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

AND

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

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“See! Caltech made you happy.”

-Agnes Tong
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ABSTRACT

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

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

Chapter 3 presents kinetic studies of the aryl oxygen bond in the systems outlined in Chapter 2. Using a series of nickel(0) diphosphine terphenyl ether complexes the kinetics of aryl oxygen bond activation was studied. The activation parameters of oxidative addition for the model systems were determined. Little variation was observed in the rate and activation parameters of oxidative addition with varying electronics in the model system. The cause of the lack of variation is due to the ground state and oxidative addition transition state being affected similarly. Attempts were made to extend this study to catalytic systems.
Chapter 4 investigates aryl oxygen bond activation in the presence of additives. It was found that the addition of certain metal alkyls to the nickel(0) model system lead to an increase in the rate of aryl oxygen bond activation. The addition of excess Grignard reagent led to an order of magnitude increase in the rate of aryl oxygen bond activation. Similarly the addition of AlMe$_3$ led to a three order of magnitude rate increase. Addition of AlMe$_3$ at -80 °C led to the formation of an intermediate which was identified by NOESY correlations as a system in which the AlMe$_3$ is coordinated to the ether moiety of the backbone. The rates and activation parameters of aryl oxygen bond activation in the presence of AlMe$_3$ were investigated.

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

Chapter 6 extends the studies of chapter 5 to cobalt complexes. The synthesis of cobalt dialuminum glyoxime metal complexes is described. The electrochemistry of the cobalt complexes was investigated. The electrochemistry was compared to the observed electrochemistry of a zinc analog to identify the redox activity of the ligand. In the presence of acid the cobalt complexes were found to electrochemically reduce protons to dihydrogen. The electronics of the ancillary aluminum ligands were found to affect the potential of proton reduction in the cobalt complexes. These potentials were compared to other diglyoximate complexes.
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CHAPTER 1

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

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

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

While few experimental studies had been done some computational studies had been undertaken where it was found that a nickel arene interaction was of present prior to the activation of the aryl oxygen bond. Our group has been focusing on several novel terphenyl diphosphine scaffolds. These terphenyl diphosphines were found to encourage metal arene interactions with a variety of metals. Given that the ligands predisposed the metal to interact with the arene we envisioned observing intramolecular reactivity with an ether moiety in close proximity with the central arene
ring. Hence we come to the main ligand of this thesis. We developed a diphosphine terphenyl containing an ether moiety in the central arene of the terphenyl. Using this novel diphosphine studies were undertaken to gain mechanistic insight into the mechanism of aryl oxygen bond activation. From this system, in collaboration with my colleagues Sibo Lin and Guy A. Edouard, a mechanism for the reductive cleavage of aryl oxygen bond was able to be worked out, which we were able to extend to catalytic systems.

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

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

The second part of my thesis deals with the study of iron and cobalt glyoxime complexes. What sets these compounds apart is the large aluminum linker between the glyoximes. The aluminum linkers and the ancillary ligands on the aluminum were found to affect the chemistry and geometry of the metal center. The structural and
electrochemical parameters of the iron complex were investigated. Analogous cobalt complexes were studied for proton reduction as a function of the aluminum linkers.
CHAPTER 2

Mechanistic Studies of Aryl-Oxygen Bond Activation in a Nickel(0) Diphosphine-Ether Complex

The text for this chapter was taken in part from:
ABSTRACT

In order to understand the mechanism of the reductive cleavage of aryl ethers by nickel, the reactivity of terphenyl diphosphine aryl alkyl ethers with nickel precursors was studied. A series of nickel(0) complexes containing nickel-arene interactions adjacent to a methyl aryl ether bond were isolated. Heating these systems led to aryl-oxygen bond activation and generation of nickel-aryl-alkoxide complexes. Formal $\beta$-H elimination from these species produced a nickel-aryl-hydride that can undergo reductive elimination and decarbonylation in the presence of the formed aldehyde to regenerate a nickel(0) complex. Upon observing reactivity with aryl methyl ethers the investigations were extended to ethyl, isopropyl, aryl, and benzyl aryl ether linkages, which are structurally relevant to lignin biomass. The reported complexes map out a plausible mechanism for the reductive cleavage of aryl ethers catalyzed by nickel, involving $\beta$-H elimination from a nickel alkoxide rather than cleavage of the nickel-oxygen bond by H$_2$. The studies provide insight into the mechanistic possibilities of the cleavage of aryl oxygen bonds in both small organics and also lignin biomass.
**INTRODUCTION:**

The elaboration of the aryl carbon-oxygen bond to a variety of functional groups has emerged as a versatile synthetic tool in organic methodology,\(^1\) as phenol precursors are readily available and synthetic modification of the aromatic ring is facile. Phenol derived electrophiles are very valuable. Phenol derived electrophiles are naturally abundant and or can be readily prepared from other accessible aromatic compounds. Currently there are over 50,000 phenol and aryl polyol derivatives commercially available. This is in direct contrast with aryl, polyaryl, vinyl, allyl, and alkyl halides, which are typically used as electrophiles in cross coupling. Although a variety of these precursors can be provided on large scale industrially, they are still far less naturally available, and at times economically and environmentally challenging.\(^{1a,b}\)

Substitution of arenes containing oxygen moieties is quite facile, indicating another advantage of phenolic precursors. Electrophilic aromatic substituents can be introduced into the aromatic ring via a number of pathways, notably through substitution. It is possible to control the formation of ortho-substituted arenes through the use of directed ortho-metallation. Oxygen containing moieties such as phenols, ethers, carbamates, and sulfonates have been shown to direct lithiation of the ortho position of the arene (Scheme 2.1).\(^{1a,b}\) Quenching of the lithium species with an electrophilic species leads to the functionalization of the arene. These functionalized arenes can be used as electrophiles in cross coupling reactions leading to the facile synthesis of complex organic compounds.
Scheme 2.1 Ortho directed lithiation

While the availability and ease of functionalization of phenolic precursors makes their advantages apparent, the implication of an aryl oxygen cleaving strategy is not simple. Aryl ether bonds are significantly stronger than their aryl halide counterparts making the direct activation of aryl-oxygen substrates challenging. Typically aryl oxygen moieties must be converted to the more reactive phosphinates, sulfonates, or triflates. Because of the strength of the aryl oxygen bonds, harsh conditions are typically required, which lead to deleterious side reactions hindering formation of the desired cross-coupled product.

Nickel-based catalysts have proven versatile in the conversion of substrates with aryl C-O or C-S bonds in comparison to well-known palladium catalysts. Although cross-coupling of phenolic substrates tends to require prior conversion to the more reactive sulfonates, recent advances show that aryl phosphates, aryl esters, aryl carbamates, aryl ethers and even free phenols can be used as electrophiles in cross-coupling reactions. In a complementary approach, the conversion of aryl C-O to aryl-H bonds has been recognized as a valuable strategy for removing an oxygen-based directing group from an aryl ring. Silanes have been utilized as a hydride source for this transformation. Additionally, stoichiometric intramolecular aryl C-O activation has been reported with rhodium and palladium pincer complexes. In the context of biomass conversion to alternative fuels and chemicals, the depolymerization of lignin, a significant component of biomass containing aryl ether linkages, is a considerable
Recently, an appealing strategy involving the cleavage of lignin-like aryl C-O bonds via nickel-catalyzed hydrogenolysis was reported by Hartwig et al. (Scheme 2.2). Given the general interest in the conversion of aryl C-O bonds, detailed mechanistic insight including the nature of the intermediates is instrumental in developing practical catalysts.

