



University
of Victoria

Graduate Studies

Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

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BSc Hons. (University of Toronto, 2014)

**“The Role of the M-PR₂ Fragment in Hydrophosphination:
From Mechanisms to Catalysis”**

Department of Chemistry

Tuesday, July 30, 2019

9:00 A.M.

Elliott Building

Room 226

Supervisory Committee:

Dr. Lisa Rosenberg, Department of Chemistry, University of Victoria (Supervisor)

Dr. Cornelia Bohne, Department of Chemistry, UVic (Member)

Dr. Scott McIndoe, Department of Chemistry, UVic (Member)

Dr. Rogério de Sousa, Department of Physics and Astronomy, UVic (Outside Member)

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Dr. Linda Welling, Department of Economics, UVic

Abstract

In this thesis, the synthesis and reactivity of metal complexes containing phosphide (PR_2^-) and phosphonium (PR_2^+) ligands for the hydrophosphination of alkenes were investigated. The mechanisms of hydrophosphination mediated by these M-PR_2 fragments were explored.

Based on previous work in the Rosenberg group, $\text{Ru}(\eta^5\text{-indenyl})$ complexes were explored and developed as catalysts for hydrophosphination. It was determined that Ru phosphido complexes are key intermediates in the hydrophosphination of electron deficient alkenes. A detailed study on the mechanisms of hydrophosphination catalyzed by the phosphido complexes $\text{Ru}(\eta^5\text{-indenyl})(\text{PPh}_2)(\text{L})(\text{PPh}_3)$ (**4a**, $\text{L} = \text{NCPH}$; **b**, $\text{L} = \text{PPh}_2\text{H}$; **c**, $\text{L} = \text{CO}$) was performed. Evidence for product inhibition was found for this catalyst system using Reaction Progress Kinetic Analysis. Product inhibition is consistent with the observed catalyst resting state of a complex containing product phosphines and the determination that substitution of the product phosphine from Ru is rate-limiting. The ancillary ligands (L) of **4** were found to influence catalytic activity by enabling catalyst deactivation ($\text{L} = \text{NCPH}$) or off-cycle processes including alkene telomerization ($\text{L} = \text{CO}$). Proposed mechanisms for catalysis were devised based on these findings. These results are important mechanistic insights that will be useful for designing new catalysts for hydrophosphination.

The viability of metal phosphonium complexes as intermediates in hydrophosphination was also explored. Three Mo phosphonium complexes were synthesized via P-H bond hydride abstraction from coordinated secondary phosphines, PR_2H . These complexes were found to mediate the stoichiometric hydrophosphination of alkenes and ketones. In particular, *trans*- $[\text{Mo}(\text{CO})_3(\text{PPh}_2\text{H})_2(\text{Pph}_2)]^+$ (**13**) mediates the hydrophosphination of a wide scope of alkenes that includes ethylene, propene and 1hexene, which are challenging substrates for metal-catalyzed hydrophosphination. Preliminary attempts were conducted to render this synthetic phosphonium-mediated hydrophosphination catalytic. These results provide evidence for the putative steps of a hydrophosphination cycle utilizing metal phosphonium complexes as intermediates.

The phosphonium complexes *trans*- $[\text{Mo}(\text{CO})_4(\text{PR}_2\text{H})(\text{PR}_2)]$ (**12a** $\text{R} = \text{ToI}^p_2$, **b** $\text{R} = \text{Ph}$) were also investigated as Lewis acid catalysts for hydrosilylation. A tentatively assigned $\eta^1\text{-HSiEt}_3$ adduct of **12a**, $[\text{Mo}(\text{CO})_4(\text{PTol}^p_2\text{H})(\text{PTol}^p_2\{\text{HSiEt}_3\})]$ (**20a**), was observed by low temperature $^{31}\text{P}\{^1\text{H}\}$ NMR and was studied computationally. Complex **12b** is proposed to behave as a Lewis acid catalyst for hydrosilylation. An off-cycle equilibrium is proposed that results in the formation of EtSi^+ . This work is an example of P(III) Lewis acid catalysis, of which there are few examples in the literature.