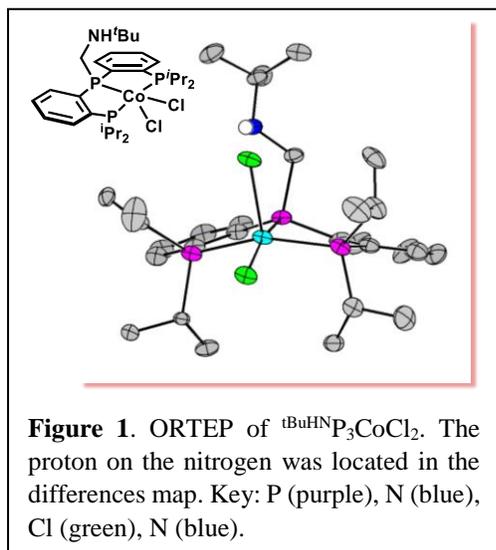


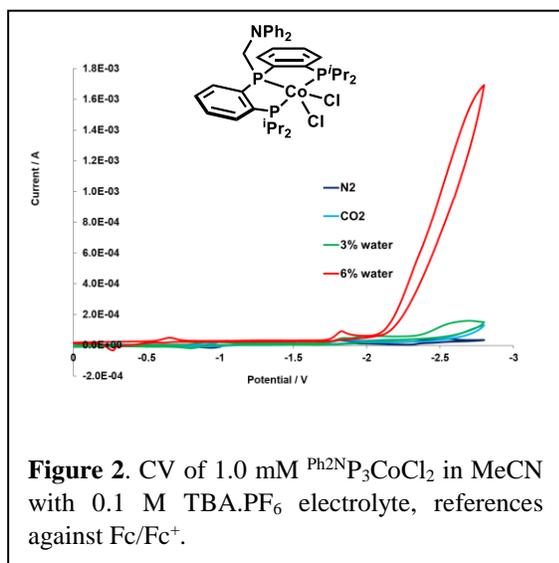
Over the past year, we have focused on understanding the role of amines in electrocatalytic CO<sub>2</sub> reductions. In our proposal, we sought to look at second coordination sphere effects, in terms of Lewis and Bronsted acids. The ligands we prepared were not stable upon metalation to Ni, Pd, and Pt, precluding electrocatalytic studies. We then slightly shifted gears and focused on understanding the role that amines play or can play in electrocatalytic reduction of CO<sub>2</sub>, and below I discuss two research directions that we took with this idea.

**Incorporation of amines in the second coordination-sphere.** We developed new tris(phosphino) ligands that feature a single pendent amine. This ligand can be put on CoCl<sub>2</sub>, and an exemplary structure is shown below (Figure 1). This



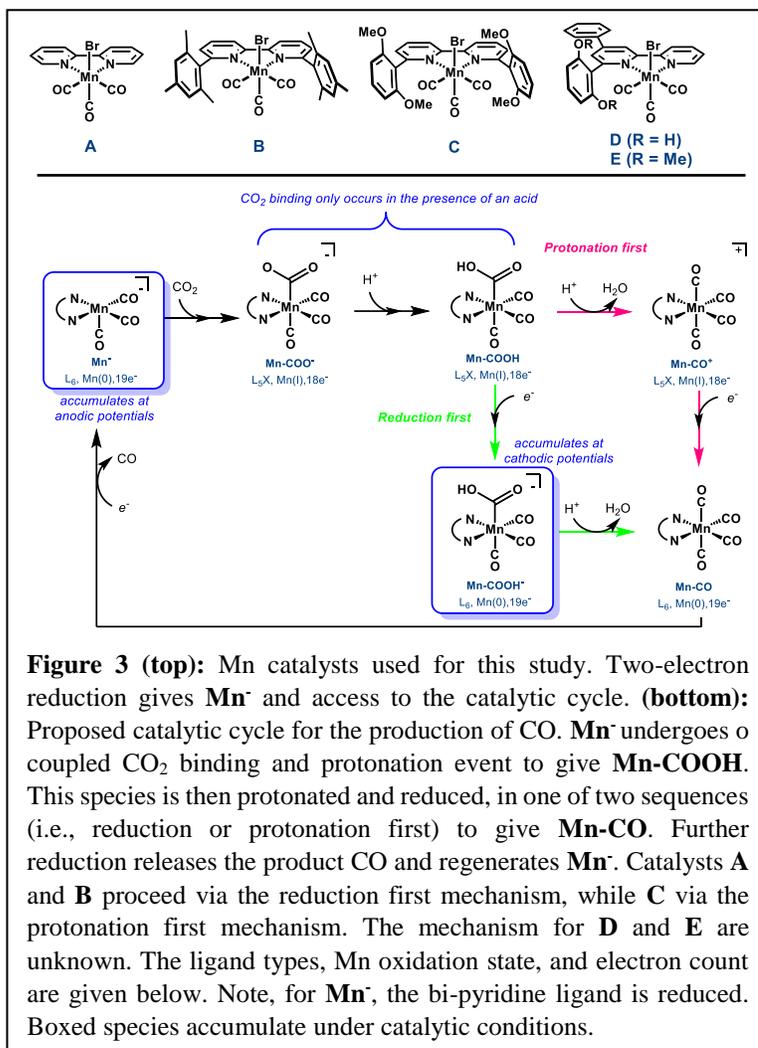
complex features a secondary alkyl amine, and the amine proton is in hydrogen-bonding range to one of the chlorides. This suggests to us that it is poised for proton-transfer to small molecule substrates that are coordinated to the metal.