Scheme 2.2 Several Catalytic Nickel Systems for the Cross Coupling and or Reductive Cleavage of Aryl Oxygen Bonds in Relevant Substrates

In the Agapie group several diphosphine terphenyl ligand precursors have been previously synthesized. When metallated with nickel, these scaffolds were found to support mono- and dinuclear complexes that exhibit a variety of strong nickel-arene interactions (Scheme 2.3). Specifically the meta-terphenyl diphosphine was found to predispose the nickel center toward an interaction with the carbon at the 2'-position of the central arene ring or an interaction with the arene π-system in that area. As metal-arene interactions have been proposed to precede the cleavage of aryl-X bonds, we envisioned this m-terphenyl diphosphine as a scaffold for a model system to provide
mechanistic insight into the reductive cleavage of aryl-oxygen bonds. A m-terphenyl diphosphine could be synthesized containing a carbon-O bond in the ipso-position of the central terphenyl ring (Scheme 2.4). The close proximity of the central arene and carbon-O bond should engender reactivity. Herein, we report detailed mechanistic studies of the nickel-mediated reductive cleavage of an aryl-ether with pendant phosphines.

**Scheme 2.3 Several Nickel Terphenyl Diphosphine Systems**

**Scheme 2.4 Design of Alkyl Ether Terphenyl Scaffold**
RESULTS & DISCUSSION:

**Ligand Synthesis:**

Synthesis of the alkyl ether terphenyl ligands was accomplished via the procedure shown in Scheme 2.1. A substituted phenol can be treated with a 2:1 mixture of sodium iodide and sodium chlorite in the presence of acid to form the desired diiodophenol. The diiodophenol can be alkylated with a variety of alkyl halides in acetone utilizing potassium carbonate as a base to form the diidoalkoxybenzene. Treatment of the diodo precursor with 2-bromophenyl boronic acid under Suzuki coupling conditions yields the dibromide terphenyl ether backbone. A lithium halogen exchange followed by treatment with diisopropylchlorophosphine leads to the formation of the desired diphosphine terphenyl ether ligand. This synthesis is highly modular and several ligand variants have been synthesized. The functional group in 4'-position of the phenol can easily be changed by varying the starting phenol, which allows for variation of the electronics of the central arene.

**Scheme 2.5 Diphosphine Terphenyl Methyl Ether Synthesis**
Using the general procedure outlined in Scheme 2.5 several variants of ligands were synthesized. The main diphosphine discussed in this chapter, contains a dimethylamino group in the \textit{para}-position of the central ring and was synthesized using a modified procedure (Scheme 2.6). Starting from 4-nitrophenol, the dibromide terphenyl ether with a para-nitro group can be synthesized in a fashion similar to other substituted phenols. Variation of the ether can be achieved by reaction of the phenol with different alkyl halide precursors (Scheme 2.5). Reduction of the nitro group was achieved via treatment of the dibromo terphenyl with ammonium chloride in the presence of excess iron powder in an acetone water mixture. This transformation can also be done in a 10:1 ethanol water mixture using excess iron powder and concentrated hydrochloric acid. Reductive amination of the terphenyl amine leads to the desired dibromo terphenyl dimethylamine ligand precursor after purification via flash chromatography. This dimethylamine terphenyl can be used to synthesize the diphosphine analogous to that shown in the general procedure (Scheme 2.6).
Scheme 2.6 Diphosphine dimethylamino terphenyl alkyl ether synthesis

Ligands containing alkyl ethers can easily be synthesized via reaction of a diiodo phenolic precursor with the desired alkyl halide. The synthesis of a diaryl ether on this scaffold, however, requires a different approach to install the aryl group. The most promising method was found to be coupling of a phenol with a diaryl iodonium triflate salt. Asymmetric diaryl iodonium triflate salts can easily be synthesized through a one-pot reaction of an aryl iodide with benzene in the presence of m-chloroperoxybenzoic acid and triflic acid. Coupling of these asymmetric diaryl iodonium reagents with a phenol leads to the formation of a diaryl ether containing the most electronegative arene of the diaryl iodonium reagent.

With this in mind the synthesis of a terphenyl diaryl ether ligand was attempted starting from the diiodo phenol (Scheme 2.7).
nitrophenol with sodium hydroxide in the presence of a variety of diaryl iodonium triflate salts did not result in the formation of the desired diaryl ether presumably due to the electronics of the arene. However, coupling of the more electron rich 2,6-diiodo-4-tertbutylphenol with (4-nitrophenyl)(phenyl) iodonium triflate proceeded smoothly to form the desired 4-nitrophenyloxy-2,6-diiodo-4-tertbutylbenzene cross coupling precursor (Scheme 2.7). Cross coupling followed by a reduction and reductive amination of the nitro substituent lead to the desired dibromide. Analogous to the previous diphosphines the terphenyl dibromide can be phosphinated upon purification by flash chromatography to yield the desired diaryl ether terphenyl diphosphine (Scheme 2.7).
All the diphosphine ether ligands synthesized exhibit NMR behavior consistent with hindered rotation around the carbon-carbon bond between the central terphenyl ring and the outer terphenyl arenes (Figure 2.1). These properties arise due to the ether moiety at the *ipso*-carbon at the central terphenyl ring and the isopropyl substituted phosphines. Analysis of the diphosphine ether ligands via $^{31}$P NMR spectroscopy typically reveals two peaks between 0 and 5 ppm. Changes in the ratio of the $^{31}$P resonances are dependent on the identity of the ether in the *ipso*-position. A similar analysis by $^1$H NMR spectroscopy reveals broadening of the resonances corresponding to the ether moiety and resonances for the outer rings. For the benzyl variant 1^Bn (Scheme 2.6) a pair of doublets and a singlet is observed for the methylene protons. This is consistent with two species in solution, the major species, which gives the two doublets, is consistent with an *anti* like configuration where the phosphines are on different sides of the plane of the central arene ring (Figure 2.1). In such a configuration, the two methylene protons are in different environments, and hence diastereotopic. Each diastereotopic proton would split the resonance of the other
proton causing the observation of two doublets. Similarly the observed singlet is consistent with a *syn* conformation of the two outer phosphines (Figure 2.1). With both phosphine groups on the same side of the central arene plane the methylene protons would be in similar environments and a singlet is observed by $^1$H NMR spectroscopy.

![Figure 2.1. Hindered rotation around substituted terphenyl rings. *Syn* atropisomer corresponds to both phosphines on the same side of the central arene ring. The *anti* atropisomer corresponds to phosphines on either side of the central ring.](image)

Interconversion between the *syn* and *anti* atropisomers can be achieved at higher temperatures. Variable temperature $^1$H NMR studies show a coalescence of peaks in the aromatic region and the isopropyl methane protons and sharpening of the resonances of the isopropyl methyl groups and the methoxy group as shown in Figure 2.2. Similarly variable temperature $^{31}$P NMR studies show coalescence of the phosphorous resonances assigned to the *syn* and *anti* atropisomers at higher temperatures. All diphosphine ethers synthesized exhibit similar peak coalescence at higher temperatures.
**Figure 2.2.** Variable temperature NMR spectra of 1. Stacked $^1$H NMR spectra on the left and $^{31}$P NMR spectra on the right.

