# Catalytic Synthesis of Phosphorous Containing Small Molecule, Polymeric and Pre-Ceramic Materials for use in Aerospace Systems

**Steven G. Dannenberg, University of Vermont**

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## Background & Significance

*Provide an introduction that provides background context and NASA significance for the study. 150 words maximum.*

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

*Concisely describe the specific goals of the project. 150 words maximum.*

The goals of this project were to discover highly active, earth abundant, hydrophosphination and dehydrocoupling catalysts. Our original hypothesis was that iron pyridine(diimine) (PDI) catalysts would be active and allow for the catalytic synthesis of phosphorous containing small and polymeric molecules to act as both functional and pre-ceramic materials. The expected outcomes of the project were: 1) the exploration of hydrophosphination and dehydrocoupling of phosphines and targeted main group molecules with a series of iron PDI catalysts; 2) Potentially more facile methods to generate known phosphorous containing small molecules, polymers, and ceramic precursors; and 3) Possible synthesis of materials with new physical and electrical properties for aerospace systems and beyond.

## Summary of Key Findings

*Describe the key outcome of your work in terms suitable for an educated, but non-expert reader. 300 words maximum.*

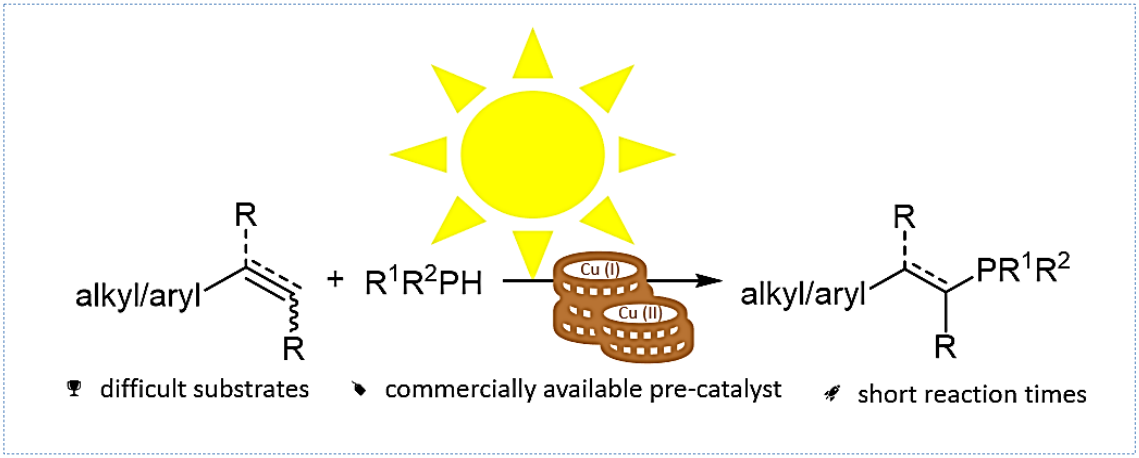
We discovered that commercially available Bis(acetylacetonato)copper(II) ($Cu(acac)_2$, **1**), a reagent found in most laboratories, is a highly active hydrophosphination catalyst. **1** is superior in terms of activity when compared to both our initially proposed iron PDI complexes or literature catalysts. Under thermal conditions, the activity of **1** is comparable to some of the best previously reported catalysts. However, under ambient temperature irradiation centered at 360 nm, the conversions are remarkable. Many reactions with **1** are complete in minutes, rarely reported unactivated substrates achieve high conversions within hours and several new substrates are accessible.

This discovery represents a potential change in the way hydrophosphination will be approached in the future. **1** is unique among active hydrophosphination catalysts because it can be handled from a benchtop without special conditions, it is air- and water-stable, is easy to handle, and exhibits low-toxicity. These properties, in conjunction with the high activity of **1**, allow for any synthetic chemist or materials scientist to use hydrophosphination for exploitation in late stage diversification of organic molecules or modification of materials.

The photocatalytic conditions are critical in this reaction. Furthermore, light appears to be a general strategy for enhanced hydrophosphination reactivity as several copper compounds exhibited improved reactivity under irradiation.

Mechanistic work suggests diverging pathways depending on the substrate, redox activation of copper, and formation of a copper-phosphido intermediate, all of which inform further catalyst development. The next step in this project is to further explore the reactivity of **1** in additional bond forming reactions, and to synthesize new active enantioselective catalysts using what we have learned.

In conclusion, this simple, bench-stable, inexpensive catalyst is highly effective and places hydrophosphination in the hands of many more synthetic chemists. This work has been submitted to the Journal of the American Chemical Society for publication.




Photocatalytic Hydrophosphination with Air-Stable and Commercially Available Bis(acetylacetonato)copper(II) ($Cu(acac)_2$, **1**)