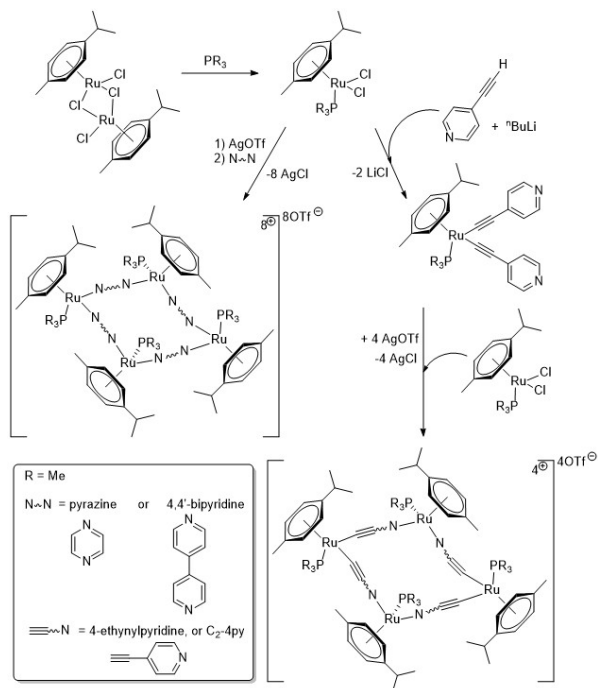


Tunable Molecular Squares using Coordination-Driven Self Assembly

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The use of organometallic transition metal complexes has had a significant impact in the field of organic chemistry as these complexes function as catalysts, and now nearly all organic syntheses of any complexity include at least one metal-catalyzed reaction. Metal containing complexes also have biological roles. For example, mixed valence compounds are ones which contain versions of the same metallic element in different oxidation states. A known mixed valent compound exists in the Oxygen Evolving Center (OEC) in Photosystem II of photosynthetic organisms and contains a Mn_4CaO_5 cubic-shaped core in the active site where the Mn ions are in the III and IV oxidation states. The difference in oxidation energy of these Mn ions allows electrons to move through the compound as water is reduced to dioxygen using light energy.



Scheme 1. Proposed synthesis of ruthenium-based molecular squares.

This summer we will be working on the synthesis of electronically tunable molecular squares involving ruthenium in the four corners. The Ru ions are proposed to be able to electronically communicate with one another via bridging ligands. This will be accomplished by using a facially coordinating tridentate ligand and a monodentate phosphine ligand, which would create a template for coordination driven molecular self-assembly through bridging ligands while providing an opportunity for different R groups to attach to the phosphine (Scheme 1). This is a collaborative project between the Lee and Pienkos research groups who propose the synthesis of a mixed-valence ruthenium molecular square where prior work with a tetradentate ligand has been replaced with p-cymene and a monodentate phosphine (PR_3).

This system will maintain 90° bond angles for the bridging ligands of either deprotonated 4-ethynylpyridine (4-C₂-py), 4,4'-bipyridine (bipy), or pyrazine (pyrz) as shown in

Scheme 1. We hypothesize that by varying the electronic and/or steric nature of the R group on the monodentate phosphine we can tune the planarity of the bridging ligand and therefore enhance the electronic communication between the metals.

In addition to working on a current challenge in inorganic chemistry, you will learn synthetic inorganic and organometallic chemistry, including 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 Orlando, FL in 2025.

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*.