The cyclic voltammogram of  $R^2N^3P_3\text{CoCl}_2$  ( $R = \text{Ph}$  or  $\text{Bz}$ ) shows two electrochemical reductions in THF. Upon addition of acids that range from H<sub>2</sub>O, phenol, and HBF<sub>4</sub>, no peak enhancement indicative of catalysis ensues, suggesting that these complexes cannot catalytically produce H<sub>2</sub>. Upon bubbling CO<sub>2</sub> through the solution, a catalytic peak is observed (Figure 2). Both CO<sub>2</sub> and acid are required to observe the catalysis, and bulk electrolysis shows that CO forms selectively (no formate or H<sub>2</sub> are detected by IC and GC, respectively). While these catalysts are not stable, with no current being observed after two minutes of bulk electrolysis, they are remarkable in that they do not react with protons to give H<sub>2</sub>, producing CO selectively under electrocatalytic conditions. In higher oxidation states,  $R^2N^3P_3\text{CoCl}_2$  can hydrogenate CO<sub>2</sub> to give formate and trace MeOH. Thus, the catalyst selectivity can be tuned by changing the oxidation state. The electrocatalysis of these species are currently being studied, parallel to the hydrogenation work. We anticipate being able to measure pertinent thermochemical parameters at both the high and low oxidation-states, allowing for better understanding of the selectivity.



**Use of carbamates as CO<sub>2</sub> surrogates.** A challenge in electrocatalytic reduction of CO<sub>2</sub> is achieving high current densities. Catalysis is limited by the low solubility of CO<sub>2</sub> in organic solvents. To circumvent this, we are interested in using amines to capture the CO<sub>2</sub> to give carbamates and carbamic acids. While direct reduction of these species should occur at more negative potentials, we hypothesized that electrocatalysts that can reduce CO<sub>2</sub> may also be able to reduce carbamates because of the high over-potential. As an initial target, we sought to determine if Mn-based electrocatalysts (Figure 1) can reduce dimethylammonium dimethyl carbonate (DMC), which is our CO<sub>2</sub> surrogate. We have prepared all the Mn complexes, and begun to explore the electrocatalytic reduction of DMC. The Mn complexes do serve as electrocatalysts, and give CO (by bulk electrolysis). The reductions occur at the same potential as when CO<sub>2</sub> is reduced. This indicates that we can and should be considering the reduction of carbamates, as this is the species that forms upon carbon capture. IN the absence of Mn catalyst, the DMC is electrocatalytically reduced by the glassy carbon electrode, but H<sub>2</sub> is made selectively. At present, we are doing bulk electrolysis experiments and kinetic studies to gain insight into the mechanism.

It is anticipated that these results will be published within the next year (both projects). These funds allowed my group to branch out into the area of electrocatalysis, and obtain preliminary results that we will use to seek federal funding in the next year.



**Figure 3 (top):** Mn catalysts used for this study. Two-electron reduction gives Mn<sup>-</sup> and access to the catalytic cycle. **(bottom):** Proposed catalytic cycle for the production of CO. Mn<sup>-</sup> undergoes a coupled CO<sub>2</sub> binding and protonation event to give Mn-COOH. This species is then protonated and reduced, in one of two sequences (i.e., reduction or protonation first) to give Mn-CO. Further reduction releases the product CO and regenerates Mn<sup>-</sup>. Catalysts **A** and **B** proceed via the reduction first mechanism, while **C** via the protonation first mechanism. The mechanism for **D** and **E** are unknown. The ligand types, Mn oxidation state, and electron count are given below. Note, for Mn<sup>-</sup>, the bi-pyridine ligand is reduced. Boxed species accumulate under catalytic conditions.