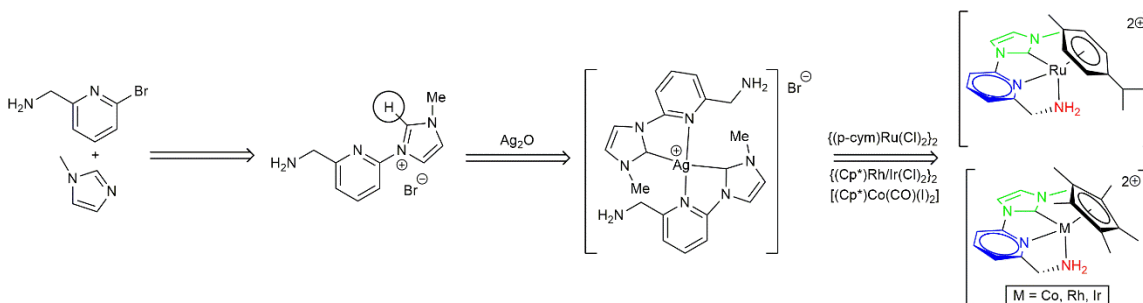


Development of a New Class of Polydentate Ligands for Coordination to Transition Metals

John P. Lee

Want to make some new metal-containing molecules! The field of organometallic chemistry is the place where we combine the rules of organic chemistry while breaking rules using inorganic chemistry. The use of organometallic transition metal complexes has had a significant impact in the field of organic chemistry as these complexes act as catalysts, and nearly all organic syntheses of any complexity include at least one metal-catalyzed reaction. Indeed, since 2001 three separate Nobel Prizes have been awarded for work in this field involving organometallic complexes with precious metals used as catalysts in organic chemistry. One area in catalysis that is currently being pursued involves metal-catalyzed electron transfer reactions. Specifically, we are interested in the electrochemical reduction of CO_2 (C^{+4}) to formate (C^{+2}), which is a net transfer of two electrons and one proton (H^+).

This summer we will be working on ligand design to go in the research direction briefly described above. This will involve the synthesis of a new mixed donor polydentate ligand. Separately, there are many tridentate ligands designed around pyridine, *N*-heterocyclic carbene (NHC) ligands have provided a wealth of new organometallic complexes, and bi- and tridentate amine ligands represent the starting point for coordination chemistry over a century ago and are still showing new chemistry today. We proposed to combine these three components using a **central pyridine** with **tethered NHC** and **amine** ligands to provide a new mixed donor facially coordinating tridentate ligand (Scheme 1). The pyridine will hold the system together as done in related tridentate ligands, the NHC is a strong electron pair donor that can be tuned sterically, and the amine can provide access to a variety of chemical transformations. For the latter, the amine could serve as a hemilabile ligand to provide an open coordination site, a source to chelate to specific metals such as cobalt(III), and/or a H^+ shuttle in electron transfer reactions that also involve proton transfer (e.g., $\text{CO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HCO}_2^-$).



Scheme 1. Proposed preparation and reactivity of the NHC/pyridine/amine tridentate ligand.

In addition to working on current challenges in the field of inorganic chemistry, you will learn synthetic inorganic and organometallic chemistry, which includes air-free chemistry in a nitrogen filled glove box and Schlenk techniques. A significant amount of the Department's instrumentation will be used for characterization, which includes: NMR spectroscopy, infrared and UV-vis spectroscopy, electrochemistry, and single-crystal X-ray diffraction. In addition, you will be encouraged to present your work at the Regional American Chemical Society meeting held in Atlanta, GA in 2024.

Students in my group have gone on to pursue a PhD in chemistry at UTK, Texas A&M and Delaware, pursue professional degrees in medicine and pharmacy at UT Memphis, and have found positions in industry immediately after graduation. These students have presented at regional and national meetings of the American Chemical Society and in some cases had their results published in peer-reviewed journals such as *Polyhedron* and *Journal of Coordination Chemistry*.