IITB-Monash Research Academy

Indian Institute of Technology Bombay | MONASH University

An Indian-Australian research partnership

Project Title:	**Gold Complexes of N-heterocyclic Carbene Ligands Derived from Bicyclic and Tricyclic Rings having Restricted Rotation Along the Bond Containing Chiral Auxiliary in Asymmetric Catalysis**	
Project Number	**IMURA0782**	
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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

Despite been largely known as an inert coinage metal, the catalytic exploits of gold are only coming to light in recent times. This has generated an unprecedented interest in gold catalysis. In this context, we rationalised that N-heterocyclic carbenes (NHC), which are immensely successful as ligands in homogeneous catalysis, might make the otherwise inert metal, gold, active in catalysis. Subscribing to this view, we have successfully demonstrated the utility of NHC-gold complexes for producing polylactides from cyclic L-lactides under the melt polymerization conditions. The NHC-silver complexes were also demonstrated to be effective in performing the cyclic lactide polymerization reaction.

In the current study, we propose to further explore the potential of NHC-gold complexes in asymmetric catalysis. Towards this end, a series of bicyclic and tricyclic NHC ligands possessing restricted rotation along the bond containing the chiral auxiliary would be synthesized using multi-step synthetic sequences. A variety of chiral substituents of different steric demands would be incorporated on the NHC ligands, with subsequent metalation yielding the corresponding gold and silver complexes. The target NHC-gold complexes, along with their silver complex analogues, are shown in Figure 1. The catalytic scope of the NHC-gold complexes would be assessed in a variety of asymmetric chemical synthesis studies. These synthetic studies would involve realising the asymmetric intermolecular reaction chemistry of 1,3-dienes, ketones, imines and 3-phenanthrenols with chiral NHC-gold carbenoid species derived from a diazo compound and the chiral metal catalyst (Scheme 1). The chiral gold(I)-catalysed tandem cyclopropanation/Cope rearrangement of a vinyl diazo ketone with 1,3-dienes would be expected to lead to the one-step enantioselective assembly of a wide variety of partially hydrogenated azepine, cycloheptane and oxepine derivatives (Scheme 1a). Likewise, it would be envisaged that the gold(I)-mediated [2 + 2 + 1] cycloaddition of ketones and imines will produce a route to a wide range of synthetically valuable enantioenriched 1,3-dioxolanes and imidazolidines (Scheme 1b). It would be anticipated that the tandem C–H bond insertion/lactonisation of a variety of 3-phenanthrenols and cyclic diazoketone derivatives will provide a one-step synthesis of enantioenriched [*n*]-helicenes (*n* = ≥ 5, Scheme 1c). In these reactions, the initial selective nucleophilic addition at carbon would be achieved by exploiting *in situ* formed gold carbenoid species containing a chiral electron-deficient substitution pattern on the NHC ligand (highlighted in green inset) to be more carbophilic cation in nature. This new approach to [*n*]-helicene synthesis will be significant as it would reduce the number of steps to this immensely important compound class from typically greater than twelve to five from commercially available reagents. Following the footsteps of the developed gold chemistry, these catalysis studies would also be extended to the silver complexes as a measure to compare reactivities and selectivities. In

