

## Development of Transition Metal Complexes for Breaking Unreactive Chemical Bonds

### John P. Lee

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. Specifically, we are interested in the atom economical oxidation of C-H bonds of aromatic molecules and alkanes to vinyl arenes and alcohols, respectively.

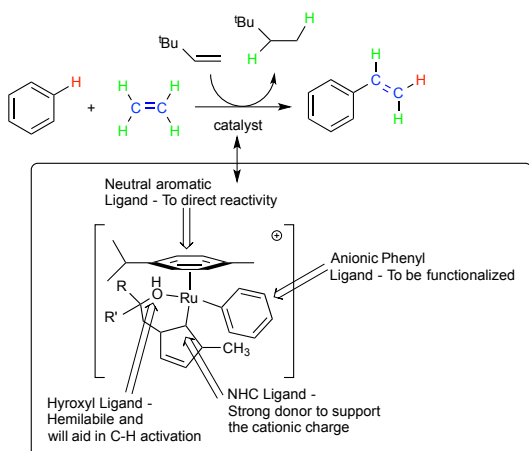
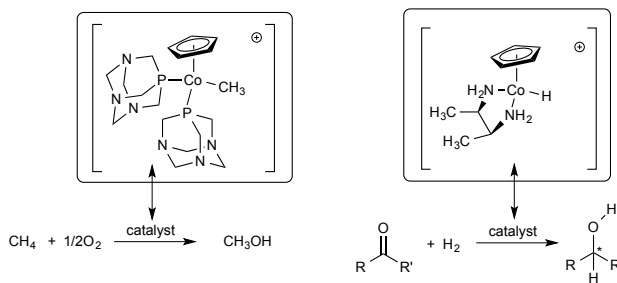


Figure 2

utilizing the cyclopentadienyl anion, Cp, and taking advantage of the NMR active nucleus  $^{59}\text{Co}$ . Long-term interest in this chemistry lies in the development of catalysts for the oxidation of methane to methanol and asymmetric hydrogenation of prochiral ketones (Figure 2). With increasing environmental concerns in regard to  $\text{CO}_2$  and the rapid depletion of fossil fuel reserves it is imperative that we develop new methods that can convert raw materials into more useful chemicals.

Figure 1



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:  $^1\text{H}/^{13}\text{C}/^{31}\text{P}/^{59}\text{Co}$  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 Columbia, SC in 2016.

This summer we will be working on two projects. The first project will involve organometallic Ru(II) complexes involving a hemilabile N-heterocyclic carbene (NHC) ligand. In particular, we are interested in exploring the chemistry around  $[\text{Ru}(p\text{-cymene})\{\text{C},\text{O}-(\text{NHC}-\text{OH})\}(\text{Ph})]$  for catalytically breaking C-H bonds of aromatic compounds and the subsequent oxidative addition across multiple bonds, which is known as oxidative olefin hydroarylation (Figure 1). The second project will involve the synthesis and characterization of Co(III) organometallic complexes. Fundamental work is needed in the exploration of Earth-abundant transition metals as catalysts for new organic transformation. Thus, specifically we will look at the chemistry of cobalt(III)