ABSTRACT

ROBBINS, LEANNA KATE. Mechanistic Studies for New Bond Forming Reactions Mediated by Oxorhenium(V) and Cp*Iridium Complexes. (Under the direction of Dr. Elon A. Ison)

This document focuses on the synthesis and characterization of new Oxorhenium(V) complexes bearing tridentate pincer ligands and of Cp*(NHC)Ir complexes and the mechanistic studies of these complexes their reactivity in new bond forming reactions. The study of mechanisms of new bond forming reactions will lead to the development of more efficient catalysts and systems that make C-C and C-O bonds.

In Chapter 2, diamidoamine (DAAm) oxorhenium(V) benzyl and benzyl derivatives were synthesized and their reactivity with CO was studied. The corresponding acetyl benzyl derivatives were isolated and characterized. The mechanism for the activation of CO via oxorhenium(V) complexes were studied. It was found through experimental and computational studies that the most likely mechanism for CO insertion was a direct insertion mechanism and not a typical two step mechanism. The ability for these complexes to undergo a direct insertion is likely due to the strong trans influence of the terminal oxo ligand.

In Chapter 3, new alky/aryl oxorhenium(V) complexes bearing thiodiethane thiol ligands (SSS) were synthesized. The ancillary ligand effects on the mechanism for CO insertion were investigated. The reaction of (SSS)Re(O) complexes with CO were studied both experimentally and computationally. CO insertion into (SSS)Re(O) complexes required harsher reaction conditions (50 ºC, 800 psi CO). It was found computationally that the most likely mechanism for CO insertion was the formation of two, high energy, CO adducts prior to CO insertion. When changing the ancillary ligand, the electronics of the metal center is altered. The alteration of electronics at the metal center allowed for the formation of CO adducts prior to CO insertion. However, the CO adducts observed computationally are high energy intermediates likely due to the trans influence of the oxo ligand.

In Chapter 4, the synthesis of new oxorhenium(V) complexes was attempted for their application in new bond forming reactions. First, the synthesis of new diamaindo amine ligands bearing trimethylsilyl (TMS) and tert-butyl dimethylsilyl(TBS) substituents were synthesized. The synthesis of new oxorhenium(V) complexes bearing TMS-DAAm or TBS-DAAm ligand frameworks was attempted. Several attempts to coordinate TMS-DAAm and TBS-DAAm ligands under a variety of conditions were unsuccessful.
Chapter 5, explores the mechanism for the formation of methanol via \( \text{Cp}^*\text{Ir}(\text{NHC})(\text{Me})(\text{Cl}) \). The kinetics for the rate of formation the novel Ir-\( \mu \)-oxo intermediate and the rate dependence on a proton source for the reaction was found. The formation of iridium oxo and iridium hydride intermediates were probed experimentally. No iridium oxo complex was able to be observed. Reactivity of the iridium hydride complex with chloride extracting reagents exhibited the formation of \([\text{Cp}^*(\text{NHC})(\text{H})]^2^+\) in all cases and not an \([\text{Cp}^*\text{Ir}(\text{NHC})\text{Cl}]^2^+\) that is observed experimentally in the methanol forming reactions. Though no new iridium intermediates were able to be isolated several new \( \text{Cp}^*\text{Ir}(\text{NHC}) \) complexes were isolated and characterized and may be used in further studies.
Mechanistic Studies of New Bond Forming Reactions Mediated by Oxorhenium(V) and Cp*Iridium Complexes

by

Leanna Kate Robbins

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Chemistry

Raleigh, North Carolina

2016

APPROVED BY:

Dr. Elon A. Ison
Committee Chair

Dr. Reza Ghiladi

Dr. Elena Jakubikova

Dr. David Shultz
DEDICATION

To my sisters, Logan and Allison
Leanna Kate Robbins was born on April 9, 1989 to Valerie Lee and David Robbins in Shenandoah, Virginia. She grew up in Big Stone Gap, VA with her two younger sisters Logan and Allison. She was interested in science at a young age and enjoyed chemistry and biology classes in high-school. Leanna graduated from Powell Valley High School and moved to Wise, Virginia to obtain an undergraduate degree in chemistry at The University of Virginia’s College at Wise. After taking inorganic chemistry in she decided to pursue a graduate degree in chemistry. After obtaining a Bachelors of Arts in Chemistry from UVa-Wise in 2011, she moved to Raleigh, NC to pursue a PhD in Chemistry at North Carolina State University. Since arriving at NC State University she has been conducting research under the direction of Elon A. Ison.
# TABLE OF CONTENTS

LIST OF TABLES.................................................................................................................. viii
LIST OF FIGURES................................................................................................................ ix

## CHAPTER 1

GENERAL INTRODUCTION..................................................................................................... 1

1.1 Background......................................................................................................................... 2

1.1.1 Organometallic Chemistry............................................................................................... 2

1.1.2 Petroleum as a Source for Petrochemical Production..................................................... 2

1.1.3 Current Technology for the Synthesis of Methanol......................................................... 2

1.1.4 Utilization of Rhenium Catalysts for Small Molecule Activation................................. 6

1.2 Scope.................................................................................................................................. 7

1.3 References............................................................................................................................ 9

## CHAPTER 2

THE SYNTHESIS AND CHARACTERIZATION OF (DAAM)RE(O)(R) COMPLEXES AND STUDY OF THE MECHANISM FOR CO ACTIVATION..................................................12

2.1 Abstract.............................................................................................................................. 13

2.2 Introduction........................................................................................................................ 13

2.2.1 Migratory Insertion of CO............................................................................................... 14

2.2.2 CO Insertion via Oxorhenium(V) Complexes.................................................................. 17

2.3 Results and Discussion......................................................................................................... 24

2.3.1 Synthesis and Reactivity of Oxorhenium(V) Benzyl and Phenyl Complexes............. 24

2.3.2 Insertion Reactions with CO............................................................................................. 27

iv
CHAPTER 3
SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF (SSS)Re(O)(R) COMPLEXES AND A COMPUTATIONAL INVESTIGATION OF ANCILLARY LIGAND EFFECTS ON THE MECHANISM FOR CO INSERTION

3.1 Abstract

3.2 Introduction

3.2.1 Background

3.2.2 Factors Affecting Migratory Insertion

3.3 Results and Discussion

3.3.1 Synthesis of New Rhenium Complexes

3.3.2 Reactivity of complexes 7-10 with CO

3.3.3 Characterization of 14
CHAPTER 4
SYNTHESIS OF NEW DIAMIDOAMINE LIGANDS AND OXORHENIUM(V) COMPLEXES

4.1 Abstract
4.2 Introduction
4.3 Results and Discussion
4.3.1 Diamidoamine Ligand Synthesis
4.3.2 Attempted Synthesis of DAAm Oxorhenium Complexes
4.3.3 Synthesis via Rhenium(III) starting materials
4.4 Conclusions
4.5 Experimental
4.6 References

CHAPTER 5
MECHANISTIC INVESTIGATION OF OXYFUNCTIONALIZATION OF Cp*Ir(NHC) COMPLEXES

5.1 Abstract
5.2 Introduction........................................................................................................122
5.3 Results and Discussion.....................................................................................125
  5.3.1 Investigation of the Mechanism of the Methanol Forming Step...............137
  5.3.2 Study of the β-hydride Elimination Step..................................................139
5.4 Conclusions......................................................................................................142
5.5 Experimental....................................................................................................143
5.6 References........................................................................................................145
LIST OF TABLES

Table 2.1. Rates for the insertion of CO into complexes 1, 4a-d, and 5 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldo
LIST OF FIGURES

Figure 1.1. Pathways to chemicals and hydrocarbon production..............................5
Figure 1.2. The Monsanto Acetic Acid Process..........................................................6
Figure 1.3. Complexes for CO insertion studies............................................................7
Figure 2.1. $^1$H NMR spectrum of complex 4a in CH$_2$Cl$_2$........................................25
Figure 2.2. Thermal ellipsoid plot for 4a.................................................................26
Figure 2.3. Thermal ellipsoid plot for 5.................................................................27
Figure 2.4. $^1$H NMR of complex 6a in CD$_2$Cl$_2$................................................28
Figure 2.5. Thermal ellipsoid plot for 6a.................................................................29
Figure 2.6. Time profile for the formation of 6a......................................................30
Figure 2.7. Hammett plot for the relative rates of addition of CO (60 psi) to complexes 4a-d in CD$_2$Cl$_2$ at room temperature.......................................................34
Figure 2.8. Eyring plot for the disappearance of 4a in the presence of CO in C$_6$D$_6$........37
Figure 2.9. Eyring plot for the disappearance of 1 in the presence of CO in C$_6$D$_6$........38
Figure 2.10. Molecular orbital diagram for oxorhenium CO adduct..........................50
Figure 2.11. Initial rates plot for the formation of 4a at 60 psi CO.............................55
Figure 2.12. Initial rate plot for the decay of 4a at 60 psi CO....................................56
Figure 2.13. Initial rate plot for the formation of 4a at 27 psi CO.............................57
Figure 2.14. Initial rates plot for the decay of 4a at 27 psi CO..................................58
Figure 2.15. Initial rate plot for the formation of 4a at 10 psi CO................................59
Figure 2.16. Initial rate plot for the decay of 4a at 10 psi CO..................................60
Figure 2.17. Plot of log(initial rate) vs. log(pCO)....................................................61
Figure 2.18  Disappearance of 4a in the presence of CO (60 psi) at 15 ºC……………..…62
Figure 2.19  Disappearance of 4a in the presence of CO (60 psi) at 25 ºC……………..…63
Figure 2.20  Disappearance of 4a in the presence of CO (60 psi) at 35 ºC……………..…63
Figure 2.21  Disappearance of 4a in the presence of CO (60 psi) at 45 ºC……………..…64
Figure 2.22  Disappeared of 4a in the presence of CO (60 psi) at 55 ºC……………..…64
Figure 2.23  Eyring plot for the disappearance of 4a in the presence of CO (60 psi) in C6D6 at temperatures 15-55 ºC………………………………………..65
Figure 2.24  Disappearance of 1 in the presence of CO (60 psi) 15 ºC……………..…66
Figure 2.25  Disappearance of 1 in the presence of CO 60 psi 25 ºC……………..…66
Figure 2.26  Disappearance of 1 in the presence of CO (60 psi) 45 ºC……………..…67
Figure 2.27  Disappearance of 1 in the presence of CO (60 psi) 55 ºC……………..…67
Figure 2.28  Eyring plot for the disappearance of 1 in the presence of CO (60 psi) in C6D6 at temperatures 15-55 ºC………………………………………..68
Figure 2.29  Time profile for the formation of 4b………………………………………..69
Figure 2.30  Time profile for the formation of 4c………………………………………..70
Figure 2.31  Time profile for the formation of 4d………………………………………..71
Figure 3.1  Lewis acid stabilized acyl complexes………………………………………..78
Figure 3.2  X-ray crystal structures of 8-10………………………………………………81
Figure 3.3  1H NMR spectrum of 7 in CDCl3………………………………………………82
Figure 3.4  Reactivity of 10 in toluene with CO at 50 ºC for up to 7 hours in a 25.0 mL glass jacket for the Parr reactor………………………………………..83
Figure 3.5  X-ray crystal structure of 11 and 12…………………………………………84
Figure 3.6  1H NMR of 11 in CDCl3…………………………………………………………85
Figure 3.7  UV-vis spectrum of 14 in CH2Cl2 at 25 ºC……………………………………86
Figure 3.8  X-ray crystal structure of 14…………………………………………………………………..87
Figure 3.9  $^1$H NMR spectra of 7-B(C6F5)3 with CO at 25 ºC monitored in a J-young NMR tube in benzene-d$_6$…………………………………………………………………..89
Figure 3.10 Preliminary X-ray crystal structure of 7·B(C$_6$F$_3$)3………………………………………91
Figure 3.11 Computational considered pathways for CO insertion…………………………………92
Figure 3.12 Computational pathways for the migratory insertion of CO in 7………………96
Figure 4.1  Representative oxorhenium complexes……………………………………………………….105
Figure 4.2 Diamidoamine trimethylsilyl, TMS-DAAm………………………………………………………..108
Figure 4.3 Organometallic complexes incorporating the TMS-DAAm ligand…………109
Figure 4.4  $^1$H NMR of TBS-DAAm in CDCl$_3$…………………………………………113
Figure 4.5  $^1$H NMR of Li$_2$TBS-DAAm in C$_6$D$_6$………………………………………………115
Figure 5.1 Shilov system……………………………………………………………………………….122
Figure 5.2 Proposed oxyfunctionalization by the Ison group……………………………………123
Figure 5.3 Proposed active intermediate for oxyfunctionalization………………………………124
Figure 5.4 Mechanism for methanol formation via 28………………………………………………126
Figure 5.5 Scan of the UV-vis spectrum for the conversion of 29 to 30 vs. time…………127
Figure 5.6 Proposed new iridium NHC complexes…………………………………………………….128
Figure 5.7 X-ray crystal structure of 31……………………………………………………………….129
Figure 5.8  $^1$H NMR spectra of the reaction outlined in scheme 5.8…………………………131
Figure 5.9  $^1$H NMR of 32 in CD$_2$Cl$_2$……………………………………………………………….132
Figure 5.10 $^1$H NMR spectrum of 33 in CD$_2$Cl$_2$…………………………………………………….133
Figure 5.11 $^1$H and $^{31}$P NMR of the reaction of 28 with PPh$_3$ and NaBArF$_4$ in CD$_2$Cl$_2$ open to air at 25 ºC after 0.5 hours……………………………………………………134
Figure 5.12  Proposed formation of Ir-PPh₃ complex……………………………………135
Figure 5.13  ¹H NMR of the reaction of 30, NaBArF₄ with tBuOOH in CD₂Cl₂ at room temperature……………………………………………………………………137
Figure 5.14  Typical plot of the decay of absorbance of 30 vs. time…………………138
Figure 5.15  Rate dependence on ethanol…………………………………………………..139
Figure 5.16.  ¹H NMR of complex 34 in CH₂Cl₂, zoom in of hydride region of the NMR………………………………………………………………………..140
Figure 5.17  ¹H NMR of complex 35 from a reaction of 34 with NaBArF₄ in CH₂Cl₂…………………………………………………………………………141
Chapter 1

General Introduction
1.1 Background

1.1.1 Organometallic Chemistry

Organometallic chemistry involves the combination of organic and inorganic chemistry, where a metal center is surrounded by an organic framework or ligand. Complexes such as these have been shown to increase reactivity, selectivity, and create new pathways for the formation of organic molecules.\(^1\) These organometallic complexes are generally employed as catalysts for many processes, where they undergo a series of transformations to give a specific product.\(^2\) Many industrial processes have been able to benefit from this enhanced reactivity and have employed the use of catalysts for reactions that are otherwise inefficient. Large industrial processes that utilize transition metals for catalysis include: alkene metathesis\(^3\) and polymerization\(^4\), CO\(^5\), C-H\(^6\), and CO\(_2\) activation\(^7\), and C-C bond formation and cleavage.

1.1.2 Petroleum as a source for petrochemical production

Petroleum, a naturally occurring source of hydrocarbons, and its products are ubiquitous in our everyday lives. A variety of useful products can be obtained from the refining of crude oil. The most common of those products is transportation fuels (gasoline, diesel, jet fuel) and accounts for over half of the petroleum used worldwide.\(^8\) Gaseous products, hydrocarbons containing C\(_1\)-C\(_4\) atoms, are also among some of the useful products obtained from oil refining. Also from refining, unsaturated hydrocarbons (ethylene, propylene, butylene) and aromatic compounds (benzene, toluene, xylenes) can be obtained. These unsaturated and aromatic compounds are synthetically useful raw materials and are utilized for the synthesis of petrochemicals. Petrochemicals account for the majority of plastics, rubber lubricants, solvents, agricultural insecticides, and synthetic fibers. However, petrochemicals make up only a small fraction, \(~6\%\)\(^9\) of the products obtained from crude oil refining, but make up for a large fraction of monetary value. Importantly, petroleum sources are utilized to produce synthesis gas (syngas), the industrial source of methanol, which is used to generate the majority of petrochemicals.

1.1.3 Current technology for the synthesis of methanol

Syngas can be derived from the partial oxidation of a hydrocarbon source such as, natural gas, petroleum, heavy oils and tar sand, coal, and biomass for the synthesis of methanol (Figure
Syngas is produced industrially by methane steam reforming to generate a mixture of carbon monoxide and hydrogen gas (Scheme 1.1)

**Scheme 1.1** Synthesis of syngas via steam reforming

\[ \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{[Ni]}} \text{CO} + 3\text{H}_2 \]

For this process a heterogeneous nickel catalyst is used at high temperatures to generate a hydrogen rich mixture of syngas. One of the largest industrial processes involves the catalytic conversion of synthesis gas (CO/H\(_2\)) to methanol (Scheme 1.2).

**Scheme 1.2**. Methanol synthesis reaction

\[ \text{CO} + 2\text{H}_2 \xrightarrow{\text{Cu/ZnO/Al}_2\text{O}_3} \text{CH}_3\text{OH} \]

Methanol is a primary feedstock for the chemical industry and is produced in quantities of 32 million tons per year. Currently, the majority (~90.0%) of methanol produced is obtained from syngas. Thus, the conversion of natural gas to syngas is the preferred method for the synthesis of methanol; however, it is of interest to pursue other routes for the conversion of petrochemicals to useful chemicals that are more efficient.

The direct conversion of synthesis gas to a bulk chemical or higher molecular weight hydrocarbon is a possible alternate route (Figure 1.1, green). One example of this type of process is the Fisher-Tropsch reaction, which is most widely used for the conversion of synthesis gas to alcohols and alkanes. This conversion of syngas to a desired product directly would reduce the need to generate another reactive intermediate such as, methanol and would allow for the continued use of the existing infrastructure for syngas production.

Alternatively, the process of steam reforming is energy intensive and the high temperatures required to generate syngas from stream reforming requires costly infrastructure to withstand these conditions. The infrastructure for this process must also be constructed in remote locations where methane reserves are located, which also makes this process inefficient. Due to the cost, most methane goes underutilized and often methane stranded in pipelines is burned in an unproductive fashion (flaring). For these reasons, it would also be
advantageous to develop a route for methanol production that bypasses the formation of syngas.

Natural gas reserves are comparable to petroleum reserves, 187.07 trillion cubic meters in 2014. However, at this point natural gas reserves are relatively underutilized. These natural gas reserves are generally located in remote areas that require the transport of natural gas to locations where it may be utilized. Due to the remote areas where natural gas is located, and its increasing demand, a potential solution is the liquefaction of natural gas to transport more easily. However, the liquefaction of natural gas presents its own set of challenges. To liquefy natural gas it must be stored at low temperatures (-162 °C) and at high pressures. The infrastructure to liquefy natural gas and the appropriate containers required for storage and transport of liquid natural gas (LNG) is energy intensive and requires a large capital investment. A possible solution to the production of LNG is the conversion of natural gas on site to a liquid product for ease of transport; this is commonly referred to as gas-to-liquid (GTL) technology. An attractive route is to convert methane (CH₄), the major component of natural gas, to methanol (CH₃OH), which is a transportable liquid (bp: 65 °C) (Figure 1.1, red). However, the current technology for the conversion of methane to methanol is not well developed. Due to the fact that methanol is currently utilized extensively by the chemical industry as a starting material and due to its ease of transport as a liquid compared to gaseous methane, developing technology for the conversion of methane to methanol would be an advantageous use of natural gas reserves.

Selectively converting methane to methanol would eliminate the need to produce syngas and reduce the costs of the infrastructure required to achieve this process. Therefore, a process that could selectively convert methane to methanol would be a competitive process for the current synthesis gas route. Another alternative to the production of syngas is the conversion of methane to another catalytic intermediate, such as, mono-halogenated methane, which could undergo hydrolysis to afford methanol (Figure 1.1, blue).

When developing or improving any of these technologies discussed above for the synthesis of bulk chemicals, an understanding of the fundamental reactions that make these processes possible is necessary. First, the technology to activate unreactive C-H bonds
selectively must exist. Specifically, the technology to activate the C-H bonds of methane (the major component of natural gas) efficiently must be improved upon. Secondly, to generate syngas, methanol, or desired chemicals from any hydrocarbon source, the ability to functionalize these bonds, (form new C/C-O bonds) is necessary. Once the processes for C-H activation and new bond forming reactions (C-C/C-O) have been developed, the mechanisms for these new processes need to be well understood. As this will lead to the development of more efficient catalysts, higher product conversion, and selectivity.

![Diagram](image)

**Figure 1.1** Pathways to chemicals and hydrocarbon production.

Important industrial processes that utilize methanol as a starting material to produce fine chemicals are the Monsanto acetic acid process\(^{12}\), BP’s Cativa process\(^{13}\), and Eastman Chemical’s acetic anhydride process\(^{14}\). The Monsanto Acetic Acid Process, contains some of the key features for developing efficient routes to fine chemicals (Figure 1.2). This process utilizes methanol as a starting material and a homogeneous transition metal catalyst, \([\text{Rh(I)}_2(\text{CO})_2]^{-1}\), to obtain acetic acid, a bulk chemical synthesized on the scale of \(~3.5\) million
tons per year\textsuperscript{15}. This process contains two key steps, a \textit{C-C bond forming step} and a \textit{C-O bond-forming step} to proceed to product. As discussed above (1.1 background), the use of catalysts lowers the activation barrier of a reaction, making the process proceed under more mild conditions. The catalyst, in this case, is also homogeneous in nature and is able to be monitored via spectroscopic methods. Monitoring the reaction and reactivity of the catalyst spectroscopically allows for the isolation of important intermediates and the ability to obtain reaction kinetics. All of these aspects allows for an \textit{understanding of the mechanism for a particular process}. In this example, Rh intermediates were isolated and characterized and the mechanism for the C-C bond-forming step of this reaction is understood to proceed by methyl migration to for a rhodium acyl intermediate.
1.1.4 Utilization of rhenium catalysts for small molecule activation

The use of rhenium complexes as a catalyst is advantageous. Though rhenium is not as electropositive as the early transition metals or as efficient at oxidative addition as many late transition metals because it occurs in the middle of the periodic table, it has access to many oxidation states, and the ability to tolerate a variety of ligand frameworks. Although rhenium is not thought to be as reactive as its first and second row transition metal counterparts due to the formation of stronger metal ligand bonds, rhenium can generally form more stable

Figure 1.2. The Monsanto Acetic Acid Process.16
complexes for the use in catalysis. The formation of stable rhenium complexes would be beneficial for the study of reaction mechanisms. Of particular interest are high-valent rhenium oxo complexes and their reactivity. Rhenium oxos have been the subject of many studies, and subsequently, a variety of oxorhenium complexes bearing diverse ligand frameworks have been synthesized.\(^{17}\)

1.2 Scope

The activation of CO is important for the utilization of syn-gas for the production of industrially relevant intermediates such as methanol or to obtain feedstock chemicals directly from syngas. In the example shown in Figure 1.2, activation of CO by transition metal complexes are commonly proposed steps for the formation of C-C bonds. Also important is the formation of acyl intermediates, which are commonly proposed in new bond forming reactions like the Monsanto Acetic Acid Process.

![Figure 1.3. Complexes for CO insertion studies.](image)

Previously, our group has studied the reactivity of high valent rhenium complexes bearing tridentate diamido amine, diamido pyridine, and thiol ligands (Figure 1.3) for the activation of CO.\(^{18}\) A novel catalytic system for syngas conversion was pursued by our lab involving C-C bond formation, and C-O bond formation to produce C\(_n^+\) oxygenates. Our lab was able to demonstrate two of these steps, C-C and C-O bond formation by oxorhenium complexes bearing the DAAm (DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C\(_6^5\)F\(_3\)) ligand framework (Scheme 1.3).

**Scheme 1.3.** DAAmRe(O) reactivity with CO.
To better understand the mechanism for the C-C bond formation step, mechanistic and kinetic investigations into the activation of CO by these high valent rhenium complexes are presented in Chapter 2. New DAAmRe(O)(Bn) complexes were synthesized and utilized to obtain reaction kinetics. It was determined experimentally and computationally utilizing Density Functional Theory (DFT) that the reaction mechanism was bimolecular and consistent with an atypical mechanism for CO insertion, a direct CO insertion mechanism. The novel mechanism for CO insertion reactions by oxorhenium complexes is importantly due to the strong trans influence of the terminal oxo ligand.

