LATE TRANSITION METALS SUPPORTED BY ARYL ETHERS AND PHENOXIDES BEARING PENDANT PHOSPHINES: MECHANISTIC INSIGHTS RELEVANT TO ETHER C-O BOND CLEAVAGE

Thesis by
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To Mom and Dad

"All things are possible to him who believes."

Mark 9:23

"For me, giving up's way harder than trying."

-Kanye West

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PREFACE

Parts of this thesis have been adapted from articles co-written by the author.

The following articles were reproduced in part with permission from the American Chemical Society:

"Nickel-Mediated Hydrogenolysis of C–O Bonds of Aryl Ethers: What Is the Source of the Hydrogen?" Paul Kelley, Sibo Lin, Guy A. Edouard, Michael W. Day, Theodor Agapie. *J. Am. Chem. Soc.* **2012**, *134* (12), 5480-5483.

"Molybdenum Catalyzed Ammonia Borane Dehydrogenation: Oxidation Specific Mechanisms." Joshua A. Buss, Guy A. Edouard, Christine Cheng, Jade Shi, Theodor Agapie. *J. Am. Chem. Soc.* **2014**, *136* (32), 11272-11275.

"Aryl Ether Cleavage by Group 9 and 10 Transition Metals: Stoichiometric Studies of Selectivity and Mechanism." Guy A. Edouard, Paul Kelley, David E. Herbert, Theodor Agapie. *Organometallics* **2015**, *34* (21), 5254-5277.

RESPECTIVE CONTRIBUTIONS

The work in this thesis is the result of collaborative efforts; general comments outlining these efforts are provided here.

Studies of carbon–oxygen bond activation were conducted in close collaboration with Dr. Paul Kelley, who completed studies of this transformation with Ni using the $-NMe_2$ substituted terphenyl diphoshpine methyl–aryl ether **1b** and aryl–aryl ether **1c** in Chapter 2. Dr. Sibo Lin complimented this work with studies of a related catalytic system and provided computational insight throughout our investigations. Dr. David E. Herbert processed all single crystal X-ray diffraction (XRD) data and provided finalized solid state structures. The late Dr. Michael W. Day solved some of the solid state structures presented earlier on this work. Mr. Larry Henling and Mr. Joshua A. Buss aided in solving the solid state structure of compound **26a**.

In Appendix A, Dr. Gyeongshin Choi synthesized 1-iminoquinolyl-3-tert-butyl-5-triphenylsilyl-phenol and completed half of the ethylene oligomerization/polymerization reactions reported in Table A.1. Salicylaldehyde precursors **41** and **42** were prepared with Ms. Jessica Sampson and Dr. Choi; precursors, particularly Neigishi coupling partners, were shared and purified for common use.

In Appendix B, molybdenum compounds **57** and **58** were first prepared by Mr. Jade Shi. Optimization of my preparations of molybdenum compounds **57-59**, their characterization, and the completion of the determination of their solid states structures was accomplished by Mr. Buss. Processing of single crystal X-ray diffraction data and determination of solid structures in the case of the molybdenum compounds was completed by Mr. Buss; for all other compounds, this work was done by Larry Henling and the late Dr. Day.

ABSTRACT

Terphenyl diphosphines bearing pendant ethers were prepared to provide mechanistic insight into the mechanism of activation of aryl C–O bonds with Group 9 and Group 10 transition metals. Chapters 2 and 3 of this dissertation describe the reactivity of compounds supported by the model phosphine and extension of this chemistry to heterogenous C–O bond activation.

Chapter 2 describes the synthesis and reactivity of aryl-methyl and aryl-aryl model systems. The metallation of these compounds with Ni, Pd, Pt, Co, Rh, and Ir is described. Intramolecular bond activation pathways are described. In the case of the aryl-methyl ether, aryl C–O bond activation was observed only for Ni, Rh, and Ir.

Chapter 3 outlines the reactivity of heterogenous Rh and Ir catalysts for aryl ether C–O bond cleavage. Using Rh/C and an organometallic Ir precursor, aryl ethers were treated with H_2 and heat to afford products of hydrogenolysis and hydrogenation. Conditions were modified to optimize the yield of hydrogenolysis product. Hydrogenation could not be fully suppressed in these systems.

