

Development of Transition Metal Complexes for Breaking Unreactive Chemical Bonds

John P. Lee

Want to make some new metal-containing molecules! The use of organometallic transition metal complexes has had a significant impact in field of organic chemistry as these complexes act as catalysts, and nearly all organic syntheses of any complexity include at least one metal-catalyzed reaction. Indeed, since 2001 three separate Nobel Prizes have been awarded for work in this field involving organometallic complexes with precious metals used as catalysts in organic chemistry. One area in catalysis that is currently being pursued is the selective activation and functionalization of bonds that are not supposed to be broken under standard laboratory conditions, so called inert chemical bonds, such as the C-H bond of hydrocarbons. Specifically, we are interested in the atom economical use of C-H bonds in organic synthesis to make new functionalized molecules.

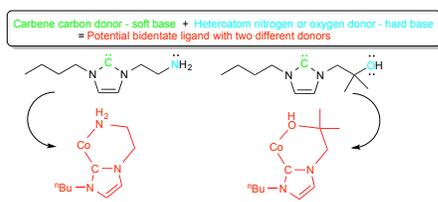


Figure 1

In many organic catalyzed reactions. In addition, the coordination chemistry of NHC ligands with Co is scant, and to date there are no examples of isolated Co(III) complexes with an NHC ligand. For the latter point, it is our hypothesis that the tethered amine or hydroxyl group will aid in the stabilization of the so far elusive Co(III)-NHC complex. In addition to the fundamental coordination chemistry between the Co(III) and the carbon-donor NHC ligand that is to be explored, we believe that these type complexes could show promise in a variety of organometallic catalytic reactions. For example, the tethered functional group could serve: as a proton source in hydrogen transfer reactions, participate in 1,2-C=O bond insertions, aid in carbon-hydrogen bond cleavage, or serve as an open coordination being hemilabile. With increasing environmental concerns in regard to CO₂ and the rapid depletion of fossil fuel reserves it is imperative that we develop reactions such as these just stated that can convert raw materials (*e.g.*, methane, benzene and hydrogen) into more useful chemicals using an Earth-abundant metal such as cobalt.

Long-term goals of this work involve the development of a greener and more atom economical use of our existing fossil fuel resources and reaction by-products. In addition to working on a current challenge in the field of inorganic chemistry, you will utilize tools from organic chemistry to prepare the *N*-heterocyclic carbene ligands while learning synthetic inorganic and organometallic chemistry, which includes air-free synthesis in a nitrogen filled glove box and Schlenk techniques. A significant amount of the Department's instrumentation will be used for characterization of the newly prepared complexes, which includes: ¹H/¹³C/³¹P/⁵⁹Co NMR spectroscopy, infrared and UV-vis spectroscopy, 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 Augusta, GA in 2018.

Students in my group have gone on to pursue a PhD in chemistry at UTK and Texas A&M, pursue professional degrees in medicine and pharmacy at UT Health Science Center 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 in published in peer-reviewed journals such as *Organometallics*, *Polyhedron* and *Journal of Coordination Chemistry*.

This summer we will be working on the preparation of cobalt complexes that contain an *N*-heterocyclic carbene (NHC) ligand bearing either a tethered amine or hydroxyl functional group (Figure 1). Fundamental work is needed in the exploration of Earth-abundant transition metals, such as cobalt, to replace precious metals (*e.g.*, Ru or Pd)

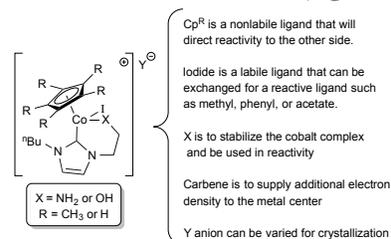


Figure 2