The exploration of the dependence the mechanism for CO insertion on the ancillary ligand is discussed in chapter 3. New oxo rhenium complexes bearing thiodiethanethiol (SSS) ligand were isolated and characterized. With these complexes in hand, their reactivity with CO was explored both experimentally and computationally. It was found that when changing the ancillary ligand of these oxorhenium complexes the electronics was drastically changed, where complexes bearing the SSS framework were found to be less electron rich than the DAAm and DAP counterparts. The most likely mechanism for CO insertion for oxorhenium SSS complexes, found computationally, was a pathway that included the formation of two CO adducts. The two CO adducts calculated are high in energy and exhibit weak rhenium carbonyl bonds. The long rhenium carbon bond lengths demonstrate the strong trans influence of the terminal oxo ligand. Also, from inspection of the geometry of the CO adduct and acyl product, it was determined that this was also a rare example of CO insertion rather than alky/aryl migration. The mechanistic studies of chapters 2 and 3 have led to a greater understanding of the role electronics play in CO activation, and more specifically, an understanding of how ancillary (DAAm, DAP, SSS) and strong trans influence ligands (oxo) govern the stabilization of CO adduct intermediates along the reaction coordinate for migratory insertion reactions.
The syntheses of new tridentate ligands and the formation of new high valent rhenium complexes for the use in carbonylation reactions is presented in chapter 4. Due to the effect of ancillary ligands on the reactivity of oxorhenium complexes, the synthesis of new rhenium complexes with tridentate ligands with varying electronics and steric was attempted. New DAAm ligands bearing trimethylsilyl (TMS) and tert-butyldimethylsilyl (TBS) substituents off the amide nitrogens were synthesized. Several attempts to coordinate the new ligands to a variety of rhenium starting materials were unsuccessful.

This thesis concludes with the exploration of the mechanism for quantitative methanol formation from Cp*Ir(NHC)MeCl at room temperature. Though systems to activate C-H bonds have been well studied, the subsequent oxyfunctionalization step to afford oxygenated C_n^+ products have been less studied. Furthermore, a system that is able to both activate and functionalize C-H bonds efficiently under mild conditions has not been found. Many studies have been completed on the Cp*Ir(PMe_3) system’s ability to activate C-H bonds of methane at and below room temperature. However, the PMe_3 system is not stable under conditions for subsequent oxidation. Cp*Ir(NHC) complexes, were proposed to be similar in electronics to the PMe_3 system, but more robust under oxidizing conditions. It had been shown previously by our group that Cp*Ir(NHC)Me(Cl) open to air at room temperature undergoes the formation of methanol in quantitative yields. In chapter 5, the rate dependence with respect to novel intermediates and a proton source was examined. The synthesis of Cp*Ir(NHC)X (X = Ph, H, C_6F_5) is described. These new iridium complexes were utilized in stoichiometric reactions to probe the intermediacy of iridium oxo formation and the formation of iridium hydride intermediates proposed in the mechanism for methanol formation. Though the formation of iridium oxo complexes was undetermined, several new Cp*Ir(NHC) complexes were isolated and characterized.

1.3 References


Chapter 2

The Synthesis and Characterization of (DAAm)Re(O)(R) Complexes and Study of the Mechanism for CO Activation

Portions of this chapter were published in Organometallics

Department of Chemistry, North Carolina State University;
Raleigh, North Carolina, 27695-8204
2.1 Abstract
The complexes [(DAAm)Re(O)(R)] [DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C6F5], 1, R = Me; 4a–d (R = benzyl, a; 4-methylbenzyl, b; 4-fluorobenzyl, c; 4-methoxybenzyl, d); and 5, R = Ph, were synthesized. CO insertion into the Re−R bond in 1 and 4a–d resulted in the formation of the acetyl complex, 2, and the (aryl)acetyl complexes, 6a–d respectively. The formation of 6a–d proceeded at a faster rate (7 h) than the formation of 2 (72 h) under the same conditions. No reaction was observed however for the phenyl complex 4 with CO. Kinetics for CO insertion into the various Re−R bonds were examined, and the experimental rate law was determined to be Rate = k_{obs}[Re][CO]. The activation parameters for CO insertion into 1 and 4a were determined to be ΔG⧧ (298 K) = 24(1) kcal/mol. The enthalpy of activation ΔH⧧ was determined to be 9(1) and 10(3) kcal/mol for 1 and 4a, respectively, and the entropy of activation, ΔS⧧, was −49(2) and −36(4) cal/mol·K. Computational studies (M06) are consistent with the hypothesis that the rate of CO insertion is dependent on the strength of the rhenium–carbon bond. Thus, experimental and computational data suggest that the most likely mechanism for the insertion of CO into the Re−R bond in oxorhenium complexes is a direct insertion mechanism.

2.2 Introduction
The migration of an anionic ligand X to a cis unsaturated ligand Y to form a M-Y-X complex and a new Y-X bond is a common transformation for many organotransition metal complexes and is depicted in Scheme 2.1. These reactions are commonly referred to as migratory insertion reactions. Migratory insertion steps are included in many catalytic processes. These steps are particularly important for the formation of new bonds, specifically C-C and C-O bonds. As shown in Scheme 2.1, the nucleophilic attack of ligand X on the unsaturated ligand Y results in a the formation of an intermediate that is generally trapped by a labile ligand, L, to form a new product. Common examples of unsaturated ligands, Y, include, but are not limited to, carbon monoxide, ketones, olefins and alkynes. In contrast, a less common mechanism for intramolecular migratory insertion involves the insertion of an unsaturated ligand into a M-X bond to form the product M-Y-X, is depicted in Scheme 2.2. This process proceeds by the insertion of an unsaturated ligand, Y, into a metal-X bond.
Scheme 2.1. General scheme for the nucleophilic attack of an unsaturated ligand Y by and anionic ligand X

\[
\begin{array}{c}
\text{Scheme 2.2. General scheme for and intramolecular insertion of an unsaturated ligand into a M-X bond}
\end{array}
\]

Y = CO, alkyne, olefin, ketone

2.2.1 Migratory insertion of CO
The migratory insertion of carbon monoxide into a metal alkyl bond to form a metal acyl is a well-known transformation in organometallic chemistry. There are two types of migratory insertion mechanisms for the formation of metal acyl complexes: (1) intermolecular direct insertion of CO into a metal alkyl bond and (2) intramolecular migratory insertion of CO to form a metal acyl (Scheme 2.3). Direct insertion proceeds by the attack of CO at a metal alkyl bond (Scheme 2.3a). The intramolecular mechanism could involve CO insertion (Scheme 2.3b), or alkyl migration (Scheme 2.3c). There are many examples of intramolecular migration of an alkyl to form a metal acyl, and there are fewer examples of intramolecular CO insertion into metal alkyl bonds. Examples of a direct insertion have been reported in our lab for oxorhenium(V) complexes.
One of the earliest mechanistic studies of intramolecular CO migratory insertion was performed with pentacarbonyl alkylmanganese complexes (Scheme 2.4).\textsuperscript{5} The manganese complex [Mn(CO)\textsubscript{5}Me] was treated with \textsuperscript{13}CO by Calderazzo and co-workers and evaluated for the stereochemical outcomes of migratory insertion. If methyl migration were to occur, the *cis* (A), the *trans* (B), and the \textsuperscript{13}C labeled acyl (C) products would be observed in a 2:1:1 ratio respectively. If CO insertion were to occur only the *cis* (A) and \textsuperscript{13}C labeled acyl (C) product would be observed in a 3:1 ratio, respectively. Importantly, the *trans* (B) product, cannot be formed from CO insertion. Only the product ratio consistent with methyl migration was observed. It was also determined that migratory insertion occurred intramolecularly with the migrating CO ligand originating from the metal center because the observed products contained a \textsuperscript{13}C labeled acyl ligand.
**Scheme 2.4.** The migratory insertion of CO into pentacarbonyl alkylmanganese complexes\(^5\)

Wojcicki and coworkers have found that asymmetric iron alkyl complexes [CpFe(CO)(PPh\(_3\))R] (R = alkyl) retain configuration when CO insertion occurred and inverted configuration when alkyl migration occurred (Scheme 2.5).\(^6\) These studies suggest that several factors govern whether the reaction proceeds by CO insertion or alkyl migration. In nitromethane, alkyl migration (A) to form the (R) enantiomer is observed and in HMPA, CO insertion (B) results in the formation of the (S) enantiomer. Thus, these studies have shown that the factors that influence the mechanism for migratory insertion are vast and can become complex. The mechanism for migratory insertion is dependent on the migrating group, solvent, incoming nucleophile, the relative stability of the metal acyl, and the metal center itself.\(^1\)\(^,\)\(^7\)
**Scheme 2.5.** The migratory insertion of CO with asymmetric iron alkyl complexes

Though the intramolecular formation of a metal acyl from a $\text{M(CO)}_n\text{R}$ complex, is commonly proposed, one can envision that the intermolecular formation of a metal acyl from an $\text{M-R}$ complex and CO can also be a relevant mechanism. A metal alkyl could undergo a direct CO insertion into a metal alkyl or aryl bond without prior formation of a CO adduct (Scheme 2.3a). However, until recent reports from our lab, there were no prior examples of the direct insertion of CO into a metal alkyl bond.  

**2.2.2 CO Insertion via Oxorhenium(V) Complexes**

Previously our lab has shown a new pathway for C-O and C-C bond forming reactions using high-valent oxorhenium complexes. Addition of CO to $[(\text{DAAm})\text{Re(O)(CH}_3\text{)}]$ [DAAm = N’N-bis(2-arylaminoethyl)methylamine; ary1 = C$_6$F$_5$] (1) resulted in the formation of the CO acetate complex $[(\text{DAAm})\text{Re(O}_2\text{CCH}_3\text{)(CO)}]$ (3) (Scheme 2.6).  

Under select conditions, the addition of CO to 1 led to the formation of the acyl intermediate $[(\text{DAAm})\text{Re(O)(C(O)CH}_3\text{)}]$ (2), and the addition of CO to 2 resulted in the formation of the CO acetate complex 3. The mechanism for the transformation of 1, to the
acyl intermediate 2, and the subsequent formation of the CO acetate product, 3, was studied both experimentally and computationally.

**Scheme 2.6.** Two-step mechanism for the activation of CO by 1

These studies led to the conclusion that the formation of 3 from 1 occurs via two distinct steps: (1) direct insertion of CO into the Re-carbon bond of complex 1 to yield complex 2 and (2) a 1, 2 migration of the acyl ligand of complex 2 to the terminal oxo followed by addition of CO to form complex 3. The formation of 2 proceeds by direct insertion of CO into the Re-carbon bond without the prior formation of a CO adduct. As discussed above, the traditionally accepted organometallic mechanism for CO insertion is intramolecular insertion, which proceeds first, through a CO adduct followed by insertion of CO into the M-R bond (Scheme 2.3b and Scheme 2.3c). This is the first example of a proposed direct insertion of CO into a metal-alkyl bond.

Experimentally, our lab has shown through $^1$H NMR studies proceeds by the decay of 1 and the formation of 2 without the formation a CO adduct; once a large enough concentration of 2 is reached it is converted into 3. Our lab has also shown through $^{13}$C
labeling studies that the acyl carbon is the carbon in the acetate ligand in the final product $3$ (Scheme 2.7).$^{4c}$

**Scheme 2.7.** $^{13}$C labeling studies show the reaction of $2^*$ with CO formed $3$

![Chemical structure](image)

Computationally (B3PW91) our lab has studied the mechanism for the formation of acetate complex $3$ from $1^{4d}$. For the formation of $2$, three possible pathways for the of CO to the metal center were proposed. In pathway A, CO approaches $syn$ to the pathway B, CO approaches $syn$ to the rhenium amide bond, and in pathway C, CO approaches $trans$ to the terminal oxo ligand (Scheme 2.8).
Scheme 2.8. Possible pathways for the approach of CO to complex 1

For both pathway A and B a CO adduct was found to be an intermediate in the formation of an oxorhenium(V) acyl complex (Scheme 2.9). Pathway A is overall exergonic $\Delta G^\circ = -11.7$ kcal/mol, however, it is unlikely for the formation of 2, because of the relatively high activation energy ($\Delta G^\ddagger = 32.8$ kcal/mol). Though the free energy of activation for pathway B to form the CO adduct has a lower energy barrier than that of pathway A, the CO adduct is relatively unstable and the transformation is unlikely because the overall process is endergonic ($\Delta G^\circ = 38.2$ kcal/mol) and the pathway does not lead to the correct product 2 anti.
Scheme 2.9. Two possible pathways for the approach of CO to 1 and the pathway for the formation of 2, via the formation of a CO adduct.

The lowest energy pathway for the formation of the oxorhenium acyl intermediate 2 is Pathway C (Scheme 2.10), the direct insertion of CO. In this pathway, CO approaches the oxorhenium methyl complex 1, trans to the oxo ligand. This pathway is exergonic overall ($\Delta G^\circ = -12.6$ kcal/mol) and proceeds through a reasonable barrier with a free energy of activation of 15.7 kcal/mol.

Scheme 2.10. Pathway C for the formation of 2
Addition of CO to complex 2 was also explored computationally to investigate the acyl migration step of the mechanism (1). The most viable pathway involves the addition of CO to 2_{anti}, which results in the formation of a CO adduct, (Int 1), a metallolactone-like structure. In Int 1 the structure the Re-C_{acyl} bond most resembles a double bond due to the significant \( \pi \) back-donation from the \( d_{xy} \) orbital into the \( \pi^* \) orbital of the acyl fragment. This results in a polarization of the acyl C-O bond, where a partial negative charge exists on the acyl oxygen. The polarization of this bond allowed for the formation of a bond between the acyl oxygen and carbon monoxide. The formation of this bond allowed for the stabilization of the CO ligand trans to the oxo. The formation of the \( \kappa^1 \) acetate structure, (Int 2), proceeded through TS 1, where the C_{CO}-O_{acyl} bond breaks disrupting the \( \pi \) back-donation between Re-C_{acyl} bond and results in partial negative charge on the terminal oxo ligand and partial positive charge on the acyl carbon and facilitates the 1,2 acyl migration. The \( \kappa^2 \) binding of the acetate ligand results in the formation of 3.

**Scheme 2.11.** Computations for 1,2 acyl migration. Ancillary ligands omitted for clarity.
Prior to these studies, there were no examples, to the best of our knowledge, of the intermolecular direct insertion of CO into a metal–alkyl bond. The support for this mechanism came primarily from computational studies; there was no unambiguous experimental evidence for direct CO insertion. Therefore, in this chapter, a kinetic investigation is presented.

Oxorhenium(V) benzyl and phenyl complexes were synthesized so that the electronics of the oxorhenium complexes could be modified (Scheme 2.12). Activation parameters for the insertion of CO were acquired to determine the viability of a direct insertion mechanism. Finally, new computational data were acquired and provided additional insight into the insertion reaction. While neither, the computational nor the experimental data by themselves are sufficient to account for all observations, the synergy between the experimental and computational data provides clarity for the proposed mechanism and builds a strong case for the hypothesis of direct CO insertion proposed in this work.

Scheme 2.12. Proposed oxorhenium(V) benzyl derivatives

\[
\begin{align*}
\text{Re} & \quad \text{Ln} \quad \text{O} \\
& \quad \text{C} \quad \text{H} \\
\text{R} & \quad \text{H} \\
\end{align*}
\]

\[
R = \text{H, Me, F, OMe}
\]
2.3 Results and Discussion

2.3.1 Synthesis and Reactivity of Oxorhenium(V) Benzyl and Phenyl Complexes.
The complexes [(DAAm)Re(O)(R)] \[DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C₆F₅\], 4a–d (R = benzyl, 4a; (4-methylphenyl)methyl, 4b; (4-fluorophenyl)methyl, 4c; (4-methoxyphenyl)methyl, 4d; and 5, R = Ph, were synthesized from the oxorhenium(V) chloride complex [(DAAm)Re(O)(Cl)]⁺ and the corresponding Grignard reagents (Scheme 2.13).

Scheme 2.13. Synthesis of oxorhenium(V) benzyl derivatives

\[
\begin{align*}
\text{Cl} & \quad \text{N} & \quad \text{N} & \quad \text{N} & \quad \text{C}_6\text{F}_5 \\
\text{Re} & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{N} & \quad \text{Re} & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{N} & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{C}_6\text{F}_5 & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{N} & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{N} & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv \\
\text{C}_6\text{F}_5 & \quad \equiv & \quad \equiv & \quad \equiv & \quad \equiv
\end{align*}
\]

R = benzyl (4a); (4-methylphenyl)methyl (4b); (4-fluorophenyl)methyl (4c); (4-methoxyphenyl)methyl (4d); Ph (5)

The \(^1\)H NMR spectrum of 4a (Figure 2.1) is representative of the series of benzyl complexes synthesized. A singlet at 4.55 ppm is observed for the two benzylic protons. The methylene protons from the ligand backbone are observed as four distinct multiplets at 4.31, 3.51, 3.12, and 2.85 ppm. The methyl group on the amine nitrogen is observed as a singlet at 3.43 ppm, while the aromatic protons are observed from 6.61 to 6.86 ppm.
Figure 2.1. $^1$H NMR spectrum of complex 4a in CD$_2$Cl$_2$. Peaks that are indicative of complex 4a are shown in red. The benzylic protons resonate at $\delta$ 4.55 ppm and the methyl attached to the amine in the ligand backbone resonates at 3.12 ppm.

Thermal ellipsoid plots for 4a and 5 (Jessica Smeltz) are shown in Figures 2.2 and 3. X-ray quality crystals for both complexes were obtained by the slow diffusion of pentane into methylene chloride solutions of 4a or 5. In both complexes, rhenium occupies a distorted square pyramidal coordination environment with the oxo ligand in the apical position. The Re1—C1 bond length in 4a (2.155 Å) is similar to the Re—Me bond (2.122 Å) in 1.\textsuperscript{4a, 4c} However, the Re—C1 bond length (2.072 Å) in 5 is significantly shorter. This type of contraction is normal and has been attributed to the change from sp$^3$ carbons in 1 and 4a to an sp$^2$ carbon in 5.\textsuperscript{9}
Figure 2.2. Thermal ellipsoid plot for 4a. Ellipsoids are at the 50% probability level. Hydrogen atoms were omitted and the pentafluorophenyl group is shown in wireframe format for clarity. Selected bond lengths (Å) and angles (deg): Re1—O1, 1.6880(18); Re1—N1, 1.963(2); Re1—N3, 1.963(2); Re1—C1, 2.155(2); Re1—N2, 2.185(2). O1—Re1—N1, 119.42(10); O1—Re1—N3, 122.73(10); N1—Re1—N3, 116.99(9); O1—Re1—C1, 98.19(9).
Figure 2.3. Thermal ellipsoid plot for 5. Ellipsoids are at the 50% probability level. Hydrogen atoms were omitted and the pentafluorophenyl group is shown in wireframe format for clarity. Selected bond lengths (Å) and angles (deg): Re1—O1, 1.685(3); Re1—N1, 1.966(4); Re1—N3, 1.981(4); Re1—C1, 2.072(4); Re1—N2, 2.154(4). O1—Re1—N1, 110.84(19); O1—Re1—N3, 111.82(18); N1—Re1—N3, 137.00(17); O1—Re1—C1, 105.31(17); N1—Re1—C1, 86.91(16); N3—Re1—C1, 87.06(17); O1—Re1—N2, 116.54(16); N1—Re1—N2, 78.02(15); N3—Re1—N2, 78.57(16).

2.3.2 Insertion Reactions with CO.

The addition of CO (60 psi) to 4a—d at room temperature resulted in the formation of the corresponding 2-(aryl)acetyl complexes 6a—d (Scheme 2.14). The $^1$H NMR spectrum of 6a is representative of the 2-(aryl)acetyl complexes (Scheme 2.4). A shift of the aromatic protons to $\delta$ 7.10 ppm (6a) from 6.86 ppm (4a) was observed. There is also a substantial change in the chemical shift for the benzylic protons, $\delta$ 4.55 ppm (4a), compared to 3.53 ppm in 6a. It is worth noting that the formation of complex 6a proceeded at a faster rate (7 h) than the formation of corresponding acetyl complex [(DAAm)Re(O)C(O)CH$_3$], 2 (72 h), under the same conditions.

![Reaction Scheme]

Figure 2.4. $^1$H NMR of complex 6a in CD$_2$Cl$_2$. Peaks indicative of complex 8 are shown in red. The benzylic protons shift to 3.5 ppm and the N-Me protons shift to 3.25 ppm and are highlighted in blue. The methylene backbone is shown in green.

One sharp peak was observed in the FTIR spectrum for the CO bond of the acyl ligand in complexes 6a–d (1592 cm$^{-1}$). Similar IR stretches have been reported for a number of acyl complexes. For example, Bergman and co-workers have reported that [CpRe(CO)$_2$
(COCH₃)(CH₃)] has an IR stretching frequency of 1630 cm⁻¹. Similarly, Gladysz and co-workers have reported IR stretches for [CpRe(NO)(PPh₃)(C(O)CH₃)] and [CpRe(NO)(PPh₃)(C(O)CH₂Ph)] of 1545 and 1558 cm⁻¹, respectively. The corresponding CO stretch in the acyl complex 2 is observed at 1587 cm⁻¹ and DAP analogue at 1599 cm⁻¹.

X-ray quality crystals for 6a were obtained by the slow diffusion of pentane into a concentrated solution of 6a in methylene chloride at room temperature (Figure 2.5). The rhenium center occupies a distorted square pyramidal environment with the oxygen in the apical position. The Re₁—C acyl bond length (2.028 Å) in 6a is comparable to the Re₁—C acyl (2.026 Å) bond length in the corresponding acetyl complex, 2. The Re—C₁ bond length decreases from 2.155 Å in complex 4a to 2.028 Å in complex 6a.

**Figure 2.5.** Thermal ellipsoid plot for 6a. Ellipsoids are at the 50% probability level. Hydrogen atoms were omitted, and the pentafluorophenyl group is shown in wireframe format for clarity. Selected bond lengths (Å) and angles (deg): Re₁—O₁, 1.6921(18); Re₁—N₁, 1.973(2); Re₁—N₃, 1.978(2); Re₁—C₁, 2.028(2); Re₁—N₂, 2.169(2). O₁—Re₁—N₁, 111.93(10); O₁—Re₁—N₃, 111.69(9); N₁—Re₁—N₃, 135.86(10); O₁—Re₁—C₁, 106.15(10).

In contrast, when insertion reactions of CO with 5 were attempted, 5 remained the major product in solution (by ¹H NMR and FTIR spectroscopy), as well as small amounts of decomposition even after 6 d under harsh reaction conditions (800 psi CO, 80 °C). The difference in reactivity between 1, 4a, and 5 may be attributed to the stronger Re—C₁ bond strength in 5 compared to 1 and 4a (vide supra).
2.3.3 Kinetics of Insertion Reactions.

The isolation of a series of oxorhenium(V) aryl/alkyl complexes and the subsequent insertion of CO to form the corresponding 2-(aryl)acetyl derivatives has allowed for an examination of the kinetics for this reaction. The reaction of 4a with excess CO at 60 psi (~30 equiv) in methylene chloride at room temperature was monitored by $^1$H NMR spectroscopy. The rate of formation of 6a and the rate of disappearance of 4a were monitored over time (Figure 2.6 (left)). The total rhenium concentration ([4a] + [6a]) remains relatively unchanged during the course of the reaction. From these plots, pseudo-first-order observed rate constants $k_{obs}$ of 6.6(2) Å × 10$^{-1}$ s$^{-1}$ (4a) and 8.4(5) Å × 10$^{-1}$ s$^{-1}$ (6a) were obtained. The dependence on CO pressure was also examined by a log(initial rates) vs log(pCO) plot for CO pressures of 10, 27, and 60 psi (Figure 2.6 (right)). A slope of 0.9(1) was obtained for the log/log plot.

**Figure 2.6.** Time profile for the formation of 6a (left). Reactions were performed with complex 4a (0.00278 mmol) and CO at 60 psi (0.0834 mmol) in a J. Young NMR tube (0.5 mL) in CH$_2$Cl$_2$ (0.25 mL) at room temperature for 11 h in a Varian 400 MHz NMR. The concentration was calculated using an internal standard, hexamethyldisiloxane (4.5 × 10$^{-4}$ mmol), which was added to the reaction mixture. Each point on the graph represents a single data point. Observed rate constants of 6.6(2) × 10$^{-1}$ s$^{-1}$ (4a) and 8.2(5) × 10$^{-1}$ s$^{-1}$ (6a)
were obtained. Plot of log(initial rate) vs log(pCO) (right). Initial rates were determined for CO pressures 60, 27, and 10 psi. Each data point represents the average initial rate for the formation of 6a and decay of 6a at each respective CO pressure. The order with respect to CO was determined from the slope of the log/log plot, 0.9(1).

