

**FUNDAMENTAL STUDIES OF CARBON OXYGEN BOND ACTIVATION
IN NICKEL DIPHOSPHINE ETHER COMPLEXES**

AND

**METALLOMACROCYCLES AS LIGANDS: SYNTHESIS AND
CHARACTERIZATION OF ALUMINUM-BRIDGED BISGLYOXIMATO
COMPLEXES OF IRON AND COBALT**

Thesis by
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“See! Caltech made you happy.”

-Agnes Tong

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ABSTRACT

In order to develop better catalysts for the cleavage of aryl-X bonds fundamental studies of the mechanism and individual steps of the mechanism have been investigated in detail. As the described studies are difficult at best in catalytic systems, model systems are frequently used. To study aryl-oxygen bond activation, a terphenyl diphosphine scaffold containing an ether moiety in the central arene was designed. The first three chapters of this dissertation focus on the studies of the nickel complexes supported by this diphosphine backbone and the research efforts in regards to aryl-oxygen bond activation.

Chapter 2 outlines the synthesis of a variety of diphosphine terphenyl ether ligand scaffolds. The metallation of these scaffolds with nickel is described. The reactivity of these nickel(0) systems is also outlined. The systems were found to typically undergo a reductive cleavage of the aryl oxygen bond. The mechanism was found to be a subsequent oxidative addition, β -H elimination, reductive elimination and (or) decarbonylation.

Chapter 3 presents kinetic studies of the aryl oxygen bond in the systems outlined in Chapter 2. Using a series of nickel(0) diphosphine terphenyl ether complexes the kinetics of aryl oxygen bond activation was studied. The activation parameters of oxidative addition for the model systems were determined. Little variation was observed in the rate and activation parameters of oxidative addition with varying electronics in the model system. The cause of the lack of variation is due to the ground state and oxidative addition transition state being affected similarly. Attempts were made to extend this study to catalytic systems.

Chapter 4 investigates aryl oxygen bond activation in the presence of additives. It was found that the addition of certain metal alkyls to the nickel(0) model system lead to an increase in the rate of aryl oxygen bond activation. The addition of excess Grignard reagent led to an order of magnitude increase in the rate of aryl oxygen bond activation. Similarly the addition of AlMe_3 led to a three order of magnitude rate increase. Addition of AlMe_3 at $-80\text{ }^\circ\text{C}$ led to the formation of an intermediate which was identified by NOESY correlations as a system in which the AlMe_3 is coordinated to the ether moiety of the backbone. The rates and activation parameters of aryl oxygen bond activation in the presence of AlMe_3 were investigated.

The last two chapters involve the study of metalla-macrocycles as ligands. Chapter 5 details the synthesis of a variety of glyoxime backbones and diphenol precursors and their metallation with aluminum. The coordination chemistry of iron on the aluminum scaffolds was investigated. Varying the electronics of the aluminum macrocycle was found to affect the observed electrochemistry of the iron center.

Chapter 6 extends the studies of chapter 5 to cobalt complexes. The synthesis of cobalt dialuminum glyoxime metal complexes is described. The electrochemistry of the cobalt complexes was investigated. The electrochemistry was compared to the observed electrochemistry of a zinc analog to identify the redox activity of the ligand. In the presence of acid the cobalt complexes were found to electrochemically reduce protons to dihydrogen. The electronics of the ancillary aluminum ligands were found to affect the potential of proton reduction in the cobalt complexes. These potentials were compared to other diglyoximate complexes.

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CHAPTER 1

General Introduction

This dissertation is focused on two main areas, specifically the study of aryl oxygen bond activation in a nickel(0) diphosphine terphenyl ether complex and the study of aluminum glyoxime macrocycles and the effects of sterics and electronics on the coordination and chemistry of the central metal center.

The efficient elaboration of aryl oxygen bonds to a variety of functional groups is emerging as a versatile tool in organic methodology. One very important use of aryl oxygen moieties is for the facile modification of arene rings. These substituents can be introduced into the aromatic ring via a number of pathways, notably electrophilic aromatic substitution. One widely used example is for the lithiation of arene rings where the aryl-lithium salt can be quenched with an electrophilic species leads to derivatization of the ring.

Although the utility of aryl oxygen groups cannot be understated, their removal is not straightforward. The aryl oxygen bond is strong and hence resists efforts at its activation. Some catalytic systems have been developed albeit the systems typically suffer from low turnover and low rates. Another utility of this cleavage is in cross coupling. Cross coupling of aryl ethers allows for the utilization of phenolic precursors in organic synthesis. While catalytic systems have been developed few in-depth mechanistic studies have been done on the reactivity of aryl oxygen bonds with nickel.

While few experimental studies had been done some computational studies had been undertaken where it was found that a nickel arene interaction was of present prior to the activation of the aryl oxygen bond. Our group has been focusing on several novel terphenyl diphosphine scaffolds. These terphenyl diphosphines were found to encourage metal arene interactions with a variety of metals. Given that the ligands predisposed the metal to interact with the arene we envisioned observing intramolecular reactivity with an ether moiety in close proximity with the central arene

ring. Hence we come to the main ligand of this thesis. We developed a diphosphine terphenyl containing an ether moiety in the central arene of the terphenyl. Using this novel diphosphine studies were undertaken to gain mechanistic insight into the mechanism of aryl oxygen bond activation. From this system, in collaboration with my colleagues Sibio Lin and Guy A. Edouard, a mechanism for the reductive cleavage of aryl oxygen bond was able to be worked out, which we were able to extend to catalytic systems.

From there I directed myself to studies on the effect of electronics in aryl oxygen bond activation (Chapter 3). I was able study the rate of oxidative addition in great detail in variants of the nickel diphosphine discussed in chapter two. I was able to show that the rates and kinetics of oxidative addition are not affected significantly by the electronics of the ether. This is proposed to result from similar changes in the energy of the ground and transition states. Attempts were made to extend these studies to actual catalytic systems however due to the complexity of the systems the conclusions were always less than satisfying.

However, during the kinetic studies I was able to observe the acceleration of aryl oxygen bond activation in the presence of Lewis metal alkyls. Through careful low temperature studies we were able to ascertain that the Lewis acidic metal is coordinated to the ether moiety. The rate was found to show a dependence on Lewis acidic metal alkyl hinting a much more complicated mechanism.

The second part of my thesis deals with the study of iron and cobalt glyoxime complexes. What sets these compounds apart is the large aluminum linker between the glyoximes. The aluminum linkers and the ancillary ligands on the aluminum were found to affect the chemistry and geometry of the metal center. The structural and

electrochemical parameters of the iron complex were investigated. Analogous cobalt complexes were studied for proton reduction as a function of the aluminum linkers.