**Metallation of the Methyl Ether Diphosphine: Nickel(0) Model Systems**

**Methyl ether**

Addition of an equivalent of Ni(COD)$_2$ to the diphosphine scaffold 1 at 20 °C led to generation of a new species 2 over the course of 13 hours, according to NMR spectroscopy (Scheme 2.8). Metallation of 1 with Ni(COD)$_2$ is slow (13 hours) consistent with hindered rotation of the terphenyl backbone. Comparatively, para- and meta-terphenyl diphosphines, which do not contain ether backbones, are metallated at a much faster rate. The $^{31}$P and $^1$H NMR spectra give a singlet and sharp resonances respectively indicative of the absence of the rotation of the terphenyl backbone that is observed in the free ligand. The $^{31}$P NMR chemical shift of 2 (40.7 ppm) is similar to
that reported for the \( p \)-terphenyl diphosphine supported nickel(0) (40.4 ppm). Similarly, the protons assigned to the central arene resonate almost 1 ppm more upfield (5.84 ppm) compared with those of the free phosphine (6.73 ppm) in the \(^1\)H NMR spectrum of 2, whereas the ether \( \text{OCH} \) peak is only slightly shifted (3.13 ppm vs. 3.17 ppm, 1 vs. 2). These data are consistent with the formation of a nickel(0) species with interactions between the metal center and the aromatic \( \pi \)-system, but not the ether oxygen. Through the aforementioned NMR studies, complex 2 was assigned as a nickel(0) complex with the metal center coordinated to the two phosphine and central arene (Scheme 2.8).

**Scheme 2.8 Synthesis of nickel(0) compound 2**

![Scheme 2.8 Synthesis of nickel(0) compound 2](image)

The assignment and spectroscopic findings of 2 were confirmed by a single-crystal X-ray diffraction (XRD). X-ray quality crystals of 2 were grown out of pentane at -32 °C. In the solid state the metal center is bound by two phosphines and interacts with two carbon centers of the central arene as predicted by NMR studies (Figure 2.3). The short Ni-C distances (1.96-2.09 Å) indicate strong interactions between the metal center and central arene. Consequently, some C-C distances of the central ring are consistent with partial localization of the double bonds. For 2 the C8-C9 and C10-C11 bonds (1.368(2) and 1.360(2) Å, respectively) are shorter than the rest of the central
arene C-C bonds by >0.06 Å. The aryl C-O bond is angled 16.76 ° away from the metal center, consistent with partial sp³ hybridization of the 2′-position of the central ring (C18, Figure 2.3) due to the Ni-C interaction. Notably, an intermediate displaying η²-interactions between Ni(0) and the double bond adjacent to the oxygen was found computationally to precede C-O bond activation in the cross coupling of phenolic derivatives. Complex 2 is the only example of such an arrested intermediate characterized by crystallography, according to a Cambridge Structural Database search.

Figure 2.3 Solid-state structure of 2 (left). Solvent molecules, anions, and select hydrogen atoms not shown for clarity. Diagram of central arene bond lengths in 2 (right).

Complex 2 was found to convert to new species in solution at 45 °C or over an extended period of time at 20 °C (Scheme 2.9). After the first 12 hours at 45 °C a new product 3 was observed by NMR spectroscopy, in mixture with starting material. The same species can also be observed in a mixture after five days at 20 °C. Monitoring the reaction mixture by ¹H NMR spectroscopy reveals a shift in the peak corresponding to
the central arene ring downfield at 6.78 ppm, which is very close to the central arene resonances of the ligand precursor 1 (6.72 ppm). Additionally, the OCH₃ resonance is shifted nearly 0.5 ppm downfield from 3.17 ppm in 2 to 3.66 ppm in complex 3. Hydrolysis of 3 and analysis of the liberated organic products by ESI mass spectrometry reveals a terphenyl diphosphine moiety without the methoxy group. This is consistent with activation of the aryl-oxygen bond to form a nickel(II) methoxide. Due to the shifts in the central arene and methoxy resonances and the identity of the ligand complex 3 was assigned as a nickel(II) methoxy species where the nickel has activated the sp² aryl-oxygen bond. Compound 3 is similar to a nickel(II) PCP complex which gives similar ¹H NMR resonances for the central arene and methoxy group at 6.85 ppm and 3.90 ppm respectively.¹³

**Scheme 2.9 Synthesis of nickel(II) methoxide complex 3**

Upon further heating of 3, a new species, 4, is observed (Scheme 2.10). The central arene protons of this complex are also shifted relative to 2 in the aromatic region (6.79 ppm vs. 5.84 ppm) and are quite similar to the arene resonances in the nickel(II) methoxide complex 3 (6.78 ppm). Intriguingly, the OCH₃ signal is absent and upfield triplet is observed in the hydride region of the ¹H NMR spectrum (-2.87 ppm). This upfield peak is consistent with the formation of a Ni(II) hydride.
Compound 4 was found to be isolable in 55% yield by precipitation from THF upon stirring 2 at 20 °C for seven days. The central arene resonances suggest a PCP pincer type coordination similar to that of 3. Analysis of the ligand by ESI mass spectrometry also supports this assignment for 4. Unfortunately, efforts to obtain X-ray quality single crystals of 4 or 3 have been unsuccessful to date.

**Scheme 2.10 Synthesis of nickel(II) hydride 4 from complex 2**

![Scheme 2.10 Synthesis of nickel(II) hydride 4 from complex 2](image)

In order to obtain structural insight into compounds 3 and 4 an analog with a better crystallization profile was synthesized. Treatment of 4 with excess methyl iodide at 20 °C for 14 hours generated a new species assigned as a Ni(II) iodide, 5; an XRD study of this species confirmed the above assignments for compounds 3 and 4 (Scheme 2.11). Gratifyingly, the nickel center was found in the same plane as the central arene as predicted by cleavage of the aryl–O bond. The Ni–C distance (1.919(1) Å) is consistent with an aryl C–Ni bond and is similar to other PCP pincer complexes. The diphosphine ligand framework, bound in pseudo-C2 fashion, acts as a classical tridentate diphosphine-aryl pincer, but with six-member chelates involving aryl-aryl linkages. The solid-state structure is consistent with the NMR spectroscopic data for 4 and 5 indicating the absence of the methoxy group and the lack of
interaction with the π-system of the arene. Most importantly, the structure shows cleavage of the aryl C–O bond and displacement of oxygen by nickel.

**Scheme 2.11 Synthesis of nickel (II) iodide 5 from complex 4**

![Scheme 2.11](image)

<table>
<thead>
<tr>
<th>angles (°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P2-Ni-P1</td>
<td>166.680(17)</td>
</tr>
<tr>
<td>C-Ni-I</td>
<td>161.06(4)</td>
</tr>
<tr>
<td>P2-Ni-I</td>
<td>99.972(12)</td>
</tr>
<tr>
<td>P1-Ni-I</td>
<td>93.156(13)</td>
</tr>
<tr>
<td>C-Ni-P2</td>
<td>84.30(4)</td>
</tr>
<tr>
<td>C-Ni-P1</td>
<td>83.98(4)</td>
</tr>
</tbody>
</table>

**Figure 2.4** Solid-state structure of 5 (left). Solvent molecules, anions, and select hydrogen atoms not shown for clarity. Table of relevant angles in 5 (right).

Attempts were made to independently synthesize a nickel(II) methoxide on this PCP backbone in order to confirm the identity of 3. One route to 3 is the reaction of 4 with methanol. Sigma bond metathesis of the methanol and 4 could form 3 and release
hydrogen. Treatment of 4 with methanol at 20 °C, gratifyingly, led to the reformation of species 3, albeit not quantitatively (as identified by \( ^1H \) and \( ^{31}P \) NMR spectroscopy). Alternatively complex 3 can be synthesized through a salt metathesis between 5 and sodium methoxide. Indeed, treatment of 5 with sodium methoxide at 20 °C does led to the formation of 3, albeit in a mixture with 4 and other unidentified species. Although the nickel(II) methoxide could not be synthesized by these alternate routes without contamination from 4, the independent methods of generation are consistent with identity of 3 being a nickel(II) aryl-methoxide. This is the product of oxidative addition of the aryl C O bond to nickel(0). Similar stoichiometric reactions mediated by rhodium and palladium have been reported.
Scheme 2.12 Alternate Syntheses of 3 from 4 and 5