**Rate Law for CO Insertion.** Two mechanisms were considered for the insertion of CO. In mechanism A, CO directly inserts into the Re–R bond to form the oxorhenium (V) 2-(aryl)acetyl complex (Scheme 2.15). In the second mechanism, upon addition of CO, there is prior formation of a CO adduct, followed by insertion of CO into the rhenium alkyl or aryl bond to form the product (Scheme 2.16).

**Scheme 2.15.** Mechanism A (Direct Insertion).

\[
\text{Rate} = k_1 [\text{CO}] [\text{Re}] \quad (1)
\]

when \([\text{CO}] >> [\text{Re}]\)

\[
\text{Rate} = k_{\text{obs}} [\text{Re}]
\]

\[
k_{\text{obs}} = k_1 [\text{CO}] \quad (2)
\]
Scheme 2.16. Mechanism B (Two Step Mechanism)

\[ R = \text{H, Ar} \]

\[
\text{Prior Equilibrium} \\
K = \frac{k_2}{k_3} = \frac{[\text{Int}]}{[\text{Re}][\text{CO}]} \\
[\text{Re}]_r = [\text{Re}]+[\text{Int}] \\
\text{Where } [\text{Re}]_r = \text{total rhenium concentration} \\
[\text{Int}] = \frac{k[\text{Re}]_r[\text{CO}]}{1+K[\text{CO}]} \\
\text{Subst in (3): Rate} = \frac{k_3K[\text{Re}]_r[\text{CO}]}{1+K[\text{CO}]} \\
\text{Rate} = \frac{k_3[\text{Re}]_r[\text{CO}]}{k_2+k_3} \\
\text{Steady State Approximation} \\
\text{Rate} = k_3[\text{Int}] \\
[\text{Int}]_{ss} = \frac{K[\text{Re}][\text{CO}]}{k_3+k_3} \\
\text{Rate} = \frac{k_3[k_3][\text{Re}][\text{CO}]}{k_2+k_3} \\
\]

The rate law for mechanism A (Equation 1, Scheme 2.15) is second order overall. However, since reactions were performed under pseudo first order conditions with excess CO, the rate law simplifies to Equation 2, where the rate is first order in Re and the observed rate constant, \(k_{\text{obs}}\), is dependent on CO pressure. The experimental data are consistent with this mechanism. For mechanism B, the derived rate equation depends on the lifetime, or concentration of the intermediate, CO adduct, (\text{Int}) (Scheme 2.16). If the CO adduct is a steady state intermediate, the rate law is given by equation 4. According to this rate equation a first order dependence in rhenium, as well as, CO is expected.

However, under conditions where the assumption that the CO adduct is a steady state intermediate does not apply, mechanism B will then involve a prior-equilibrium between Re, CO and the intermediate CO adduct. As shown in Equation 7 the rate law for this mechanism predicts a mixed order dependence on CO. This rate law is only consistent with our data in the regime where the value of \(k_3[\text{CO}]\) is negligible relative to \(k_2\). This suggests that within the concentration range of the kinetic experiments (CO pressure 26-60 psi), a two-step
A mechanism with a prior-equilibrium step is not a viable mechanism for the activation of CO via these oxorhenium(V) aryalkyl and aryl complexes.

**Hammett data.** For the proposed one-step direct insertion mechanism, it is expected that the rate would be affected by the electronics of the *para*-position of the benzyl ligand. A study of the rate for different *para*-substituted benzyl derivatives 4a-d was performed to examine the role played by the electronics of the benzyl ligand (Scheme 2.17). $^1$H NMR spectroscopy was used to measure the rate of product formation over 11 h for each derivative. A Hammett plot was used to determine if there is a linear correlation between rate and the electronics of the benzyl ligand (Figure 2.7). From the Hammett plot, no linear correlation between the rate and electronics was observed, however, the electronics of the *para* position of the benzyl ligand did have some effect on the rate as in general the reaction rate was slower for electron-withdrawing substituents. It has been reported by J. D. Cotton and co-workers that the substitution of the *para*-position of molybdenum benzyl complexes results in an increase in the rate of CO insertion with the increasing donating ability of the *para* substituent.$^7b$ From the results of the kinetic data they were able to obtain a reaction constant $\rho = -0.97$ from the corresponding Hammett plot. Because there is no linear correlation between the sigma values and reaction rates, in our system, the electronics of the substituent in the para position of the aryl group may not be the strongest influence on reaction rate.
Scheme 2.17. Synthesis of acetyl benzyl complexes

\[
\begin{align*}
\text{Re} & \quad \text{C}_6\text{F}_5 \quad \text{N} \quad \text{O} \quad \text{CH}_2R \\
& \xrightarrow{\text{CO (60 psi)}} \quad \text{CD}_2\text{Cl}_2, \text{rt, 11 h} \\
& \quad \text{R} = \text{phenyl (6a); (4-methylphenyl) (6b); (4-fluorophenyl) (6c); (4-methoxyphenyl) (6d)}
\end{align*}
\]

Figure 2.7. Hammett plot for the relative rates of addition of CO (60 psi) to complexes 4a-d in CD$_2$Cl$_2$ at room temperature.

\[
\log\left(\frac{k_X}{k_H}\right) = 4.48 \times 10^{-1}
\]

\[
\sigma
\]

\[
\begin{align*}
p-\text{Me} & \quad p-H \\
& \quad p-\text{OMe} \\
& \quad p-F
\end{align*}
\]
Correlation with bond dissociation energy. The effect on the rate could be related to the stability of the radical upon homolytic cleavage of the metal carbon bond, where it is generally understood that the strength of a bond is related to bond dissociation energy (BDE) and the stability of the its radical (Scheme 2.18).\textsuperscript{12} The trend in the rate for CO activation with these benzyl complexes, the methyl complex, and the previously synthesized phenyl complex may be best interpreted in this manner.

Scheme 2.18. General representation of the homolytic cleavage of R-H bond to form two free radicals\textsuperscript{12}

\[ \text{R—H} \longrightarrow \text{R}^+ + \text{H}^+ \quad \Delta H = \text{BDE} \]

We can rationalize that the differences in the rate of insertion are related to the strength of the Re—C bond. The rate of insertion in 1 is much slower than the rate of insertion in 4a, which is consistent with the relationship between radical stability and bond dissociation (Table 2.1). The BDE for a C—H bond in methane is larger than that of toluene due to the stability of a benzylic radical in toluene compared to a methyl radical. Likewise, the BDE for sp\textsuperscript{3}-hybridized bonds would be less for sp\textsuperscript{2}-hybridized bonds, which is consistent with the experimental result that no CO insertion is observed with 5. Also, one can rationalize the trend within the substituted benzyl complexes, where we would expect the donating 4-methylbenzyl complex to have a faster rate due to the increased stability of the free radical and a smaller BDE than that of the benzyl and 4-fluorobenzyl complexes (Table 2.1).\textsuperscript{2e, 5}

Table 2.1. Rates for the insertion of CO into Complexes 1, 4a-d, and 5.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$10^5 k_{obs}$ (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.22</td>
</tr>
<tr>
<td>4a</td>
<td>8.42</td>
</tr>
<tr>
<td>4b</td>
<td>8.34</td>
</tr>
<tr>
<td>4c</td>
<td>7.14</td>
</tr>
<tr>
<td>4d</td>
<td>7.74</td>
</tr>
<tr>
<td>5</td>
<td>No Reaction</td>
</tr>
</tbody>
</table>
It is generally understood that electron-withdrawing groups slow the rate of insertion and that electron-donating groups increase the rate of insertion reactions.\textsuperscript{3, 6, 13} Electron-withdrawing groups strengthen M—C bonds and make insertion reactions less favorable. For the insertion of CO into complexes 4a-d, a better comparison of the rate of insertion may not be electronics but rather, metal carbon bond strength. Though the factors that affect metal carbon bond strengths are complex, linear correlations between the metal carbon bond strengths and carbon hydrogen bond strengths have been determined.\textsuperscript{14} The precedence for the correlation of metal-carbon bond strengths and C—H bond strengths and the difficulty of measuring metal—carbon bond strengths, the C—H bond strengths of methane and toluene derivatives were used to correlate the rates of CO insertion. The strong correlation between reaction rate and reported bond dissociation energy supports a direct insertion mechanism. However, these data may also be consistent with a mechanism where a CO adduct is formed and then CO inserts.

**Determination of Activation Parameters.** To investigate the activation parameters of the reaction, variable-temperature kinetic experiments for the CO insertion reaction with 1 and 4a were completed for a temperature range of 15−55 °C (Scheme 2.8 and 2.9). The enthalpy of activation, $\Delta H^*$, was found to be 9(1) kcal/mol for 1 and 13(1) kcal/mol for 4a, and the entropy of activation, $\Delta S^*$, found was −49(2) for 1 and −36(4) cal/mol·K for 4a. Thus, the overall free energies of activation, $\Delta G^*$ (298 K), were 24(1) kcal/mol for both 1 and 4a.
Figure 2.8. Eyring plot for the disappearance of $4\text{a}$ in the presence of CO (60 psi) in C$_6$D$_6$ at temperatures 15-55 °C. Activation parameters were obtained from non-linear fits to the Eyring Equation: $k_{\text{obs}} = 2.084 \times 10^{10} \cdot e^{\frac{M_1}{R}} \cdot e^{\frac{M_2}{RT}}$ where $M_1 = \Delta S^\dagger / R$ and $M_2 = -\Delta H^\dagger / R$
Figure 2.9. Eyring plot for the disappearance of 1 in the presence of CO (60 psi) in C₆D₆ at temperatures 15-55 °C. Activation parameters were obtained from non-linear fits to the Eyring Equation: 

\[ k_{obs} = 2.084 \times 10^{10} \cdot e^{\frac{M_1}{R} \cdot \frac{M_2}{RT}} \]

where \( M_1 = \Delta S^\ddagger / R \) and \( M_2 = -\Delta H^\ddagger / R \)

Activation parameters, specifically entropies of activation, for other CO insertion reactions, have been reported. For example, Bassetti and coworkers found \( \Delta S^\ddagger = -13 \text{ cal·mol}^{-1}\text{K}^{-1} \) for the reaction of [Rh(L)(CO)]PF₆ (L = 1,6-bis(benzylthiomethyl)(pyridine)). Heck and co-workers reported values from −6.1 to 5.4 eu for migratory insertion for the complexes I(PR₃)(CO)RPt, while Haynes and co-workers reported values of −16 and −9.1 eu for migratory insertion into [MeRh(CO)I₂(dppms)] (dppms = Ph₂PCH₂P(S)Ph₂) and [MeRh(CO)I₂(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂), respectively. In these examples, migratory insertion is proposed to proceed first through a CO adduct. The entropies of activation for the reaction of 1 and 4a with CO are significantly more negative than these reported values and are consistent with an ordered transition state and the bimolecular nature of the proposed direct insertion mechanism.
2.3.4 Computational Data for CO Insertion

Density Functional Theory (DFT) calculations were utilized to try to obtain a closer approximation to the differences in the barrier for insertion. Furthermore, DFT was used to calculate the barrier for insertion for complex 5 where no reactivity was observed experimentally. Previously reported calculations on the carbonylation 1 were explored with the B3PW91 functional and (6-31G) basis set.\textsuperscript{15} The geometry of 1 was optimized using different functionals by a member of our lab and is summarized in Table 2.2. The amount of deviation in the bond lengths of the calculated structure from the crystal structure for 1 was calculated. The %deviation was less than 1.0% for all functionals with the exception of BP86. The activation energy for the direct insertion transition state was also calculated using the various functionals. The functional M06\textsuperscript{16} gave the activation energy closest to experiment as well as a %deviation less than 1% for the bond lengths of 1. The M06 functional was used for all other calculations.
Table 2.2. Comparison of bond lengths for 1 and activation energies for different functionals.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Functional</th>
<th>% Deviation of Bond Lengths$^a$</th>
<th>$\Delta G^\ddagger$ (kcal/mol)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BP86</td>
<td>1.30</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>M06</td>
<td>0.97</td>
<td>19.0</td>
</tr>
<tr>
<td>3</td>
<td>B3LYP</td>
<td>0.92</td>
<td>17.2</td>
</tr>
<tr>
<td>4</td>
<td>B3PW91</td>
<td>0.89</td>
<td>15.3</td>
</tr>
<tr>
<td>5</td>
<td>B3PW91, GD3$^c$</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>6</td>
<td>PBE0</td>
<td>0.88</td>
<td>n/a</td>
</tr>
<tr>
<td>7</td>
<td>M06L</td>
<td>0.79</td>
<td>11.3</td>
</tr>
</tbody>
</table>

$^a$Geometries were calculated in the gas phase using the specified functional with the SDD basis set for rhenium and 6-31G(d,p) for all other atoms. $^b$Solvent energies were computed with geometries optimized in the gas phase (SDD with an added $f$ polarization function for rhenium and 6-31G(d,p) for all other atoms) using the SMD method$^{17}$, with benzene as the solvent, and with SDD basis set with an added $f$ polarization function for rhenium and 6-311+G(d,p) for all other atoms as implemented in Gaussian 09. $^c$The dispersion corrections were assessed using Grimme’s D3 parameter set.

Gas phase energies for the activation energy of the direct insertion transition state were calculated using various basis sets for C, H, N, O, and F atoms in Table 2.3. Similarly, the basis set on rhenium was varied and the activation energy was calculated with for each basis set on rhenium (Table 2.4). The 6-311G++(d,p)$^{18}$ on C, H, N, O and F and SDD$^{19}$ with an $f$
polarization$^{30}$ on rhenium gave the activation energy closest to the experimentally obtained value.

**Table 2.3.** Choice of basis set for atoms C, H, N, O and F.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Basis Set</th>
<th>$G^\ddagger$ (kcal/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6-31G(d,p)</td>
<td>15.3</td>
</tr>
<tr>
<td>2</td>
<td>6-311G(d,p)</td>
<td>18.2</td>
</tr>
<tr>
<td>3</td>
<td>6-311+G(df,p)</td>
<td>18.0</td>
</tr>
<tr>
<td>4</td>
<td>6-311++G(d,p)</td>
<td>19.0</td>
</tr>
<tr>
<td>5</td>
<td>6-311++G(2d,2p)</td>
<td>18.4</td>
</tr>
<tr>
<td>6</td>
<td>6-311++G(3df,2pd)</td>
<td>18.7</td>
</tr>
</tbody>
</table>

$^a$Geometries were optimized in the gas phase with the M06 functional and employed the SDD basis set on Re with an added $f$ polarization and 6-31G(d,p) basis set on all other atoms. Energies were corrected with geometries optimized in the gas phase using the SMD method, with benzene as the solvent, and with the SDD basis set for rhenium and listed basis set for all other atoms as implemented in Gaussian 09.
Table 2.4. Choice of basis set for rhenium.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Basis Set</th>
<th>$\Delta G^\ddagger$ (kcal/mol)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LANL2TZ</td>
<td>17.8</td>
</tr>
<tr>
<td>2</td>
<td>cc-pVDZ-PP</td>
<td>18.0</td>
</tr>
<tr>
<td>3</td>
<td>cc-pVTZ-PP</td>
<td>18.3</td>
</tr>
<tr>
<td>4</td>
<td>cc-pVQZ-PP</td>
<td>18.3</td>
</tr>
<tr>
<td>5</td>
<td>SDD($f$)</td>
<td>19.0</td>
</tr>
</tbody>
</table>

$^a$Geometries were optimized in the gas phase with the M06 functional and employed the SDD basis set on Re with an added $f$ polarization function and 6-31G(d,p) basis set on all other atoms. Energies were calculated by utilizing the gas phase optimized structures above with the M06 functional, in addition a solvent correction using the SMD model with benzene as the solvent was utilized to obtain the energy of activation. The 6-311++G(d,p) basis set for the C, H, N, O and F atoms.

From this screening the M06 functional with a 6-311++(d,p) basis set for all atoms (C, H, N, O and F) except for rhenium where a SDD basis set with an added $f$ polarization, was utilized for all calculations from this point forward. With the new computational methods and experimental data at hand, the previous computational data obtained were revisited. It was found experimentally, that the barrier for insertion was 24(1) kcal/mol for both complexes 1 and 4a. With this information, two things needed to be addressed: first, it was previously calculated that the barrier for insertion was 15.7 kcal/mol, which is significantly lower than experimentally obtained value for $\Delta G^\ddagger$. Second, the barrier for insertion experimentally for 1 and 4a was found to be the same, which does not account for the difference in the rate of insertion between the two complexes, (1, 72 h; 4a, 7 h).

As before, pathway A (Scheme 2.19) involves the approach of CO syn to the terminal oxo which results in the formation of a CO adduct, that CO adduct undergoes methyl group
migration to give the acyl product. The rate-determining step of pathway A is CO insertion, which proceeds with a barrier of 29.0 kcal/mol. In pathway B, the approach of CO syn to the rhenium amide bond was considered, which resulted in the formation of a CO adduct followed by methyl migration to afford an acyl product. The acyl product observed in pathway B was not the correct geometry, and the barrier to methyl migration to generate this acyl product was 52.3 kcal/mol, which is an unrealistic barrier considering this reaction proceeds at room temperature in 3 d. Lastly, the approach of CO \textit{trans} to the terminal oxo ligand, pathway C, resulted in the direct insertion and the formation of the acyl product in a single step. The barrier for this insertion was 19.0 kcal/mol. Again, this barrier for insertion is the lowest calculated barrier making pathway C the most likely mechanism for CO insertion. The barrier for insertion via pathway C, 19.0 kcal/mol, is a closer (compared to previous calculations with B3PW91) approximation of the experimentally determined energy of activation, 24(1) kcal/mol.
Having obtained calculations in the M06 functional and confirmed that direct insertion, pathway C, was the most likely pathway for CO insertion for 2. Pathway C was then explored for complexes 4a and 5 (Scheme 2.20). Complex 4a proceeds with a barrier of 19.1 kcal/mol and the benzyl ligand undergoes a rotation prior to direct insertion. Though a better approximation to the experimentally observed energies of activation for 1 and 4a was obtained computationally, we are still not able to distinguish between the differences in rates for those complexes (Scheme 2.20).
Scheme 2.20. Comparison of Computational and Experimental Results for 1 and 4a.

Lastly, pathway C was explored for 5. The barrier for direct insertion into 5 is 22.1 kcal/mol, 3.0 kcal/mol higher in energy for both 1 and 4a. The larger barrier for this insertion is likely due to the ability for CO to directly insert into an sp²-hybridized bond. This result is consistent with our experimental data where CO insertion was not observed in 5, even under more harsh reaction conditions such as high temperatures, high CO pressure, and longer reaction times. It is also important to note that the difference in CO insertion is only 3.0 kcal/mol between 1, 4a, and 5.

The energies of activation for the insertion of CO into the Re—R bond of [(DAAm)Re(O)(R)] (R = methyl, 1; benzyl, 4a; and phenyl, 5) were calculated using this method and are also summarized in Table 2.5. These results are again consistent with experimental observations, as insertion into the Re—phenyl bond in 5 resulted in the least favorable barrier (22.1 kcal/mol). Further, as described above, this complex did not react
with CO at 800 psi and 80 °C. Neither the computational nor the experimental methods however, were able to distinguish between the small difference in the activation energies between 1 and 4a.

**Table 2.5.** Thermodynamic and Kinetic Data for Insertion of CO (TS1) into the Re—R Bond of 1 (R = Me); 4a (R = benzyl) and 5 (R = phenyl).

<table>
<thead>
<tr>
<th>[(DAAm)Re(O)(R)]</th>
<th>$\Delta G^\circ$ (kcal/mol)</th>
<th>$\Delta G^\ddagger$ (kcal/mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = methyl (1)</td>
<td>-9.3 (-9.7)</td>
<td>19.0 (17.9)</td>
</tr>
<tr>
<td>R = benzyl (4a)</td>
<td>-10.3 (-11.8)</td>
<td>19.1 (26.9)</td>
</tr>
<tr>
<td>R = phenyl (5)</td>
<td>-7.5 (-10.1)</td>
<td>22.1 (19.5)</td>
</tr>
</tbody>
</table>

*Structures were optimized with Gaussian 09 in the gas phase with the M06 functional and employed the SDD basis set on Re with an added f polarization and the 6-31G(d,p) basis set on all other atoms. Energetics were calculated with the 6-311++G(d,p) basis set for C, H, N, O and F atoms and the SDD basis set with an added f polarization function on Re as implemented in Gaussian 09. Reported energies utilized analytical frequencies and the zero point corrections from the gas phase calculations and included solvation corrections, which were computed using the SMD model as implemented in Gaussian 09.

Here, 3.0 kcal/mol is the difference between reaction and no reaction observed experimentally. It may also be noted that the difference between reaction times and rates for 1 (3 d) and 4a (16 h) will not result in a large difference in the free energy of activation and may not be distinguishable with the current computational method. The trend in reactivity is consistent with a dependence of the rate of insertion on the strength of the Re—R bond. This is confirmed by inspection of the optimized structures for the transitions states for CO insertion into 1, 4a, and 5 (Table 2.6).
Table 2.6. Comparison of Calculated Transition State Structures for Methyl (1), Benzyl (4a) and Phenyl Complexes (5)

<table>
<thead>
<tr>
<th>[(DAAm)Re(O)(R)]</th>
<th>Re-R</th>
<th>Re-Amine</th>
<th>Re-CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = methyl (1)</td>
<td>2.361</td>
<td>2.338</td>
<td>1.974</td>
</tr>
<tr>
<td>R = benzyl (4a)</td>
<td>2.453</td>
<td>2.368</td>
<td>1.983</td>
</tr>
<tr>
<td>R = phenyl (5)</td>
<td>2.249</td>
<td>2.381</td>
<td>1.981</td>
</tr>
</tbody>
</table>

M06 optimized structures from the transition states for CO insertion into 1, 4a, 5. Structures were optimized with Gaussian 09 in the gas phase and employed the SDD basis set on Re with an added f polarization and the 6-31G(d,p) basis set on all other atoms. Selected bond lengths are in angstroms (Å). For clarity, most hydrogen atoms were omitted and the pentafluorophenyl group and ligand backbone is shown in wireframe format.

From Table 2.6, it is evident that the most significant change in the transition state is the lengthening of the Re–R bond in the order 4a > 1 > 5. The Re–benzyl transition-state bond length, for example, is 0.2 Å longer than the Re–phenyl transition-state bond length. Further, selected bond lengths for optimized structures for 1, 4a, and 5 and their corresponding transition states are shown in Table 2.7. The transition states in all complexes feature a significant weakening of the Re–R bond. The extent of this bond weakening
(expressed as the %deviation from the Re–R bond in the ground-state structure) follows the order 4a > 1 > 5, which is again consistent with the observed reactivity for these complexes.

**Table 2.7. %Deviation of the TS Re—R Bond from the Ground State Structures in 1, 4a, 5.**

<table>
<thead>
<tr>
<th>R</th>
<th>Re-R (Å)</th>
<th>TS Re-R (Å)</th>
<th>%Deviation(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>2.120</td>
<td>2.361</td>
<td>11.4</td>
</tr>
<tr>
<td>benzyl</td>
<td>2.154</td>
<td>2.453</td>
<td>13.9</td>
</tr>
<tr>
<td>phenyl</td>
<td>2.079</td>
<td>2.175</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\(^a\) %Deviation = 100*(Re—R bond length – TS Re—R bond length)/(Re—R bond length).

\(^b\) Structures were optimized with Gaussian 09 in the gas phase with the M06 functional and employed the SDD basis set on Re with an added f polarization and the 6-31G(d,p) basis set on all other atoms. Energetics were calculated with the 6-311G++(d,p) basis set for C, H, N, O and F atoms and the SDD basis set with an added f polarization function on Re as implemented in Gaussian 09. Reported energies utilized analytical frequencies and the zero point corrections from the gas phase calculations and included solvation corrections, which were computed using the SMD model as implemented in Gaussian 09.

**2.4 Conclusions.**

In this chapter, we have provided additional evidence for an unusual mechanism for the insertion of CO into M– R bonds. Methyl, benzyl, and phenyl complexes have been synthesized and characterized. In addition, these complexes were treated with CO, and the rate of formation of the corresponding acyl complex was examined. The observed rate of insertion of CO into the Re–R (R = methyl, benzyl, and phenyl) bond was benzyl > methyl > phenyl. This rate reflects the strength of the Re–R bond.
The rate law was acquired for the benzyl complexes and is consistent with a bimolecular reaction between the rhenium complex and CO. In addition, activation parameters were acquired for the reaction of CO with the benzyl (4a) and the methyl complex (1). The activation parameters acquired for 1 and 4a (ΔG* (298 K) = 24(1) kcal/mol) are also consistent with the observed rates of insertion. Further, the entropies of activation (ΔS* = −49(2), 1; −36(4), 4a; cal/mol·K) reflect a bimolecular reaction between CO and the rhenium complexes. The Re–R bond in the calculated (DFT(M06)) transition states is lengthened and follows the trend benzyl (4a) > methyl (1) > phenyl (5), which again reflects the trend observed experimentally.

