

Public Abstract

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Ph.D.

Chemistry

Alkene-Oxo and Alkene-Alkene Coupling on Pt(II)

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The topic of this dissertation is the detailed investigations of various reactions involving Pt(II) complexes and alkenes. These studies are important, because they can help understand and improve complicated transition-metal catalyzed processes such as burning of fossil fuels, manufacturing common organics, polymers, etc. Many of these processes are heterogeneous rendering their investigations incredibly complicated due to the lack of simple techniques available to study surface reactions. Reactions of soluble model complexes can be easily and accurately monitored with a variety of techniques (NMR, IR, UV, etc.). Information gained from these systems can also be used to propose mechanisms for complex homogeneous processes. This dissertation essentially deals with such model reactions.

Tetranuclear Pt(II) oxo complex $[(\text{COD})_4\text{Pt}_4(\mu^3\text{-O})_2\text{Cl}_2](\text{BF}_4)_2$ (**1**) (COD = 1,5-cyclooctadiene) was found to readily oxidize a variety of alkenes (ethylene, norbornenes and propylene). The most significant discovery resulted from the norbornene reaction, which gave platinaoxetane $[(\text{COD})_2\text{Pt}_2(\text{OC}_7\text{H}_{10})\text{Cl}]\text{BF}_4$ (**4**), the first metallaioxetane obtained from the direct reaction of an oxo complex and an alkene. Our results suggest that oxo complexes and metallaioxetanes are possible species to consider in catalytic alkene oxidation pathways.

A facile alkene-exchange reaction was observed between platinaoxetane **4** and a benzonorbornene-derivative giving a new platinaoxetane and free norbornene in contrast to other metallaioxetanes that insert alkenes into the M-O bond. This demonstrates unexpected reactivity in platinum-alkene oxidation chemistry. Kinetic studies revealed that the reaction is catalyzed by possibly more than one electrophilic catalyst.

Cationic Pt(II) complexes $(\text{COD})\text{Pt}(\text{OTf})_2$ and $[(\text{COD})\text{Pt}(\text{THF})(\text{OTf})]\text{OTf}$ were found to readily react with alkenes such as norbornenes, cyclopentene, propylene and ethylene. Two common features of these reactions were alkene C-H bond cleavage and triflic acid elimination. Norbornenes, cyclopentene and ethylene gave alkene-coupled products, while propylene resulted in a simple allyl complex. The formation of triflic acid instead of reductive C-H coupling by proposed hydride intermediate species is remarkable.