The mechanism of the hydride formation in 4 was probed through deuterium labeling studies. A ligand containing a deuterated methoxide was synthesized through the use of $d$-iodomethane in the phenol protection. 1-$d$ metallation with nickel(0) produced 2-$d$, the deuterated analog of 2. Subjection of 2-$d$ to elevated temperatures in this complex leads to a nickel methoxide complex 3-$d$, which is identical to 3, albeit without resonances for the methoxy group. Further heating of 3-$d$ leads to the formation of the nickel(II) deuteride 4-$d$. Complex 4-$d$ gives no signal in the hydride region of the $^1$H NMR spectrum, but otherwise displays the same peaks as 4. This is consistent with the formation of a nickel-deuteride through a $\beta$-hydrogen elimination of the methoxide to presumably form formaldehyde, as the methoxy group is the only source of deuterium in the reaction mixture other than $d$-benzene. This study
confirms the methoxy group as the source of hydrogen (deuterium). β-hydrogen elimination could occur via a five-coordinate intermediate, although, in coordinatively saturated systems it has been proposed to occur via alkoide dissociation or in bimolecular fashion. Given the strain observed in the chelates in 5, dissociation of a phosphine arm may also be possible, opening up a cis coordination site for β-hydrogen elimination. Further studies will be required to elucidate the mechanism of β-hydrogen in the present system.

**Scheme 2.13 Synthesis of 4-d from 2-d**

![Scheme 2.13](image)

Although its generation does not require dihydrogen, hydride 4 is a potential intermediate in the hydrogenolysis of the aryl-O bond. Complex 2 was heated to 100 °C, generating new species, 6, in over 90% yield (1H NMR spectroscopy) within two hours. The Ni-H peak is absent from the 1H NMR spectra of the product and a new triplet is present (6, 6.51 ppm) assigned to an aryl ipso-C-H. Infrared (IR) spectroscopy revealed an absorption indicative of a terminal Ni(0)-CO (6, 1917 cm⁻¹) (Scheme 2.14). The identity of this complex was confirmed through the independent synthesis of the Nickel(0) ipso-H complex 7. Addition of a sub stoichiometric amount of carbon monoxide to this complex leads to the formation of 6 and starting material as identified by NMR and IR spectroscopy (Scheme 2.15).
Intrigued by the presence of the ipso-H and the carbonyl group, we hypothesized that the ipso-H and carbonyl in 6 were the product of a reductive elimination and decarbonylation of formaldehyde from the previously isolated nickel(II) hydride 4. To this end, reductive elimination in the 4 was investigated as the source of the ipso-H. Surprisingly, heating 4 to 100 °C for over 6 hours does not result in reductive elimination to form 7 and heating for extended periods resulted in decomposition of 4. However, the addition of sub stoichiometric amounts of carbon monoxide to 4 does result in the generation of 6, albeit slowly in a mixture with several other unidentifiable products. This behavior indicates that another ligand facilitates the reductive elimination step in 4.
Acidic ligands have been previously reported to facilitate reductive elimination in nickel(II) square planar complexes. Intrigued by the ligand facilitated reductive elimination, other ligands were investigated. The addition of less π-acidic ligands such as pyridine or trimethyl phosphine did not result in reductive elimination in 4 even after heating at 100 °C. As formaldehyde is proposed to be generated through the β-H elimination to form 4, paraformaldehyde was tested for facilitation of the reductive elimination. Treatment of 4 with paraformaldehyde immediately leads to the formation of several unidentified species at room temperature. Heating this mixture to 60 °C results in the formation of 6 within four hours.

The reaction of the hydride 4 with formaldehyde could proceed through several mechanisms. The nickel(II) hydride could undergo a sigma bond metathesis with formaldehyde to release dihydrogen forming a nickel(II) formyl complex. The formyl can undergo a deinsertion of the carbonyl to form a five coordinate nickel(II) carbonyl hydride, this transient species could undergo reductive elimination to form 6. Alternatively formaldehyde can act as a fifth ligand and coordinate to the 4 and facilitate reductive elimination to form 7, which can then decarbonylate formaldehyde releasing dihydrogen and forming 6.

In order to gain insight into these mechanistic possibilities the nickel(0) complexes were tested for decarbonylation reactivity. Treatment of 7 with paraformaldehyde quickly resulted in a vigorous release of dihydrogen and a color change from dark red to red orange. Analysis by ¹H and ³¹P NMR spectroscopy revealed the quantitative formation of 6 in under 10 minutes at 20 °C. Interestingly, all the meta nickel(0) complexes (7, 2, 2₃Bu, and 2₃CF₃) discussed undergo decarbonylation
with paraformaldehyde. As the nickel(0) complexes are competent for the decarbonylation of formaldehyde it is entirely possible that 4 coordinates formaldehyde as a fifth ligand and undergoes reductive elimination to form 7 with formaldehyde coordinated. As we have observed experimentally 7 can quickly undergo decarbonylation to quantitatively generate 6.

A possible mechanism for the reductive cleavage of anisoles with nickel has been outlined using the nickel(0) diphosphine ether model system 2 (Scheme 2.16). Starting from a nickel(0) metal center (2) the complex can undergo oxidative addition to form a nickel(II) methoxide (3). The nickel(II) methoxide species (3) undergoes β-hydrogen elimination to form a nickel(II) hydride (4) and formaldehyde. In the presence of formaldehyde, the hydride (4) undergoes reductive elimination and decarbonylation to form a nickel(0) carbonyl complex (6). Overall, an anisole has been reductively cleaved forming an arene, carbon monoxide, and dihydrogen, with the methoxy group providing the required reducing equivalents (Scheme 2.17).
Inspired by these mechanistic results, the reactivity of the nickel model complex 2 was assessed in the presence of two prominent reductive cleavage additives, hydrogen and silanes. In a catalytic system with dihydrogen it is feasible to propose that the nickel(0) can add into the aryl oxygen bond forming a nickel(II) alkoxide, which could undergo sigma bond metathesis with dihydrogen to form a nickel(II) hydride and an alcohol. To investigate the feasibility of this mechanistic possibility the reactivity of 2 was explored in the presence of dihydrogen. Using 2-d₃ it should be possible to observe whether sigma bond metathesis is feasible through a labeling study,
as a successful sigma bond metathesis would lead to the formation of 4. A vessel charged with 2-d3 and 4 atm of dihydrogen was heated to 45 °C. Under these conditions only β-hydrogen elimination was observed as only 4-d1 was identifiable by 1H NMR spectroscopy. The results of the labeling study show that in this system, β-hydrogen elimination from the alkoxide is more favorable than sigma bond metathesis of dihydrogen, for the formation of 4 (Scheme 2.18). Overall this suggests that the sigma bond metathesis of dihydrogen through a nickel(II) intermediate might not be a viable mechanistic step for the reductive cleavage of aryl bonds.

Scheme 2.18 Reactivity of 2-d3 in the presence of H2

As silyl hydrides are also used as hydride sources in the reductive cleavage of aryl oxygen bonds, the reactivity of the model complex was investigated in the presence of triethylsilane (Scheme 2.19). In a catalytic system one can postulate that a
nickel(0) catalyst could undergo oxidative addition of an aryl ether to form a nickel(II) alkoxide, which can undergo transmetallation with silane, producing a nickel(II) hydride, followed by reductive elimination releasing arene and forming the nickel(0) catalytic species. This mechanistic possibility can be probed through a labeling study of 2 and labeled silane, where the identity of the ipso-H, in 6 will indicate silane transmetallation. Heating 2 to 80 °C in benzene in the presence of two equivalents of Et₃SiD for three hours generated less than 10% 6-d₁. A larger excess of Et₃SiD (10 equivalents) led to more deuterium incorporation (ca 20% 6-d₁).