The unusual reactivity observed for oxorhenium(V) complexes described here appears to stem from the strong trans influence of the oxo ligand, which does not allow for the formation of stable carbonyl complexes. The electronics of the oxo ligand influences the mechanism for insertion, because the strong trans influence of an oxo ligand in the axial position of these square pyramidal oxorhenium molecules strongly destabilizes complexes with a ligand (in this case CO) trans it. Further, strong π donation from these d² metal complexes results in unusually strong rhenium carbon bonds (see Figure 2.10).
Figure 2.10. Molecular orbital diagram for oxorhenium CO adduct.

2.5 Experimental

General Considerations. [DAAMRe(O)Cl] was prepared as previously reported⁸; all other reagents were purchased from commercial sources and used as received. ¹H, ¹³C, and ¹⁹F NMR spectra were obtained on 300 or 400 MHz spectrometers at room temperature. Chemical shifts are listed in parts per million (ppm) and referenced to their residual protons or carbons of the deuterated solvents, respectively. ¹³C NMR spectra of acetyl complexes were obtained on a 500 MHz spectrometer. All reactions were run under an inert atmosphere with dry solvents unless otherwise noted. High pressure reactions were performed in a stainless steel Micro Bench Top Reactor. FTIR spectra were obtained in KBr thin films. Elemental analyses were performed by Atlantic Micro Laboratories, Inc.

General Procedure of the Synthesis of Oxorhenium Benzyl Complexes. The respective Grignard reagent (4.63 mmol) was added dropwise to a stirred solution of the [DAAmRe(O)Cl] (aryl = C₆F₅) (1.00 g, 1.54 mmol) in dichloromethane (15.0 mL) and allowed to stir for 30 min. Water was added (50 mL × 3), and the organic layer was extracted and dried over Na₂SO₄. The mixture was filtered, and solvent was removed under reduced pressure. The resultant residue was dissolved in a minimal amount of dichloromethane and precipitated upon the addition of hexanes. The resultant precipitate was filtered. The precipitate was washed with methanol to yield the final product.
[(DAAm)Re(O)CH$_2$Ph], 4a. Complex 3a was obtained as a blue solid in 49.8% yield. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.86 (m, 3 H), 6.61 (d, 2 H), 4.55 (s, 2 H), 4.31 (m, 2 H), 3.51 (m, 2 H), 3.43 (s, 3 H), 3.12 (H), 2.85 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 151.6, 129.7, 127.2, 123.6, 70.8, 64.9, 51.1, 36.1. Anal. Calcd for C$_{24}$H$_{18}$F$_{10}$N$_3$ORe: C, 38.92; H, 2.45; N, 5.67. Found: C, 38.69; H, 2.23; N, 5.68.

[(DAAm)Re(O)(CH$_2$(C$_6$H$_4$-p-CH$_3$))], 4b. Complex 4b was obtained in 60.0% yield as a blue-green solid. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.71 (d, 2 H), 6.48 (d, 2 H), 4.50 (s, 2 H), 4.31 (m, 2 H), 3.51 (m, 2 H), 3.43 (s, 3 H), 3.11 (m, 2 H), 2.84 (m, 2 H), 2.19 (s, 3 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 148.3, 133.3, 129.4, 127.8, 70.6, 64.9, 51.2, 35.3, 20.3. Anal. Calcd for C$_{25}$H$_{20}$F$_{10}$N$_3$ORe·0.5(CH$_2$Cl$_2$): C, 38.42; H, 2.66; N, 5.27. Found: C, 39.00; H, 2.51; N, 5.57.

[(DAAm)Re(O)(CH$_2$(C$_6$H$_4$-p-OCH$_3$))], 4c. Complex 3c was obtained as a blue crystal. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.50 (m, 4 H), 4.52 (s, 2 H), 4.33 (m, 2 H), 3.70 (s, 2 H), 3.54 (m, 2 H), 3.44 (s, 3 H), 3.11 (m, 2 H), 2.84 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 156.6, 143.4, 130.5, 112.4, 70.7, 65.1, 51.1, 35.5. Anal. Calcd for C$_{25}$H$_{20}$F$_{10}$N$_3$O$_2$Re·0.5(CH$_2$Cl$_2$): C, 37.67; H, 2.60; N, 5.17. Found: C, 38.10; H, 2.58; N, 5.35.

[(DAAm)Re(O)(CH$_2$(C$_6$H$_4$-p-F))], 4d. Complex 4d was obtained in a 21.0% yield as a blue-green solid. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.61 (m, 4 H), 4.51 (s, 2 H), 4.31 (m, 2 H), 3.51 (m, 2 H), 3.43 (s, 3 H), 3.13 (m, 2 H), 2.86 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 160.96, 147.58, 130.92, 113.29, 70.85, 64.97, 51.26, 34.60. Anal. Calcd for C$_{24}$H$_{17}$F$_{10}$N$_3$ORe: C, 38.00; H, 2.26; N, 5.54; Found: C, 37.88; H, 2.35; N, 5.41.

[(DAAm)Re(O)C(O)CH$_2$Ph], 6a. Complex 4a (200 mg, 0.270 mmol) was added to a Parr reactor and dissolved in dichloromethane. The reactor was purged and pressurized with CO (60 psi) and allowed to stir at room temperature for 6 h. The solvent was removed under reduced pressure, and the orange residue was dissolved in a minimal amount of dichloromethane. Excess hexanes were added to precipitate a brown impurity, which was removed by filtration. Solvent was removed from the resultant filtrate to yield 5a in 73.6% yield as an orange solid. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 7.10 (m, 3 H), 6.63 (d, 2 H), 4.51 (m, 2 H), 3.82 (m 2 H), 3.51 (s, 2 H), 3.27 (s, 3 H), 3.18 (m, 2H), 3.02 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$
[(DAAm)Re(O)C(O)(CH$_2$(C$_6$H$_4$-p-CH$_3$))], 6b. Complex 4b (104 mg, 0.138 mmol) was added to a 25 mL storage tube with a stir bar and dissolved in dichloromethane (5 mL). The mixture was subjected to three freeze–pump–thaw cycles. The reaction was purged and pressurized with CO (60 psi) and allowed to stir at room temperature for 7 h. Solvent was removed under reduced pressure to give an orange residue. The residue was dissolved in a minimal amount of dichloromethane. Excess hexanes were added to precipitate an orange impurity. Solvent was removed from the resultant filtrate to yield 5b as an orange solid in 38.9% yield. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.91 (d, 2 H), 6.53 (d, 2 H), 4.50 (m, 2 H), 3.82 (m, 2 H), 3.46 (s, 3 H), 2.27 (s, 3 H), 3.17 (s, 2 H), 3.02 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 259.32, 135.42, 129.41, 127.99, 126.77, 69.45, 67.24, 67.01, 47.06. FTIR: 1592 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{20}$F$_{10}$N$_3$O$_2$Re·0.5(CH$_2$Cl$_2$): C, 38.58; H, 2.57; N, 5.09. Found: C, 39.00; H, 2.51; N, 5.57.

[(DAAm)Re(O)C(O)(CH$_2$(C$_6$H$_4$-p-OCH$_3$))], 6c. Complex 4c was obtained as an orange solid in a 50.8% yield. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.64 (m, 4 H), 4.53 (m, 2 H), 3.83 (m 2 H), 3.75 (s, 2 H), 3.43 (s, 3 H), 3.28 (s, 3 H), 3.20 (m, 2 H), 3.03 (m 2 H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 259.6, 130.4, 130.2, 113.6, 69.6, 67.2, 66.4, 55.6, 47.1. FTIR: 1592 cm$^{-1}$. Anal. Calcd for C$_{26}$H$_{20}$F$_{10}$N$_3$O$_2$Re·0.5(CH$_2$Cl$_2$): C, 37.84; H, 2.52; N, 5.00. Found: C, 37.93; H, 2.44; N, 5.13.

[(DAAm)Re(O)C(O)(CH$_2$(C$_6$H$_4$-p-F))], 6d. Complex 4d (104 mg, 0.137 mmol) was added to a storage tube (25 mL) with a stir bar and was dissolved in dichloromethane (5 mL). The reaction mixture was subjected to three freeze–pump–thaw cycles. The reaction was purged and pressurized with CO (60 psi) and was allowed to stir at room temperature for 8 h. Solvent was removed under reduced pressure, and an orange residue was obtained. The residue was dissolved in a minimal amount of dichloromethane, and excess hexanes were added to precipitate an orange impurity. Solvent was removed from the residual filtrate to yield 5d in 33.3% yield. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 6.81 (m, 2 H), 6.66 (m 2 H), 4.51 (m, 2 H), 3.82 (m, 2 H), 3.48 (s, 2 H), 3.27 (s, 3 H), 3.17 (m, 2 H), 3.03 (m, 2 H). $^{13}$C NMR (CD$_2$Cl$_2$):
δ = 259.60, 136.54, 128.98, 129.02, 129.20, 69.54, 67.12, 66.78, 47.03. FTIR: 1591 cm$^{-1}$.

Anal. Calcd for C$_{25}$H$_{17}$F$_{11}$N$_3$O$_2$Re: C, 38.17; H, 2.18; N, 5.34. Found: C, 37.99; H, 2.10; N, 5.41.

[DAAmRe(O)(Ph)], 5. In a glovebox, phenyl magnesium bromide (3.0 M in diethyl ether) (292.0 µL, 0.438 mmol) was added to [DAAmRe(O)(Cl)] (200.0 mg, 0.146 mmol) dissolved in ~10.0 mL of dichloromethane. The solution was removed from the glovebox and washed with DI water (3 × 10 mL). The solution was dried over sodium sulfate and concentrated under reduced pressure. Excess pentane was used to precipitate the red powder (282.1 mg, 64.4% yield). Two isomers of the product were found by $^1$H NMR spectroscopy. $^1$H NMR (CD$_2$Cl$_2$): δ = 6.63 (m, 6H), 6.18 (t, 3H), 5.39 (m, 2H), 4.54 (m, 4H), 4.24 (m, 2H), 4.00 (dd, 2H), 3.86 (m, 2H), 3.73 (dd, 2H), 3.42 (s, 3H), 3.26 (dd, 2H), 2.97 (m, 2H), 2.52 (s, 3H). $^{19}$F NMR (CD$_2$Cl$_2$): δ = −148.09 (m, 2F), −149.99 (dd, 1F), −150.49 (dd, 1F), −163.90 (t, 1F), −164.57 (t, 1F), −166.19 (m, 1F), −167.08 (m, 1F), −168.06 (m, 2F). Anal. Calcd for C$_{23}$H$_{16}$F$_{10}$N$_3$ORe: C, 38.02; N, 5.78; H, 2.22. Found: C, 37.66; N, 5.24; H, 2.26.

Computational Methods. Theoretical calculations have been carried out using the Gaussian 09 implementation of M06 density functional theory.\textsuperscript{16} All geometry optimizations were carried out in the gas phase using tight convergence criteria (“opt = tight”) and pruned ultrafine grids (“Int = ultrafine”). The basis set for rhenium was the small-core (311111,22111,411) → [6s5p3d] Stuttgart–Dresden basis set and RECP combination (SDD)\textsuperscript{19} with an additional f polarization function. The 6-31G(d,p) basis set\textsuperscript{15} was used for all other atoms. Cartesian d functions were used throughout; that is, there are six angular basis functions per d function. All structures were fully optimized, and analytical frequency calculations were performed on all structures to ensure either a zeroth-order saddle point (a local minimum) or a first-order saddle point (transition state: TS) was achieved. The minima associated with each transition state was determined by animation of the imaginary frequency and, if necessary, with intrinsic reaction coordinate (IRC) calculations. Energetics were calculated with the 6-311++G(d,p)\textsuperscript{18} basis set for C, H, N, O, and F atoms and the SDD basis set with an added f polarization function on Re.\textsuperscript{20} Reported energies utilized analytical frequencies and the zero-point corrections from the gas phase optimized geometries and
included solvation corrections that were computed using the SMD method,\textsuperscript{17} with benzene as the solvent, as implemented in Gaussian 09. In this method, an IEFPCM calculation is performed with radii and electrostatic terms from Truhlar and coworkers’ SMD solvation model.

2.6 Supplemental Kinetic Data

2.6.1 General Procedure for CO dependence data.

4a (0.0027 mmol) in CD\textsubscript{2}Cl\textsubscript{2} (0.25 mL) was added to a J. Young NMR tube (0.50 mL) at room temperature and was degassed. The reaction was pressurized with CO (60-10 psi) and placed in a 400 MHz NMR spectrometer. The highest pressure allowable in the J. Young NMR tube was 60 psi. The reaction was monitored for 11 h. Concentrations were calculated using an internal standard, hexamethylcyclotrisiloxane (4.5 x10\textsuperscript{-5} mmol) that was added to the reaction mixture. The first ~10% of product formation or reactant disappearance was plotted against time to obtain the initial rates of the reaction. The log of the initial rates was plotted against the log of CO pressure to obtain the order with respect to CO.
Figure 2.11. Initial rates plot for the formation of 4a at 60 psi CO. Concentrations were calculated using an internal standard, hexamethylcyclotrisiloxane (4.5 x 10^-5 mmol) that was added to the reaction mixture.
**Figure 2.12.** Initial rate plot for the decay of 4a (0.0027 mmol) at 60 psi CO. Concentrations were calculated using an internal standard, hexamethyldicyclohexasiloxane (4.5 x10^{-5} mmol) that was added to the reaction mixture.
Figure 2.13. Initial rate plot for the formation of 4a at 27 psi CO. Concentrations were calculated using an internal standard, hexamethyldicyclotrisiloxane (4.5 x10^5 mmol) that was added to the reaction mixture.
Figure 2.14. Initial rates plot for the decay of 4a (0.0027 mmol) at 27 psi CO. Concentrations were calculated using an internal standard, hexamethyldisiloxane (4.5 x 10^-5 mmol) that was added to the reaction mixture.
Figure 2.15. Initial rate plot for the formation of 4a at 10 psi CO. Concentrations were calculated using an internal standard, hexamethylcyclotrisiloxane \((4.5 \times 10^{-5} \text{ mmol})\) that was added to the reaction mixture.
Figure 2.16. Initial rate plot for the decay of 4a (0.0027 mmol) at 10 psi CO. Concentrations were calculated using an internal standard, hexamethyldicyclotrisiloxane (4.5 x10^{-5} mmol) that was added to the reaction mixture.
Figure 2.17. Plot of log(initial rate) vs. log(pCO). The initial rates were obtained by monitoring formation of 6a and disappearance of 3a for the initial ~10% of the reaction at CO pressures of 60, 27 and 10 psi. Each data point represents the natural log of an average of the initial rate of formation of 6a and initial rate of decay of 4a at each respective CO pressure.

2.6.2 General Procedure for Eyring Data for the Disappearance of 4a.
To a J Young NMR tube, a solution of 4a (0.0108 M) in benzene-d$_6$ (0.25mL) was added via syringe. An internal standard, 1,3,5-trimethoxybenzene (0.0108 M) was used to calculate the decay of 4a and was added directly into the reaction mixture. The reaction was degassed and pressurized with CO (60 psi). The reaction was then placed in an oil bath when temperatures were above 25 °C and a circulating cold bath for temperatures 25 °C and below. $^1$H NMR spectroscopy was used to monitor the disappearance of 4a for 5 half-lives.
Figure 2.18. Disappearance of 4a in the presence of CO (60 psi) at 15 °C.
Figure 2.19. Disappearance of 4a in the presence of CO (60 psi) at 25 °C.

Figure 2.20. Disappearance of 4a in the presence of CO (60 psi) at 35 °C
Figure 2.21. Disappearance of 4a in the presence of CO (60 psi) at 45 °C.

Figure 2.22. Disappearance of 3a in the presence of CO (60 psi) at 55 °C.
Figure 2.23. Eyring plot for the disappearance of 3a in the presence of CO (60 psi) in C₆D₆ at temperatures 15-55 °C. Activation parameters were obtained from non-linear fits to the Eyring Equation: 

\[
k_{\text{obs}} = 2.084 \times 10^{10} \cdot e^{\frac{M_1}{R} \cdot \frac{1}{T}} \cdot e^{\frac{M_2}{R} \cdot \frac{1}{T}}\]  

where \(M_1 = \Delta S^\ddagger / R\) and \(M_2 = -\Delta H^\ddagger / R\)

2.6.3 General Procedure for Eyring Data for the Disappearance of 1. 
To a J Young NMR tube a solution of 1 (0.0108 M) in benzene-d₆ (0.25mL) was added via syringe. An internal standard, 1,3,5-trimethoxybenzene (0.0108 M) was used to calculate the decay of 1 and was added directly into the reaction mixture. The reaction was degassed and pressurized with CO (60 psi). The reaction was then placed in an oil bath when temperatures were above 25 °C and a circulating cold bath for temperatures 25 °C and below. ¹H NMR spectroscopy was used to monitor the disappearance of 1 for 5 half-lives.
Figure 2.24. Disappearance of 1 in the presence of CO (60 psi) at 15 °C.

Figure 2.25. Disappearance of 1 in the presence of CO (60 psi) at 25 °C
Figure 2.26. Disappearance of 1 in the presence of CO (60 psi) at 45 °C.

Figure 2.27. Disappearance of 1 in the presence of CO (60 psi) at 55 °C.
Figure 2.28. Eyring plot for the disappearance of 1 in the presence of CO (60 psi) in C₆D₆ at temperatures 15-55 °C. Activation parameters were obtained from non-linear fits to the Eyring Equation: 

\[ k_{\text{obs}} = 2.084 \times 10^{10} \cdot e^{\frac{M_1}{R} \cdot e^{\frac{M_2}{RT}}} \]

where \( M_1 = \Delta S^\ddagger / R \) and \( M_2 = -\Delta H^\ddagger / R \)

2.6.4 General Procedures for Hammett Data.
To a J. Young NMR tube (0.5 mL) of the respective rhenium starting material (0.0027 mmol) was added to CD₂Cl₂ (0.25 mL) and degassed. The reaction mixture was pressurized with CO (60 psi) at room temperature and monitored for 11 h in a Varian 400 MHz NMR. Concentration was calculated using an internal standard, hexamethylcyclotrisiloxane (4.5 x10⁻⁴ mmol) that was added to the reaction mixture. These conditions were carried out for complexes 4a-d.
Figure 2.29. Time profile for the formation of 4b. Reactions were performed with complex 4b (0.00278 mmol), and CO at 60 psi (0.0834 mmol) in a J. Young NMR tube (0.5 mL) in CD$_2$Cl$_2$ (0.25 mL) at room temperature 11 h in a Varian 400 MHz NMR. Concentration was calculated using an internal standard, hexamethylocyclotrisiloxane, (4.5 x10$^{-4}$ mmol) that was added to the reaction mixture, each point on the graph represents a single data point.
Figure 2.30. Time profile for the formation of 4c. Reactions were performed with complex 4c (0.00278 mmol), and CO at 60 psi (0.0834 mmol) in a J. Young NMR tube (0.5 mL) in CD$_2$Cl$_2$ (0.25 mL) at room temperature 11 h in a Varian 400 MHz NMR. Concentration was calculated using an internal standard, hexamethyldicyclosiloxane, (4.5 x10$^{-4}$ mmol) that was added to the reaction mixture, Each point on the graph represents a single data point.
**Figure 2.31.** Time profile for the formation of 4d. Reactions were performed with complex 4d (0.00278 mmol), and CO at 60 psi (0.0834 mmol) in a J. Young NMR tube (0.5 mL) in CD$_2$Cl$_2$ (0.25 mL) at room temperature 11 h in a Varian 400 MHz NMR. Concentration was calculated using an internal standard, hexamethylocyclotrisiloxane, (4.5 x10$^{-4}$ mmol) that was added to the reaction mixture, each point on the graph represents a single data point.
2.6.5 Additional Syntheses

Scheme 2.21. Attempted Synthesis of Re-CH₂TMS Complex

In an attempt to synthesize other oxorhenium complexes with –X ligands of the formula –CH₂R to compare the reactivity with CO, the reaction of the oxorhenium chloride starting material with the trimethylsilyl Grignard reagent (Scheme 2.21). Various solvents, temperatures, reaction time, and equivalents of Grignard were used but decomposition of the rhenium chloride substituent was observed in every case (Scheme 2.22).

Scheme 2.22 Attempted synthesis of new alkyl DAAmRe(O) complexes
The synthesis and characterization of 5 was previously reported in the unpublished results of Jessica L. Smeltz, a member of our lab. The reactivity of 5 with CO was explored, however, no insertion was observed even after increased temperature, pressures, and reaction times (Scheme 2.23). After two days of reactivity of 800 psi at 80 °C only the composition of 5 was observed via $^1$H NMR.

The synthesis of the (DAP)Re(O)(Et) complex was carried out utilizing the corresponding DAP chloride starting material and Zn(Et)$_2$ as a transmetallating agent (Scheme 2.24). The ethyl complex was synthesized in a 56% yield and isolated as a red solid. The reactivity with
CO and complex (DAP)Re(O)(Et) was monitored via a J. Young tube reaction. The corresponding acetyl complex was formed at 60 psi of CO in benzene at 80 °C, the same conditions reported for other DAP analogs 4b.

2.7 References.
Chapter 3

Synthesis, Characterization and Reactivity of (SSS)Re(O)(R) Complexes and a Computational Investigation of Ancillary Ligand Effects on the Mechanism for CO Insertion

Portions of this chapter were submitted for publication in Organometallics. Robbins, L. K.; Lilly, C. P.; Sommer, R. D.; and Ison, E. A. *Organometallics, 2016,* Submitted.
Lambic, N. S.; Lilly, C. P.; Robbins, L. K.; Sommer, R. D.; and Ison, E. A. *Organometallics.* 2016, Accepted.
Department of Chemistry, North Carolina State University;
Raleigh, North Carolina, 27695-8204
Abstract.

Several oxorhenium complexes bearing an SSS pincer ligand were isolated and characterized and their reactivity with carbon monoxide was explored. The corresponding oxorhenium (V) acyl derivatives were also isolated and characterized. Harsh reaction conditions (400 psi CO, 50 °C, 3-7 h) were required for all carbonylation reactions of the oxorhenium(V) complexes. The mechanism for carbonylation was explored computationally. The most likely mechanism for carbonylation of these (SSS)Re(O) complexes is the formation of a CO adduct followed by insertion of CO into the rhenium alkyl or aryl bond.

Introduction

3.2.1 Background

The migratory insertion of unsaturated substrates into metal ligand bonds is a common step included in many large catalytic processes, such as: hydroformylation, hydrogenation, and olefin polymerization. The insertion of carbon monoxide into metal ligand bonds, carbonylation, is one of most well-known migratory insertion reactions and examples of the insertion of carbon monoxide are known for most transition metals. Important large-scale industrial processes that utilize this reaction include the carbonylation of methanol to generate acetic acid in the Monsanto Acetic Acid Process and BP’s Cativa Process. Eastman Chemical’s Acetic Anhydride Process also involves the carbonylation of methyl acetate to generate acetic anhydride on an industrial scale. Hydroformylation utilizes the migratory insertion of carbon monoxide in a reaction with olefin and molecular hydrogen to produce aldehydes as first discovered by Otto Roelen at BASF. Because of the utility of carbonylation as a source for new C—C bond formation, understanding the mechanism for this reaction is important for the design of new catalysts.

Three types of mechanisms are proposed for the carbonylation of metal alkyl/aryl complexes and are depicted in Chapter 2, Scheme 2.3. It is important to note, again, that the commonly accepted mechanism for carbonylation reactions is of the type (b) and (c) in Scheme 2.3.
3.2.2 Factors affecting migratory insertion

As discussed in Chapter 2, many mechanistic studies to determine whether CO insertion or alkyl migration has occurred have been performed by studying the stereochemistry at the metal center. Generally, it was found that alkyl migration, as opposed to CO insertion, is the predominant mechanism. Factors such as solvent, entering ligand, migrating group, and the ancillary ligand have been shown to affect the mechanism for migratory insertion. For example, the rates of migratory insertion were found to be faster in polar solvents for complexes of the form RMn(CO)$_5$ as reported by Mawby and co-workers. The nucleophilicity of the solvent was also found to affect the rate of reaction for the migratory insertion reactions of Mo(CO)R complexes. Solvent has also been found to act as a trapping agent, and stabilize reactive intermediates in the migratory insertion reactions of [CpFe(CO)$_2$R] complexes.

