

N-Heterocyclic Carbene (NHC) Supported Metal Complexes: Structural Diversity and Understanding of the Structure-Activity Correlation

Arnab Rit*

Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600036

(arnabrit@iitm.ac.in)

Abstract: Ancillary ligands are known to play crucial roles in the activity of any metal complexes and their stereoelectronic parameters are normally considered as important factors to tweak their properties thus, essentially their reactivity. Over the past few decades, N-Heterocyclic carbenes (NHCs) have established themselves as an elite class of ligands in various fields such as organometallic chemistry, homogeneous catalysis, material chemistry, metallopharmaceuticals.¹ From the catalysis perspective, detailed understanding of the combined steric and electronic influence of the ancillary NHC ligand in transition metal catalyzed transformations would be useful for the development of future efficient catalyst systems.² To study such effects, we have synthesized a range of mono- and bimetallic complexes (Fig. 1a) and to understand the influence of ligand variations, all these complexes were tested in different catalytic transformations which revealed that substantial tailoring of activity is possible either by altering their stereoelectronic profiles or introducing cooperative effect.³ Further, multi-ligand self-assembly involving these uniquely designed NHC ligand systems (Fig. 1b) resulted in unique equilibrium between the two forms (tri- and tetranuclear complex) in solution, unprecedented in C_{NHC}-donor based chemistry.

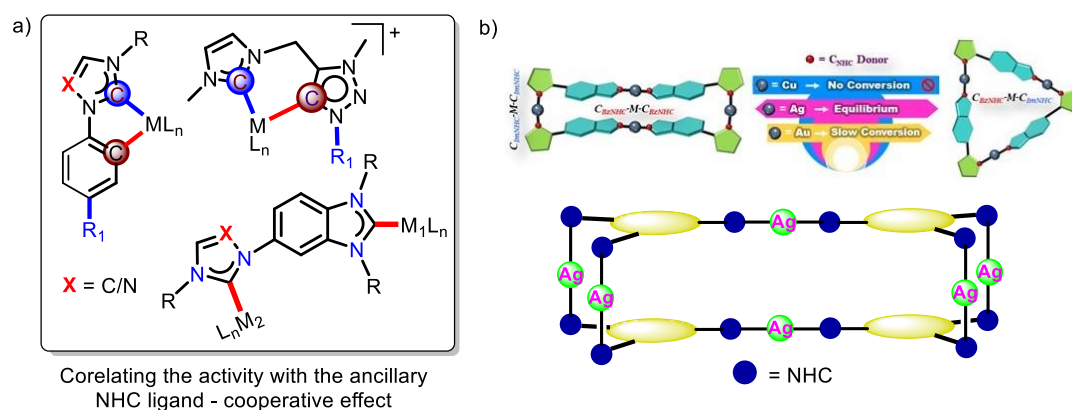


Figure 1. (a) Different types of metal-NHC complexes used in this study and (b) Cartoon representation of the ligand design for self-assembly process.

References:

1. a) Gardiner, M. G.; Ho, C. C. *Coord. Chem. Rev.* **2018**, *375*, 373. b) Peris, E. *Chem. Rev.* **2017**, *118*, 9988. c) Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755.
2. a) Bolje, A.; Hohloch, S.; van der Meer, M.; Košmrlj, J.; Sarkar, B. *Chem. -Eur. J.* **2015**, *21*, 6756. b) Tiwari, C. S.; Illam, P. M.; Donthireddy, S. N. R.; Rit, A. *Chem. -Eur. J.* **2021**, *27*, 16581.
3. a) Bauri, S.; Donthireddy, S. N. R.; Illam, P. M.; Rit, A. *Inorg. Chem.* **2018**, *57*, 14582. b) Donthireddy, S. N. R.; Illam, P. M.; Rit, A. *Inorg. Chem.* **2020**, *59*, 1835. c) Kumar, S.; Patra, D. K.; Rit, A. *Chem. -Eur. J.* **2023**, DOI: 10.1002/chem.202302180. d) Illam, P. M.; Tiwari, C. S.; Rit, A. *Chem. Sci.* **2022**, *13*, 13387. e) Nishad, R. C.; Kumar, S.; Rit, A. *Angew. Chem. Int. Ed.* **2022**, *61*, e202206788.