As there is an isotope effect favoring the formation of 6, the effect of triethylsilane with 2-d₁ was also investigated. Treatment of 2-d₁ with Et₃SiH (2 equiv) generated 6-d₁ and 6 in a 1:1 ratio. The increased isotopic incorporation from Et₃SiH vs. Et₃SiD is consistent with normal isotope effects for β-hydrogen elimination (conversion of 3 to 4) and σ-bond metathesis between 3 and silane to generate 4. An unidentified species was observed by ¹H and ³¹P NMR spectroscopy, in amount proportional to the label incorporation from SiX (X=D or H) into 6. This is consistent with decreased generation of formaldehyde and hence lower formation of the nickel carbonyl species upon reductive elimination / decarbonylation. These results indicate that the mechanism involving β-hydrogen elimination (Scheme 2.19) is favored vs. interception of the nickel methoxide by silane, at low concentration of silane.
Scheme 2.19 Labeling studies of 2 with Triethylsilane

The mechanism for the reductive cleavage of the aryl-oxygen bond outlined with complex 2 was found to be the same for the other nickel(0) terphenyl diphosphine methyl ether variants. The tert-butyl variant 2tBu was found to undergo a mechanism identical to the dimethyl amino variant. Interestingly the trifluoromethyl variant 2CF3 showed some deviation in the formation of the final nickel(0) carbonyl product. Heating of 2CF3 to 100 °C for 1.5 hours produces both 6CF3 and 7CF3 in a 1:1 ratio. This could be due to the lack of reactivity between 3CF3 and formaldehyde and formaldehyde acts like a fifth ligand promoting reductive elimination to form 4CF3. 7CF3 undergoes decarbonylation much slower (3 hours) than the more electron donating 7 (less than 10 minutes), which can explain the observed 7CF3, reductive elimination followed by a slow decarbonylation leads to a mixture of species.
Metallation of the Methyl Ether Diphosphine: Nickel(II) Phenoxide Halide Systems

Treatment of a colorless solution of the diphosphine terphenyl ether 1 with an equivalent of yellow Ni(II)Cl_2(DME) (DME = dimethoxyethane) in THF results in the formation of a green compound (8) (Scheme 2.20) over the course of several hours. The ^31P NMR spectrum shows a shift in the phosphorous resonances of the free diphosphine to a new resonance at 13.46 ppm. The ^1H NMR reveals several broad resonances in the alkyl region between 0 and 4 ppm which can be assigned to the dimethylamine group and isopropyl groups of the ligand, however there is no assignable methoxy resonance indicating C-O bond activation. Mass analysis of the organics after hydrolysis of 8 reveals the mass for the diphosphine phenol, leading to the assignment of 8 as a nickel(II) phenoxide chloride complex (as shown scheme 2.20). This is consistent with Ni(II)X_2 reacting in a fashion similar to boron tribromide, where the Lewis acidic nickel center coordinates to the methoxy group and eliminates MeX, forming a nickel(II) phenoxide chloride. This is reminiscent of reactivity observed in the treatment of other phosphine ethers and diphosphine ethers with group 10 metals. The observed reactivity appears to be limited to metal halides, treatment of the ligand with other nickel(II) salts such as Ni(II)OTf (OTf = trifluoromethyl sulfate) does not lead to the formation of a similar phenoxide complex and only starting materials are observed by ^1H and ^31P NMR spectroscopy. The rate of the formation of the phenoxide complex is also dependent on the identity of the ether. Treatment of 1^t or 1^iPr leads to the formation of the same nickel(II) phenoxide chloride complex albeit at a significantly reduced rate with 1^iPr being the slowest, while addition of a nickel(II) halide to 1^iPr does not lead to the formation of 8.
Scheme 2.20 Reactivity of 1 with NiCl$_2$(DME)

A single crystal X-ray diffraction study of a crystal of 8 grown from a concentrated solution in benzene confirmed the tentative structure (Figure 2.5). From the solid state structure we can see that the Ni(II)Cl$_2$ has activated the sp$^3$ C–O bond to form a nickel phenoxide species. Interestingly two different structures were obtained from the crystal and differ in the structural identity of the dimethylamine group on the central arene. One structure contains what appears to be a dimethylamine in the backbone and displays C–N–C angles of 111.42°, 109.77°, and 115.64° which are consistent with a tetrahedral geometry (angles 109.5°) around the amine nitrogen. The other structure contains what appears to be a planar imine as the angles around the nitrogen are 120.53°, 118.57°, and 119.62° which is consistent with planar geometry (angles 120°) making this more consistent with an imine group rather than an amine group. The N–C$_\text{ar}$ bond length is much shorter in the imine like system (1.383 Å) than in the amine structure (1.432 Å). Observation of the imine and amine structures in the unit cell suggests that the dimethylamino phenoxide is capable of redox chemistry similar to iminoquinones.
Although the geometry of the amino group hints at redox activity of the phenoxide, the bond lengths of the arene do not. Little difference is observed in the bond lengths of the two central arene rings in the crystal structures (Figure 2.5). For a para-iminoquinone both the N–Ar and O–Ar bonds are shorter than typical N and O-Ar bonds. As an alternate explanation the two structures could differ due to packing of the molecules in the crystal. Further investigation of the molecules of this type is needed to identify whether the aminophenoxide is capable of acting as a redox active ligand in these Ni-POP complexes.
Metallation of the Methyl Ether Diphosphine: Nickel(I) Systems

The cleavage of C–X bonds are typically proposed to proceed through a nickel(0/II) mechanism, where a nickel(0) catalyst undergoes oxidative addition of a substrate to form a nickel(II) species which can transmetallate and undergo reductive elimination to reform the nickel(0) catalyst. Analogies can quickly be drawn between mechanism and observed intermediates in nickel(0/II) mechanisms as intermediates
are readily and conveniently observable by NMR spectroscopy. Although nickel(0/II) appears to be common, it has been proposed that the cleavage of some C-X bonds can proceed through a nickel(I/III) mechanism in addition or lieu of a nickel(0/II) mechanism (Scheme 2.21). This mechanism has been proposed for the cross coupling of aryl halides, alkyl halides and more recently in the activation of aryl oxygen bonds.

**Scheme 2.21 A possible nickel(I/III) mechanism for cross coupling**

For aryl ethers, Martin et al. developed a system for the reductive cleavage of C-O bonds based on nickel(0), tricyclohexylphosphine, and silane as the reducing agent. Using this system the reductive cleavage of aryl ethers was observed catalytically, however only when the phosphine was tricyclohexylphosphine. Through further experimental and computational investigations of the system, it was proposed that the catalytic cycle goes through a nickel(I) intermediate (Scheme 2.22). In the catalytic cycle a nickel(I) diphosphine silane is generated from Ni(COD)₂, PCy₃, and Et₃SiH through a comproportionation event. The nickel(I) diphosphine silane is the key catalytic species. The nickel(I) silane coordinates the substrate in an η₁-fashion and
undergoes a migratory insertion event and generate a benzyl nickel species. From this benzyl nickel species MeOSiR₆ is eliminated followed by a migration of the nickel center, resulting in the formation of the nickel(I) arene. This complex undergoes transmetallation with triethylsilane to generate the reduced arene and regenerating the nickel(I) silane catalyst. In order to gain insight into the possibility of a nickel(I) intermediate and investigate the cleavage of aryl-O bonds by nickel(I) a nickel(I) terphenyl diphosphine ether was synthesized.

Scheme 2.22 Proposed mechanism for aryl-O bond activation containing nickel(I) species

We have studied aryl-oxygen bond activation facilitated by nickel in a terphenyl diphosphine ether system. From our studies vide supra the activation of the aryl-oxygen bond proceeds through a nickel(0/II) mechanism in the model system. Given the evidence for nickel(I) species in activation of aryl-X bonds in catalytic systems, attempts were made to gain mechanistic insight in the role of nickel(I) in aryl-O bond activation using our model system.