Many studies have shown that the migrating alkyl group affects the rate of migratory insertion and it was generally found that the rate of insertion increases with the electron releasing nature of the migrating ligand, and decreases as the migrating ligand becomes electron withdrawing. In a study by Cotton and co-workers, the rates of migratory insertion of CO in Mn(CO)$_5$R complexes, were found to decrease in the order: $R = \text{n-Pr} > \text{Et} > \text{Ph} > \text{Me} >> \text{CH}_2\text{Ph} > \text{CF}_3$. The metal carbon bond strength has also been shown to affect the rate of insertion, as well as, the mechanism (CO insertion or alkyl migration) of the reaction.

The rates and mechanism of migratory insertion have been well documented with regards to the effect of incoming ligands, especially in the case of entering phosphine and phosphite ligands. In general, with increasing steric bulk of the incoming phosphine ligands, the rate of migratory insertion decreases. It has been shown that increasing nucleophilicity of the entering ligand increases the rate of migratory insertion. The rate of migratory insertion of CO has been shown to increase in the presence of a Lewis acid, because the Lewis acid will stabilize the acyl products by binding at the acyl oxygen (Figure 3.1, (a)). Also, the oxygen of the acyl ligand can coordinate to stabilize coordinatively unsaturated complexes (Figure 3.1, (b), (c)).
Figure 3.1. Lewis acid and $\eta^2$ acyl stabilized complexes

While the effects on the migratory insertion of CO into metal alkyl and aryl bonds have been well documented, the effect of the ancillary ligands on the rate and mechanism of migratory insertion reactions has not been extensively studied. In order to gain further insights into the factors influencing the mechanism for migratory insertion, specifically the effect of the ancillary ligand in high valent rhenium oxo complexes, we have synthesized a series of oxorhenium (SSS) (SSS = 2-mercaptoethylsulfide) chelating ligands. In this chapter, we report the synthesis and characterization of oxorhenium(V) alkyl, aryl and hydride complexes with these ligands along with their reactions with CO.

In the previous chapter and in publications by our lab, we have shown that oxorhenium(V) complexes bearing tridentate diamidoamine (DAAm) (DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C$_6$F$_5$) and diamidopyridine (DAP) ligands undergo an unprecedented mechanism for CO insertion (Scheme 3.1). It was found from mechanistic, kinetic, and computational studies that the most likely mechanism for the insertion of CO into rhenium-alkyl/aryl bond was a direct insertion mechanism ((a) Scheme 2.3) and not the typical two-step intramolecular mechanism (Scheme 2.3, (b) and (c)). As mentioned in the previous chapter, the mechanism for CO insertion is largely impacted by the strong trans influence of the axial oxo ligand in these square pyramidal oxorhenium(V) complexes. Importantly, these high valent oxo complexes differ from typical CO insertion reactions of low valent metal carbonyl complexes, in that the CO adduct is destabilized relative to the starting complex (Scheme 2.17, Chapter 2). In some cases, the CO adduct will be so destabilized that insertion into the metal alkyl/aryl bond will proceed directly without the formation of a CO adduct, this was found to be true for DAAm and DAP oxorhenium(V) complexes. With these data in mind and the limited data found in the literature, the effect of
the ancillary ligand on the mechanism of migratory insertion was explored with high-valent oxorhenium(V) complexes.

**Scheme 3.1.** Mechanism for CO insertion into (DAAm)Re(O)(V) complexes

![Scheme 3.1](image)

1.) Rate of insertion Bn > Me > Ph
2.) Bimolecular kinetics
3.) Large Negative $\Delta S^\ddagger$

### 3.3 Results and Discussion

#### 3.3.1 Synthesis of new rhenium complexes

The previously reported (SSS)Re(O)(Me) complex was synthesized from methyltrioxorhenium in the presence of excess triphenylphosphine. NMR and IR spectral data are consistent with reported literature (Scheme 3.2).

**Scheme 3.2.** Synthesis of complex 7

![Scheme 3.2](image)

A series of alkyl and aryl complexes bearing the SSS ligand framework, (SSS)Re(O)R, (R = Et, 8; Ph, 9; Bn, 10), were successfully synthesized from the corresponding transmetalating reagent (Scheme 3.3) and (SSS)Re(O)Br. The complexes were isolated in moderate yields and all complexes were air and moisture stable.
X-ray quality crystals of all compounds were obtained by vapor diffusion of pentane into a concentrated solution of 8-10 in methylene chloride. The geometry around rhenium is best described as distorted square pyramidal, with an oxo ligand occupying the axial position and the tridentate SSS ligand in the equatorial plane. A comparison of the bond lengths and angles in the three structures is depicted in Table 3.1. Bond lengths and angles for all three structures are remarkably similar. There is only a small decrease in the rhenium—carbon bond lengths in proceeding from 8-10 (Entry 1).
Table 3.1. Selected bond lengths and angles for 8-10.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bond</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re—C</td>
<td>2.16</td>
<td>2.11</td>
<td>2.17</td>
</tr>
<tr>
<td>2</td>
<td>Re—S₂</td>
<td>2.35</td>
<td>2.35</td>
<td>2.34</td>
</tr>
<tr>
<td>3</td>
<td>Re—S₁</td>
<td>2.29</td>
<td>2.29</td>
<td>2.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle (º)</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. O—Re—S₁</td>
<td>116</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>5. O—Re—S₂</td>
<td>109</td>
<td>108</td>
<td>109</td>
</tr>
<tr>
<td>6. S₁—Re—S₃</td>
<td>128</td>
<td>128</td>
<td>128</td>
</tr>
<tr>
<td>7. C—Re—S₂</td>
<td>149</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

Figure 3.2. X-ray crystal structures for 8-10. Thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (º). For 8: Re1—O1, 1.6901(15); Re1—C₅, 2.157(2); Re1—S₂, 2.3498(6); Re1—S₁, 2.291(5); Re1—S₃, 2.2890(5); S₂—Re1—C₅, 149.33(6); O₁—Re1—C₅, 101.16(9); S₁—Re1—S₃, 127.138(19). 9: Re1—O1, 1.6831(14); Re1—C₅, 2.1101(17); Re1—S₂, 2.3461(4); Re1—S₁, 2.2803(4); Re1—S₃, 2.2886(4); S₂—Re1—C₅, 150.36(5); O₁—Re1—C₅, 101.81(7); S₁—Re1—S₃, 127.852(17). 10: Re1—O1, 1.6861(15); Re1—C₅, 2.1694(19); Re1—S₂, 2.3360(5); Re1—S₁, 2.2878(5); Re1—S₃, 2.2901(5); S₂—Re1—C₅, 149.99(5); O₁—Re1—C₅, 102.10(8); S₁—Re1—S₃, 127.730(19).

All new SSS rhenium complexes (8-10) were fully characterized using ¹H NMR, ¹³C NMR and IR spectroscopies. The ¹H NMR spectra of 7-10 all exhibit four distinct multiplets, each integrating to two protons, corresponding to the four diastereotopic protons of the ethylene backbone. The chemically inequivalent protons arise from two protons being
syn to the terminal oxo ligand and two protons being trans to the terminal oxo. The diastereotopic nature of the protons of tridentate ethylene bridged ligands around rhenium oxo complexes have been well documented.\textsuperscript{18a}

A representative $^1$H NMR spectrum of 7 illustrating the splitting pattern of the SSS ligand observed experimentally is shown in Figure 3.3. Four multiplets corresponding to the ethylene backbone resonate at 4.1, 3.9, 3.0, and 1.9 ppm. Each multiplet integrates to two protons and the protons of the Re—Me group resonates as a singlet at 3.0 ppm that is overlapping with one of the ligand backbone resonances. All SSS complexes also exhibit a distinct Re=O stretch in the FT/IR spectrum at 963-972 cm$^{-1}$. Terminal Re=O stretches have been observed for many Re$^V$ complexes and was the subject of a review article, Re$^V$(O) have been found to exhibit IR stretching frequencies at 912-995 cm$^{-1}$.\textsuperscript{20} The Re=O stretch in the IR was reported for several other terminal oxo rhenium complexes, [Re(O)(MeCCMe)$_2$], [Re(O)(PhCCPh)$_2$], and [Re(O)(PhCCPh)$_2$]Na$^+$ at 975, 972, and 824 cm$^{-1}$ respectively.\textsuperscript{21}
The reactivity of complexes 7-10 with CO was explored. The addition of CO (400 psi) to complexes 7, 8, and 9 in toluene at 50 °C from 3-8 h resulted in the corresponding acyl derivatives (Scheme 3.4). It is important to note that the formation of the acetyl derivatives 11, 12, and 13 required harsher reaction conditions than those previously reported by our
group (Chapter 2) bearing the DAAm ligand framework. Complex 10 did not result in any isolatable benzyl derivative. The formation of a new rhenium complex was observed after one hour by $^1$H NMR spectroscopy, however, the new species was never able to be isolated Figure 3.4. Even under milder reaction conditions (15-300 psi, 25-80 °C, 2-16 h), no new stable rhenium complex was isolated.

![Diagram of complex formation](image)

**Figure 3.4.** Reactivity of 10 with CO. Conditions: Reactions performed in a 25.0 mL glass-lined Parr reactor with 10, (25.0 mg, 0.0561 mmol) in toluene (10.0 mL) and CO (200 psi) at 50 °C for up to 7 h. The spectral data represent (bottom to top), starting material (0 h), 1, 3, and 7 h time points, as the crude reaction mixture in CD$_2$Cl$_2$.

Complexes 11-13 were characterized by $^1$H, $^{13}$C NMR, and FTIR spectroscopies. The FTIR spectra all exhibit a strong C=O stretch for the acyl group from 1602-1631 cm$^{-1}$. Similarly, other CO stretches for acyl complexes have been reported in the literature. For example, Bergman and coworkers have reported that [CpRe(CO)$_2$(COCH$_3$)(CH$_3$)] has an IR stretching frequency of 1630 cm$^{-1}$. Filippou and coworkers reported an IR stretching frequency of 1618 cm$^{-1}$ for the complex [CpRe(CO)$_2$C(O)Ph(Br)]$^{23}$ Hoffman and coworkers reported IR
stretches of 1505 cm\(^{-1}\) for [Re(O)(C(O)R)R\(_2\)(PMe\(_3\))], (R = CH\(_2\)SiMe\(_3\)).\(^{24}\) The corresponding DAAm analog, 2 exhibits a CO stretch 1587 cm\(^{-1}\) and the recently reported DAAm benzyl complexes (4a-d) exhibits a CO stretch at 1592 cm\(^{-1}\). Similarly, the DAP analogue exhibits an acyl stretch at 1599 cm\(^{-1}\) and the benzoyl analogue at 1557 cm\(^{-1}\). Importantly, the DAAm and DAP analogs of these oxorhenium(V) alkyl and aryl complexes result in lower stretching frequencies for the acyl ligands than the SSS complexes. The higher CO stretching of the acyl ligand of 6-8 is due to a more electron poor rhenium center, and thus less \(\pi\) backbonding into the \(\pi^*\) orbital of the acyl ligand from the metal center. The resonance forms of the acyl ligand are represented in Scheme 3.5. The SSS acyl complexes have a major contribution from resonance form A, evident by less \(\pi\) backbonding. Conversely, DAAm acyl complexes have a major contribution from the carbene resonance form B, due to increased \(\pi\) backbonding.

**Scheme 3.5.** Representation of resonance forms of Re-acyl complexes. Ancillary ligands omitted for clarity.

![Scheme 3.5](image)

X-ray quality crystals of 11 and 12 were obtained via the slow diffusion of pentane into a concentrated solution of the rhenium compound in methylene chloride. The geometry around the metal center can be described as distorted square pyramidal with the terminal oxo ligand in the apical position. Representative crystal structures of 11 and 12 are shown in Figure 3.5. The Re1—C3 bond length of 7 (2.16 Å) and Re1—C5 (2.10 Å) of 8 decreases in complex 11 (2.08 Å) and 12 (2.16 Å). Importantly, the Re—C\(_{\text{acyl}}\) bond length for the previously reported DAAm complex [DAAmRe(O)(C(O)CH\(_3\))] is 2.03 Å and DAP complex [DAPRe(O)(C(O)CH\(_3\))] is 2.04 Å, significantly shorter than the Re—C\(_{\text{acyl}}\) bond length for 11 and 12, 2.10 and 2.08 Å respectively. This is likely due to the increased \(\pi\) back-bonding from the metal center to the CO \(\pi^*\) orbital bearing the more donating DAAm ligand compared to the less donating SSS framework.
Figure 3.5. X-ray crystal structure of 11 and 12. Ellipsoids are at 50% probability. Hydrogens have been omitted for clarity. Selected bond lengths (Å) for 11: Re1—O1, 1.691(2); Re—S1, 2.3327(6); Re—S2, 2.2920(5); Re—C3, 2.077(3); O—Re—C, 104.63(11); S2—Re—O, 114.759(14). Selected bond lengths (Å) for 12: Re1—O1, 1.6899(15); Re1—S2, 2.3524(5); Re1—S1, 2.2922(6); Re1—S3, 2.2832(5); Re1—C5, 2.100(2); O1—Re1—C5, 103.72(8); S3—Re1—S1, 129.35(2); C5—Re1—S2, 148.64(6).
A representative $^1$H NMR spectrum of 11 in CDCl$_3$ is shown in Figure 3.6.

![NMR spectrum image]

Figure 3.6. $^1$H NMR spectrum of 11 in CDCl$_3$.

3.3.3 Characterization of 14

Because of the significant difference in the conditions for CO insertion between the SSS and DAAm complexes, studies were attempted to determine the mechanism of CO insertion for complexes 7-9. Upon workup of the reaction of complexes 7-9 with CO the formation of a bimetallic species was observed in all cases. The species was NMR inactive, however, it was characterized by IR and UV-vis spectroscopy, as well as, X-ray crystallography. Complex 14 could be formed independently by heating complex 7 at high CO pressures (800 psi) in benzene for 8 h (Scheme 3.6). The dark red bimetallic rhenium
complex was isolated and is both air and moisture stable. Complex 14 exhibits three terminal CO stretches in the FTIR spectrum: 2012, 1939, and 1871 cm\(^{-1}\).

X-ray quality crystals were obtained from the slow diffusion of pentane into a concentrated solution of 14 in methylene chloride. The bimetallic species (Figure 3.8) contains a bridging SSS ligand between each rhenium center in the equatorial plane. The geometry about each rhenium center is best described as octahedral, where a terminal carbonyl ligand occupies the axial position of Re1 and S5 of the tridentate sulfur ligand occupies the axial position of Re2. The bimetallic rhenium complex was also characterized by UV-vis spectroscopy. The UV-vis spectrum of 14 was obtained in methylene chloride at room temperature (Figure 3.7). Three separate absorbances \(\lambda = 347, 447, 554 \text{ nm}\) were observed. Because of the formation of 14 under the conditions for all acyl products, attempts to obtain reaction kinetics were unsuccessful. To explore ancillary ligand effects on migratory insertion, the reaction of complexes 7-10 with CO was explored computationally.
Figure 3.7. UV-vis spectrum of 14 (0.05 M) in CH$_2$Cl$_2$ (2.5 mL) at 25 ºC, $\lambda_{\text{max}}$ = 557, 447, 347 (sh), 277 nm.
Scheme 3.6. Synthesis of complex 14

![Scheme Diagram](image)

**Figure 3.8.** X-ray crystal structure of 14. Ellipsoids are at 50\% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Re1—S1, 2.4754(6); Re1—S3, 2.4691(6); Re2—S1, 2.5282(6); Re2—S3, 2.5219(6); Re2—S4, 2.2638(7); Re2—S5, 2.4658(6); Re2—S6, 2.2753(6); Re1—C1, 1.919(3); Re1—C2, 1.937(3); Re1—C3, 1.924(3); Re2—C8, 1.883(2); C1—Re1—S3, 94.75(8); C8-Re2-S3, 100.24(8); C1—Re1—S2, 176.14(8); S5—Re2—S3, 83.440(19); C8—Re2—S5, 174.33(8); C3—Re1—S1, 173.65(8); S4—Re2—S1, 164.02(2); Re1—S1—Re2, 100.30(2).

### 3.3.4 Synthesis and reactivity of (SSS)Re(O)(H)

The synthesis of the corresponding hydride complex, 15, was carried out from the (SSS)Re(O)Br starting material and (H)Sn(Bu)$_3$ in THF at room temperature for 30 min (Scheme 3.7). The transmetallation affords the air and moisture stable complex (SSS)Re(O)H in good yield. The deuterated analog, complex 15-D was prepared in a similar manner from (D)Sn(Bu)$_3$, to compare spectroscopically with 15. A singlet at 8.40 ppm, which corresponds to the Re—H resonance was observed in the $^1$H NMR spectrum of 15. The resonance at 8.40 ppm was absent in the $^1$H NMR of 15-D. By FTIR spectroscopy, the
Re—H stretch was observed at 2019 cm\(^{-1}\), and is observed as a single band of weak intensity, which shifted to lower frequency in the deuterated complex. Complex 15 exhibited poor solubility in most organic solvents. Poor-moderate solubility was achieved in CH\(_2\)Cl\(_2\), CHCl\(_3\), CH\(_3\)CN, and DMSO at room temperature, and increased solubility was observed in CH\(_3\)CN and DMSO at elevated temperatures (80 °C).

**Scheme 3.7.** Synthesis of 15/15-D

![Scheme 3.7. Synthesis of 15/15-D](image)

The reactivity of 15 with CO was explored experimentally. However, no reaction of 15 with CO was observed even at elevated temperatures and CO pressure. Starting materials were isolated at the end of the reactions with CO (Scheme 3.8).

**Scheme 3.8.** Reactivity of 15 with CO

![Scheme 3.8. Reactivity of 15 with CO](image)

Similarly, the reactivity of 15 was explored with other saturated substrates. In the presence of ethylene at 60 psi at elevated temperatures no reaction was observed and only starting materials were obtained at the end of the reaction (Scheme 3.9). The reaction of 15 with benzaldehyde was monitored by \(^1\)H NMR spectroscopy in toluene and acetonitrile at elevated temperatures; however, no reaction was observed only starting materials were recovered (Scheme 3.10).

**Scheme 3.9.** Reactivity of 15 with ethylene

![Scheme 3.9. Reactivity of 15 with ethylene](image)

**Scheme 3.10.** Reactivity of 15 with benzaldehyde

![Scheme 3.10. Reactivity of 15 with benzaldehyde](image)
The reactivity of 15 was explored with Lewis acid reagents. It has been shown by our group that the addition of a Lewis acid to oxorhenium DAAm and DAP complexes drastically alters the reactivity of the complexes.\textsuperscript{25} The synthesis of a Lewis acid/base adduct from 15 was attempted using similar reported procedures for DAAm and DAP analogs.\textsuperscript{25-26} The reaction of 15 with varying equivalencies of BF\textsubscript{3}·OEt\textsubscript{2} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Scheme 3.11) only resulted in decomposition and no discernable organometallic complexes via \textsuperscript{1}H NMR spectroscopy.
Scheme 3.11. Reaction of 15 with Lewis acids

\[ \text{Solvent, } T \]

BF\(_3\)-OEt\(_2\) (5-15 equiv) or B(C\(_6\)F\(_5\))\(_3\) (3-5 equiv)

Not Observed

Scheme 3.12. Synthesis and reactivity of 7\(\cdot\)B(C\(_6\)F\(_5\))\(_3\).

After 6 hours

Starting material

\[ \text{ppm} \]

Figure 3.9. \(^1\)H NMR spectra of 7\(\cdot\)B(C\(_6\)F\(_5\))\(_3\) (10 mg, 0.0113 mmol) with CO (60 psi) at 25 °C monitored in a J Young NMR tube in benzene-\text{d}_6 (0.25 mL). Spectral data are shown (bottom to top) for starting material (0 h) and 1, 3, and 6 h of reactivity.
Similarly, the reactivity of complex 7 with Lewis acids was also explored. The reaction of 7 with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in methylene chloride at room temperature resulted in the formation of 7·B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Scheme 3.12). The formation of 7·B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was confirmed by the chemical shifts in the \textsuperscript{1}H NMR spectrum compared to the \textsuperscript{1}H NMR shifts of 7 in situ. X-ray quality crystals were obtained from the slow diffusion of pentane into a concentration solution of 7·B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} under a nitrogen atmosphere. A preliminary structure is shown in Figure 3.10. The geometry is best described as distorted square pyramidal with the oxo and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} ligand occupying the axial position. Complex 7·(B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} is structurally similar to the previously reported DAP and DAAm borane adducts.\textsuperscript{25-26}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure310.png}
\caption{Preliminary X-ray crystal structure of 7·B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}. Ellipsoids are at 50\% probability; hydrogen atoms have been omitted for clarity. Selected bond lengths (\textAA{}), angles (\textdegree{}): Re1—S1, 2.259; Re1—S3, 2.249; Re2—S1, 2.312; Re1—C, 2.122; Re—O, 1.748; O—B, 1.553; B—O—Re, 167.84; S1—Re—S2, 120.06; C—Re—O, 103.71; C—Re—S3, 146.45; O—Re—S2, 109.84.}
\end{figure}
The reaction of $7 \cdot \text{B}(\text{C}_6\text{F}_5)_3$ was explored with CO and monitored by $^1\text{H}$ NMR spectroscopy. At mild temperatures and pressures of CO, complex $7 \cdot \text{B}(\text{C}_6\text{F}_5)_3$ was converted to a new organometallic complex as observed by $^1\text{H}$ NMR spectroscopy but quickly decomposes (Figure 3.9). Attempts to isolate the product under varied conditions were not successful.

3.4 DFT calculations.

Recently, the possible mechanisms for the insertion of CO into oxorhenium(V) complexes with DAAm and DAP ancillary ligands were explored computationally.\textsuperscript{15b, 18b, 18c} The most likely mechanism for the migratory insertion of these complexes was a direct insertion mechanism (Scheme 2.3 (a), Chapter 2) and not the commonly proposed two-step mechanism that included the formation of CO adducts. In order to examine the effect of the ancillary ligand on the mechanism for the migratory insertion of CO into alkyl/aryl bonds with SSS ligands, a computational study was pursued.

For the calculations in this chapter, structures were optimized in the gas phase with the M06\textsuperscript{27} functional as implemented by Gaussian 09 with the 6-31G(d,p)\textsuperscript{28} basis set on C, H, S, and O and the Stuttgart-Dresden\textsuperscript{29} basis set and relativistic effective core potential (RECP) combination (SDD) on Re with an additional f polarization function.\textsuperscript{30} Energetics were calculated with the 6-311++G(d,p)\textsuperscript{31} basis set for C, H, S and O atoms and the same basis set and RECP on Re as above. Reported energies utilized analytical frequencies and the zero-point corrections form the gas phase calculations and included solvation energies, which were computed using the SMD\textsuperscript{32} model with benzene as the solvent. Three possible pathways were considered for the approach of CO to the metal center computationally (Figure 3.11.)
Figure 3.11. Computationally considered pathways for CO insertion.

Because complex 7 is five coordinate, the trajectories considered were syn to the rhenium-methyl bond (a), syn to the rhenium-sulfide bond (b), and finally, trans to the terminal oxo ligand (c).

Scheme 3.13. Pathway A.

Pathway A. Attack of CO syn to the rhenium methyl bond. The approach of CO syn to the Re—Me bond (Scheme 3.13) results in the CO adduct 16. The geometry of 16 at the rhenium center is best described as distorted octahedral, where the oxo—rhenium—carbonyl bond angle is 87.2°. The oxo—rhenium—methyl bond angle is 147.4° and the rhenium—methyl bond is elongated (2.35 Å) compared to the rhenium—methyl bond length in 7 (2.14 Å). The elongation of the rhenium—methyl bond in 16 is likely due to the trans influence of the terminal oxo ligand. The formation of 16 is endergonic overall (ΔG° = 17.4 kcal/mol) for the addition of CO and the activation barrier is 33.7 kcal/mol. Migration of the methyl group to CO results in the formation of 11syn. The formation of 6syn from 16 is exergonic (ΔG = -5.4 kcal/mol) and proceeds at a barrier of ΔG‡298 = 17.7 kcal/mol. Complex 11syn
isomerizes to the experimentally observed product $11_{\text{anti}}$ (Scheme 3.14). The isomerization reaction is exergonic overall ($\Delta G^o = -7.5$ kcal/mol) and proceeds with a barrier of 5.5 kcal/mol).