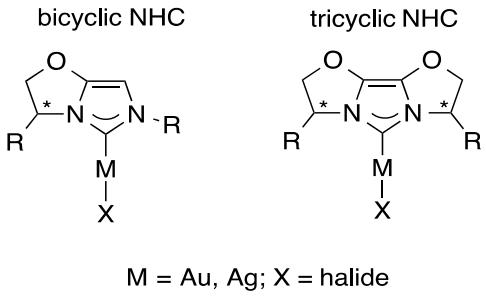
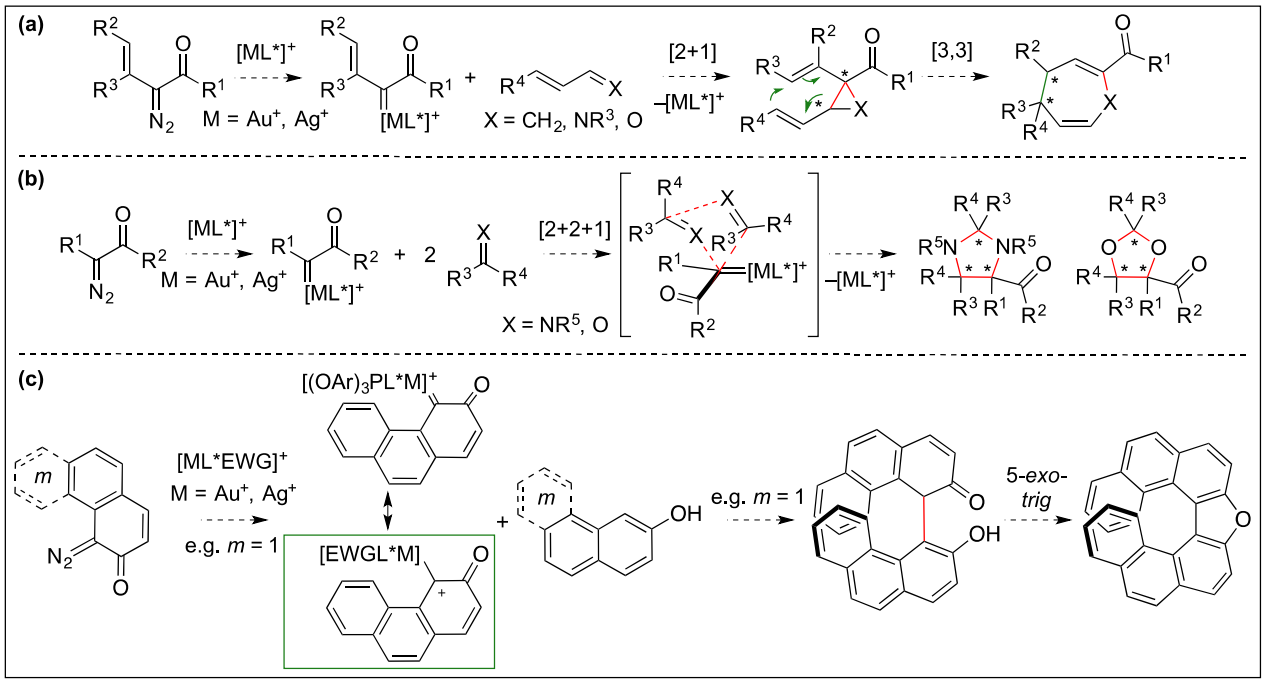


Figure 1. Proposed NHC-gold and -silver complexes for asymmetric catalysis

order to obtain an insight on the catalyst mode of action, a thorough mechanistic study would be undertaken using experimental and computational methods. The knowledge obtained from these investigations would, in turn, help to design improved catalysts for the studied transformations.



Scheme 1. Intermolecular reactivities of chiral NHC-metal carbenoid species

Project aims

Define the aims of the project

(*i*). To synthesize a series of bicyclic and tricyclic NHC ligands possessing restricted rotation along the bond containing the chiral auxiliaries.
(*ii*). To synthesis gold and silver complexes of these bicyclic and tricyclic NHC ligands.
(*iii*). To explore the utility of the gold and silver NHC complexes in a variety asymmetric transformations including that of the asymmetric intermolecular reactions of 1,3-dienes, ketones, imines and 3-phenanthrenols,
(*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 new bicyclic and tricyclic NHC ligands possessing restricted rotation along the bond containing the chiral auxiliaries would be synthesised.
(*ii*). Several new gold and silver complexes of these bicyclic and tricyclic NHC ligands would be synthesized.
(*ii*). The utility of these gold and silver NHC complexes in a variety asymmetric transformations including that of the asymmetric intermolecular reactions of 1,3-dienes, ketones, imines and 3-phenanthrenols would be explored.
(*iii*). The mechanistic insights on the mode of action of these gold and silver NHC complexes for the asymmetric catalysis tried would 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 Philip Wai Hong Chan (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