Nickel(I) systems have been previously synthesized on similar terphenyl diphosphine scaffolds in our group through a comproportionation of nickel(II) and
nickel(0) precursors. Treatment of the dimethylamino terphenyl diphosphine methyl ether 1 with a 1:1 mixture of NiCl\textsubscript{2}DME and NiCOD\textsubscript{2} led to a mixture of nickel(II) phenoxide chloride 8, and 2 (Scheme 2.23 A). This mixture of products emphasizes the reactivity of the ligand with nickel(II) halide precursors. The nickel(II) phenoxide forms at a rate faster than 2. This is due either to the dissociation of COD from the nickel(0) precursor or the nickel(II) halide only needs to coordinate a single phosphine to undergo the cleavage of the sp\textsuperscript{3} C-O bond. Fortunately, the nickel(0) complex 2 can be oxidized to form a nickel(I) complex, i.e. 2 can be oxidized by NiCl\textsubscript{2}DME to form a nickel(I) chloride complex 9 and nickel black (Scheme 2.23 B). Filtration from the nickel black led to the isolation of 9 as a bright yellow solid.

**Scheme 2.23 Synthesis of 9 from Ni(COD)\textsubscript{2} and NiCl\textsubscript{2}(DME)**

Complex 9 is paramagnetic and hence gives broad peaks ranging from -5 to 20 ppm in the \textsuperscript{1}H NMR spectrum. No resonances are observed by \textsuperscript{31}P NMR spectroscopy for compound 9. Hydrolysis of the complex with HCl and subsequent analysis by ESI mass spectrometry gives the mass of the terphenyl diphosphine 1. The mass of 1 provides evidence for a nickel(I) chloride coordinated to the two diphosphines with
the ether still intact (Scheme 2.23). Treatment of 9 with a halide abstraction agent such as AgOTf or TlOTf leads to the formation of a nickel(I) triflate complex 9\textsuperscript{OTf}. Compound 9\textsuperscript{OTf} can be reduced with cobaltocene to regenerate the nickel(0) complex 2 providing further evidence for the identity of both complexes 9 and 9\textsuperscript{OTf}. Nickel(I) complexes can be synthesized with different anions through the use of other oxidizing agents, for example treatment of 2 with ferrocenium hexafluorophosphate leads to the formation of complex 9\textsuperscript{PF6}. With several nickel(I) complexes the reactivity of the nickel(I) center with the aryl-O bond was investigated.

**Scheme 2.24 Synthesis of different variants of 9**

Complex 9 was found to be very robust. Heating 9 in benzene to 80 °C did not lead to any observed reactivity. Similarly heating complex 9 to 140 °C in xylenes does not result in aryl-O bond cleavage or any form of reactivity as only 9 was observed by
'H NMR after heating and the diphosphine 1 was observed by ESI mass spectrometry after hydrolysis of the reaction mixture. It was hypothesized that the lack of reactivity in 9 was due to coordination of the chloride to the nickel center, to this end reactivity was investigated with nickel(I) complexes without coordinating anions 9^{OTf} and 9^{PF6}. Heating 9^{OTf} in xylenes (140 °C) or the 9^{PF6} in MeCN (80 °C) did not lead to any observed reactivity.

In the mechanism proposed by Martin et. al. the silane of the nickel(I) species plays a critical part in the cleavage of the aryl oxygen bond (migratory insertion and silanol elimination). To investigate the possibility of aryl oxygen bond activation by migratory insertion and alcohol elimination the synthesis of other nickel(I) complexes was attempted. Initially the synthesis of nickel(I) aryl and alkyl complexes were targeted. Treatment of 9 with MeMgBr or MeMgCl in THF, toluene, or benzene leads to the clean generation of 2 within minutes. The addition of larger Grignards such as benzyl, phenyl, and mesityl also leads to the formation of 2 and the coupled aryls (as observed by GC-MS) within minutes. Complex 9 presumably quickly undergoes transmetallation to form a nickel(I) aryl complex. Two of these nickel(I) aryl species rapidly undergo either a radical recombination or a bimolecular reductive elimination to form the biaryl and 2. Treatment of 9 with other reagents such as lithium or sodium triethylborohydride, triethyl silane (to form a nickel(I) hydride), and triethyl silyl potassium (to form a nickel(I) silyl species) all led to formation of 2.
Scheme 2.25 Transmetallation reactivity of 9

Isopropyl Ether

Intrigued by the observed mechanism for the terphenyl diphosphine methyl ether system, our investigation was expanded to observe if this mechanism is general to all aryl ethers. Nickel(0) model systems were targeted containing a variety of different ethers. To model the reductive cleavage of secondary alcohols, an isopropyl aryl ether was targeted. Synthesis of the diphosphine terphenyl isopropyl ether ligand proceeded according to scheme 2.6 and resulted in the diphosphine 1\textsubscript{iPr}. Treatment of 1\textsubscript{iPr} with nickel(0) COD\textsubscript{2} at 20 °C in THF resulted in the formation of the nickel(0) diphosphine terphenyl isopropyl ether complex 2\textsubscript{iPr} (Scheme 2.26). A shift is observed in the \textsuperscript{31}P NMR spectrum where a single peak is observed at 39.20 ppm (vs. -2.41 and -4.54 of 1\textsubscript{iPr}) for 2\textsubscript{iPr}, this is comparable to the \textsuperscript{31}P NMR shift of the methoxy variant 2 (40.7 ppm). By \textsuperscript{1}H NMR spectroscopy a downfield shift in the central arene ring resonance of 2\textsubscript{iPr} is observed, in comparison to the free ligand (5.78 ppm vs. 6.75 ppm) similar to what is observed in complex 2 (5.84 ppm). A doublet is observed at 0.68 ppm along with a septet at 3.90 ppm assigned to the isopropyl ether methyl groups and methine respectively. The resonances are relatively unchanged from what is observed
in the free terphenyl isopropyl ether where two doublets are observed at 0.70 and 0.73 ppm and a septet at 3.83 ppm.

**Scheme 2.26 Synthesis of 2**

With 2 in hand, reactivity studies were undertaken. Unsurprisingly the nickel(0) complex 2 undergoes oxidative addition to form a proposed nickel(II) isopropoxide species 3 as identified by $^{31}$P NMR spectroscopy. To date attempts to isolate complex 3 have resulted in failure. The proposed nickel(II) isopropoxide gives a $^{31}$P NMR resonance at 23.65 ppm, which is in the range of the $^{31}$P resonance of 2 (27.23 ppm). $\beta$-H elimination quickly occurs in 3 to form the previously characterized 4 and acetone as observed by $^1$H and $^{31}$P NMR. The reductive elimination in the presence of acetone is facile forming 7 (Scheme 2.27). All four species (2, 3, 4, and 7) can be observed by $^1$H and $^{31}$P NMR after 22 hours in THF at 20 °C. In comparison, with 2 the final product 6 is not observed by $^1$H and $^{31}$P NMR under these conditions (20 °C for 22 hours) only 3 and a small amount of 4 could be observed in addition to starting material. Heating of 2 at 100 °C for one hour results in complete conversion to 7 and acetone. The reductive cleavage of a secondary aryl ether results in the formation of a ketone and an arene (Scheme 2.28). The observed mechanism mirrors that observed with the methyl terphenyl ether diphosphine oxidative addition, followed by $\beta$-H elimination and subsequent reductive elimination.
However, in the ether case the formed acetone shows that a ketone can act as a fifth ligand to promote reductive elimination to form the arene.

