

PRF Annual Report on Research

1. DNI 58841
2. Asymmetric C-C Bond Construction Utilizing Organoboron Reagents via Cooperative Catalysis for the Synthesis of Chiral Amines from Petrochemical Feedstock
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4. N/A

Our research conducted during this grant period has resulted in the discovery of a new class of Cu-NHC catalysts that allow for a significant improvement of transition-metal-catalyzed addition reactions. The catalytic system stems from the idea of unsymmetrical modification of the ligand scaffold, which collectively leads to (1) significantly improved synthesis of sterically-bulky NHC ligands; (2) rational modification of the buried volume and chelating properties; (3) exploration of new ligand space; and (4) facile introduction of the peripheral substitution. At present, a library of ten distinct Cu-NHC catalysts has been prepared. Five catalysts have been fully characterized by the x-ray crystallography. The catalysts can be classified into the following classes: (1) sterically-bulky; (2) chelating; and (3) peripherally-substituted catalysts with a general structure based on imidazolylidene ring. Although investigation of catalytic properties did not reveal activity in the nucleophilic addition of organoboranes to polar bonds, we have demonstrated that these novel catalysts are extremely active in β -hydroboration, α -hydroboration and carboboration reactions. Using this catalyst system, the reactions can be conducted at 0.02 mol% loading under open air, room temperature conditions to provide tri-substituted vinylboronates, while the synthesis of tetra-substituted vinylboronates proceeds efficiently at 1.0 mol% loading. At present, we have investigated the scope of these reactions, demonstrating high activity in fifteen examples with excellent functional group tolerance (halides, nitro, cyano, polar heterocycles). We anticipate to complete this work and submit the preliminary communication by the end of this calendar year. More broadly, the developed catalyst scaffold is applicable to other metals, including precious metals, such as Pd, Rh, Ir and coinage metals, such as Au. Our preliminary investigations resulted in the synthesis and isolation of representative metal-NHC catalysts based on Pd and Rh. Investigation of the catalytic activity of these catalysts in metal addition reactions is ongoing.

In terms of impact, the development of new more efficient ligands and catalysts represents one of the most important areas of catalysis, including conversion of simple petrochemical feedstock chemicals to complex and valuable materials. This type of catalysts is among most routinely employed across various subfields of chemistry. The catalysts developed during the life of this grant have already been shown to be more effective than the most reactive catalysts reported in the literature to date for the synthesis of boronates. We are optimistic that further investigation of the catalytic properties will uncover the catalyst system for the nucleophilic addition of organoboronates to polar bonds, which will set the stage for the asymmetric addition. Dr. Qun Zhao has been fully involved in the development of the above-noted reactions. The grant has enabled Dr. Qun Zhao to gain experience in NHC ligand synthesis and Cu-NHC catalysis, which has been instrumental in his future career prospects in academia. The grant has enabled the PI to research novel NHC ligands and develop new transition-metal-catalyzed addition reactions for the conversion of simple petroleum-derived chemicals into valuable products. The ligand scaffold is applicable to other metals, setting the stage for a much broader research project. We are optimistic that further investigations in the second year will demonstrate utilizing Cu-NHCs as reactive catalysts for the controlled addition of organoboranes and other nucleophiles to petroleum-derived feedstocks.

We are extremely grateful for the support from the ACS PRF. The grant has been essential in securing the results and jump-starting the research on Cu-NHC catalysis. We hope to explore the activity of Cu-NHC catalysts in the second year of the grant and plan external grant submissions to federal agencies in the following years.