

“Heterodehydrocoupling as a Route for Synthesizing Main Group Silicon–Element Bonds”

Matthew B. Reuter, Chemistry
AY 2020-2021 Progress Report

Background & Significance

Polymers and ceramics comprise an important group of materials that have a diverse array of chemical applications. Notably, ceramics are critical to the realm of aerospace technologies due to their intrinsic chemical resilience, mechanical prowess, and thermal stability. Importantly, many of these materials are comprised of main group element–element (i.e., E–E or E–E’) bonds. However, synthetic routes to forming these moieties are dominated by stoichiometric transformations, which not only form large quantities of waste but may also need additional purification steps that increase the overall waste generated from these reactions. Bond formation via dehydrocoupling reactions is a solution to stoichiometric transformations, as dihydrogen gas is the sole by-product of these reactions which also simplifies purification steps. Moreover, the liberation of dihydrogen gas provides an excellent kinetic and thermodynamic driving force, which accelerates the reaction to more stable products.

Project Goals

The general goals of this work were to synthesize metal heterodehydrocoupling compounds to catalytically form main group Si–E bonds, which could be utilized to form small molecules, polymers, and ceramics. This work was based upon the derivatization of iron dimer $\text{Cp}_2(\text{CO})_4\text{Fe}_2$ (**1**) which was found to couple small molecules such as silanes and alcohols, and silanes and amines. The two types of catalysts that were targeted were mixed-phosphine iron dimers and on-cycle iron-nucleophiles. The mixed-phosphine iron dimer (**2**) derivatives were expected to activate completely under visible-light irradiation compared to **1**, given the steric encumbrance of these species. The on-cycle iron-nucleophiles (**3**), either $\text{Cp}(\text{CO})_2\text{FeNR}_2$ or $\text{Cp}(\text{CO})_2\text{FeOR}$, were expected to rapidly form Si–E bonds, as these compounds completely overcome the necessary photoirradiative activation step encountered with **1**.

Summary of Key Findings

Initially, the synthesis of mixed-phosphine dimers **2** was targeted, however, after approximately a dozen reaction iterations, it was found that the route to these compounds was both extraneous and inefficient. Indeed, synthesis of these proposed dimers is several steps compared to **1**, which is also commercially available, and the resulting yields were far too small for even characterization. As a result, the on-cycle nucleophiles **3** were next targeted, however, similar to **2**, these compounds were shown to be too reactive for isolation and quantification. In the realm of applicability, the limitations related to both compounds makes them unfeasible for large-scale use. Yet, although both the mixed-phosphine dimers and on-cycle nucleophiles were abandoned, an alternative route to this type of reactivity was pursued that combined the goals of both projects, namely via in-situ catalyst activation with $\text{Cp}(\text{CO})(\text{PR}_3)\text{FeBr}$ and $\text{LiN}(\text{SiMe}_3)_2$. Importantly, these in-situ activation reactions revealed the critical role the simple lithium amide, $\text{LiN}(\text{SiMe}_3)_2$, plays in Si–N heterodehydrocoupling. Indeed, catalytic amounts of $\text{LiN}(\text{SiMe}_3)_2$ rapidly dehydrocouple both substituted and unsubstituted amines with primary, secondary, and tertiary silanes. Notably, the excellent reactivity of this compound in

small molecule coupling under ambient conditions rivals that of highly active *d*- and *f*-block catalysts. Current work is poised at publishing on small molecule Si–N heterodehydrocoupling with $\text{LiN}(\text{SiMe}_3)_2$. Future work is aimed at expanding this reactivity to other nucleophilic substrates such as alcohols, thiols, and phosphines, as well as exploring the potential of these products to form polymers and ceramics.

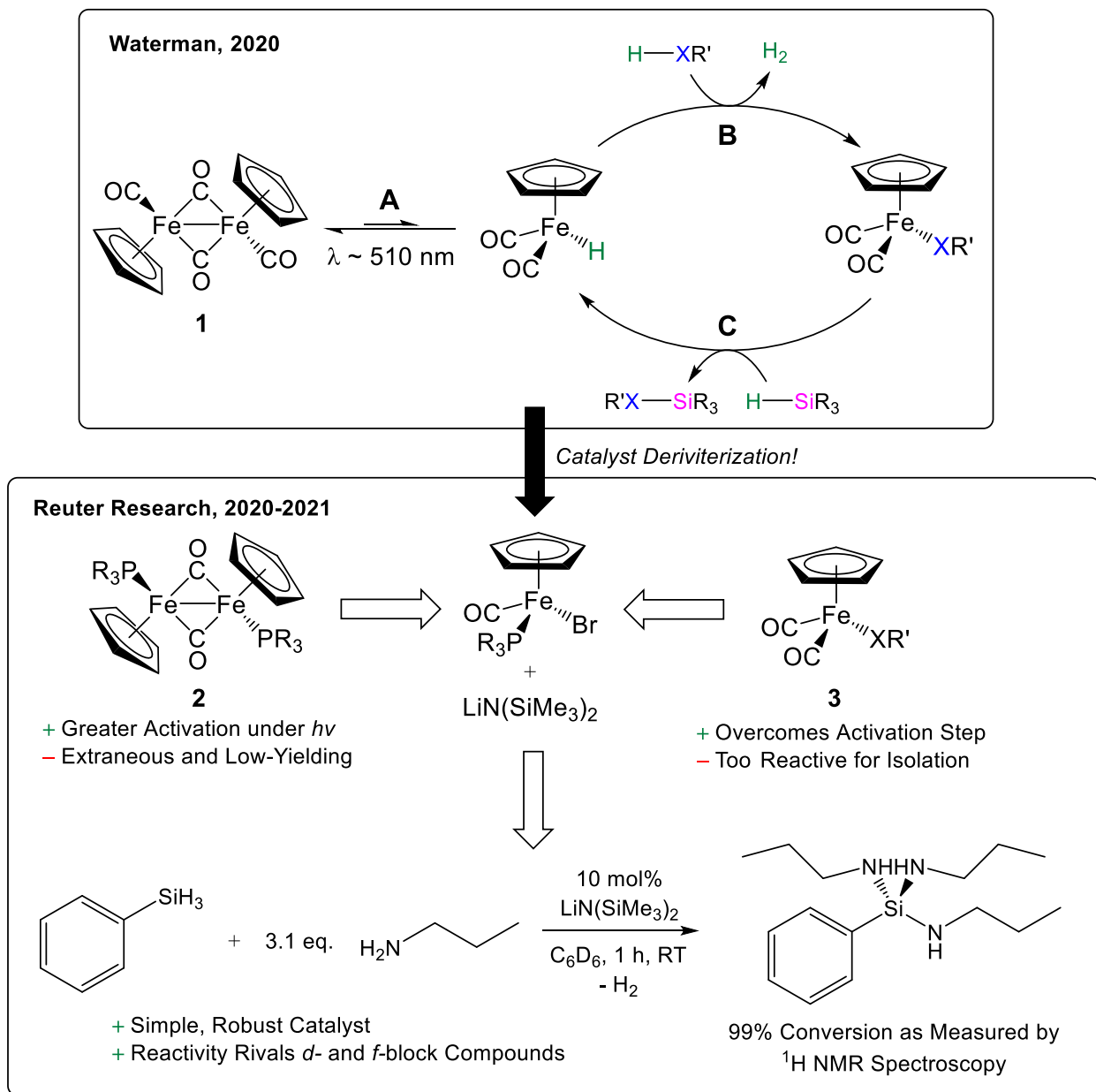


Figure 1. Research goals and key findings related to funded research.