Appendix A describes initial investiagtions of bisphenoxyiminoquinoline dichromium compounds for selective C_2H_4 oligomerization to afford α-olefins. The synthesis of monometallic and bimetallic Cr complexes is described. These compounds are compared to literature examples and found to be less active and non-selective for production of α-olefins.

Appendix B describes the coordination chemistry of terphenyl diphosphines, terphenyl bisphosphinophenols, and biphenyl phosphinophenols proligands with

molybdenum, cobalt, and nickel. Since their synthesis, terphenyl diphosphine molybdenum compounds have been reported to be good catalysts for the dehydrogenation of ammonia borane. Biphenyl phosphinophenols are demonstrated provide both phosphine and arene donors to transition metals while maintaining a sterically accessible coordination sphere. Such ligands may be promising in the context of the activation of other small molecules.

Appendix C contains relevant NMR spectra for the compounds presented in the preceeding sections.

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CHAPTER 1

General Introduction

This dissertation deals primarily with the synthesis, metallation, and reactivity of terphenyl diphosphines and monophosphines with mid- to late-transition metals. An emphasis is placed on aryl C–O bond activation of terphenyl diphosphines bearing pendant methyl and aryl ethers. Efforts towards the synthesis of bisphenoxyiminoquinoline dichromium complexes tethered by a rigid terphenyl linker for selective oligomerization of ethylene are also described.

Aryl C–O bond activation is of interest in the context of conversion of biomass to hydrocarbons as well as aromatic compounds that are useful precursors in the preparation of pharmaceuticals and commodity chemicals. It is also a fundamental transformation in the elaboration of arene rings (e.g., through cross-coupling reactions). In aryl–alkyl ethers, the aryl C–O is stronger than the alkyl C–O bond; thus, engendering selectivity for catalytic aryl bond activation is an ongoing topic of research.

Our group has investigated terphenyl diphosphines which enfore metal-arene interactions. In the literature, computational studies had identified a nickel-arene interaction proximal to an aryl C–O bond as a key intermediate on the pathway of aryl C–O bond cleavage. We prepared a series of terphenyl diphosphines bearing pendant alkyl and aryl ethers which position transition metals in close proximity to aryl C–O bonds. With Ni, a mechanism for reductive cleavage of aryl-alkyl ether C–O without the addition of exogenous reductant was elucidated through a stoichiometric study with our terphenyl model system. This mechanism was shown to be relevant to a catalytic system. These stoichiometric studies were extended to Group 9 and Group 10 transition metals; Rh and Ir were found to activate the aryl C–O bond of our model system in the presence of an alkyl C–O bond (Chapter 2).

Having demonstrated that mechanisms determined in our stoichiometric system were operative in reported Ni-catalyzed C–O bond cleavage technology, we attempted to design new Rh- and Ir-catalyzed methodologies for selective aryl ether C–O bond cleavage (Chapter 3). In the absence of exogenous ligand, Rh/C and organometallic Rh and Ir precursors were found to be precatalysts for reactions which yielded hydrogenolysis and hydrogenation products of aryl ethers in the presence of neat aryl ether, heating, and H_2. Although reaction conditions were optimized for hydrogenolysis product, hydrogenation was observed all reactions.

From there, this dissertation continues with a discussion of efforts towards the synthesis of terphenyl bisphenoxyiminoquinoline dichromium complexes envisioned to be precatalysts for selective olefin oligomerization (Appendix A). Activities are an order of magnitude less than those reported in the literature for monometallic phenoxyiminoquinoline Cr compounds. A distribution of α-olefins is observed in this reaction. Optimization of the described reaction conditions and substitution of the phenoxyiminoquinoline proligand is suggested as a strategy towards engendering higher activity and selectivity in this system.

Lastly, terphenyl, terphenyl phenoxide, and biphenylphenoxide complexes of mid- to late-transition metals are dicussed in an appendix (Appendix B). These compounds display hemilabile metal-arene interactions, hard and soft donors, and open coordination sites which are attractive design principles for the activation of small molecules (e.g., CO_2, H_2, N_2) by low-coordinate, low-valent transition metal complexes.