**Scheme 2.27 Observed \( 2^\text{nd} \) Model System Reactivity**

![](image)

**Scheme 2.28 Overall Isopropyl aryl ether Reductive Cleavage Products**

![](image)

**Ethyl Ether**

As acetone showed no reactivity with the nickel(0) precursor in comparison to formaldehyde, which displayed decarbonylation under the same conditions, it was hypothesized that a more complex aldehyde could engender composite reactivity within the system. To explore this possibility a terphenyl diphosphine ethyl ether \( 1^n \)
was targeted. Compound 1 was synthesized via the fore mentioned synthesis route (Scheme 2.29). Mixing a solution of 1 with Ni(0)COD at 20 °C results in the formation of a new Ni(0) terphenyl diphosphine ether complex 2. A resonance is observed by 31P NMR at an unremarkable shift of 40.56 ppm, consistent with the other synthesized terphenyl diphosphine ether complexes. 1H NMR shows a similar shift in the central arene resonances (5.85 ppm) indicative of a metal arene interaction as seen with other variants. The ethoxide moiety of 2 shows resonances (a quartet and doublet) at 3.58 and 0.51 ppm corresponding to the methylene and methyl of the ethoxide respectively. These shifts are similar for the ethoxide peaks observed in 1 (3.48 and 0.63 ppm for the methylene and methyl respectively) albeit without the isomer broadening.

Scheme 2.29 Synthesis of 2

Upon heating the Ni center of 2 under goes an oxidative addition of the aryl oxygen bond resulting in a new species 3. 31P NMR spectroscopy reveals a resonance at 27.33 ppm. This new species is believed to be the nickel(II) oxidative addition product similar to 3. Further heating results in reductive elimination to form the nickel(II) hydride 4 as observed by NMR spectroscopy and acetaldehyde. Further heating results in the formation of a mixture of three complexes in varying ratios dependent on the heating temperature. The three species were identified as, the
previously identified Ni° carbonyl complex 6, a Ni° species generated from reductive elimination of a proton 7, and a Ni° complex resulting from the reductive elimination of a methyl group 10 (Scheme 2.30). The overall reaction is the reductive cleavage of an ethyl aryl ether and formation of benzene, toluene, carbon monoxide and hydrogen (Scheme 2.31).

**Scheme 2.30 Observed 2° Model System Reactivity**

From the mixture of species formed it is probable that there are several competing processes active. For the formation of tolyl complex 10 from heating 2° it is postulated that the nickel(II) hydride 4 reacts with the formed acetaldehyde resulting in a transient nickel(II)-acyl complex and hydrogen. This species is proposed to quickly undergo decarbonylation and reductive elimination to form complex 10 (Scheme 2.24). The carbon monoxide generated could be used to form complex 6 as the nickel(II) hydride 4 is capable of reacting with carbon monoxide to form the
reductively eliminated product 7. The formation of the proton species could also arise from 4 coordinating acetaldehyde as a fifth ligand, leading to reductive elimination.

**Scheme 2.31 Overall Ethyl aryl ether Reductive Cleavage Products**

In order to probe the mechanism of 2 further studies were carried out. If the proposed mechanism was possible, the isolable nickel hydride 4 should be able to react with acetaldehyde to form the observed ratio of products. When 4 is mixed with excess acetaldehyde little reactivity is seen at room temperature, however heating to reaction conditions identical to the aforementioned studies results in the formation of the methyl reductive elimination product coordinated to a carbonyl ligand 11 which was not observed in the heating of 2 (Scheme 2.32). It is also possible that the acetaldehyde can undergo decarbonylation from a nickel(0) species forming carbon monoxide and methane similar to what is observed in reactions of 2 or 7 in the presence of formaldehyde at room temperature. However, acetaldehyde does not react with 2, 7, and 7u at room temperature and reacts over the course of days with heating at 90°C resulting in a small amount of nickel(0) carbonyl species, starting material, and small amounts of decomposition products as denoted by the observation of free ligand by 31P NMR spectroscopy (Scheme 2.33). Due to the lessened reactivity of the acetaldehyde it is probable that the two described mechanisms result in the observed products, as the acetaldehyde can act as a fifth ligand for 4 resulting in the formation...
of the reductive elimination species 7 and alternatively acetaldehyde can react with the hydride to undergo deacylation to form dihydrogen and a nickel(II) acyl complex, which can follow the ascribed pathway and form 10.

**Scheme 2.32 Reactivity of 4 with acetaldehyde**

![Scheme 2.32 Reactivity of 4 with acetaldehyde](image)

**Scheme 2.33 Reactivity of nickel(0) model systems with acetaldehyde**

![Scheme 2.33 Reactivity of nickel(0) model systems with acetaldehyde](image)

**Benzyl Ether**

In an attempt to further study the effect of variation of the ether a ligand containing a benzyl ether in the ipso position was synthesized. Treatment of the ligand with Ni(COD)$_2$ in THF for 25 hours results in the formation of a new species 12. Analysis by $^{31}$P NMR spectroscopy reveals a single resonance at 18.42 ppm which is inconsistent with the aforementioned nickel(0) systems, but similar to a previously reported nickel(II) chloride phenoxide complex (8) which gives a $^{31}$P NMR resonance at 13.45 ppm. By $^1$H NMR spectroscopy the protons on the central aryl ring of the
terphenyl core resonate at 7.15 ppm, which is closer to that of the free ligand indicating the absence of interactions between the central arene and the Ni center. Similarly the benzyl methylene protons are shifted from the doublets centered at 4.43 ppm observed in the free ligand to a triplet at 1.35 ppm, which is similar to resonances for nickel alkyl species. The observation of a triplet for the benzyl methylene protons indicates coupling from the phosphines, suggesting the methylene is interacting with the nickel metal center. This data lead to the assignment of 12 as a Ni(II) benzyl phenoxide complex (Scheme 2.34).

Scheme 2.34 Synthesis of 12 from 1

Gratifyingly, single crystals were grown from diethyl ether at room temperature, which upon preliminary analysis by single crystal x-ray diffraction resulted in the expected 12 structure. In order to further probe this system the reaction of the Benzyl ether ligand over time revealed the presence of another species by $^{31}$P NMR spectroscopy with a phosphorous resonance at 40.60 ppm, which is consistent with the other nickel(0) systems. Due to the weak benzyl oxygen bond this nickel(0) species quickly undergoes oxidative addition to form the isolated nickel(II) species 12. This result is unsurprising, as the benzyl oxygen bond is known to be weaker than the aryl oxygen bond.
**Diaryl Ether**

The need for a $\beta$-hydrogen is essential for the reductive cleavage of alkyl ethers in our nickel(0) model system. The absence of a $\beta$-hydrogen would lead to an inhibition of formation of a nickel(II) hydride and hence no reductive elimination. Investigation of this possibility lead to the synthesis of a terphenyl diphosphine containing an diaryl ether. A diaryl ether variant was synthesized via a coupling of a sufficiently nucleophilic 2,6-diiodophenol with a diaryliodonium triflate salt in the presence of base and following the route outlined in scheme 2.7. The developed synthesis can be used on the diaryl precursor to result in a ligand containing a diaryl ether $^{10}$Ar. Treatment of the terphenyl ligand with Ni(COD)$_2$ at room temperature results in the formation of a new species 13 (Scheme 2.35).

