Notice of the Final Oral Examination
for the Degree of Master of Science

of

ROBIN THERON

BSc (University of Saskatchewan, 2013)

“Real-time Investigation of Catalytic Reaction Mechanisms by Mass Spectrometry and Infrared Spectroscopy”

Department of Chemistry

Wednesday, June 10, 2015
1:00 P.M.
David Turpin Building
Room A144

Supervisory Committee:
Dr. Scott McIndoe, Department of Chemistry, University of Victoria (Supervisor)
Dr. Dennis Hore, Department of Chemistry, UVic (Member)

External Examiner:
Dr. Jason Hein, Department of Chemistry and Chemical Biology, University of California Merced

Chair of Oral Examination:
Dr. Falk Herwig, Department of Physics and Astronomy, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies
Abstract

Electrospray ionization mass spectrometry (ESI-MS) has been applied to the realtime study of homogeneous organometallic reactions. ESI-MS as a soft ionization technique is amenable to fragile organometallic complexes, and as a fast and sensitive technique is ideal for detecting low concentration intermediates within reactions. Pressurized sample infusion (PSI) was used for continuous sample infusion into the mass spectrometer, granting the air-free conditions necessary for these reactions to be successful, and resulting in reaction profile data that contains information about the dynamics of speciation of the catalyst. Collision induced dissociation (CID) was used to probe the binding affinities of various bisphosphine ligands as well as in characterizing intermediates in reactions.

PSI ESI-MS was applied to the hydroboration reaction of the alkene tert-butylethene using the amine-borane $\text{H}_3\text{B} \cdot \text{NMe}_3$ catalyzed by $[\text{Rh(xantphos})]+$ fragments to show how the reaction progresses from substrates to products. PSI ESI-MS was also applied to the hydrogenation of a charge-tagged alkyne $[\text{Ph}_3\text{P}(\text{CH}_2)_4\text{C}_2\text{H}]^+\text{[PF}_6^-]$, catalyzed by a cationic rhodium complex $[\text{Rh(PcPr}_3\text{)}^2(\eta_6\text{-FPh})]^+\text{[B}\{\text{3,5-(CF}_3\text{)2C}_6\text{H}_3}\}_4^- \quad (\text{PcPr}_3 = \text{triscyclopropylphosphine}, \text{FPh} = \text{fluorobenzene}).$ This work demonstrated the use of ESI-MS in conjunction with NMR, kinetic isotope effects and numerical modeling for determining a mechanism of reaction. The hydroacylation reaction of a substituted aldehyde and an alkyne catalyzed by $[\text{Rh(PiPr}_2\text{NMePiPr}_2\text{)}(\eta_6\text{-FPh})]^+\text{[B}\{\text{3,5-(CF}_3\text{)2C}_6\text{H}_3}\}_4^- \quad (\text{PiPr}_2 = \text{diisopropylphosphine})$ was studied by PSI ESI-MS while employing charged tags, allowing for observation of reaction progress and some key intermediates.

A new concept for mechanistic analysis has been developed: coupling of an orthogonal spectroscopic technique with PSI ESI-MS. This new method was applied to the same hydroacylation reaction studied with charged tags. The use of IR in conjunction with ESI-MS led to rate information about the overall reaction along with dynamic information about catalytic speciation. Coupling of these techniques allows for detection over many magnitudes of concentration.