IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	**Design, Synthesis and Utility of the Nickel Complexes of N/O-functionalized N-heterocyclic Carbene Complexes in Cross-Coupling Reactions and in Enantioselective Cyclopropanation Reactions**	
Project Number	**IMURA0783**	
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IITB Department:	Department of Chemistry	

Research Clusters: Research Themes:

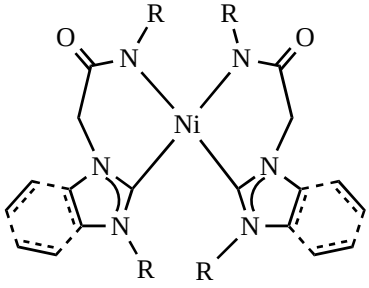
Highlight which of the Academy's CLUSTERS this project will address? *(Please nominate JUST **one.** For more information, see www.iitbmonash.org)*	**Highlight which of the Academy's Theme(s) this project will address?** *(Feel free to nominate more than one. For more information, see www.iitbmonash.org)*	

1	*Material Science/Engineering (including Nano, Metallurgy)*	***1***	*Advanced computational engineering, simulation and manufacture*
2	*Energy, Green Chem, Chemistry, Catalysis, Reaction Eng*	2	*Infrastructure Engineering*
3	*Math, CFD, Modelling, Manufacturing*	3	*Clean Energy*
4	*CSE, IT, Optimisation, Data, Sensors, Systems, Signal Processing, Control*	4	*Water*
5	*Earth Sciences and Civil Engineering (Geo, Water, Climate)*	5	*Nanotechnology*
6	*Bio, Stem Cells, Bio Chem, Pharma, Food*	6	*Biotechnology and Stem Cell Research*
7	*Semi-Conductors, Optics, Photonics, Networks, Telecomm, Power Eng*	7	*Humanities and social sciences*
8	*HSS, Design, Management*	8	Design

The research problem

Define the problem

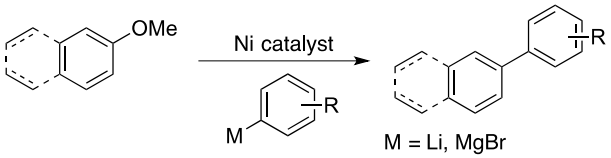
Following the footsteps of palladium, nickel catalysis is increasingly getting popular these days. Nickel, being significantly cheaper than palladium, seems attractive as a viable substitute. The fact that the nickel exhibits similar geometric and electronic preferences to that of palladium, makes the metal all the more promising a candidate to study as an alternative. Because of the aforementioned reasons, we became interested in exploring the catalytic potential of nickel. In this regard, we have recently reported the utility of nickel in bifunctional catalysis namely, in base-free Michael addition reactions using amido-functionalised N-heterocyclic carbene ligands. The effort assumes relevance in the backdrop of the fact that though the N-heterocyclic carbenes have been extremely successful as ligands in homogeneous catalysis, their utility in bifunctional catalysis remains surprisingly overlooked.



Here in the current study, we propose to further the cause of nickel catalysis. In particular a series of nickel complexes of amido-functionalised N-heterocyclic carbene ligands bearing imidazole, triazole and benzimidazoles would be synthesised with the objective of exploring their potential in various catalytic reactions. The target nickel N-heterocyclic carbene complexes are shown in the figure provided alongside. A variety of substituents with different electronic and steric requirements would be put on the N-heterocyclic carbene ligands with the aim of performing a comprehensive structure-function correlation study. Additionally, detailed mechanistic studies would be undertaken for improving the catalysts performances.

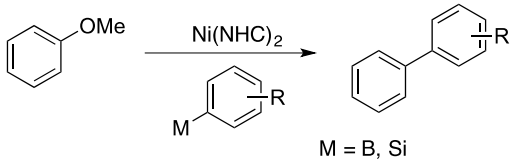
The Ni-NHC complexes synthesised in the first part of the project will be applied in a number of catalytic reactions, including cross-coupling reactions and enantioselective cyclopropanations.

