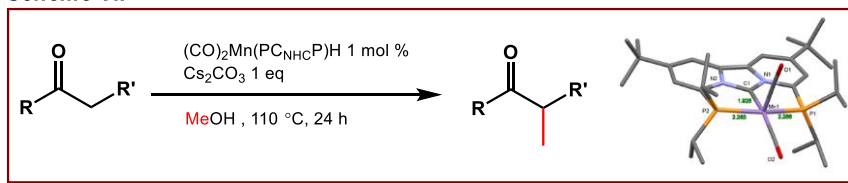
Scheme VI



combination with commercially available potassium *tert*-butoxide and pinacolborane, catalyzes the hydroboration of nitriles, carbonates, and esters at room temperature and with near quantitative yields in less than three hours. Additional studies demonstrated that other earth-abundant metal triflate salts can facilitate this reaction as well, which is further discussed in this report. Overall, these results suggest that elaborate catalyst designs based on strong-field or redox noninnocent ligands may not be necessary, and the earth-abundant metal triflate salts itself are effective catalyst for challenging $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ bonds hydroboration.

In the last work, I was exploring a novel $\text{MnPC}_{\text{NHC}}\text{P}$ complex, where the N-Heterocyclic carbene cantered strong pincer ligand can act as

Scheme VII



a spectator ligand and can provide a strong ligand field environment to the complex.⁴ In general, hydrogen borrowing reactions are privileged with metal ligand co-operativity. In this work we explored a $\text{MnPC}_{\text{NHC}}\text{P}$ complex, which can catalyse the hydrogen borrowing reactions without having a traditional metal ligand cooperative site. The mechanistic understanding of this transformation is highly interesting, and our investigation is in progress.

List of Publications

1. Mondal, M.; **Thenarukandiyil, R.**; Gupta, S. K.; Choudhury, J. “Labile Coordination Approach for Modulation of Electronic Properties in Ruthenium(II) and Iridium(III) Complexes within “N-Heterocyclic Carbene (NHC)–Pyridyl” Dynamic Platform.” *Dalton Trans.* **2014**, 43, 9356–9362.
2. **Thenarukandiyil, R.**; Choudhury, J. “Rhodium(III)-Catalyzed Activation and Functionalization of Pyridine C–H Bond by Exploring a Unique Double-Role of ‘N-Heterocyclic Carbene–Pyridyl’ Ligand Platform.” *Organometallics* **2015**, 34, 1890–1897.
3. **Thenarukandiyil, R.**; Thrikkykkal, H.; Choudhury, J. “Rhodium(III)-Catalyzed Non-aromatic sp^2 C–H Activation/Annulation using NHC as a Directing and Functionalizable Group.” *Organometallics* **2016**, 35, 3007–3013.
4. **Thenarukandiyil, R.**; Gupta, S. K.; Choudhury, J. “Unraveling the Crucial Competition of Two C–H and Two M–C Bonds in Guiding the Mechanism of Rhodium(III)-Catalyzed C–H Activation-Annulation.” *ACS Catal.* **2016**, 6, 5132–5137.
5. Semwal, S.; Mukkatt, I.; **Thenarukandiyil, R.**; Choudhury, J. “Small ‘Yaw’, Large ‘Bite’ and Electron-Rich Metal: Revealing a Stereoelectronic Synergy to Enhance Hydride Transfer Activity.” *Chem. Eur. J.* **2017**, 23, 13051–13057.
6. **Thenarukandiyil, R.**; Dutta, C.; Choudhury, J. “Switching of Reaction Pathway from C–C Rollover to C–N Ring-Extension Annulation.” *Chem. Eur. J.* **2017**, 23, 15529–15533.
7. **Thenarukandiyil, R.**; Maji, B.; Choudhury, J. “Remote Coordination Approach for Electronic Tuning of a Rhodium(I)-N-Heterocyclic Carbene (NHC) Complex.” *Inorg. Chim. Acta.* **2019**, 487, 419–423.
8. Garhwal, S.; Kroeger, A. A.; **Thenarukandiyil, R.**; Fridman, N.; Karton, A.; de Ruiter, G. “Manganese-Catalyzed Hydroboration of Terminal Olefins and Metal-Dependent Selectivity in Internal Olefin Isomerization–Hydroboration.” *Inorg. Chem.* **2021**, 60, 494–504.
9. **Thenarukandiyil, R.**; Satheesh, Vanaparthi; Shimon, L. J. W.; de Ruiter, G. “Hydroboration of Nitriles, Esters, and Carbonates Catalyzed by Simple Earth-Abundant Metal Triflate Salts.” *Chem Asian J.* **2021**, 16, 999–1006.
10. **Thenarukandiyil, R.**; Paenurk, E.; Wong, A.; Fridman, N.; Karton, A.; Ménard, G.; Gershoni-Poranne, R.; de Ruiter, G. “Extensive Redox Non-Innocence in Iron Bipyridine-Diimine Complexes: a Combined Spectroscopic and Computational Study” *Inorg. Chem.* **2021**, 60, 18296–18306.

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References

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