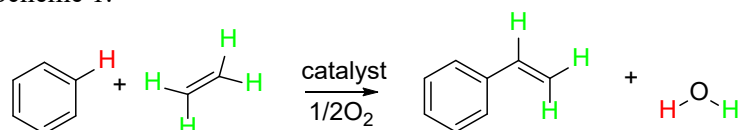


Development of Transition Metal Complexes for Breaking Unreactive Chemical Bonds

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. 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 production of vinyl arenes from a one-step reaction between benzene and ethylene using oxygen as the hydrogen acceptor, which is known as oxidative hydrophenylation and is shown in Scheme 1.



Scheme 1

This summer we will work on the synthesis and characterization of the catalyst to be used in the reaction shown above. This catalyst will contain 2 different transition metals and will be in the same phase as the organic reactants, which classifies it as a homogenous (same phase) heterobimetallic (2 different metals) catalyst and is shown below in Figure 1. Each piece of the “puzzle” shown in Figure 1 is proposed to play an integral role in the reactivity. The key piece of the puzzle (aka our hypothesis) is the *trans*-bidentate ligand on the Pd(II). The ligand is referred to in this way as it spans 180° (*trans*) and has two coordination sites via the nitrogen on the pyridines that will bite into the Pd(II) center (bidentate). Our hypothesis is that this *trans*-bidentate ligand will direct reactivity toward the acetate leaving groups during the C—H activation step. The Co(III) will provide the hinge to hold the catalyst together, has a similar ionic radius as Ti(IV) shown to make a related compound, and is easier to work with than Ti(IV) while still remaining inexpensive as a 1st row transition metal.

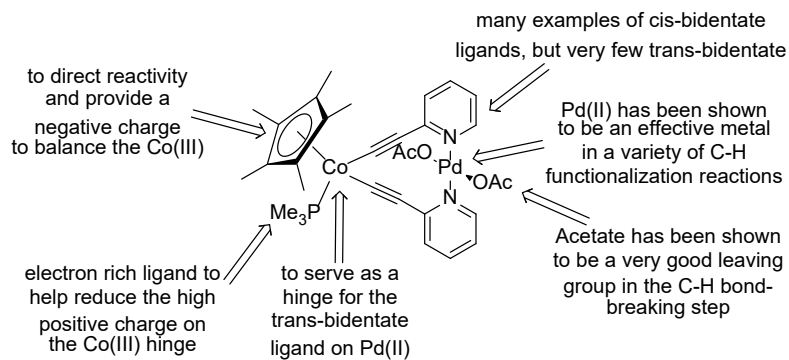


Figure 1

This proposed reaction is of interest as it represents a greener and more atom economical use of our existing fossil fuel resources. 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: $^1\text{H}/^{13}\text{C}/^{31}\text{P}/^{19}\text{F}$ 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 Birmingham, AL in 2021.