Phosphorous-Containing Small Molecules and Materials for Aerospace Systems

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Background & Significance

Phosphorus-based small molecules and materials have promising properties for the aerospace industry including energy storage via hydrogen fuel cells, 3D printing materials, novel electronic properties, molecular wires, CO_2 activation and storage, low temperature elasticity, and lightweight heat resistant materials. Additionally, these molecules are integral molecules in organic synthesis, catalysis, materials science, and biologically active molecules.

Despite an increase in interest and demand for these materials, there is a paucity of methods to form the phosphorous–phosphorous (P–P), phosphorous–carbon (P–C), and phosphorous–element (P–E) bonds necessary to make these materials, especially via efficient and sustainable methods.

Metal catalyzed hydrophosphination and dehydrocoupling are promising reactions to form these bonds and materials. Hydrophosphination is the addition of a phosphorous – hydrogen (P–H) bond across an unsaturated substrate and is 100% atom economical. Dehydrocoupling has the potential to generate these compounds with only H_2 as a byproduct.

Project Goals

The goals of this project were to expand upon the methods for P-C and P-P bond formation. Last year we discovered that commercially available Bis(acetylacetonato)copper(II) ($Cu(acac)_2$, **1**), a reagent found in most laboratories, is a highly active hydrophosphination catalyst. This year, our goals were to publish last year's work, elucidate the mechanism, and expand the scope and selectivity of copper catalyzed hydrophosphination.

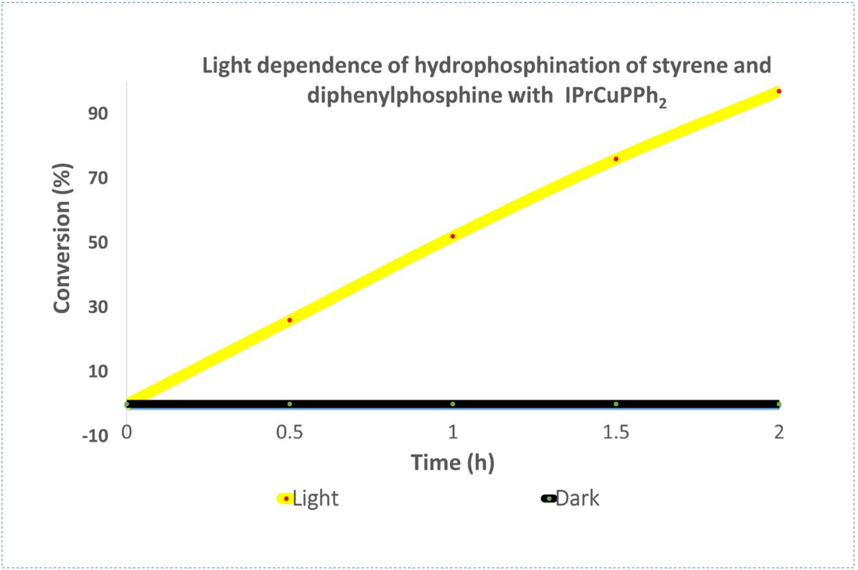
Summary of Key Findings

We were able to publish that $Cu(acac)_2$ is the most active catalyst for the hydrophosphination of unactivated alkenes to date (S. G. Dannenberg and R. Waterman, Chem. Commun. 2020, 56, 14219-14222).

A second manuscript focusing on the mechanism of catalysis is forthcoming. Our findings suggest an insertion-based mechanism that differs dramatically from previous late metal hydrophosphination catalysts. We were also able to demonstrate that styrene can only insert into an NHC-copper phosphido under irradiation. Continued study will allow us to make further improvements to reactivity by studying the factors that increase or decrease the length of the Cu-P bond.

We also obtained single crystal X-ray diffraction (XRD) data of potential catalytic intermediate with the molecular composition of $(Ph_2P)_4Cu_4[P(^tBu)_3]_2$. The key to isolating this intermediate was addition of electron rich P^tBu_3. As there are few reports of these types of compounds, our finding will be an important addition to the literature. Importantly, this compound is more catalytically active than **1** and led to the discovery that copper (I) compounds, such as Cu(I)OAc, are also more active than **1**. This is an improvement over our state of the art catalyst.

I have also made substantial progress towards enantioselective hydrophosphination to generate phosphines that are chiral-at-carbon. I successfully synthesized and tested several chiral catalysts. As predicted, these compounds were active under irradiation and we were able to achieve high yields and up to 18% enantioselective excess (ee). Despite modest selectivity, it is a promising first example of selectivity with these previously unstudied substrates. It also provides a proof of concept that reaction kinetics can be tuned to select for one enantiomer preferentially by addition of a chiral ligand. We anticipate that systematic modification and optimization of conditions will lead to improved selectivity. This work is now underway.



Demonstration of the necessity of light in copper catalyzed hydrophosphination