

Ph.D. Open Seminar

Department of Chemistry

Speaker: Shrivats Semwal (Thesis Advisor: Dr. Joyanta Choudhury)

Roll No: 1220221

Topic of Seminar: Stereo-electronically Tuneable and Stimuli-Switchable Organometallic Complexes for Transfer Hydrogenation, Hydrogenation and Dehydrogenation Catalysis: Toward Reversible Energy-Storage and Delivery

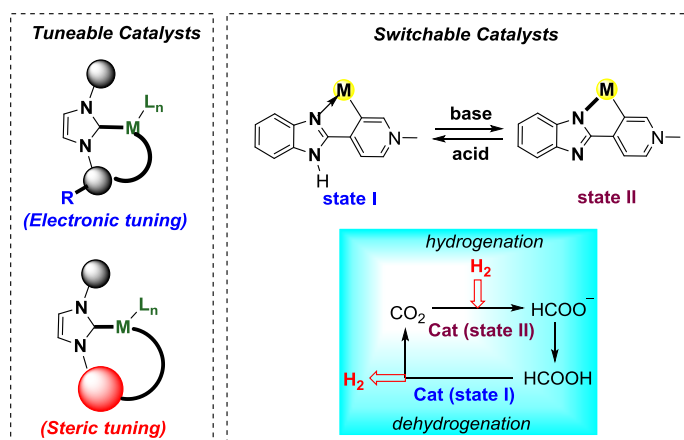
Date: January 19, 2018

Time: 4.00 PM

Venue: L1 (LHC)

Abstract:

Metal hydrides play important role in wide array of chemical reactions involving (transfer) hydrogenation and dehydrogenation^[1]. Easy transfer of hydride ion (hydricity) is expected to increase the overall rate of a (transfer) hydrogenation reaction, provided metal hydrides are involved in the rate-limiting step of the catalytic cycle. Homogeneous catalysis provides opportunity of tuning ligand backbone in order to optimize stereo-electronic influence at the catalytic metal center to achieve better hydride transfer. The first part of my thesis deals with this important issue in the context of transfer hydrogenation catalysis with five- and six-membered cyclometalated iridium-NHC (NHC = N-heterocyclic carbene) complexes.^[2] The investigation revealed that there exists an interesting multidimensional synergy among relevant stereoelectronic factors present within the metal complexes — yaw angle, bite angle, ligand electronic, as well as electronic of the metal center, to govern the hydride donor ability (hydricity) of the complexes during catalysis. Thus the six-membered chelate complexes having small yaw and large bite angles, strong donor ligand, and electron-rich metal, were found to be better catalysts than their five-membered analogues.^[2] In the second part of my thesis, hydrogenation and dehydrogenation reactions were explored by extending the application of the emerging class of stimuli-responsive artificial switchable catalysts. A novel type of pH-driven “molecular coordination switch” was developed with Ir- and Ru-NHC-based complexes.^[3] These pH-switchable catalysts were applied for hydrogenation and dehydrogenative coupling of imines and amines respectively.^[3] Finally, this type of switchable hydrogenation/dehydrogenation application was extended toward developing an efficient reversible chemical hydrogen-storage/delivery system based on the greenhouse gas (GHG) CO₂ and its hydrogenated counterpart, formic acid (FA, HCO₂H).^[4] In this seminar, all the above results will be discussed in detail.



References:

- [1] Morris, R. H. *Chem. Rev.* **2016**, *116*, 8588 and references therein. [2] (a) Semwal, S.; Ghorai, D.; Choudhury, J. *Organometallics* **2014**, *33*, 7118; (b) Semwal, S.; Mukkatt, I.; Thenarukandiyil, R.; Choudhury, J. *Chem. Eur. J.* **2017**, *23*, 13051. [3] (a) Semwal, S.; Choudhury, J. *ACS Catal.*, **2016**, *6*, 2424; (b) Semwal, S.; Choudhury, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 5556. [4] Semwal, S.; Choudhury, J. *Manuscript Submitted*.