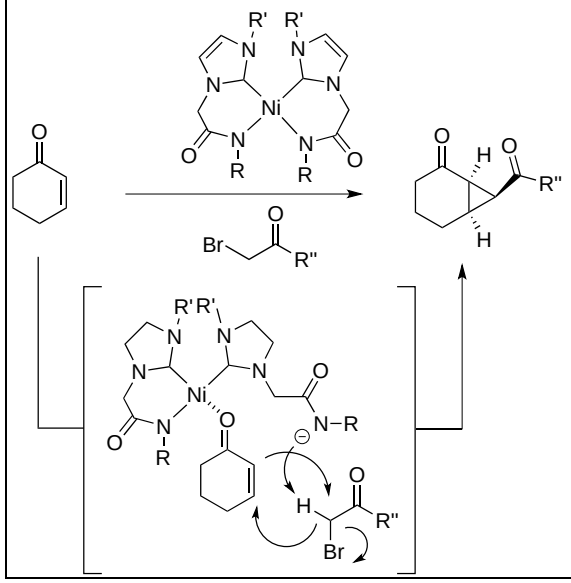
Known reactions



Nickel catalysed cross-coupling reactions using aryl ethers as the electrophilic component is, potentially, a very sustainable method, due to the availability of aryl ethers from biological sources such as lignin. The limiting factor in these reactions is the difficult oxidative addition of Ni^0 into the C-O bond, often requiring the additional activation of naphthalene substrates. Bis-NHC nickel complexes are highly electron rich, which will aid in the oxidative addition, allowing for cross-coupling of unactivated substrates under milder conditions and lower catalyst loadings. In addition, the use of milder nucleophiles, such as those based on boron and silicon will be examined, to improve the practicality and utility of these reactions.

Proposed reaction





Enantioselective cyclopropanation reactions will also be developed, utilising the bifunctional Lewis acid/Brønsted base activity of chiral nickel NHC complexes. Lewis acid activation of the alpha-beta unsaturated carbonyl is accompanied by the amide group acting as a base to deprotonate the bromo-carbonyl, controlling the facial selectivity of the cyclopropanation reacti

Project aims

Define the aims of the project

(*i*). To synthesize amido-functionalised NHC ligands bearing imidazole, triazole and benzimidazoles rings.
(*ii*). To synthesis nickel complexes of these amido-functionalised NHC ligands.
(*iii*). To explore the utility of the nickel NHC complexes in a number of catalytic transformations namely, the cross-coupling and enantioselective cyclopropanation reactions.
(*iv*). To carry out a detailed mechanistic study, involving experimental and computational means, for obtaining a better understanding of the catalytic cycles. The knowledge in turn would be used in designing better catalysts.

Expected outcomes

Highlight the expected outcomes of the project

(*i*). Several amido-functionalised NHC ligands bearing imidazole, triazole and benzimidazoles rings would be synthesised.
(*ii*). Several nickel complexes of these amido-functionalised NHC ligands would be synthesized.
(*ii*). The utility of these nickel complexes with the amido-functionalised NHC complexes a number of catalytic transformations namely, the cross-coupling and enantioselective cyclopropanation reactions would be explored.
(*iii*). The mechanistic insights on the mode of action of these nickel NHC complexes for these catalytic transformations tried also be studied.

How will the project address the Goals of the above Themes?

Describe how the project will address the goals of one or more of the 6 Themes listed above.

The proposed would develop improved high performing catalysts for transformations that would be useful to the Clean Energy goal.

Capabilities and Degrees Required

List the ideal set of capabilities that a student should have for this project. Feel free to be as specific or as general as you like. These capabilities will be input into the online application form and students who opt for this project will be required to show that they can demonstrate these capabilities.

A PhD student having Masters degree in Inorganic or Organic Chemistry is required to carry out the project.

Potential Collaborators

Please visit the IITB website www.iitb.ac.in OR Monash Website www.monash.edu to highlight some potential collaborators that would be best suited for the area of research you are intending to float.

(a). Professor Prasenjit Ghosh (from IIT Bombay)
(b). Professor Joel Hooper (from Monash University)

Select up to **(4)** keywords from the Academy's approved keyword list **(available at http://www.iitbmonash.org/becoming-a-research-supervisor/)** relating to this project to make it easier for the students to apply.

Chemistry
Catalysis
Nanotechnology and Nanosceince
Biosciences