PRF#: 57257-DNI3
Project Title: Developing Ruthenium-Boryl Catalysts for Olefin Metathesis
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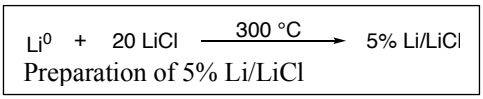
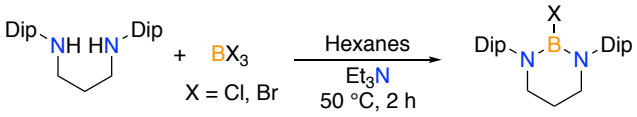
Progress of the Research: The project is aimed at developing the chemistry of boron analogues of the ubiquitous N-Heterocyclic carbene ligands (NHCs). The project is broken down into three sections: ligand synthesis, metal complex synthesis, and catalysis with the metal complexes. The ultimate goal is to advance the knowledge on the properties of N-heterocyclic boryl ligands (NHBs) and prepare Grubbs-type ruthenium olefin metathesis catalysts featuring NHBs. In regards to ligand development, our inspiration is from the seminal paper by Nozaki and coworkers (*Science*, 2006) on the synthesis of a boryl-lithium complex. This compound is viewed as an anionic variant of Arduengo's NHC and acts as a nucleophile as well as coordinates to metals, although examples of the latter are minimal.

Given that the five-membered unsaturated boryl-lithium complex is known and is a viable precursor to metal complexes, we have been working on reproducing the synthesis. It is a challenging synthesis but we have experimental evidence that we have been able to prepare it. The lithiation of the bromo-diazaborole is a lengthy reaction at low temperature (-20 °C) and the boryl lithium species is not stable above these temperatures or in the solid-state and accordingly, must be used in situ. We have attempted to use commercial sources of lithium metal but achieve yields lower than the literature (quantified by trapping reactions). From these efforts, we believe that the literature method using lithium powder (rather than commercial lithium) is likely the best protocol for this transformation. We have developed a method to deposit lithium metal onto lithium chloride (5% by weight) in order to achieve the similar high surface area of the powder. Examining this mixture in other known lithiations results in more rapid reaction times than commercial lithium pellets with reproducible results. From these investigations, it appears that the Li/LiCl mixture is easier to prepare and handle in comparison to lithium powder. Efforts are ongoing to utilize this mixture for the reduction. In addition, we are also preparing lithium powder since it is not commercially available to replicate Nozaki's reduction conditions.



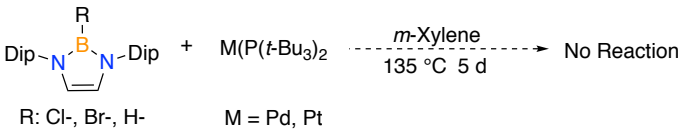
Preparation of 5% Li/LiCl

We have conducted calculations on a variety of model compounds that indicate the sigma-donating and pi-accepting properties of boryl ligands are dependent on the ring size as well as the substitution on the backbone. From these preliminary calculations, we recognized that the unknown saturated six-membered NHB has significantly different properties than Nozaki's five-membered NHB. This has become a target and we have successfully prepared the ligand precursor, a diaminohaloborane where the halide is either chlorine or bromine. The lithiation of these species will be attempted in due course.



Synthesis of six membered N-heterocyclic boryl precursor. Dip = 2,6-diisopropylphenyl

We have also attempted a method alternative to transmetallation to introduce boryl ligands on transition metals. Recognizing that it is possible for boron-halides/hydrides to undergo oxidative addition with late transition metals, we reacted unsaturated five-membered Cl-, Br-, and H-diaminoboranes with $Pd(P^tBu_3)_2$ and $Pt(P^tBu_3)_2$. Unfortunately, no reactivity was observed by ^1H, ^{11}B, or ^{31}P NMR spectroscopy, even at elevated temperatures (135 °C) after 5 days.



Attempts of preparing metal-boryl complexes via oxidative addition.

Impact on research career: This award has been a tremendous boost to my career and research program for multiple reasons. It has enabled me to branch out to a new project that has very little preliminary data and otherwise, may have had significant difficulties obtaining funding for. The funds have been primarily used to support students working on the project that has enabled them to focus their time on research. The students involved in the project have been able to learn a variety of areas of chemistry including ligand design, catalyst design, advanced inorganic synthesis, and critical thinking that should prepare them for their own independent careers. This award has also helped strengthen my tenure package as being recognized as an ACS PRF Doctoral New Investigator is viewed with prestige in the community.