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**BSc (Chemistry and Chemical Engineering), Ecole Supérieure de
Chimie Organique et Minérale Compiègn, France, 2011**
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Jules Vernes Amiens, France, 2013**

DEPARTMENT OF CHEMISTRY

TITLE OF THESIS: INVESTIGATION OF P-H, O-H, AND Si-H
OXIDATIVE ADDITION INVOLVING
GROUP 9 METAL PSiP COMPLEXES

TIME/DATE: 9:30 am, Tuesday, March 19, 2019

PLACE: Room 3107, The Mona Campbell Building, 1459
LeMarchant Street

EXAMINING COMMITTEE:

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

Dr. Fran Cozens, Department of Chemistry, Dalhousie University (Reader)

Dr. Alex Speed, Department of Chemistry, Dalhousie University (Reader)

Dr. Mark Stradiotto, Department of Chemistry, Dalhousie University
(Reader)

Dr. Laura Turculet, Department of Chemistry, Dalhousie University
(Supervisor)

DEPARTMENTAL REPRESENTATIVE: Dr. Erin Johnson, Department of Chemistry,
Dalhousie University

CHAIR: Dr. Peter Duinker, PhD Defence Panel, Faculty
of Graduate Studies

ABSTRACT

Group 9 transition metal pincer complexes have shown remarkable reactivity with respect to E-H (E = main group element) bond activation chemistry. In this context, this research focuses on developing new Ir and Rh complexes supported by bis(phosphino)silyl ligands of the type $[\kappa^3\text{-}(2\text{-Cy}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]$ (Cy-PSiP). A prominent feature of this ligand is the presence of a highly *trans*-labilizing and electron donating silyl group located at the central anionic position. These properties may allow for the stabilization of reactive, coordinatively unsaturated compounds. This document details the synthesis of neutral and cationic (Cy-PSiP)M (M = Ir, Rh) complexes, and their application towards E-H bond oxidative addition (E = P, O, and Si) reactions.

With the goal of observing E-H bond oxidative addition mediated by the (Cy-PSiP)M system, considerable progress has been made in isolating unusual monomeric phosphido-hydride, alkoxy-hydride, and silyl-hydride species. In particular, several examples of successful Ir-mediated P-H, O-H and Si-H bond oxidative addition were demonstrated. Furthermore, phosphido-hydride species showed interesting reactivity in subsequent E-H bond activation featuring alkynes, hydrosilanes, and H₂. Migratory insertions of CO₂ and isocyanates involving alkoxy-hydride complexes were also observed.

Efforts were undertaken to generate silylene species (Cy-PSiP)Ir(H)(=SiR₂) from complexes of the type (Cy-PSiP)Ir(H)(SiRR') (R = H, Cl; R' = Ph, Mes). While such silylene species remain elusive, a better understanding of the behaviour of Ir-silyl complexes was garnered.

Lastly, syntheses of cationic M^{III} complexes of the type [(Cy-PSiP)MR]⁺X⁻ (M = Ir, Rh, R = H, Me; X = OTf, BF₄, B(C₆F₅)₄) were explored. Challenges were encountered, associated with either the reactivity or the stability of the synthesized complexes. The inclusion of a neutral L donor resulting in complexes of the type [(Cy-PSiP)MRL]⁺X⁻ (L = PMe₃) afforded increased stability, allowing for the isolation of Ir-methyl cations.