Bimetallic Complexes for Small Molecule Activation

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Thornton Research Group – Virginia Tech Chemistry Department

Thornton Research Group

The Thornton Research group was welcomed into Virginia Tech in August of 2020 with the aim to overcome challenging transformations, such as the conversion of hydrocarbons into commonly-used products, using inorganic complexes. In order to convert common hydrocarbons (example, petroleum feedstocks) into useful and chemically valuable compounds, the C-H bonds must be selectively cleaved off to form more reactive compounds. The focus of their research is to develop systems using first-row transition metals (which are abundant and cheap) to cleave C-H bonds or other strong bonds (example C-O in CO_2) using either polarized metal-metal interactions or bimetallic complexes inspired from enzymatic systems.

titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper
22	23	24	25	26	27	28	29
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
47.867	50.942	51.996	54.938	55.845	58.933	58.6934	63.546

My Role: Undergraduate Researcher

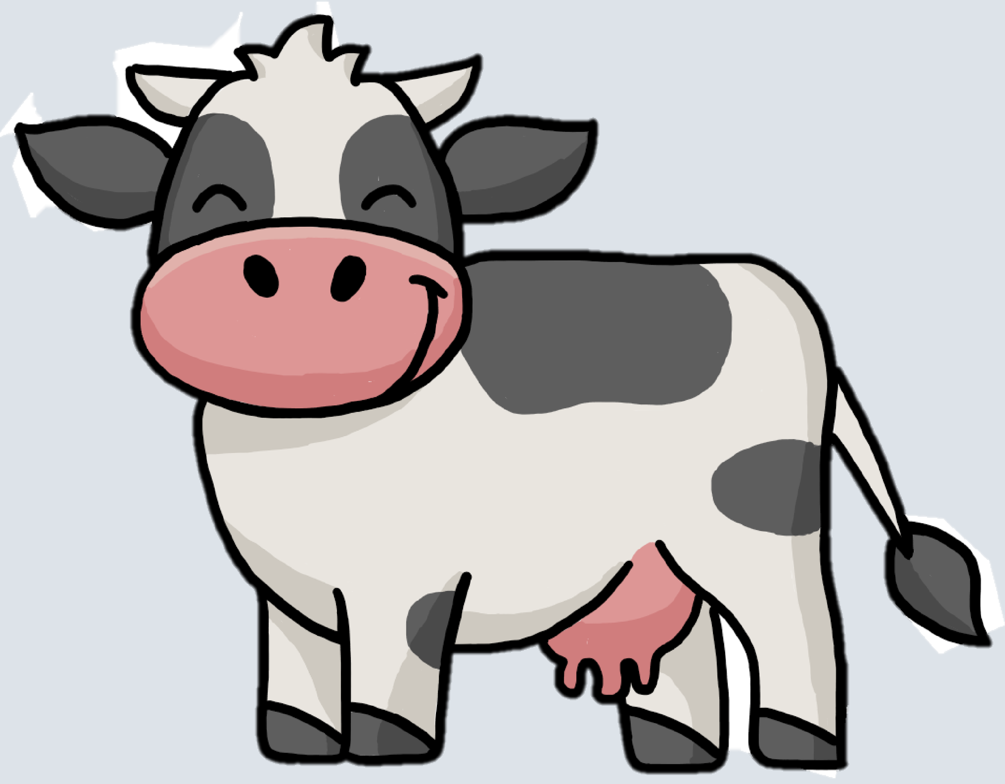
My research within the Thornton Research Group was under Professor Diana Thornton and my graduate student mentor Matthew Williams. I worked as an undergraduate researcher with the responsibility of synthesizing bimetallic ligands and testing their reactivity from August 2022 to May 2023 on Virginia Tech Campus. Personally, I chose this experience to be more involved in research and to explore my love for chemistry and understand the research process as a possible career path.

Why is this Important?

Methane is known to be a pollutant that is produced from various processes and environments such as agricultural and livestock farming, oil and gas production, and landfills. Its abundance in the atmosphere is harmful to the earth, contributing to global warming. Methane is better at trapping heat than carbon dioxide, making it significantly more harmful in the long run.

At the industrial level, methane activation methods demand high levels of energy and resources to successfully convert the pollutant to methanol. Nature provides a solution for this with the presence of methane monooxygenase enzymes that convert available methane into methanol. However rare they are, they provide inspiration for synthetically made molecules that can react with methane similarly.

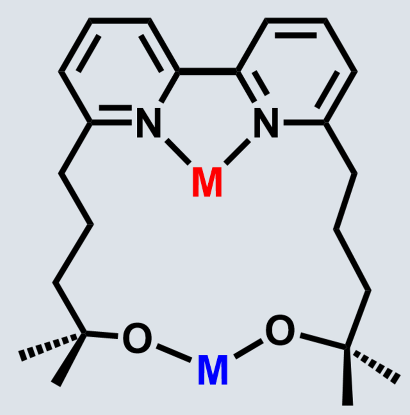
Our goal is to provide a cheaper and more readily available process to create the useful form of methanol to recycle the methane in the atmosphere. Methanol is popularly used as an industrial solvent and provides an efficient way to use the abundance of methane.



