



University
of Victoria

Graduate Studies

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

of

PAUL GRAY

B.ScH (Acadia University, 2012)

“Cationic Complexes of the Group 13-15 Elements Supported
by N-, P-, and O-based Ligands”

Department of Chemistry

Thursday, July 5, 2018

9:00 A.M.

Clearihue Building

Room B017

Supervisory Committee:

Dr. Neil Burford, Department of Chemistry, University of Victoria (Supervisor)

Dr. David Berg, Department of Chemistry, UVic (Member)

Dr. Robin Hicks, Department of Chemistry, UVic (Member)

Dr. Jay Cullen, School of Earth and Ocean Sciences, UVic (Non Member)

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Dr. Kim M. Baines, Department of Chemistry, Western University

Chair of Oral Examination:

Dr. Christopher Eagle, Department of Mathematics and Statistics, UVic

Abstract

This dissertation presents the synthesis and characterization of a variety of neutral and cationic complexes featuring Group 13-15 element centres stabilized by N-, P-, and O-based donors. Unique aluminum and gallium cationic complexes are obtained from equimolar reactions of the metal halide with the chelating alkyl phosphine dmpe. However, using the analogous amine donor tmeda, neutral adducts are preferred for aluminum as well as for GaCl₃, while cations are obtained for GaBr₃ and GaI₃. New cations of Ge(II) and Sn(II) were also discovered, featuring the coordination of either bipyridine ligands or dmpe. Utilizing bipyridine led to the expected mono and dicationic chelate complexes, however, using dmpe led to the formation of unprecedented tetracationic molecules. The reactivities of the bipyridine complexes were investigated with a variety of substrates which showcased their Lewis acidity as well as their ability to be oxidized. Finally, a new series of high oxidation-state main group cations have been synthesized using a variety of ligands. The ligand choice was found to be an important role in compound isolation as ligand degradation occurred for some of the compounds due to their high electrophilicity. Additionally, the Lewis acidity of some of the complexes leads to interesting reaction chemistry including sp³ C-H activation. Overall, the results presented herein represent new coordination chemistry for the main group elements and opens the door towards new reactivity pathways including small molecule activation and catalysis.