Public Abstract

First Name:Nandita

Middle Name:Malathi

Last Name:Weliange

Adviser's First Name:Paul

Adviser's Last Name:Sharp

Co-Adviser's First Name:

Co-Adviser's Last Name:

Graduation Term:FS 2011

Department:Chemistry

Degree:PhD

Title:ALKENE OXIDATION BY PLATINUM(II)-OXO/HYDROXO COMPLEXES

The dissertation is an investigation of the reactivity between alkenes and Pt(II) complexes. These reactions are important as they are used for the synthesis of various useful chemicals. An important aspect of such studies is an understanding of the mechanisms by which reactions take place.

Mechanistic investigations of formation of platinaoxetane $[(\text{COD})_2\text{Pt}_2(\text{OC}_7\text{H}_{10})\text{Cl}][\text{BF}_4]$ (2) lead to the identification of intermediacy of Pt- μ -hydroxo complex $(\text{COD})_2\text{Pt}(\text{OH})_2^{2+}$ (4) and protonated- μ -platinaoxetane $[(\text{COD})\text{Pt}(\text{OH})(\text{C}_7\text{H}_{10})]^+(5)$. A proposed mechanism for the transformation is described.

Pt- μ -hydroxo complex 4 also reacts readily with ethylene, propylene and 1- μ -butene. All three reactions, resembling Wacker chemistry, yield alkene oxidation products: acetaldehyde, acetone and ethyl- μ -methyl ketone, respectively. A proposed mechanism for these alkene oxidations is described.

Pt- μ -hydroxo complex 4 also reacts with cyclohexene. In this case the reaction takes an allylic C- μ -H activation pathway to produce the cyclohexyl allyl complex $[(\text{COD})\text{Pt}(\text{C}_6\text{H}_9)]^+$ (55). In arriving at these results kinetic studies and NMR spectroscopy were heavily used.