My Projects

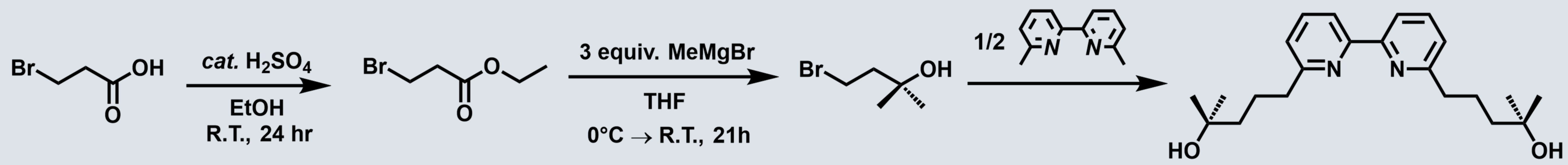
Overall Goal: to synthesize bimetallic complexes with polar metal-metal interactions and test their reactivity for cleaving strong bonds. Polar metal-metal interactions can be obtained by having two distinct metals, two metals in different oxidation states, or two of the same metals with different coordination environments. Upon synthesizing a compound with one of the latter properties, reactivity will be performed to test their ability to cleave bonds starting with weak (easily reactive) bonds and building towards stronger bonds such as those in CO_2, H_2, CH_4, and N_2.

O/N - ligands



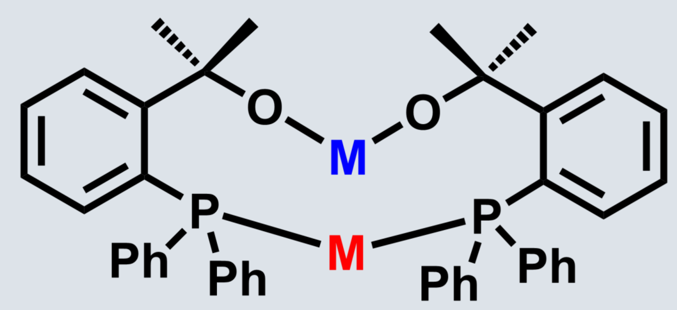
My role in this project began over the summer of 2022 and I was working in the lab 4 hours each day to build this ligand (shown to the left, inspired from *Eur. J. Inorg. Chem.* **2003,** 467-474) and then to test its reactivity with different metals. My main work consisted of conducting organic chemistry reactions to prepare this ligand from 3-bromopropionic acid as seen in the scheme below.

