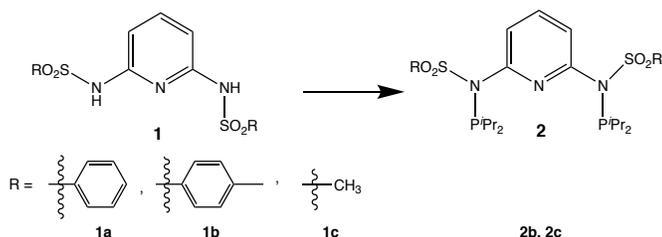
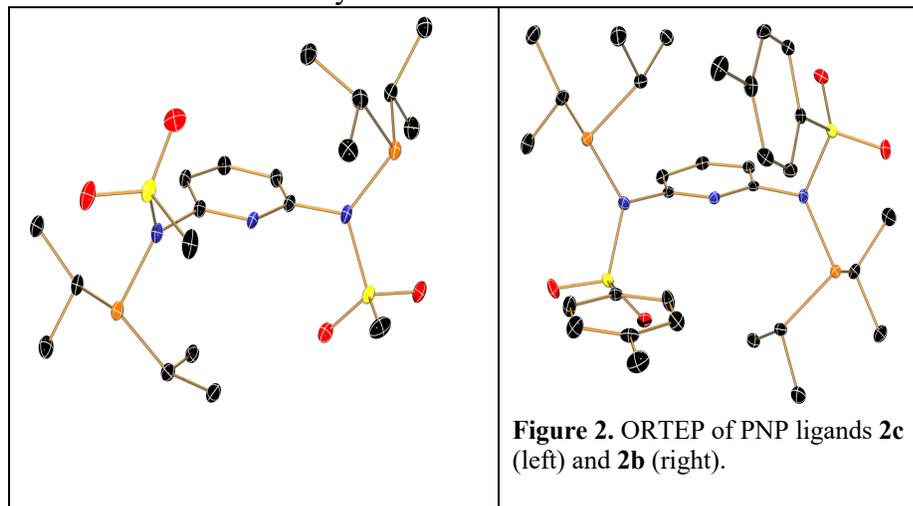


1. PRF#: UR 59227
2. Project title – Development of Fe pincer Complexes for CO<sub>2</sub> Reduction
3. PI name, affiliation – Abby R. O'Connor, The College of New Jersey

The O'Connor lab has made progress towards the goals set out in our proposal to prepare to new pincer iron complexes for CO<sub>2</sub> reduction. *Our objectives in year 1 focused on ligand preparation and metalation strategies.* My group prepared the new, desired PNP pincer ligands that possess proton responsive sulfonamide moieties. Students in my lab initially prepared three 2,6-disulfonylaminopyridines that possess different substituents on the sulfonyl moieties (Figure 1, **1**). This was achieved using a modified literature procedure.<sup>1</sup> With the pyridine derivatives in hand, we conducted the synthesis of the PNP ligand via addition of different chlorophosphines to the 2,6-disulfonylaminopyridines (**1**) under basic conditions in THF (Figure 1, **2**). These new ligands were characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. The molecular structure for two derivatives (**2b**, **2c**) was determined using X-ray crystallography (Figure 2). The crystal structures were obtained in collaboration with Chirik lab at Princeton University.



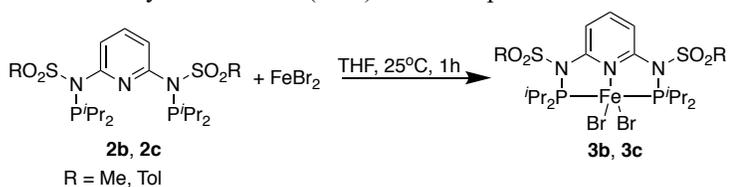
**Figure 1.** 2,6-Disulfonylpyridines (**1**) and PNP (**2**) ligands prepared.



