Results from Summer 2015

Justin Hoffman
Department of Chemistry and Biochemistry
Faculty Advisor, Dr. Seth Brown

This summer, my research was intended to be on the subject of osmium complexes. First, I was planning on synthesizing a tetradentate noradamantinediamine ligand, which would be forced into a planar conformation when bound to osmium, ideally creating dioxo complexes with the oxos *trans* to each other. Second, I was also planning on synthesizing osmium complexes with the already known "Clip" ligand, which is generally seen in a bent conformation, leading to *cis* dioxo complexes. These two complexes could be used to compare non-classical and classical reactions. I was also planning on briefly finishing up a previous project with non-innocent [ONO]-rhenium complexes.

The osmium chemistry did not go as planned. I was first unable to synthesize the new ligand after multiple setbacks. Next, though I found methods to synthesize some osmium complexes with most-likely bound Clip ligands, I was not able to purify them or characterize the final products.

However, the rhenium chemistry I meant to briefly revisit ended up taking some unexpected turns which were of high priority. I had previous studied the mechanism of *fac,anti*-[ONO]ReO(μ-O)$_2$ReO[ONO] with PPh_3 and had believed that the product-determining and rate-determining steps were the same. However, when $P(C_6H_{11})_3$ was used instead, it was shown that this was not the case. This also meant we were able to answer more questions about the reaction beyond the first step. For example, what actually reacts with phosphine in the product-determining step? Assuming the dimer is broken up by the first step, this means two possibilities

stand out, [ONO]ReO_2 and [ONO]$ReO_2(PPh_3)$. To investigate whether the relevant intermediate was or was not ligated, the dimer was reacted with pyridine, which was unable to react with the oxygen groups, thus forming dimer and [ONO]ReO_2(py) at equilibrium. Variable-temperature NMR determined that the rate of exchange was much less than a second. This reaction was also determined to be first-order in pyridine. Next, we are investigate the reaction of this adduct with PPh_3. If it reacts while not ligated, the rate law will be $rate = k\frac{[Re][PPh_3]}{[py]}$, meaning pyridine would inhibit the rate. However, if it reacts while ligated, the rate law will be zero-order in pyridine. These tests have started, but are not yet complete.