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**BSc (Chemistry), University of Manitoba, 2014**

**DEPARTMENT OF CHEMISTRY**

**TITLE OF THESIS:** ADVANCES IN PALLADIUM AND NICKEL CATALYZED CROSS-COUPLING REACTIONS

**TIME/DATE:** 9:30 am, Wednesday, December 6, 2017

**PLACE:** Room 1014, Kenneth C. Rowe Management Building, 6100 University Avenue

**EXAMINING COMMITTEE:**

Dr. Jennifer Love, Department of Chemistry, University of British Columbia (External Examiner)

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

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

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

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

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

**CHAIR:** Dr. Elizabeth Cowley, PhD Defence Panel, Faculty of Graduate Studies

**ABSTRACT**

Homogeneous organometallic complexes have become an indispensable tool as they are employed as catalysts for a large number of chemical transformations. Ancillary ligands, organic molecules that bind to the metal center, are critical for fine tuning the performance of these catalysts. The initial portion of this thesis describes a comparative survey of several state-of-the-art ligands for Pd catalyzed C-O cross-coupling reactions. As part of this survey two sets of conditions are employed: reactions carried out at 90 °C, using 1 mol % Pd, and room temperature reactions, using 7 mol % Pd. In these comparisons, it was found that Rockphos was the ligand of choice for reactions at room temperature, as well for electron rich electrophiles. The Josiphos variant, CyPF-*t*Bu, was the optimal ligand for reactions at elevated temperatures, as well as for activated electrophiles.

Many ligands that have found use in Pd chemistry have been repurposed for use in Ni catalysis. While this an effective strategy, it is not necessarily ideal. The bisphosphine PAd-Dalphos has been tailored for Ni catalyzed monoarylation of ammonia, and primary amines. Here, ammonium, methylamine, and ethylamine salts are successfully used as cross-coupling partners employing microwave heating. High yielding reactions, utilizing as little as 1 mol % Ni can be completed in as little as 5 minutes under these conditions.

In an effort to establish trends of reactivity in Ni catalysis, the complex (DPEphos)Ni(mesityl)Br was developed for both C-N, C-C cross-coupling reactions. This complex was first established in the cross-coupling of secondary amines, and azoles with activated aryl chlorides. The observation of PhB(OH)<sub>2</sub> required as a catalyst activator lead to the development of this complex as a catalyst for C-C cross-coupling using unstable 5-membered heterocyclic boronic acids for challenging biheteroaryl formation. Here reactions conducted at room temperature were found to be comparable to the previous state-of-the-art Ni catalysis. In addition, 3-pyridinyl-boronic acids were also successfully employed. While the scope of reactivity with such challenging substrates was modest, the work herein represents a step forward as only a small handful of examples exist for Ni catalyzed reactions.