**Scheme 3.14** Isomerization pathway from $11_{\text{syn}}$ to $11_{\text{anti}}$

\[ \begin{align*} 11_{\text{syn}} & \xrightarrow{\text{TS 3}} 11_{\text{anti}} \\ -5.4 \text{(-2.3)} & \quad -7.5 \text{(-4.6)} \end{align*} \]

*The large barrier for the addition of CO to 7 via TS 1, ($\Delta G^\ddagger_{298} = 33.7$ kcal/mol) makes pathway A unlikely for the formation of 11.*

**Pathway B, the addition of CO syn to the rhenium—sulfido bond.** The approach of CO syn to the rhenium—sulfido bond of 7 resulted in the formation of CO adduct 17, which is endergonic overall ($\Delta G^o = 9.3$ kcal/mol) (Scheme 3.15).

**Scheme 3.15.** Pathway B.

Adduct 17, has both the CO and methyl ligand in the equatorial plane and the SSS is now arranged around rhenium in a facial orientation. Complex 17 is structurally similar to 16 and is also best described as distorted octahedron around rhenium with the oxo—rhenium—carbonyl bond angle 87.1º. The formation of 17 is more favorable than the formation of 16 from Pathway A by 8.1 kcal/mol and proceeds at a lower barrier ($\Delta G^\ddagger_{298} = 16.9$ kcal/mol). The increased stabilization of 17 may be due to the orientation of the sulfur ligand trans to
the terminal oxo ligand, whereas, 16 has two strong trans influence ligands (methyl and oxo) trans to one another.

From 17, methyl migration occurs to afford the acyl product 18. The formation of 18 is unfavorable overall ($\Delta G^o = 37.7$ kcal/mol) and proceeds with a large barrier of activation, TS 5, ($\Delta G^{‡}_{298} = 49.4$ kcal/mol). Pathway B does not lead to the experimentally observed product, and is also thermodynamically and kinetically unfavorable.

**Pathway C, attack of CO trans to the oxo ligand.** Finally, the approach of CO trans to the terminal oxo ligand was considered (Scheme 3.16).

**Scheme 3.16.** Pathway C

![Scheme 3.16](image)

Initial addition of CO trans proceeds with an activation barrier of 12.7 kcal/mol, is endergonic overall ($\Delta G^o = 12.2$ kcal/mol) and results in the formation of the CO adduct 19. Adduct 19 is then distorted to generate a new CO adduct 20. The transformation is endergonic overall ($\Delta G^o = 21.6$ kcal/mol) and proceeds with a barrier of 23.0 kcal/mol. The major structural differences for 19 and 20 are summarized in Table 3.2.

In proceeding from 19 to 20 the oxo—rhenium—carbonyl bond angle is decreased from 172° in 19 to 140° in 20 (Entry 4); the rhenium—carbonyl bond is decreased significantly from 2.46 Å in 19 to 2.04 Å in 20 (Entry 3) and the rhenium methyl bond is increased from 2.5 Å in 19 to 2.26 Å in 20 (Entry 2). The barrier for insertion (TS 8) is 21.9 kcal/mol. Thus this elementary step (TS 8, 20 -11) is essentially barrierless (0.3 kcal/mol). These data suggest that the most likely pathway for the formation of 11 is
Pathway C, which results in the formation of two distinct CO adducts before proceeding to product.

Pathway C describes the stepwise insertion of CO into the rhenium-methyl bond of 7. There have been many mechanistic studies aimed at clarifying the exact nature of the migrating group (CO insertion versus alkyl/aryl migration) in metal-alkyl/aryl carbylation reactions. Generally, it has been established that alkyl/aryl migration is the dominant mechanism compared to CO insertion.\textsuperscript{4, 11a, 33} However, based on the geometry of the acyl product 11 (acyl ligand cis to oxo) and the vibrational analysis of TS 8, it is evident that the mechanism here (Pathway C) involves a rare example of CO insertion.

More importantly, because the ancillary SSS chelate ligand is not very donating, the effect on the mechanism for insertion is: a) CO adducts are stabilized relative to the DAAm and DAP analogs where a direct CO insertion mechanism was observed. The reduced electron density at rhenium results in harsher reaction conditions (400 psi CO, 50 °C) for carbylation when the SSS ligand is employed compared to the corresponding DAAm and DAP complexes. The computational data for the three calculated pathways are summarized in Figure 3.12.
Table 3.2. M06 optimized structures for 19 and 20, and comparison of selected bond lengths and angles. Structures were optimized in the gas phase with the 6-31G* basis set\(^3\) on C, H, S, and O and the SDD basis set and effective core potential on Re. The basis set on Re was augmented with a single f polarization function. Hydrogens have been omitted for clarity.

![M06 optimized structures for 19 and 20](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bond (Å)</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re-C(_{\text{Methyl}})</td>
<td>2.15</td>
<td>2.02</td>
</tr>
<tr>
<td>2</td>
<td>Re-S</td>
<td>2.38</td>
<td>2.67</td>
</tr>
<tr>
<td>3</td>
<td>Re-C(_{\text{Carbonyl}})</td>
<td>2.46</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>Angle (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>O-Re-C(_{\text{Carbonyl}})</td>
<td>172.0</td>
<td>140.1</td>
</tr>
<tr>
<td>5</td>
<td>S-Re-C(_{\text{Methyl}})</td>
<td>152.3</td>
<td>163.3</td>
</tr>
</tbody>
</table>
Figure 3.12. Computational pathways for the migratory insertion of CO in 7. Structures were optimized in Gaussian 09 in the gas phase with the M06 functional and employed the SDD basis set on Re with an added f polarization and the 6-31G(d,p) basis set on all other atoms. Energetics were calculated with the 6-311++G(d,p) basis set for C, H, S, and O atoms and the SDD basis set with an added f polarization function on Re as implemented in Gaussian 09. Reported energies utilized analytical frequencies and the zero point corrections form the gas phase calculations and included solvation corrections, which were computed using the SMD model as implemented in Gaussian 09.
3.4.1 Pathway C for complexes 8-10, and 15.

Scheme 3.17. M06 data for CO insertion into 15

The reactivity of 15 with CO was also explored computationally according to Pathway C, the lowest energy pathway computed for the carbonylation of 7. The formation of the trans CO adduct, 21, in this case directly proceeds to the formyl product, 22. The inability to observe the formation of a second CO adduct in this case is likely due to the relatively high energy and thus instability of the second adduct. For complex 15, CO insertion from adduct 21 has a small barrier for the formation of 22 (2.1 kcal/mol). It is likely in changing the R substituent on rhenium the electronics are altered in such a way that the second CO adduct is strongly destabilized and thus not observed computationally.

The activation barrier for CO insertion into the rhenium—hydride bond is 17.9 kcal/mol and the formation of 22 is an endergonic process overall at 0.6 kcal/mol (298 K) (Scheme 3.17). The unfavorable thermodynamics accounts for the lack of insertion observed experimentally for 15. Unfavorable CO insertion into metal hydrides to form transition metal formyl complexes is not unprecedented.\(^{35}\) This arises from the increased bond strength of a M—H of the starting material compared to M—C of the product.\(^{35}\) Metal formyl complexes have been synthesized by other means\(^ {36}\) although there have been a few reports of the synthesis of formyl complexes via radical, Rh(OEP)(H), (OEP = octaethylprophyrin),\(^ {37}\) and insertion, Th(OR)(C(O)H), (R = C(C(CH\(_3\))\(_3\))\(_2\)),\(^ {16a}\) reactions.

Similarly, Pathway C for 8 and 9 involves insertion from a trans CO adduct (23 and 24) with a barrier of 21.6 and 20.4 kcal/mol respectively (Scheme 3.18). Again, the inability to form a second CO adduct is likely due to the relative high energy of the intermediate compared to the starting materials and the small energy of activation between the two CO
adducts which, contributes to a relatively short life-time for the adduct. The formation of both 12 and 13 are exergonic overall (-9.3 (12) and -5.9(13) kcal/mol respectively).

**Scheme 3.18.** Pathway C calculated for 12 and 13.

Finally, Pathway C was explored for the benzyl complex, 10 (Scheme 3.19). The formation of 27 was exergonic overall (-7.3 kcal/mol) and both CO adducts were found computationally. Complex 25 which contains a CO ligand trans (172°) to the oxo ligand is distorted to reduce the oxo—rhenium—carbonyl bond angle to 153° with a barrier of 19.2 kcal/mol. The new CO adduct, 26, undergoes insertion to generate 27 with a low barrier (18.4 kcal/mol).

3.5 Conclusions

The effect of the ancillary ligand on the mechanism for migratory insertion of CO in high valent oxorhenium complexes has been clarified by synthesizing a series of oxorhenium complexes that contain (SSS) (SSS = 2-mercaptoethylsulfide) chelating ligands. Unlike, the DAAm and DAP analogs, SSS ligands result in complexes that appear to be less electron rich at rhenium. As a result, CO adducts are slightly stabilized and calculated as intermediates on the potential energy surface. Data suggest that the most likely mechanistic pathway results in the formation of two distinct CO adducts before proceeding to product. Thus the most likely pathway with SSS ligands describes the stepwise insertion of CO into the rhenium—methyl bond of 7 rather than the concerted direct CO insertion observed for DAAm and DAP complexes. Based on the geometry of the acyl product and the vibrational analysis of the carbon—carbon bond forming step, it is evident that the mechanism here involves CO insertion. Thus the calculated mechanism with SSS ligands is a rare example of CO insertion rather than alkyl/aryl migration.

3.6 Experimental

Complex 7 and (SSS)Re(O)Br\textsuperscript{38} were synthesized as previously reported. All other reagents were purchased from commercial resources and used as received. \textsuperscript{1}H, \textsuperscript{13}C NMR spectra were obtained on 300 or 400 MHz Varian Mercury spectrometers at room temperature. Chemical shifts are listed in parts per million (ppm) and referenced to their residual protons or carbons of the deuterated solvents respectively. All deuterated solvents were obtained from Cambridge Isotopes Laboratory. All reactions were run open to air unless otherwise noted. FTIR spectra were obtained on a JASCO FT/IR-4100 instrument in KBr thin films. High-
pressure reactions were performed in a stainless steel Parr 4590 Micro Bench Top Reactor. Elemental analyses were performed by Atlantic Micro Labs, Inc.

[(SSS)Re(O)CH₃], 7. An alternative to the original synthesis by Shan and coworkers (Inorg. Chem. 2003, 42, 2362-2367) was utilized for the synthesis of 7. Methyl trioxorhenium (111 mg, 0.447 mmol) and triphenylphosphine (117 mg, 0.447 mmol) was added to a 25.0 mL scintillation vial and dissolved in a minimal amount of methylene chloride. 2, 2’-Thiodiethanethiol (58 µL, 0.45 mmol) was added via syringe to the reaction mixture. The mixture was left to stand for 24 h undisturbed. The resulting red crystals were filtered and washed with diethyl ether (~10 mL) to afford 7 in a 52% yield (90.3 mg, 0.244 mmol).

(SSS)Re(O)Ph, 9. In a 25.0 mL scintillation vial, (SSS)Re(O)Br (0.691 mmol, 300 mg) and Zn₂Ph (1.38 mmol, 303 mg) was dissolved in ~15 mL THF in a nitrogen filled glove box. The reaction was stirred for 0.5 h at room temperature. The resulting mixture was extracted with CH₂Cl₂ (25.0 mL × 3) and washed with a saturated NaCl solution (50.0 mL × 3). The organic layer was dried over NaSO₄ and filtered. The filtrate was reduced in vacuo to afford the concentrated product. Excess pentanes (~ 50.0 mL) were added to afford the product as a red powder (0.506 mmol, 219 mg) 73% yield. ¹H NMR (CD₂Cl₂) 𝛿: 7.2 (d, J = 7.4 Hz, 2H), 7.1 (dd, J = 6.9, 1.4 Hz, 2H), 7.0 (t, J = 6.6 Hz, 1H), 4.3 (m, 2H), 4.1 (m, 2H), 3.1 (m, 2H), 2.1 (m, 2H). ¹³C NMR (CD₂Cl₂) 𝛿: 138.2, 128.1, 124.9, 48.4, 44.7. Elemental Analysis (C₁₀H₁₃S₃O-Re): Theoretical: C: 27.83; S: 22.28, H: 3.04. Found C: 27.96, S: 22.56, H: 3.00.

(SSS)Re(O)Bn, 10. In a 25 mL scintillation vial, (SSS)Re(O)Br (300 mg, 0.691 mmol) was dissolved in 10.0 mL of dry CH₂Cl₂ in a nitrogen filled glove box. BnZnBr, (5.5 mL of a 0.5 M solution in THF) was added. The reaction mixture was stirred at room temperature for 0.5 h. The product was extracted with CH₂Cl₂ (25.0 mL × 3) and washed with a saturated NaCl solution (25.0 mL × 3). The organic layer was dried with NaSO₄ and filtered, and the filtrate was reduced in vacuo. To the concentrated solution, excess hexanes were added (50.0 mL) to afford a grey precipitate. The precipitate was filtered and dried to afford product (0.202 mmol, 88.5 mg) 44% yield. ¹H NMR (CD₂Cl₂) 𝛿: 7.3 (m, 4H), 7.0 (m, 1H), 5.0 (s, 2H, benzylic), 4.1 (m, 2H), 4.0 (m, 2H), 3.0 (m, 2H), 1.9 (m, 2H). ¹³C NMR (CD₂Cl₂) 𝛿: 130.1, 127.5, 124.6, 49.7, 44.5, 33.2. Elemental Analysis (C₁₁H₁₅S₃O-Re·CH₂Cl₂): Theory: (C:
27.17; H: 3.23; S: 18.13) Found: (C: 27.82; H: 3.10; S: 20.13). Despite several attempts satisfactory elemental analysis could not be obtained for this molecule.

(SSS)Re(O)Et, 7. In a 25.0 mL scintillation vial (SSS)Re(O)Br (0.691 mmol, 300 mg) was dissolved in 15.0 mL of THF. (Et)2Zn (1.38 mL of a 1.0 M solution in ether) was added to a stirred reaction mixture, and the resulting dark brown solution was allowed to stir for 1 h at room temperature. Solvent was removed in vacuo and the residual brown residue was dissolved in a minimal amount of methylene chloride. Addition of excess pentanes resulted in dark precipitate. Filtration afforded a pale yellow/orange powder (0.345 mmol, 132 mg, 50% yield). 1H NMR (CD2Cl2) δ: 4.14 (m, 2H), 3.94 (m, 2H), 3.83 (q, J = 7.4 Hz, 2H), 3.00 (m, 2H), 2.28 (t, J = 7.4 Hz, 3H), 1.79 (m, 2H). 13C NMR (CD2Cl2), δ: 49.3, 44.2, 24.3, 24.1. Elemental analysis (C6H13S3ORe): Theoretical: C: 18.79; S: 25.08; H: 3.42. Found C: 18.90; S: 24.91; H: 3.46.

General procedure for complexes 11-13. In a 25 mL glass liner, 11-13 and a stir bar was added and dissolved in 15 mL of toluene. The glass liner was added to a Parr reactor and allowed to stir. The reactor was pressurized with carbon monoxide (400 psi) and heated to 50 ºC for 3-7 h. The reactor was then cooled to room temperature and depressurized. The reaction mixture was concentrated under reduced pressure and filtered over celite. To the resulting filtrate, excess pentanes were added to afford an orange precipitate. Filtration of the precipitate gave a pale orange powder.

(SSS)Re(O)(O)CH3, 11. Reaction of 7 (300 mg, 0.813 mmol) with CO for 7 h. Isolated (129 mg, 0.325 mmol), 40% yield. 1H NMR (CDCl3) δ: 4.3 (m, 2H) 3.9 (m, 2H), 3.0 (m, 5H) 2.1 (m, 2H). 13C NMR (CDCl3) δ: 245.0, 52.2, 46.3, 43.0. IR (FTIR, KBr pellet, cm-1): ν(C-Oacyl) 1620(s); ν(Re-O) 968 (s). Elemental Analysis (C6H11S3O2Re): Theoretical: C: 18.13; S: 24.19; H: 2.79. Found C: 18.35, S: 24.49, H: 2.75.

(SSS)Re(O)(O)CH2CH3, 12. Reaction of 8 (152 mg, 0.395 mmol) with CO for 7 h. Isolated (51.8 mg, 0.126 mmol), 31% yield. 1H NMR (CDCl3) δ: 4.3 (m, 2H) 3.9 (m, 2H) 3.3 (q, J = 7.7 Hz, 2H) 3.1 (m, 2H) 2.0 (m, 2H) 1.4 (t, J = 7.4 Hz, 3H). 13C NMR (CDCl3) δ: 248.2,
Elemental Analysis (C_{10}H_{13}S_{3}O_{2}Re·(0.5)CH_{2}Cl_{2}): Theoretical: (C: 19.84; H: 3.11) Found: (C: 19.84; H: 3.20) IR(FTIR, KBr pellet, cm\(^{-1}\)): \(\nu(CO_{acyl})\) 1631(s).

(ŠŠS)Re(O)C(O)Ph, 13. Reaction of 9 (150 mg, 0.348 mmol) with CO for 3 h. Isolated (41.1 mg, 0.0895 mmol) 26% yield. \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.0 (m, 2H), 7.48 (m, 3H, aromatic), 4.33 (m, 2H), 3.92 (m, 2H), 3.14 (m, 2H), 2.19 (m, 2H). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\)) \(\delta\): 246.6, 132.9, 129.6, 128.9, 47.8, 44.5. Elemental Analysis (C\(_{10}\)H\(_{13}\)S\(_3\)O\(_2\)Re·(0.5)H\(_2\)O): Theoretical: C: 28.19; H: 3.01. Found C: 28.05; H: 2.78. FTIR (KBr pellet, cm\(^{-1}\)): \(\nu(Re-O)\) 963 (s).

(ŠŠS)Re(O)H, 15. In a 25 mL scintillation vial (300 mg, 0.691 mmol) of (ŠŠS)Re(O)Br was dissolved in THF (15 mL) in a nitrogen filled glove box. Tributyltin hydride (0.279 mL, 1.38 mmol) was slowly added and the reaction allowed to stir for 0.5 h. The reaction mixture was then concentrated in vacuo. Excess hexanes (30 mL) was added to the concentrated mixture and the resulting powder was filtered, washed with ether and dried under vacuum. (ŠŠS)Re(O)H (183 mg, 0.515 mmol) was obtained as a black powder (74% yield). \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.40 (s, 1H, Re-H) 4.16 (m, 2H, -S-CH2-) 3.83 (m, 2H, -S-CH2-) 2.84 (m, 2H, -S-CH2-) 1.60 (m, 2H –S-CH2-). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 46.16, 47.25. Elemental Analysis: (C\(_4\)H\(_9\)S\(_3\)ORe) Theoretical: (C: 13.51; H: 2.55; S: 27.05). Found (C: 13.72; H: 2.68; S: 27.27). IR(FTIR, KBr pellet, cm\(^{-1}\)): \(\nu(Re-H)\) 2030 \(\nu(Re-O)\) 969 (ŠŠS)Re(O)D was prepared in the same manner with Bu\(_3\)SnD.

\([(ŠŠS)Re(CO)\(_3\)Re(CO)(ŠŠS)]\), 14. Complex 7 (300 mg, 0.813 mmol) was added to a 25.0 mL glass liner with stir bar and dissolved in toluene (~15.0 mL). The glass vial was added to a Parr reactor and pressurized with carbon monoxide (800 psi) and heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature, depressurized and the solvent was evaporated in vacuo. The resulting red powder was collected in 26% yield (83.5 mg, 0.106 mmol) (FTIR, KBr pellet, cm\(^{-1}\)): \(\nu(C-O)\) 2012 (bs); 1939 (bm); 1871 (bm). UV-vis: \((\lambda_{\text{max}}:\ 557 \text{ nm})\), 0.05 M in CH\(_2\)Cl\(_2\). Elemental analysis: (C\(_{12}\)H\(_{16}\)S\(_6\)O\(_4\)Re\(_2\)) Theoretical (C: 18.24; S: 24.38; H: 2.04), Found (C: 18.42; S: 24.37; H: 2.05).
Computational Methods. Computations were performed on clusters provided by NC State Office of Information Technology High Performance Computing (HPC). Theoretical calculations have been carried out using the Gaussian 09 implementation of M06 density functional theory. All geometry optimizations were carried out in the gas phase using tight convergence criteria (“opt = tight”) and pruned ultrafine grids (“Int = ultrafine”). The basis set for rhenium was the small-core (311111,221111,411) → [6s5p3d] Stuttgart-Dresden basis set and relativistic effective core potential (RECP) combination (SDD) with an additional f polarization function. The 6-31G(d,p) basis set was used for all other atoms. Cartesian d functions were used throughout, i.e., there are six angular basis functions per d function. All structures were fully optimized and analytical frequency calculations were performed on all structures to ensure either a zeroth-order saddle point (a local minimum) or a first-order saddle point (transition state: TS) was achieved. The minima associated with each transition state was determined by animation of the imaginary frequency and, if necessary, with intrinsic reaction coordinate (IRC) calculations.

Energetics were calculated at 298.15 K with the 6-311++G(d,p) basis set for C, H, N, O and F atoms and the SDD basis set with an added f polarization function on Re. Reported energies utilized analytical frequencies and the zero point corrections from the gas phase optimized geometries and included solvation corrections which were computed using the SMD model, with benzene as the solvent as implemented in Gaussian 09.

3.7 References


Chapter 4

Synthesis of New Diamidoamine Ligands and Oxorhenium(V) Complexes

Department of Chemistry, North Carolina State University;
Raleigh, North Carolina, 27695-8204
4.1 Abstract
The synthesis of new diamidoamine ligands bearing trimethylsilyl (TMS-DAAm) and tert-butyldimethylsilyl (TBS-DAAm) substituents and their lithiated derivatives are described. Several oxorhenium(V) starting materials were utilized for the attempted synthesis of new complexes incorporating these ligands, however these attempts were unsuccessful. Re(III) starting materials were also attempted, but were also unsuccessful.

4.2 Introduction
Rhenium has been shown to form several organometallic complexes that catalyze a variety of reactions.\(^1\) The Ison lab has studied oxorhenium complexes with diamidoamine (DAAm) and diamidopyridine (DAP) ligands (Figure 4.1) and has shown diverse reactivity of the resulting oxorhenium DAAm and DAP complexes. For example, it has been shown that oxorhenium complexes catalyze oxygen atom transfer reactions, and hydrosilylation reactions, perform carbonylation reactions, and new C—C and C—O bond forming reactions.\(^1\text{c},^2\)

![Figure 4.1. Representative oxorhenium complexes](image)

When the ligand is changed from DAAm to DAP the reactivity is varied. For example, in Scheme 4.1, the oxorhenium(V)methyl complex, 1, reacts with CO to yield the oxorhenium(III) acetate complex 3. However, the DAP analogue does not react with CO to result in a oxorhenium(III) acetate complex is observed. This is likely due to the more rigid nature of the DAP ligand and its stability compared to the DAAm ligand.
Scheme 4.1. The activation of CO by DAAm and DAP complexes

Thus, the electronics at the metal center, and the rigidity and reactive nature of the complex are altered by varying the ancillary ligand. Therefore, the development of a variety of ligands for the synthesis of new oxorhenium complexes is warranted. In order to determine which ligands to employ for new rhenium complexes, Cassandra Lilly collected computational data for several different ligand frameworks. The energetic pathways for the formation of the respective acetate products from the corresponding acyl complexes were found for several ligands, three are shown in Table 2. As shown in Entry 1, when the C₆F₅-DAAm ligand is employed, the formation of 3 is exergonic overall and has a free energy of activation for the acyl transition state of 26.0 kcal/mol and 27.2 kcal/mol for 1,2 acyl migration transition state. In contrast, when the trimethylsilyl substituted diamidoamine ligand (TMS-DAAm) was employed (Entry 3), the acyl transition state is 4 kcal/mol lower in energy than the C₆F₅-DAAm ligand and a 1,2 acyl migration transition state that is 5.5 kcal/mol lower in energy and is overall more exergonic. Because the energetic pathway for the formation of a Re(III)acetate complex is more favorable when the N₃TMS ligand set is employed, it would be advantageous to attempt to synthesize a new oxorhenium(V) complex bearing the N₃TMS ligand framework.
Table 4.1. The energetic pathway for the formation of a Re(III) acetate complex employing different ligand frameworks

![Energetic Pathway Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ln</th>
<th>Acyl</th>
<th>Acyl T.S.</th>
<th>AcyCOAdd</th>
<th>Migrate T.S.</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DAAm</td>
<td>0.0(0.0)</td>
<td>26.0(26.9)</td>
<td>23.4(23.9)</td>
<td>27.2(25.8)</td>
<td>-36.5(-35.3)</td>
</tr>
<tr>
<td>2</td>
<td>DAP</td>
<td>0.0(0.0)</td>
<td>N/A</td>
<td>22.8(25.9)</td>
<td>26.2(28.7)</td>
<td>-28.4(-25.1)</td>
</tr>
<tr>
<td>3</td>
<td>TMS-DAAm</td>
<td>0.0(0.0)</td>
<td>21.3(21.5)</td>
<td>17.8(18.6)</td>
<td>21.7(20.9)</td>
<td>-49.3(-48.9)</td>
</tr>
</tbody>
</table>

Gas phase energies were calculated using the B3PW91 functional with the SDD basis set for rhenium and 6-31G(d, p) for all other atoms. Solvation energies were computed geometries optimized in the gas phase (parentheses) using the SMD method, with dichloromethane as the solvent, as implemented in Gaussian 09.
4.3 Results and Discussion

4.3.1 Diamidoamine Ligand Synthesis

Our lab is interested in the utilization of a new oxorhenium complex bearing the diamidoamine ligand framework using a trimethylsilyl (TMS) substituent (Figure 4.2).

