

Bimetallic Catalysis Project Summer Research

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Human activity in recent decades has rapidly accelerated global climate change, in large part due to the release of greenhouse gasses into the atmosphere through the combustion of fossil fuels. To mitigate the devastating impacts of climate change in future years, it is crucial that we replace the use of fossil fuels with renewable sources of energy such as wind, solar, and hydroelectric. However, because many renewable energy sources are by nature intermittent, there exists a significant need for efficient mechanisms to store energy from renewable sources for later use. While hydrogen gas (H_2) has been proposed as a possible storage mechanism for renewable energy, H_2 cannot be readily compressed or liquified under reasonable conditions, limiting its practicality in applications that require high-density fuels such as petroleum-based transportation industries. However, combining sustainable hydrogen production with subsequent carbon fixation (hydrogenating small molecules such as CO_2) would solve the problems associated with using hydrogen as a synthetic fuel, providing a sustainable mechanism for the synthesis of high-density liquid fuels such as methanol, formic acid, and liquefied methane¹. In this proposed carbon-neutral energy cycle², energy from renewable sources would be used to produce hydrogen gas through electrolysis. Next, a heterobimetallic catalyst would be used to hydrogenate small, carbon-based molecules to produce synthetic liquid fuels, using the hydrogen gas produced in the previous step along with carbon dioxide captured from the atmosphere. Finally, these liquid fuels could later be burned to release their stored energy and complete a carbon-neutral energy cycle.

The overarching goal of our project is the development of a heterobimetallic catalyst that would drive the hydrogenation of small, carbon-based molecules such as CO_2 to produce high-energy-density, synthetic liquid fuels. This catalyst would play a critical role in a proposed carbon-neutral energy cycle that combines hydrogen production with carbon fixation to generate synthetic liquid fuels that could efficiently store energy from renewable sources. The organic scaffold for our proposed bimetallic catalyst contains two ligands tethered together: a cyclopentadiene (Cp) group and an N-heterocyclic carbene (NHC) group^{3,4,5}. With two different binding sites, this Cp-NHC bifunctional ligand would be poised to form bonds with two disparate transition metals, a key part of our catalyst design. We hypothesize that the proposed bimetallic complex would be an efficient catalyst for fuel production because of its bimetallic nature: one metal supports a nucleophilic hydride designed to attack a carbon source such as CO_2 , while the other metal supports a relatively electrophilic hydride designed to complete the catalytic cycle.

This summer, we synthesized, isolated, and characterized via NMR and Liquid Chromatography Mass Spectrometry two versions of the Cp-NHC bifunctional ligand that will serve as the organic scaffold for our proposed catalyst. The synthetic pathways for each version of the bifunctional ligand are shown below in Figure 1. The final step in the synthesis of each ligand, the elimination of one of the two imidazole (NHC) groups, proved particularly difficult due to the reaction's air and moisture sensitivity. When exposed to air and/or "wet" solvents, decomposition rapidly occurred, yielding a dark, tar-like sludge rather than the desired solid product. We were able to address the air/moisture sensitivity of this final step by drying solvents with 3Å molecular sieves and using Schlenk line and glove box techniques to maintain inert conditions. Having synthesized two versions of the Cp-NHC bifunctional ligand, we plan to begin metalation experiments this fall as we attempt to construct our proposed bimetallic catalyst.

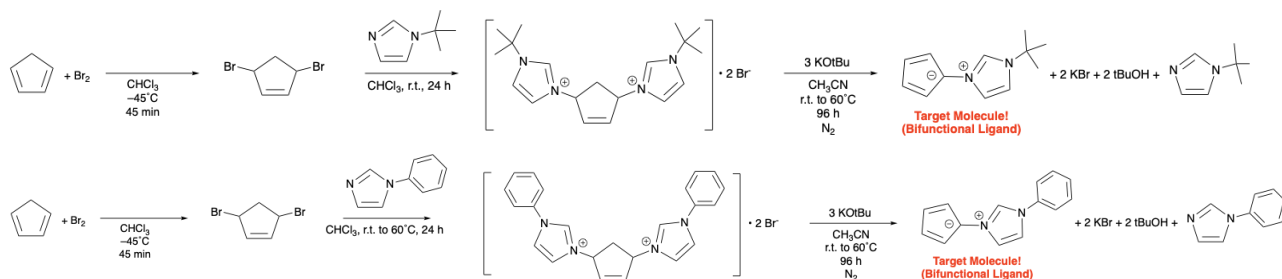


Figure 1. Shown above are the synthetic pathways for the two Cp-NHC bifunctional ligands produced this summer in the Tate Lab. The NHC group used in the first pathway is 1-butylimidazole, and the NHC group used in the second pathway is 1-phenylimidazole.

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References:

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