Development of New Catalysts Through the Synthesis and Characterization of High-valent Metal Complexes

Keit Dine,1 Bart Iwan,1 and Wei-Tsung Lee1
1Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL 60660, USA

Introduction

Efforts have been made to develop new catalytic materials based on transition metals. Transition metal complexes are often used in catalysis because the metal center can take on multiple oxidation states.1,2 Traditionally, these metal complexes utilize rare metals like gold, platinum, and palladium because of their ability to control the properties of reactivity. Since these metals are expensive, new metal complexes need to be developed that are both inexpensive and functions as efficient catalysts. To develop a more cost-effective catalyst design, a focus was placed on the synthesis of high-valent, first-row, transition metal complexes. First-row transition metals have the potential to form high-valent metal complexes which are stabilized by coordinating with strong electron-donating ligands. To this end, metal complexes supported by a rigid CNC-pincer ligand, CNC2Bu(ImdBu)2, were synthesized and characterized.

Background

- The scaffolding of high-valent metal complexes are electron-rich ligands.
- Imidazole base ligands have the potential to form carbenes upon deprotonation.3
- Carbenes are of interest because of their strong electron donating properties, a powerful catalytic feature.4

Fig. 1: First and Second Generation Ligands

Results

- CNC CNC2Bu(ImdBu)2 pincer Ligand has been synthesized successfully (Scheme 1).
- Ligand had been successfully modified through alkylation (Scheme 2).
  - Installing electron donating groups likely increases carbene activity
  - Carbene formed after deprotonation with 3 equivalents of lithium diisopropylamide (LDA)
- The Fe complex has been synthesized successfully (Scheme 3).
  - Red reaction turns into a blue product after workup
  - Suggestive of solvent binding
  - NMR shows some paramagnetic activity

Future Work

- Synthesize ligand and make more precursor (Scheme 1)
- Produce more modified ligand (Scheme 2)
- Synthesize metal complex using different first-row transition metal salts (Scheme 3)
- Obtain crystal structures and begin reactivity studies

Acknowledgments

I give sincere thanks and appreciation to Dr. Wei-Tsung Lee for giving me the opportunity to join his research lab and mentoring me. This research is also supported by Adriana Lugosan, who trained and assisted me. In addition, I would like to thank Bart Iwan for synthesizing the precursor. I would also like to show gratitude to Loyola University Chicago for funding this work.

References

3. Alba Vellé, Andrea Cebollada, Ramón Macias, Manuel Iglesias, María Gil-Moles, Pablo J. Sanz Miguel ACS Omega 2017 2(4), 1292-1399
4. Jan C. Bernhammer, Ning Xi Chong, Ramasamy Jothibasu, Binbin Zhou, and Han Vinh Huynh Organometallics 2014 33(13), 3607-3617