![Figure 4.2. Diamidoamine trimethylsilyl, [TMS-DAAm]](image)

The trimethylsilyl diamidoamine ligand, [TMS-DAAm], was previously synthesized by Bertrand and coworkers. A reaction of N-methyldiethylenediamine and n-Butyl lithium afforded the lithiated ligand \textit{in situ}. The addition of TMSCl to the reaction mixture gave the TMS-DAAm ligand and LiCl as it was warmed to room temperature (Scheme 4.2).

![Scheme 4.2. Synthesis for [TMS-DAAm]](image)

Bertrand and several others have used this ligand to synthesize several organometallic complexes (Figure 4.3). Complexes containing the TMS-DAAm framework, [(MeN(CH$_2$CH$_2$NTMS)$_2$)AlMe] have been reported to catalyze the ring opening polymerization of (D,L)-lactide. Other complexes such as, [(MeN(CH$_2$CH$_2$NTMS)$_2$)Ti(NNPh$_2$)(py)] have been shown to perform new reactions with alkynes and hydrazines to form 1,2 aminated products. The zirconium complex [(MeN(CH$_2$CH$_2$NTMS)$_2$)ZrCl$_2$] has been shown to catalyze the polymerization of olefins. However, no oxorhenium complexes containing the TMS-DAAm ligand have been reported.
Figure 4.3. Organometallic complexes incorporating the TMS-DAAm ligand.

4.3.2 Attempted Synthesis of DAAm Oxorhenium Complexes.

The chelation of DAAm ligands to several different rhenium complexes has been reported and was utilized by our lab to make new DAAm rhenium complexes.\textsuperscript{4,7} Similar procedures were used in an attempt to chelate the TMS-DAAm ligand with rhenium (Table 4.2). Triphenylphosphine, TMS-DAAm, and methyltrioxorhenium, [Re(O)\textsubscript{3}(CH\textsubscript{3})], were allowed to react for five days, which resulted in no product formation and only the decomposition of catalyst and triphenylphosphine oxide, (entry 1). Adding [N\textsubscript{3}TMS] to [Re(O)(Cl)\textsubscript{3}(OPPh\textsubscript{3})(SMe\textsubscript{2})] or [Re(O)(Cl)\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}] also resulted in no product formation, (entries 2 and 3). Extended reaction times and other solvent systems were also unsuccessful for the formation of a new complex. Interestingly, the formation of a diamidoamine oxorhenium(V) complex, where the loss of TMS substituent from the diamidoamine was observed by \textsuperscript{1}H NMR spectroscopy. Reactions utilizing other oxorhenium starting materials were unsuccessful (entries 4 and 5).
Table 4.2. The energetic pathway for the formation of a Re(III) acetate complex employing different ancillary ligands.

![Diagram of Re(III) acetate complex]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Base</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re(O)₃CH₃</td>
<td>PPh₃</td>
<td>Dichloromethane/Methanol</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Re(O)(Cl)₃(SMe₂)(OPPh₃)</td>
<td>2,6 Lutidene</td>
<td>Ethanol/Methanol</td>
<td>25-80</td>
<td>1-5</td>
</tr>
<tr>
<td>3</td>
<td>Re(O)(PPh₃)₂(Cl)₃</td>
<td>2,6 Lutidene</td>
<td>Toluene/Benzene/Dichloromethane</td>
<td>25 – reflux</td>
<td>1-5</td>
</tr>
<tr>
<td>4</td>
<td>Re(O)₂(PPh₃)(I)</td>
<td>PPh₃</td>
<td>Methanol/Toluene/Benzene/DCM/Benzene/Methanol/CHCl₃ (1:10)</td>
<td>25- reflux</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Re(O)Br₄(OPPh₃)</td>
<td>None</td>
<td>Methanol/CHCl₃</td>
<td>25</td>
<td>1</td>
</tr>
</tbody>
</table>

Because of the inability to chelate TMS-DAAm to the metal center, other methods of synthesis were attempted. Bertrand and co-workers previously reported that the dilithium
salt of TMS-DAAm was prepared and used to chelate the ligand to a metal center (Scheme 4.3).

**Scheme 4.3.** Synthesis of Li₂TMS-DAAm ligand.

Table 4.3. Attempted synthesis of new oxorhenium(V) TMS-DAAm complexes using Li₂TMS-DAAm as a starting material

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re(O)(PPh₃)₂(Cl)₂</td>
<td>Toluene, Benzene, Pentane, THF</td>
<td>25</td>
<td>2 - 16</td>
</tr>
<tr>
<td>2</td>
<td>Re(O)(Cl)₃(OPPh₃)(SMe₂)</td>
<td>Toluene, benzene, Pentane, THF</td>
<td>-78 – 25</td>
<td>2 - 16</td>
</tr>
<tr>
<td>3</td>
<td>Re(O)₂(PPh₃)₂(I)</td>
<td>Benzene, Toluene</td>
<td>25</td>
<td>2 - 16</td>
</tr>
<tr>
<td>4</td>
<td>Re(O)(Br)₄(OPPh₃)</td>
<td>Benzene</td>
<td>25</td>
<td>2 - 16</td>
</tr>
</tbody>
</table>

The reaction of Li₂TMS-DAAm with the rhenium starting materials that were previously used in varying solvents and temperatures was attempted to synthesize a new oxorhenium
complex (Table 4.3). Several transition metal complexes bearing the TMS-DAAm ligand used the lithium salt Li$_2$TMS-DAAm to chelate the ligand to the metal center. [Re(O)(PPh$_3$)$_2$(Cl)$_3$], [Re(O)(Cl)$_3$(OPPh$_3$)(SMe$_2$)], and [Re(O)$_2$(PPh$_3$)$_2$(I)] were treated with Li$_2$TMS-DAAm in a variety of solvents and temperatures and were allowed to react for 16 h, however, no product formation was observed, (entries 1-4). Similar reactions have been successful for the synthesis of [(Me$_3$SiNCH$_2$CH$_2$)$_2$NMe]AlCl complexes.$^4$

Due to the continued difficulty to chelate the TMS-DAAm ligand to rhenium, more measures were undertaken to generate a new rhenium diamidoamine complex. When many of these reactions were monitored by $^1$H NMR spectroscopy, quick decomposition of catalyst was observed along with free TMS, where the TMS substituent was lost during the course of the reaction. Because of the loss of the TMS group under the reaction conditions, a new ligand bearing a bulkier silyl group was synthesized.

Tert-butyldimethylsilyl(TBS) was chosen as a bulkier substituent for the new diamido amine ligand, as the added bulk of the tert-butyl group should hinder the loss of the substituent. Methods similar to the ones described above for TMS-DAAm were used to form the TBS-DAAm ligand shown in Scheme 4.4. A representative $^1$H NMR spectrum is shown of [N$_3$TBS] in Figure 4.4. The methylene groups of the ligand backbone resonate as two multiplets at δ 2.73 and 2.20 ppm and both integrate to 4 protons. A singlet at δ 2.03 ppm corresponds to the methyl substituent on the amine nitrogen, one singlet resonates at δ 0.90 ppm and integrates to 18 hydrogens, corresponding to the tert-butyl groups and δ 0.00 ppm integrating to 12 protons corresponds to the 4 methyl groups on the silyl groups.

Scheme 4.4. Synthesis of the TBS-DAAm ligand.
Figure 4.4. $^1$H NMR spectrum of TBS-DAAm in CDCl$_3$. The methylene backbone protons are highlighted in green and exhibited two distinct multiplets at 2.73 and 2.21 ppm. The N-methyl protons are highlighted in light blue and resonate at 2.0 ppm. The tert-butyl group protons are highlighted in blue and resonate at 0.90 ppm and the four methyl groups resonate to one peak, highlighted in red, at 0.00 ppm.

The reaction of TBS-DAAm with [Re(O)(Cl)$_3$(PPh$_3$)$_2$], [Re(O)(Cl)$_3$(SMe$_2$)(OPPh$_3$)], [Re(O)$_2$(PPh$_3$)$_2$(I)], and [Re(O)(Br)$_4$(OPPh$_3$)] in benzene or dichloromethane in presence of a base for up to 5 days did not result in the formation of a new rhenium complex (Table 4.4).
Table 4.4. Attempted synthesis of a new oxorhenium(V) TBS-DAAm complex.

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Base</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Time (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re(O)₃CH₃</td>
<td>PPh₃</td>
<td>Dichloromethane</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Re(O)(Cl)₃(PPh₃)₂</td>
<td>2,6 Lutidene</td>
<td>2,6 Lutidene</td>
<td>25-80</td>
<td>1-5</td>
</tr>
<tr>
<td>3</td>
<td>Re(O)(Cl)₃(SMe₂)(PPh₃)</td>
<td>2,6 Lutidene</td>
<td>2,6 Lutidene</td>
<td>25-80</td>
<td>1-5</td>
</tr>
<tr>
<td>4</td>
<td>Re(O)₂(PPh₃)₂(I)</td>
<td>2,6 Lutidene</td>
<td>2,6 Lutidene</td>
<td>25</td>
<td>1-5</td>
</tr>
<tr>
<td>5</td>
<td>Re(O)(Br)₄(OPPh₃)</td>
<td>2,6 Lutidene</td>
<td>2,6 Lutidene</td>
<td>25</td>
<td>1-5</td>
</tr>
</tbody>
</table>

The dilithium salt of TBS-DAAm was synthesized by the same procedure used to form the Li₂TMS-DAAm salt. A representative $^1$H NMR spectrum is shown in Figure 4.5: two broad multiplets at δ 3.30 and 3.08 ppm and each multiplet integrates to 2 protons corresponding to two methylene groups, at δ 2.25 there is a broad multiplet that integrates to 4 protons from the other two methylene groups. The N-methyl protons resonate at δ 1.94 ppm and integrates to 3 protons, a broad singlet at δ 1.03 ppm integrates to 18 protons of the tertbutyl groups and two singlets at δ 0.11 and 0.09 ppm each integrates to 6 protons.
corresponding to the two methyl groups bound to the silane. Both the lithiated and protiated forms were used to synthesize a new TBS-DAAm rhenium complex using the same methods used as the TMS-DAAm ligand.

**Figure 4.5.** $^1$H NMR spectrum of Li$_2$TBS-DAAm in C$_6$D$_6$. The methylene backbone is highlighted in green and resonates to three multiplets, 3.21, 3.08, and 2.26 ppm. The N-methyl group is highlighted in light blue and resonates at 1.94 ppm. The tert-butyl groups resonate at 1.08 ppm as a singlet, highlighted in blue and the four methyl groups resonate as two singlets at 0.12 and 0.09 ppm.
The reaction of Li₂TBS-DAAm with the four rhenium starting materials in two non-chlorinated solvents, benzene and toluene, at room temperature for 16 hours is shown in Table 4.5. All attempts were unsuccessful and decomposition of the catalyst was observed. The reaction of TBS-DAAm with methyltrioxorhenium, MTO, and triphenyl phosphine in a minimal amount of methylene chloride resulted in triphenylphosphine oxide and decomposition of the complex.

**Table 4.5.** Attempted synthesis of a new oxorhenium(V) TBS-DAAm complex employing Li₂TBS-DAAm as a starting material.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Re(O)(PPh₃)₂(Cl)₃</td>
<td>Benzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>2</td>
<td>Re(O)(Cl)₃(SMe₂)(OPPh₃)</td>
<td>Benzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>3</td>
<td>Re(O)₂(PPh₃)₂(I)</td>
<td>Benzene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>4</td>
<td>Re(O)(Br)₄(OPPh₃)</td>
<td>Benzene</td>
</tr>
</tbody>
</table>

### 4.3.3 Synthesis via rhenium(III) starting materials

Because of the inability to successfully synthesize new oxorhenium diamidoamine complexes with the TMS-DAAm and TBS-DAAm ligands, we continued to attempt new methods for the synthesis of these complexes. We propose to use rhenium(III) starting materials instead to synthesize rhenium TMS-DAAm complexes (Scheme 4.5). The synthesis will be attempted with two different rhenium(III) starting materials that are commercially available. The proposed synthetic strategy is outlined in Scheme 4.5 and involves the
reaction of TMS-DAAm with a base, 2,6-Lutidine, in a variety of solvents, temperatures, and reaction times under air or O₂ to oxidize the rhenium.

It has been previously shown by our group that the attempted synthesis of new rhenium(III) complexes from the starting [Re(Cl)₃(PPh₃)₂CH₃CN] and DAP ligand did not result in the formation of a new rhenium(III) chloride complex but the oxidized (DAP)Re(O)(Cl) complex (Scheme 4.5).³⁸

**Scheme 4.5. Synthesis of rhenium(V) complexes using rhenium(III)**

Other (DAAm)Re(III) complexes have exhibited similar behavior upon exposure to air or water: the rhenium complex oxidizes to the corresponding oxorhenium(V) complex. For example, the (DAAm)Re(CO)(C₆F₅) complex synthesized in our laboratory upon exposure to an oxygen source, O₂ or H₂O, results in the formation of the oxo rhenium(V) complex (DAAm)Re(O)(C₆F₅) (Scheme 4.6).⁹

**Scheme 4.6. Reported synthesis of DAAm oxorhenium(V) complex from DAAm rhenium(III) complexes.**
**Scheme 4.7.** Attempted synthesis of oxo Re(V) complexes bearing TMS-DAAm

The synthesis of new oxo rhenium complexes bearing the TMS-DAAm and TBS-DAAm were attempted with two different rhenium(III) starting materials in the presence of a base (scheme 4.7). However, no formation of a new [(TMS-DAAm)Re(O)(Cl)] complex was observed.

**4.4 Conclusions**

Several methods to form a new oxorhenium(V) complex bearing a TMS-DAAm ligand were attempted but did not result in the formation of a new complex. A new ligand was synthesized with a bulkier silyl substituent tert-butyldimethylsilyl. Several attempts to chelate the TMS-DAAm ligand to a rhenium complex were unsuccessful.

Though a new oxorhenium(V) TMS-DAAm complex was unable to be synthesized more methods could be used to attempt to form the new rhenium complex. We proposed the use of rhenium(III) complexes as starting materials may lead to the desired product, however, after several attempts to isolate new oxo rhenium(V) products beginning from rhenium(III) starting materials was also unsuccessful.

**4.5 Experimental General Considerations.** Re(O)Cl₃(PPh₃)₂, Re(O)₂I(PPh)₂, Re(O)(OPPh₃)(SMe₂)Cl₂, Re(O)Br₄(OPPh₃), and CH₃N[CH₂CH₂N(Si(CH₃)₃)]₂, and Li₂[N₃TMS] were prepared as previously reported. All other reagents were purchased from commercial sources and used as
received. All reactions were performed under inert atmosphere using dry solvent unless otherwise noted. $^1$H and $^{13}$C NMR were obtained on a Varian Mercury 300MHz or a Varian Mercury 400 MHz spectrometer. Chemical shifts are listed in parts per million (ppm) and referenced to their residual protons or carbons of the deuterated solvents.

$\text{CH}_3\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{Si}(\text{C}(\text{CH}_3)_3)(\text{CH}_3)_2)]_2$. $\text{CH}_3\text{N}(\text{HNCH}_2\text{CH}_2)$ (5 mL, 0.021 mmol) was added to a Schlenk flask (250 mL) with stir bar and dissolved with ether. The reaction mixture was cooled to -78 °C and n-butyl lithium (16.8 mL, 0.042 mmol) was added dropwise. The reaction mixture was allowed to come to room temperature and stir for 1 h. The mixture was then cooled to -78 °C and TBSCl (6.33 g, 0.042 mmol) was added dropwise to the reaction mixture was allowed to warm to room temperature and was stirred for 16 h. [TBS-DAAm] was obtained in 95% yield as a pale yellow oil. $^1$H NMR (CDCl$_3$) $\delta$: 2.73 (m, 4 H), 2.21 (m, 4 H), 2.02 (s, 3 H), 0.90 (s, 18 H), 0.00 (s, 12 H)

$\text{CH}_3\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{Si}(\text{C}(\text{CH}_3)_3)(\text{CH}_3)_2)]_2\text{Li}_2$. $\text{Li}_2[\text{N}_3\text{TBS}]$ (1.0 g, 0.0029 mol) was added to a schlenk flask with stir bar and dissolved in pentane. The reaction mixture was cooled to -78 °C and n-butyl lithium (2.32 mL, 0.0058) was added dropwise. The solution was allowed to warm to room temperature and stired for 1 h. Solvent was removed under reduced pressure to yield a pale yellow solid. $\text{Li}_2[\text{N}_3\text{TBS}]$ was obtained in 48% yield as a pale yellow solid. $^1$H NMR (C$_6$D$_6$) $\delta$: 3.21 (m, 2 H), 3.08 (m, 2 H), 2.26 (m, 4 H), 1.94 (s, 3 H), 1.08 (s, 18 H), 0.12 (s, 6 H), 0.09 (s, 6H)

4.6 References
Chapter 5

Mechanistic Investigation of Oxyfunctionalization of Cp*Ir(NHC) Complexes

Department of Chemistry, North Carolina State University; Raleigh, North Carolina, 27696-8204
5.1 Abstract
The mechanism for the oxyfunctionalization of Cp*Ir(NHC)(Me)(Cl) (NHC = 1,3-dimethylimidazol-2-ylidene) with air (O₂), to produce methanol at room temperature was explored. New Cp*Ir(NHC)(X)(Cl), (X = Ph, C₆F₅, H) complexes were synthesized to probe the intermediacy of proposed iridium oxo and hydride species. The five-coordinate [Cp*Ir(NHC)(C₆F₅)]BAR₄ complex was also isolated and characterized. The reaction of Cp*Ir(NHC)(Me)(CH₂Cl₂) with O₂ to produce methanol was studied and the dependence of this reaction on a proton source was investigated. The reaction was found to exhibit a first order dependence on [Ir] and a zeroth order dependence on the proton source.

5.2 Introduction
For reasons outlined in the general introduction, Chapter 1, developing a catalytic system that can selectively functionalize hydrocarbons under mild conditions is of importance. There have been advances in homogeneous systems to carry out the two necessary steps to functionalize simple hydrocarbons: 1.) C-H activation and 2.) oxyfunctionalization (C-O bond formation). The earliest of these examples was developed by Shilov utilizing a Pt⁰ catalyst (Figure 5.1).¹ For the formation of an oxyfunctionalized product in this system, Pt⁴⁺ is required as an oxidant in stoichiometric quantities and the reaction is performed under acidic conditions. More recently, the Catalytica system developed by Periana and coworkers also utilizes a Pt⁰ catalyst, however, highly acidic conditions are necessary for this system.²

![Figure 5.1. The Shilov system.](image-url)

Many research efforts to improve homogeneous systems for hydrocarbon functionalization have focused on the individual steps necessary for this process. A large part of the research
has focused on selectively activating C-H bonds. As a result, there is a better understanding of the mechanism for C-H activation and catalyst development for more efficient systems for C-H activation. Of particular note is the report by Bergman and co-workers of the activation of methane at room temperature by \((\text{Cp}^*)\text{Ir}^{\text{III}}(\text{PMe}_3)\) (Scheme 5.1). 

**Scheme 5.1.** Report of methane activation by Bergman

Studies on the subsequent functionalization step have been much less developed. The functionalization of substrates that react with oxygen atom donors and \(\text{O}_2\) in a stoichiometric fashion have been reported, however, few of these examples involves a system that activates C-H bonds. Efforts recently in our lab have involved the investigation of oxyfunctionalization with systems that have been shown to activate C-H bonds (Figure 5.2).

**Figure 5.2.** Proposed oxyfunctionalization by the Ison group.

The \((\text{Cp}^*)\text{Ir}^{\text{III}}(\text{PMe}_3)\) system reported by Bergman in Scheme 5.1 performs C-H activation efficiently under mild conditions, however, under oxidizing conditions the \(\text{PMe}_3\) ligand is oxidized. The easily oxidizable nature of phosphine ligands makes this system particularly unsuitable for oxyfunctionalization of hydrocarbon substrates. Replacing the phosphine ligand with a ligand of similar electronics that is less easily oxidized is necessary for the development of a system that can both activate C-H bonds as well as functionalize them. Studies by our group and others have shown that replacement of phosphine on \((\text{Cp}^*)\text{Ir}^{\text{III}}\) complexes with an N-heterocyclic carbene (NHC) ligand could result in similar activity.
The NHC ligand should be similar in electronics and should be less likely to oxidize under conditions for oxyfunctionalization. Previously, in our group we have shown that \((\text{Cp}^*)\text{Ir}^{\text{III}}(\text{NHC})\) complexes are capable of activating C-H bonds.\(^3\text{v} \quad 3\text{w}\) For example, \([\text{(Cp}^*)\text{Ir(NHC)(H}_2\text{O}_2\text{)}_2]\text{OTf}_2\) was shown to activate the C-H bonds of benzene at 150 °C (Scheme 5.2).\(^3\text{w}\)

**Scheme 5.2.** C-H activation of benzene by \(\text{Cp}^*\text{Ir}^{\text{III}}(\text{NHC})(\text{H}_2\text{O})_2\)

Furthermore, \((\text{Cp}^*)\text{Ir}^{\text{III}}(\text{NHC})\) complexes have been shown to oxyfunctionalize \(\text{Ir-}\text{Me}\) bonds stoichiometrically.\(^6\text{c} \quad 6\text{d}\) Specifically, \([\text{(Cp}^*)\text{Ir}^{\text{III}}(\text{NHC})(\text{Py})(\text{Me})]\) under \(\text{O}_2\) pressure with HCl at 100 °C forms methanol (Scheme 5.3). However, the oxidation of \(\text{Ir-}\text{Me}\) bond under less harsh reaction conditions than were found in this system warrants investigation.

**Scheme 5.3.** Synthesis of methanol by \([\text{(Cp}^*)\text{Ir}^{\text{III}}(\text{NHC})(\text{Py})(\text{Me})]^+\)

It was proposed in this study that the active intermediate was \([\text{(Cp}^*)\text{Ir(NHC)(Me)}]^+\) a five coordinate 16-electron complex with an open coordination site, (Figure 5.3). It was hypothesized that if the dissociation of the pyridine ligand to form the unsaturated \(\text{Cp}^*\text{Ir}\) complex was more facile, oxyfunctionalization could occur under milder reaction conditions.
A (Cp*)Ir(NHC)(Me)Cl complex, 28, was synthesized in our labs and its ability to undergo oxyfunctionalization was studied. Complex 28 in the presence of NaBARF₄ and air (O₂) in CH₂Cl₂ at room temperature undergoes rapid conversion to methanol (Scheme 5.4). It was found in this study that 28 undergoes chloride abstraction and when exposed to air forms a kinetically competent Ir-oxo complex, 30, which, in the presence of a proton source quantitatively forms methanol.

**Scheme 5.4.** Formation of methanol from complex 30

Though kinetic data was obtained and the novel complex, 30 was isolated, a more detailed study of the mechanism for the formation of 30 and oxyfunctionalization reaction was needed. Also the exact role played by 30 in the mechanism is not understood and warrants the synthesis of similar analogs of this Ir^IV-µ-oxo-Ir^IV complex.

**5.3 Results and Discussion**

The proposed mechanism for the formation of methanol via complex 28 is shown in Figure 5.4. The mechanism begins with chloride abstraction by NaBARF₄ to generate a methylene chloride stabilized intermediate 29. Upon exposure of 29 to air (O₂) it rapidly forms complex 30 from the combination of 29 and an iridium oxyl intermediate. The Ir—oxyl will undergo oxygen atom insertion into an iridium methyl bond to generate an iridium methoxy complex. Once this complex is exposed to a proton source the methoxy group is protonated to generate methanol and an ethoxy iridium complex (CH₃OH forming step,
Figure 5.4. The ethoxy complex then undergoes β-hydride elimination to generate acetaldehyde and an Ir hydride which rapidly decomposes to form an iridium chloride dimer (β-hydride step, Figure 5.4.)