Left:
- M = Co, Ni, Fe
- M = Ti, V, Cr

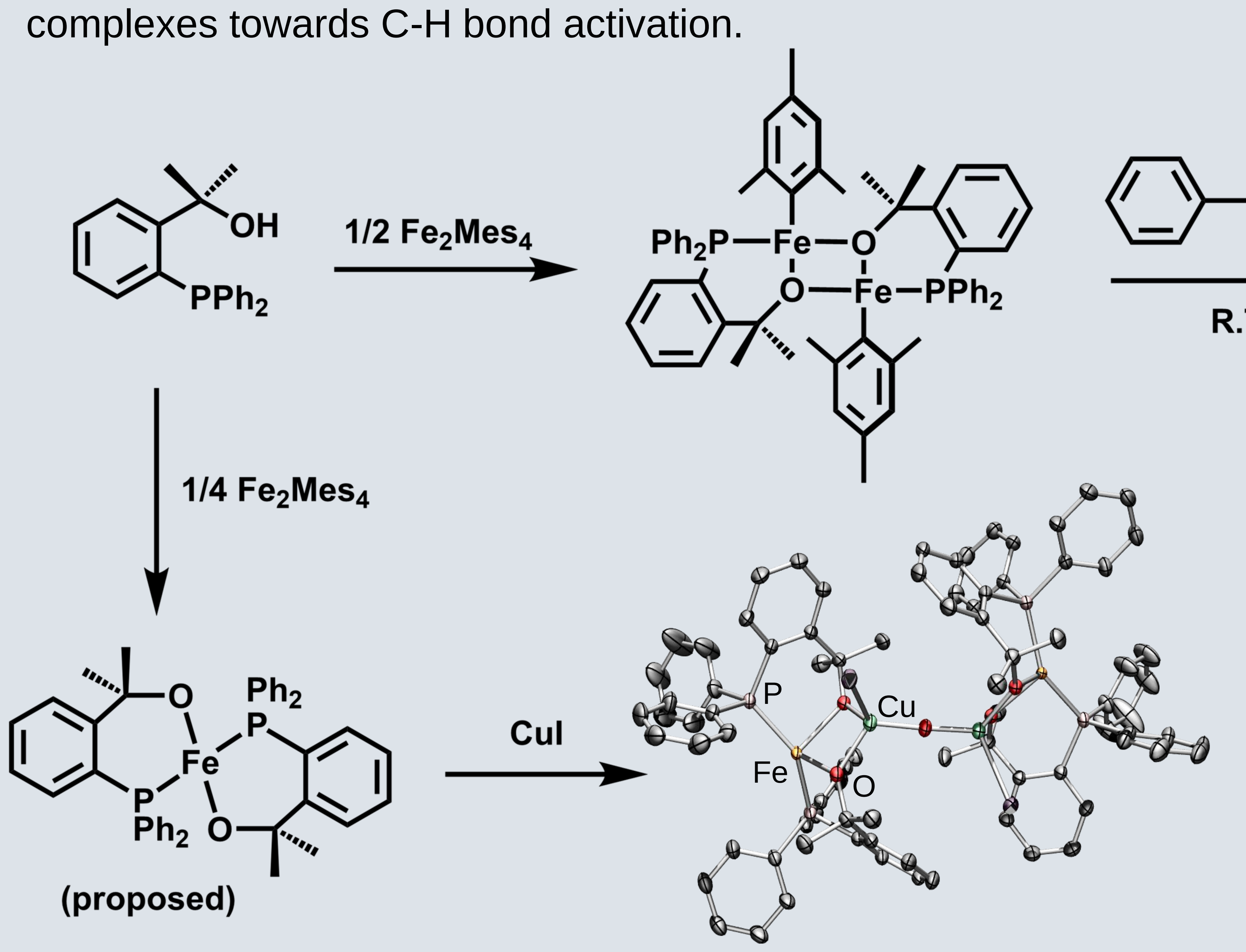


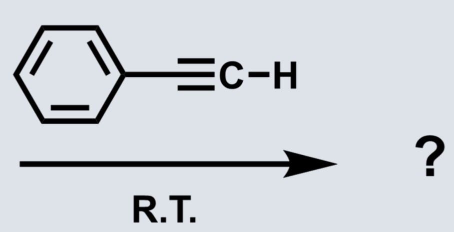
O/P - ligands

My role in this project began over the Fall 2022 semester and I will continue my work over the summer of 2023. I did research for two credit hours for the fall and spring semesters of 2022 and 2023, respectively. The compound to the right was the proposed bimetallic complex. My role was to react the alcohol ligand with various metals and test the reactivity of the resulting complexes towards C-H bond activation.



M – Co, Ni, Fe
M – Ti, V, Cr, Fe





I began working with the alcohol ligand shown and reacted it with iron mesityl in two different ways. First, as shown by the upper pathway, I reacted 2 equivalents of the alcohol with the iron compound to form an iron dimer. The two iron centers provided a possible means of activation which was tested by reacting this species with phenylacetylene (which has a very reactive and acidic C-H bond). The results showed that a reaction occurred, and we are working to identify the products formed. If the C-H bond was indeed properly activated, this is promising as we can move to testing the reactivity of the bimetallic complex with stronger bonds such as methane and carbon dioxide.

Second, I reacted 4 equivalents of the alcohol ligand with the iron mesityl which we propose to have formed an iron compound as seen in the pathway above. I began to test the addition of a second metal, beginning with copper. The resulting iron-copper complex was crystalized and confirmed by single crystal X-ray diffraction. The crystal structure confirms a hetero-bimetallic system and a metal-metal interaction which could be suitable for C-H bond activation.

Next steps – Experiment with other metal combinations in the proposed complex, test the reactivity of the iron-copper complex, and continue to investigate the reaction of phenylacetylene with the iron dimer complex.

Summary

Over the course of the past year, I have learned many valuable lessons within this laboratory. First, I have gained appreciation for the process of trial and error. The power of brainstorming with teammates and constantly discussing possible executions for the next steps of the project helped shape my motivation to keep up my effort when results were not as expected. Second, I acquired a love for research and laboratory work where the environment is always ready to teach you more. Third, I got to make my love for chemistry a real experience in my undergraduate years and I will never regret that! Although my future career may not be directly in the chemistry field, I am glad I got to explore it with talented and enthusiastic chemists.

Miyaji, A. (2011). Particulate methane monooxygenase from Methylosinus Trichosporium OB3B. *Methods in Methane Metabolism, Part B: Methanotrophy*, 211–225. https://doi.org/10.1016/b978-0-12-386905-0.00014-0
What's the deal with methane? UNEP. (n.d.). Retrieved April 13, 2023, from https://www.unep.org/news-and-stories/video/whats-deal-methane#:~:text=It%20is%20responsible%20for%20more,years%20after%20it%20is%20released.