

Development of Transition Metal Complexes for Breaking Unreactive Chemical Bonds

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Organometallic chemistry is a combination of inorganic and organic chemistry, and is broadly defined by the presence of direct metal-carbon bond(s). The metal can be a main-group, transition, or rare earth metal, and the bond with carbon can either be a single or multiple bond. The use of organometallic transition metal complexes as catalysts in organic synthesis has been very important in recent years and has been an integral part of the development of this sub-discipline of chemistry. Since 2001 three separate Nobel Prizes have been awarded for work in this field. One area in catalysis that is currently being pursued is the selective activation and functionalization of inert chemical bonds such as the C-H bond of hydrocarbons and the C=O bond of CO₂. For example, the C-H bond is as ubiquitous in organic chemistry as it is inert to chemical reactivity. Carbon dioxide represents the thermodynamic end product of carbon and is in a highly oxidized and stable form. However, through ligand design and the use of the *d* orbitals of the transition metals, the activation of these once notoriously inert chemical bonds is being realized.

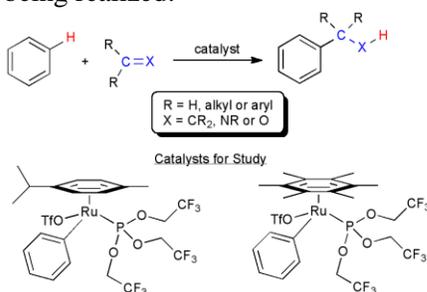


Figure 1

This summer we will be working on two projects. The first project will involve organometallic Ru(II) complexes bearing a fluorinated phosphite ligand. In particular, we are interested in exploring the chemistry around [Ru(*p*-cymene){P(OCH₂CF₃)₃}(Ph)(OTf)] and [Ru(Bz-Me₆){P(OCH₂CF₃)₃}(Ph)(OTf)] for catalytically breaking C-H bonds of aromatic compounds and the subsequent addition across multiple bonds, which is known as olefin hydroarylation (Figure 1). The second project will involve the synthesis and characterization of mixed sandwich Co(III) organometallic complexes. Fundamental work is

needed in the exploration of polydentate *N*-heterocyclic carbene (NHC) ligands with first row transition metals. Thus, specifically we will look at the chemistry of cobalt(III) utilizing the cyclopentadienyl anion, Cp, and related derivatives, and the chemistry of the NHC on cobalt(III) as a function of the Cp^R ligand. Long-term interest in this chemistry lies in the development of catalysts for the coupling of carbon dioxide and ethylene to produce acrylic acid (Figure 2). With increasing environmental concerns in regard to CO₂ and the rapid depletion of fossil fuel reserves it is imperative that we develop new methods that can convert Nature's carbon source, CO₂, into more useful chemicals.

Both catalytic reactions of interest represent a greener and more atom economical use of our existing fossil fuel resources and reaction by-products. The student 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: ¹H/¹³C/³¹P/¹⁹F/⁵⁹Co NMR spectroscopy, infrared and UV-vis spectroscopy, electrochemistry, and single-crystal X-ray diffraction. In addition, the student will be encouraged to present their work at the Regional American Chemical Society meeting held in Memphis, TN in 2015.

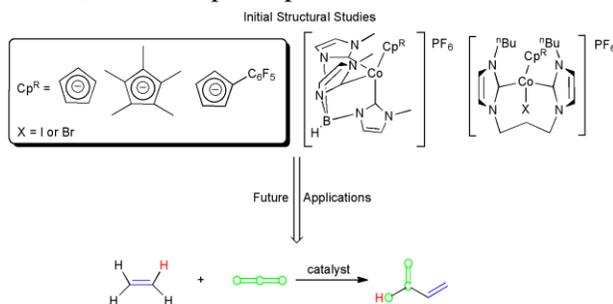


Figure 2