

PRF#: 57257-DNI3

Project Title: Developing Ruthenium-Boryl Catalysts for Olefin Metathesis

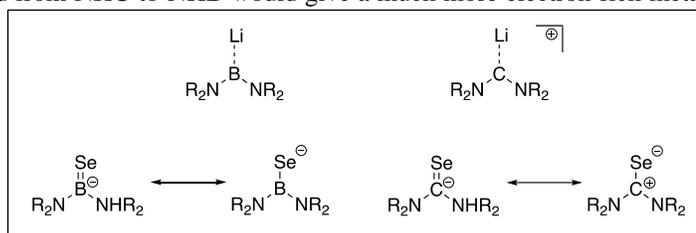
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### Progress of the Research:

In the past year, our efforts have been focused on reproducing the synthesis of the known N-heterocyclic boryl (NHB) lithium complex, assessing the properties of a variety of NHBs computationally, and attempting to prepare metal complexes. In regard to the synthesis of the NHB lithium complex, it is challenging but we have experimental evidence that we have been able to prepare it. We have attempted to use commercial sources of lithium metal but achieve yields lower than the literature. From these efforts, we believe that the literature method using lithium powder (rather than commercial lithium) is likely the best protocol. We have developed a method to deposit lithium metal onto lithium chloride (5% by weight) in order to achieve the high surface area of the powder. Kinetic experiments indicate that more rapid reaction times are observed with Li/LiCl powder than commercial lithium pellets. Comparison studies with other forms of lithiums are ongoing. We have been able to scale the synthesis and believe it could be a reductant used by many synthetic chemists as it is safer to handle than lithium powder.

Due to the lack of NHB variants that have been accessed, we have been performing calculations to assess the  $\sigma$ -donor and  $\pi$ -accepting properties of NHBs with different backbones. In this study, we have examined the geometric, thermochemical, and electronic properties of their adducts to the  $\text{Li}^+$  cation and Se atom, as compared to the analogous neutral NHCs. The studies on lithium cation adducts evaluates the  $\sigma$ -donation while the selenium complexes serve to assesses the  $\pi$ -accepting ability. The results indicate that boryl anions have a weaker  $\pi$ -accepting ability than NHCs, but it is still a non-negligible factor in the bonding interactions between boryl and the Se atom. The tuneability of the  $\pi$ -accepting capacity of boryl anions is similar to that of NHCs, indicating potential for modification of the electronic properties of metal complexes incorporating boryl ligands. The boryls are calculated to be significantly better  $\sigma$ -donors than NHCs, which suggests that replacing a ligand from NHC to NHB would give a much more electron-rich metal complex including a more negative formal charge. Using a boryl ligand with better  $\pi$ -accepting ability could potentially reduce the charge on the metal if that was desired for a given application.

Attempts to prepare metal complexes thus far have been unsuccessful. We are investigating alternative strategies to access them including metathesis and oxidative addition routes.



**Impact on research career:** The award enabled the diversification of my research program to ligand development. It also stimulated branching out into computational chemistry. The funds have supported students on this project, including Mr. Leif Laperriere who just completed his MSc thesis. The diverse aspects of the project have been excellent for training personnel. In addition, I was recently promoted to Associate Professor with tenure that was assisted by the support from this by this grant.