Figure 5.4. Mechanism for methanol formation via 28

To better understand how the formation of 30 proceeds from 29 the reaction of 29 in methylene chloride was monitored open to air over time at 0 ºC by UV-vis spectroscopy (Figure 5.5). The UV-vis spectrum of the reaction shows the disappearance of complex 29 and the absorbance of 30 appearing over time at 660 nm. Two isosbestic points are observed in the UV-vis spectrum at 407 and 540 nm. The isosbestic points indicate 29 proceeds directly to 30 without an appreciable accumulation of any other intermediates. Due to the inability to observe any intermediates via UV-vis spectroscopy other means to probe the intermediacy of the formation of an Ir-oxyl intermediate experimentally were undertaken.
Figure 5.5. Scan of the UV-vis spectrum for the conversion of 29 to 30 vs. time. Spectra were obtained every 40 s. The reaction was performed with 29 (1.0 mM), NaBAR\textsubscript{4} (1.2 mM) in CH\textsubscript{2}Cl\textsubscript{2} in an uncapped UV-vis cell open to air at 0 °C.

The proposed mechanism for the formation of 30 proceeds from the formation of an Ir—oxyl intermediate, which combines with 29 (Scheme 5.5). To probe the formation of the Ir—oxyl experimentally, the synthesis of other (Cp\textsuperscript{*})Ir(NHC)(Cl)(X), X = alkyl or aryl complexes were attempted (Figure 5.6).
Scheme 5.5. Proposed formation of 30 form an Ir-oxo

![Scheme 5.5. Proposed formation of 30 form an Ir-oxo](image)

Figure 5.6. Proposed new iridium NHC complexes

The reaction of (Cp*)Ir(NHC)Cl₂ with diphenyl zinc afforded the transmetallated product 31 at room temperature in THF (Scheme 5.6). X-ray quality crystals were obtained from the slow diffusion of pentane into a concentrated solution of 31 in CH₂Cl₂ by Matthew Lehman a member of our lab (Figure 5.7). Complex 31 is structurally similar to other Cp*Ir(NHC) complexes reported by our lab³v, ³w, ⁶c, ⁶d and the geometry is best described as a three-legged piano stool.

Scheme 5.6. Synthesis of 31

![Scheme 5.6. Synthesis of 31](image)
Figure 5.7. X-ray crystal structure of 31. Ellipsoids are at the 50% probability level. Hydrogens have been omitted for clarity. Selected bond lengths and angles (degrees): Ir1-Cl1, 2.373(4); Ir1-C11, 2.0249(19); Ir1-C16, 2.0791(18); C11-Ir1-C16, 86.86(7); C16-Ir1-Cl1, 88.20(5); C11-Ir1-C11, 91.35(5).

The reaction of 31 with NaBAR$_4$ open to air did not result in the formation of a new iridium µ-oxo species but instead the known [(Cp*)Ir(NHC)(Cl)]$_2$[BAR$_4$]$_2$ was formed and confirmed by X-ray crystallography.

Scheme 5.7. Complex 31 reactivity with O$_2$

Although the formation of a new Ir–µ–oxo complex was not observed in the reaction outlined in Scheme 5.7, the competition experiment outlined in Scheme 5.8 was performed. Presumably, if the formation of an Ir–oxyl intermediate was generated during the reaction it would have an equal likeliness of reacting with either 28 or 31 resulting in the formation of an Ir-µoxo species with both methyl and phenyl as substituents.
Scheme 5.8. Competition experiment to form new iridium η-oxo complexes.

The \(^{1}\)H NMR spectra for the reaction of 28 and 31 with O\(_2\) is shown in Figure 5.8. An NMR spectrum of the starting iridium complexes (28 and 31) with NaBAr\(_{4}\) is shown in blue, Figure 5.8. The NMR spectrum of the reaction of 28 and 31 with NaBAr\(_{4}\) after 0.5 hours is shown in green, Figure 5.8. The NMR spectrum shown in grey (Figure 5.8) is the reaction minutes after it was exposed to air; peaks corresponding to the formation of complex 30 is represented by red boxes and continue to form over time (pink NMR, Figure 5.8). Importantly, no new iridium complexes were observed. Free benzene is also observed in all NMR spectra, this is likely due to the loss of the phenyl ligand in solution, which is consistent with lack of reactivity toward oxygen for complex 27.
Figure 5.8. $^1$H NMR spectra of the reaction outlined in Scheme 5.8: 28 (7.5 mg, 0.0158 mmol), 31 (8.48 mg, 0.0158 mmol), and NaBAR$_4$ (27.0 mg, 0.0316) were dissolved in CD$_2$Cl$_2$ (0.5 mL) in a screw cap NMR tube. The spectrum shown in blue is the starting reaction and green is the reaction after 0.5 hours. Grey is the reaction immediately after being opened to air and the top spectrum(pink) is 0.5 hours after the reaction was opened to air.

Due to the instability of complex 31 in solution, other iridium complexes with the formula Cp*Ir(NHC)Cl(X) were synthesized. The reaction of Cp*Ir(NHC)(Cl)$_2$ with Zn(C$_6$F$_5$)$_2$ in THF at room temperature resulted in the formation of 32 (Scheme 5.9). Complex 32, was characterized by $^1$H and $^{19}$F NMR spectroscopies and X-ray crystallography. The $^1$H NMR spectrum of 32 in CD$_2$Cl$_2$ is shown in Figure 5.9 and exhibits three distinct singlets: the Cp* ligand resonates at 1.65 ppm integrating to fifteen protons, the N-methyl groups on the NHC ligand resonate at 3.58 ppm integrating to six protons, and the C-H groups on the NHC backbone resonate at 6.97 ppm and integrates to two protons.
Scheme 5.9. Synthesis of 32.

Figure 5.9. $^1$H NMR of 32 in CD$_2$Cl$_2$.

The reactivity of 32 was studied open to air in the presence of NaBAr$^F_4$ under conditions similar to the reaction of 31 with NaBAr$^F_4$. The reaction resulted in the formation of a stable five-coordinate iridium complex 29 (Scheme 5.10). Complex 33 was characterized by $^1$H, $^{19}$F NMR spectroscopy and X-ray crystallography. The $^1$H NMR spectrum of 33 is shown in Figure 5.10. The chemical shifts are relatively similar to 31, however, the aromatic protons from the BAr$^F_4$ counterion can be observed above 7.5 ppm. The $^{19}$F NMR spectrum of 33 is shifted from 31 where the fluorine peak corresponding to BAr$^F_4$ counterion is observed at -
63.25 ppm, and the fluorine chemical shifts corresponding the pentafluorophenyl ligand are exhibited as three distinct singlets at -118.75, -158.56, and -162.45 ppm which are shifted from the fluorine resonance in 32 (-113.15, 165.98, and -166.71 ppm).

**Scheme 5.10.** Formation of five coordinate iridium complex 33.

![Scheme 5.10](image)

**Figure 5.10.** $^1$H NMR spectrum of 33 in CD$_2$Cl$_2$.

Because no new $\mu$—oxo—iridium complexes were observed from the experiments described above, other means of probing the formation of an iridium oxyl intermediate were explored. The reactivity of metal oxo complexes has been well documented.$^8$ Common
reactivity of metal oxos include their ability to perform oxygen atom transfer reactions. With that in mind, if the formation of an iridium oxyl does occur under the reaction conditions, in the presence of an oxygen atom acceptor, new oxygenated products should be observed (Scheme 5.11).

**Scheme 5.11.** Proposed reactivity of Ir-oxo with PPh₃

\[
\begin{align*}
\text{Ir} & \quad \text{BAr}^\text{F}_4 \\
\text{N} & \quad \text{Ir} \quad \text{ClCD}_2\text{Cl} \\
\text{Me} & \quad \text{ClCD}_2\text{Cl} \\
\text{29} & \\
\end{align*}
\]

\[
\begin{align*}
\text{1/2 O}_2 & \quad \text{PPh}_3 \\
\text{Ir}^{\text{IV}} & \quad \text{OPPh}_3 + [\text{Ir}] \\
\text{Me} & \quad \text{OPPh}_3 \\
\text{28} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ir} \quad \text{Cl} \\
\text{N} & \quad \text{Ir} \\
\text{Me} & \quad \text{ClCD}_2\text{Cl} \\
\text{29} & \\
\end{align*}
\]

\[
\begin{align*}
\text{NaBAr}^\text{F}_4, \text{PPh}_3, \text{O}_2 & \quad \text{rt, CH}_2\text{Cl}_2 \\
\text{OPPh}_3 + [\text{Ir}] & \\
\text{Not Observed} & \\
\text{28} & \\
\end{align*}
\]
The reaction of 28, in the presence of PPh₃ and under the same conditions to form the Ir-µ-oxo complex, was explored (Figure 5.11). The ¹H and ³¹P NMR spectra for the crude reaction are shown in Figure 5.11. Oxygen atom transfer products were not observed, by ³¹P NMR i.e. triphenylphosphine oxide was not observed but two new phosphorus resonances were observed. Peaks corresponding to two new iridium complexes were also observed by ¹H NMR spectroscopy. However, the isolation of the two iridium complexes was unsuccessful; X-ray quality crystals obtained from the crude reaction mixture were those of (Cp*)Ir(NHC)(Cl)(PPh₃) presumably from a reaction of 28 with PPh₃, which in the presence of CH₂Cl₂ exchanges the methyl ligand for a chloride ligand as proposed mechanism in Figure 5.12.
Because the reactions to isolate or trap an iridium oxo intermediate were unsuccessful other methods to understand the activation of O$_2$ by iridium were attempted. The formation of the Ir-$\mu$-oxo complex was explored with other oxidants similar to that of O$_2$. The proposed stepwise formation of 30 from 29 is shown in Scheme 5.12. The activation of O$_2$ by 29 proceeds through the formation of an iridium peroxo species, which forms two equivalents of an iridium-oxyl, which combines with an equivalent of 29 to generate 30. Other oxidants similar to O$_2$ should be suitable for the oxidation of 29.
Scheme 5.12. Stepwise mechanism for the formation of 30 from 29

Therefore, the reaction of 28 with O atom sources as an oxidant was explored. The reaction of 28 with NaBAR$_4$ at room temperature in CH$_2$Cl$_2$ with 0.5 equiv of tert-butyl hydroperoxide was monitored by $^1$H NMR spectroscopy with an internal standard (Figure 5.13). The reaction formed 30 in 100% conversion in minutes.
Figure 5.13. $^1$H NMR spectrum of the reaction of 30 (15 mg, 0.032 mmol), NaBAR$_F^4$ (27.0 mg, 0.032 mmol) with $^t$BuOOH (2.8 µL, 0.0158 mmol) in CD$_2$Cl$_2$ (0.5 mL) at room temperature. 1,3,5 trimethoxy benzene was used as an internal standard (5.3 mg, 0.032 mmol).

The ability to use a hydroperoxide source in the place of O$_2$ as an oxidant suggests that the formation of iridium peroxo and oxo complexes are likely intermediates for the formation of 30.

5.3.1 Investigation of the mechanism of the methanol forming step
To investigate the methanol forming step of the reaction, the dependence of the reaction on the concentration of the proton source, ethanol, was examined. The decay of 30
was monitored at 660 nm over time with varying equivalents of ethanol. An example of the decay of 30 over time with 1.0 mM of ethanol is shown in Figure 5.14. The decay of 30 over time was monitored at 0.25, 0.5, 1.0, 1.5, and 2 mM ethanol and the observed rate constants were plotted against the varied concentration of ethanol (Figure 5.15). The observed rates did not vary with ethanol concentration exhibiting a zero order dependence on the rate of decay of 30. The zero order dependence on ethanol suggests that the rate-determining step must occur prior to the formation methanol.

Figure 5.14. Typical plot of the decay of absorbance of [30]_{660 \text{ nm}} vs. time. Conditions: [30] (0.4 mM); C\textsubscript{2}H\textsubscript{5}OH (1.0 mM) in 2.5 mL CH\textsubscript{2}Cl\textsubscript{2}, 25 °C. Reactions were monitored by UV-vis spectroscopy in an uncapped UV-vis cell open to air.

\[ k_{\text{obs}} = 0.005437(3) \text{ s}^{-1} \]
\[ R^2 = 0.999 \]
5.3.2 Study of the β-hydride elimination step.

Finally the β-hydride elimination step was investigated. To directly monitor the β-hydride elimination step of the reaction stoichiometrically the synthesis of iridium alkoxy species was attempted. The reaction of (Cp*)Ir(NHC)(Cl)$_2$ with KO'Bu and NaOMe in various solvents, temperature and reaction times (Scheme 5.13) did not lead to new alkoxy complexes.

Scheme 5.13. Attempted synthesis of an iridium alkoxy complex.

The formation of an iridium hydride is proposed to form immediately following β-hydride elimination of the ethoxy ligand to form acetaldehyde. The iridium hydride is then proposed to undergo ligand exchange with methylene chloride to generate [((Cp*)Ir(NHC)(Cl)]$_2^{2+}$,
which is observed at the end of the reaction in quantitative yields. Attempts to synthesize the proposed iridium hydride in CH₂Cl₂ under reaction conditions for stoichiometric reactions were attempted. A reaction of (Cp*)Ir(NHC)(Cl)₂ with tributyltin hydride in THF resulted in the formation of complex 34. The ¹H NMR spectrum of 34 is shown in Figure 5.16 and consists of a singlet just below 2 ppm corresponding to the 15 protons of the Cp* ligand, the methyl groups bound to the nitrogen of the NHC ligand resonate as two broad singlets just below 4 ppm integrating to three protons each, and the C-H protons of the NHC backbone integrating to two protons. A zoomed in region of the NMR spectrum shows the hydride resonance at -13.2 ppm integrating to one proton.

![Figure 5.16. ¹H NMR spectrum of complex 34 in CH₂Cl₂ (bottom), and hydride region (top).](image)

With complex 34 in hand, its reaction with NaBAR₄ to abstract the chloride ligand and result in the formation of the proposed cationic hydride intermediate, which in the presence of
$\text{CH}_2\text{Cl}_2$ should decompose to form $[(\text{Cp}^\ast)\text{Ir(NHC)}(\text{Cl})]^{2+}$ was explored. However, the reaction of $34$ in $\text{CH}_2\text{Cl}_2$ with an equivalent of $\text{NaBAr}^\text{F}_4$ at room temperature resulted in the known bridging hydride dimer, $[(\text{Cp}^\ast)\text{Ir(NHC)}(\text{H})]^{2+}$ in minutes. The hydride dimer was confirmed by $^1\text{H}$ NMR spectroscopy and the spectrum is shown in Figure 5.17. The $^1\text{H}$ NMR data are consistent with the reported literature. Because this reaction proceeded directly to the bridging hydride dimer, other methods to abstract the chloride ligand were explored.

![Diagram showing the reaction of 34 with NaBArF4](image)

**Figure 5.17.** $^1\text{H}$ NMR spectrum of complex 35 from a reaction of 34 (48.5 mg, 0.105 mmol) with NaBArF4 (90.93 mg, 0.105 mmol) in CH2Cl2 (1.0 mL). The hydride region is also shown.

Reactions to abstract the chloride ligand of 34 are summarized in Scheme 5.14. The use of silver, cesium and sodium salts in coordinating and non-coordinating solvents to abstract the
chloride ligand were successful but resulted in the formation of the bridging hydride dimer in all cases. The reaction of 34 with the benzyl and methyl Grignard reagents did not result in the formation of any new benzyl or methyl iridium complexes, instead the formation of the hydride dimer was observed at the end of the reaction by $^1$H NMR spectroscopy.

Scheme 5.14. Reactivity of 34 (15.0 mg, 0.0325 mmol) and chloride abstracting agent (0.0325 mmol) in d-solvent (0.5 mL).

In the presence of chloride abstracting reagents 34 undergoes rapid formation of iridium hydride dimer, 35. Under the conditions described in Figure 5.17 no chloride dimer was observed. The formation of an iridium hydride species following the $\beta$-hydride elimination step that undergoes decomposition to the observed iridium chloride dimer is unlikely under the reaction conditions. Instead, the formation of a cationic iridium complex stabilized by solvent may lead to the formation of an iridium chloride dimer (Scheme 5.15).

Scheme 5.15. Proposed formation of chloride dimer

5.4 Conclusions
The mechanism for oxyfunctionalization of Cp*Ir(NHC)(Me)(Cl) (NHC = 1,3-dimethylimidazol-2-ylidene) to undergo quantitative methanol formation at room temperature was explored. New Cp*Ir(NHC)(X)(Cl), (X = Ph, C$_6$F$_5$, H) complexes were
synthesized and utilized to probe the intermediacy of proposed iridium oxo and iridium hydride species. The synthesis of new Cp*Ir(NHC) complexes did not, however, undergo reactivity with oxygen and did not yield any new iridium oxo species. Other experiments discussed above to probe the intermediacy of metal oxo species proved unsuccessful. The dependence of the reaction on Cp*Ir(NHC)(Me)(CH₂Cl₂) complex on a proton source (ethanol) for the formation of methanol, the reaction was found for this system. Notably, the reaction was first order in 29 and was zero order in ethanol. This suggested that the reactions rate-determining step was prior to methanol formation. Also the observation of two isosbestic points suggests there is not a build-up of significant concentrations of any other intermediate in the reaction. The reactivity of 30 was explored, and was found to form the previously reported complex 31, under conditions to abstract the chloride ligand. The reactivity of 30 suggests that the formation of [Cp*Ir(NHC)(Cl)]₂²⁺ may likely proceed through the formation of a solvent bound species rather than a metal hydride.

5.5 Experimental

**General considerations.** Reagents were purchased from commercial sources and used as received. Complexes 28⁶ᵈ, 29⁶ᵈ, 30⁶ᵈ and Cp*Ir(NHC)Cl₂¹⁰ were synthesized as previously reported. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer at room temperature. ¹H, ¹³C, ¹⁹F, and ³¹P NMR chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively. Elemental analyses were performed by Atlantic Microlabs, Inc. X-ray crystallography was performed at the X-ray structural facility of North Carolina State University by Dr. Roger Sommer.

**General Procedure for ethanol dependence on the disappearance of 30.** The reaction of [29] with ethanol in CH₂Cl₂ was monitored by UV-vis at 660nm. In a nitrogen-filled glove box a solution of 29 (1.0 mM) in 2.5 mL of CH₂Cl₂ was added to a 25 mL scintillation vial. The vial was removed from the glove box and ethanol was added to the reaction mixture. A 0.5 mL aliquot of this solution was added to a cuvette and diluted to 2.5 mL in CH₂Cl₂. The cuvette was then placed in the UV-vis spectrometer at 25 °C and data was acquired with the
cell uncapped open to air. This procedure was repeated four times and values for the observed rate constants are given in Table 5.1.

### Table 5.1. Ethanol dependence on the disappearance of 30

<table>
<thead>
<tr>
<th>[EtOH] mM</th>
<th>$k_{obs} \times 10^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>5.125</td>
</tr>
<tr>
<td>0.5</td>
<td>5.234</td>
</tr>
<tr>
<td>1</td>
<td>5.437</td>
</tr>
<tr>
<td>1.5</td>
<td>5.207</td>
</tr>
<tr>
<td>2</td>
<td>5.925</td>
</tr>
</tbody>
</table>

Complex 34, (Cp*)Ir(NHC)(H)(Cl). In a 25 mL scintillation vial, Cp*Ir(NHC)Cl$_2$ (NHC = 1,3-dimethylimidazol-2-ylidene) (150 mg, 0.303 mmol) was added and dissolved in THF (5.0 mL). Bu$_3$SnH (40.8 µL, 0.152 mmol) was added dropwise to a stirred solution of iridium at room temperature. The mixture was allowed to stir for 0.5 h. Excess solvent was then removed under reduced pressure to afford a red residue. Excess pentanes was added to a concentrated solution of the resulting iridium species in methylene chloride. The mixture was then filtered to afford 34 as a red powder in 38% yield (38.0 mg, 0.0824 mmol). $^1$H NMR (CD$_2$Cl$_2$, $^\delta$: 6.94 (s, 2 H); 3.91 (bs, 3 H); 3.64 (bs, 3 H); 1.80 (s, 15 H); -13.21 (s, 1 H). $^{13}$C NMR (CD$_2$Cl$_2$) Elemental Analysis: (C$_{18}$H$_{24}$N$_2$Ir$\cdot$0.5CH$_2$Cl$_2$) Theoretical: (C: 37.05;
Complex 31, (Cp*)Ir(NHC)Ph(Cl). In a 25 mL scintillation vial with stir bar, Cp*Ir(NHC)Cl₂ (NHC = 1,3-dimethylimidazol-2-ylidene) (350 mg, 0.708 mmol) and Ph₂Zn (85.4 mg, 0.389 mmol) was added and dissolved in THF (10.5 mL). The reaction mixture was allowed to stir for 3 h at room temperature. Excess solvent was removed under reduced pressure to afford a red solid. The solid was dissolved in a minimal amount of methylene chloride and excess pentane was added to afford a clean red precipitate. The precipitate was filtered to afford 31 as a red powder in 93% yield (352 mg, 0.657 mmol).

1H NMR (CD₂Cl₂, δ): 7.21 (d, J = 1.5 Hz, 1 H); 7.19 (d, J = 1.5 Hz, 1 H); 6.90 (s, 2 H); 6.80 (m, 3 H); 3.50 (bs, 6 H); 1.66 (s, 15 H).

13C NMR (CD₂Cl₂) δ: 140.85, 126.60, 122.81, 120.62, 90.82, 38.30, 9.20. Elemental Analysis: (C₂₅H₂₃ClN₂Ir·2H₂O) Theoretical: (C: 44.08; H: 5.64; N: 5.02). Found (C: 44.15; H: 5.30; N: 5.02).

Complex 32, (Cp*)Ir(NHC)(C₆F₅)(Cl). In a 25 mL scintillation vial with stir bar, Cp*Ir(NHC)Cl₂ (NHC = 1,3-dimethylimidazol-2-ylidene) (150 mg, 0.303 mmol) and (C₆F₅)₂Zn was dissolved in THF (10.0 mL). The reaction mixture was stirred at room temperature for one hour. Excess solvent was then removed under reduced pressure and the resulting residue was dissolved in a minimal amount of methylene chloride. To the concentrated methylene chloride solution excess pentane was added to afford a dark precipitate. The precipitate was filtered to afford an orange powder in 30% yield (57.0 mg, 0.091 mmol). 1H NMR (CD₂Cl₂) δ: 6.97 (s, 2 H); 3.58 (s, 6 H); 1.65 (s, 15 H). 19F NMR (CD₂Cl₂) δ: -166.71, -165.98, -113.15. 13C NMR (CD₂Cl₂) δ: 123.87, 92.93, 83.90, 38.31, 10.02. Elemental Analysis: (C₂₅H₂₃ClF₅N₂Ir·(0.5 CH₂Cl₂)) Theoretical: (C: 38.63; H: 3.81; N: 4.19). Found (C: 38.82; H: 3.78; N: 4.13).

Complex 33, [(Cp*)Ir(NHC)(C₆F₅)]Bar₄F, (Bar₄F = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). In a 25 mL scintillation vial with stir bar, 33 was added (100 mg, 0.160 mmol) and NaBar₄F (139.0 mg, 0.160 mmol) and dissolved in CH₂Cl₂ (5.0
mL) and stirred at room temperature for 0.5 h. A dark precipitate was formed and filtered to afford the product as a red powder in 69% yield (80.4 mg, 0.0552 mmol). $^1$H NMR (CD$_3$CN,) δ: 7.71 (bm, 12 H, BAr$_4^F$), 7.16 (s, 2 H); 3.43 (s, 6 H); 1.77 (s, 15 H). $^{19}$F NMR (CD$_3$CN, δ: -63.69 (24 F, BAr$_4^F$), -115.37, -164.47, -165.88. $^{13}$C NMR (CDCl$_3$) δ: 157.0, 130.0, 124.0, 122.1, 120.6, 120.0, 119.4, 117.4, 112.7, 92.2, 32.7, 5.9. Elemental Analysis: (C$_{53}$H$_{35}$BF$_{29}$N$_2$Ir) Theoretical: (C: 43.53; H: 2.68; N: 2.26). Found (C: 43.81; H: 2.58; N: 1.92).

5.6 References