From there our attention turned to the synthesis of the requisite iron halide precursors needed to make the iron hydride catalyst (**4**). Addition of ligand **2** to FeBr<sub>2</sub> in THF resulted in formation of a yellow powder that is paramagnetic (Scheme 1). The <sup>1</sup>H NMR spectral data and color

of the complex are consistent with proposed iron complex **3** as supported by the literature.<sup>2</sup> However, all attempts to isolate crystals of the complex have not been successful. Given the likelihood that **3** is the desired complex of interest, it was used in attempts to synthesize the iron hydride (**4**, Scheme 2). To date all reactions to convert the iron halide **3** to the hydride **4** have not been fruitful.<sup>3</sup> In year 2, we will investigate coordination of transition metals to this style of ligand, as it is unknown. We will prepare metal hydride complexes from diamagnetic metal halides to ease characterization and ensure hydride formation. Once desirable conditions are identified our focus will be to synthesize iron hydride **4**.

**Scheme 1.** Synthesis of the (PNP)FeBr<sub>2</sub> complexes.



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From these initial studies, we expanded our ligand targets beyond the proposed PNP ligands to NNN pincers (**5**, Scheme 3) that possess the proton responsive sulfonamide moieties. Much to our surprise there is only one known preparation<sup>4</sup> of this style of compound. To develop greener methodology, we turned to microwave reactions to facilitate the coupling between the pyridine and sulfonamide substrates. This strategy worked exceptionally well and is a greener

method because of the lack of coupling agents and work up necessary to make these compounds. To determine the sulfonamide substrate scope, I used this newly developed methodology in a CURE style laboratory for my inorganic chemistry course in fall 2019. At the end of the semester, we prepared more than 8 derivatives using this methodology and expanded the substrate scope to include electron rich and poor sulfonamides (Scheme 3). With these ligands we will explore

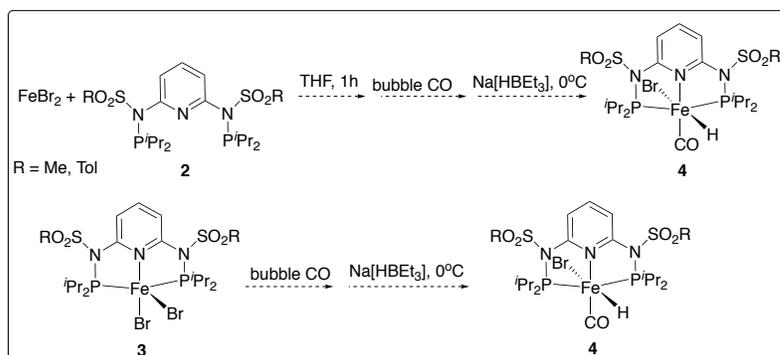
coordination to iron and evaluate the possibility of using these complexes in CO<sub>2</sub> reduction. We are currently finishing up this work and are eager to share this with the

community. This work impacted 25 students in my class and 2 student researchers in my group.

This research project, although in its infancy, has garnered successful outcomes for undergraduate students. During year 1 of the funding period, I had two female undergraduates, one from an underrepresented group in STEM, working on this project throughout the academic year. Due to my maternity leave, I was not able to work with students on this project during the 2019 summer, but I will do so the next three summers. Both female students continue to work on this project. With the expertise gained from my laboratory, one of these undergraduates obtained a highly competitive SULI. She worked at Los Alamos National Lab (LANL) for the summer investigating redox-flow batteries. Due to her love of the research at LANL she will graduate a semester early and pursue a semester-long opportunity at a National Lab for spring 2020. The other student will graduate in spring 2020 and intends to work in industry. In addition, I have identified three students to join my lab to pick up this work when the other students graduate. They have already started research in my group. This work has also impacted my career as it has allowed for a portion of my group to look at base metal chemistry. Most work in my lab has focused on noble metal catalysis. Our results should yield complexes that will react with CO<sub>2</sub>. Further expansion of work should result in submission of an NSF proposal along with several peer-reviewed publications. We will present our initial findings at the ACS meeting in Philadelphia (spring 2020).

**References:** <sup>1</sup>*J. Chin. Chem. Soc.* **2013**, *60*, 813–822. *Bull. Inst. Chem. Acad. Sin.* **1995**, 63–73. <sup>2</sup>*Organometallics* **2006**, *25*, 1900–1913. <sup>3</sup>*Organometallics* **2014**, *33*, 6905–6914., *Organometallics* **2009**, *28*, 6902–6914. <sup>4</sup>*Bioorg. & Med. Chem.* **2011**, *19*, 6827–683.

**Scheme 2.** Attempted synthesis of iron hydride (**4**).



**Scheme 3.** Greener microwave method to make NNN pincer compounds (**5**).