**Scheme 2.35 Synthesis of 13**

Analysis of 13 by $^{31}$P NMR spectroscopy reveals a new peak at 29.73 ppm. Analysis by $^{1}$H NMR spectroscopy reveals a subtle shift in the proton resonance for the central terphenyl ring, from 7.51 ppm in the free ligand to 7.22 ppm for the nickel complex. The subtle shift in the central arene ring and shift of the phosphine resonances leads to the assignment of the nickel complex 13 as a nickel(II) complex where the nickel has undergone oxidative addition to the aryl oxygen bond of the
terphenyl ring resulting in a complex similar to the nickel(II) alkoxide complexes previously synthesized. Treatment of 13 with an equivalent of MeMgBr results in the formation of a nickel(II)-methyl species 14, which is the same nickel(II) complex observed when 3 is treated with MeMgBr, providing further corroboration of the assignment. It was proposed that upon metallation with nickel(0) COD, a nickel(0) complex 15 is formed however this species quickly undergoes oxidative addition to form 13. Indeed analysis of the reaction of 10Ar over time reveals a peak at 41.56 ppm by 31P NMR consistent with a nickel(0) complex. 15 quickly undergoes oxidative addition to form 13 at 20 °C. The rate of oxidative addition is much faster due to the electronics on the phenoxide making it a better leaving group than alkoxides resulting in a weaker aryl ether bond (Scheme 2.36).

**Scheme 2.36 Treatment of 13 with Methyl Grignard**

![Scheme 2.36 Treatment of 13 with Methyl Grignard](image)

The nickel(II) complex 13 was investigated for further reactivity. Heating 13 to 100 °C does not result in any further reactivity. As predicted the lack of a β-hydrogen inhibits further reactivity in the aryl-aryl ether system. However its lack of reactivity makes it perfect for the study of sigma bond metathesis. The treatment of 13 with 4 atm of dihydrogen does not result in any reactivity, neither at 20 °C or when heated to 100 °C. Treating 13 with excess paraformaldehyde also does not result in any observed
reactivity at 20 °C, however upon heating at 100 °C for extended periods of time (72 hours) results in the formation of a small amount of 6. 6 could be formed from 13 from a sigma bond metathesis with formaldehyde to form a phenol and a nickel(II) formyl that can deinsert carbon monoxide and undergo reductive elimination to make 6. This study shows that in our model system although sigma bond metathesis or a sigma bond metathesis like mechanism may be possible it is not kinetically favorable in comparison to $\beta$-H elimination for the formation of the nickel(II) hydride.
**Conclusions:**

In summary, the mechanism of nickel-mediated reductive cleavage of aryl-ethers was investigated. Substrates with pendant phosphines allowed the isolation and characterization of intermediates along the reaction pathway. These intermediates were found to support a mechanism involving nickel(0) coordination to an arene, oxidative addition of the aryl carbon oxygen bond, followed by β-hydride elimination, and aldehyde or ketone-assisted reductive elimination of the aryl-H bond. Dihydrogen (4 atm) does not compete with the above processes. Overall the present studies provide mechanistic snapshots of a transformation of interest in organic methodology and with potential for biomass conversion.
**EXPERIMENTAL SECTION:**

**General considerations:**

Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs’ method. Benzene-$d_6$ was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. Chloroform-$d$ was also purchased from Cambridge Isotope Laboratories and vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 °C for 12 h. 2,6-diiodo-4-nitrophenol, 1,3-diiodo-2-methoxy-5-nitrobenzene, and its isotopolog with a deuterated methoxy ether were synthesized following literature procedures. 2,6-diiodo-4-nitroaniline was purchased from Sigma-Aldrich. All other materials were used as received. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Varian Mercury 300 spectrometer at ambient temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C$\textsubscript{6}$D$\textsubscript{6}$) and 7.26 ppm and 77.16 ppm (CDCl$\textsubscript{3}$) for $^1$H and $^{13}$C NMR data, respectively. $^{31}$P NMR chemical shifts are reported with respect to the instrument solvent lock when a deuterated solvent was used. IR spectra were recorded on a Thermo-Fisher Scientific Nicolet 6700 FT-IR spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon filtering the sample through a plug of silica gel. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high-resolution mass spectrometer. Elemental analysis was conducted by Midwest Microlab, LLC (Indianapolis, IN). In the following complexes, the carbons of the terphenyl backbone are assigned using the following scheme:
2,6-diiodo-4-nitrophenol was synthesized according to a modified literature procedure. A solution of 2,6-diiodo-4-nitrophenol (50.01 g, 359.5 mmol) in MeOH (1 L) was mixed with an aqueous solution (1 L in H₂O) of NaClO₂ (123.64 g, 1.09 mol) and NaI (321.04 g, 2.15 mol) in a 3 L round bottom flask. To this dark purple solution 4.5 equivalents of 12M HCl (120 ml) was added slowly using an addition funnel to prevent the temperature from rising over 35°C. Upon HCl addition the solution quickly became a slurry. The solution was stirred overnight at 20 °C. After the allocated time the slurry was filtered over Celite using a glass frit. The brown solid was eluted with ethyl acetate and washed three times with a saturated solution of sodium metabisulfite. The solvent was removed from the bright yellow organic fraction under vacuum yielding a yellow crystalline powder. Yield: 121.32 g, 86.3% ¹H NMR (d-Acetone, 300 MHz) δ 8.61 (s, 2H, central Ar-H)
1,3-diiodo-2-alkoxy-5-nitrobenzene

The 1,3-diiodo-2-alkoxy-5-nitrobenzene compounds were synthesized using a modified literature procedure for the synthesis of 1,3-diiodo-2-methoxy-5-nitrobenzene. In a 500 ml round bottom flask potassium carbonate (21.69 g, 156.9 mmol) was mixed with 20.13 g (51.5 mmol) 2,6-diiodo-4-nitrophenol in acetone (150 ml). To this slurry 10.5 ml (168.7 mmol) methyl iodide was added to the slurry via syringe. The round bottom was equipped with a reflux condenser and sealed with a septum and heated to 55°C for 12 hours. After 12 hours the solvent was removed from the orange slurry via rotovap. The solid residue was taken up in water and the organics were extracted three times with ethyl acetate (50 ml). The yellow organic fractions were combined and dried with magnesium sulfate. The ethyl acetate was removed by rotovap yielding an orange yellow solid, which smells vaguely of garlic.

1,3-diiodo-2-methoxy-5-nitrobenzene Yield: 19.08 g, 91.5% ¹H NMR (CDCl₃, 300 MHz) δ 8.64 (s, 2H), 3.94 (s, 3H)

1,3-diiodo-2-isopropoxy-5-nitrobenzene Yield: 4.13 g, 52.3% ¹H NMR (CDCl₃, 300 MHz) δ 8.66 (s, 2H), 4.96 (septet, 1H), 1.46 (d, 6H)
1,3-diiodo-2-ethoxy-5-nitrobenzene Yield: 6.23 g, 62.7% 'H NMR (CDCl₃, 300 MHz) δ 8.66 (s, 2H), 4.04 (quartet, 2H), 1.20 (t, 3H)

1,3-diiodo-2-benzyl-5-nitrobenzene Yield: 19.08 g, 91.5% 'H NMR (CDCl₃, 300 MHz) δ 8.16 (s, 2H), 7.53 (d, 2H), 7.24 (t, 2H), 7.19 (t, 1H), 4.67 (s, 2H)

1,3-diiodo-2-phenoxy-5-nitrobenzene

1,3-diiodo-2-(4-nitrophenoxy)-5-tertbutylbenzene was synthesized using a modified literature procedure for the arylation of malonates of diaryl iodonium salts. In a round bottom flask 0.75 g NaOH (18.6 mmol) and 5.00 g 2,6-diido-4-tertbutylphenol (12.4 mmol) were stirred in 20 ml THF. To this slurry was added 7.38 g (15.5 mmol) of the diaryl iodonium triflate salt. This dark brown mixture was heated to 50 °C for one hour. After the allotted time the solvent was removed in vacuo and the residue was dissolved in a 90:10 Hexanes:EtoO mixture. A yellow solid precipitated from solution. The solid was collected via filtration yielding 1,3-diiodo-2-(4-nitrophenoxy)-5-
tertbutylbenzene. Yield: 4.30 g, 66.3% ¹H NMR (CDCl₃, 300 MHz) δ 8.22 (d, 2H), 7.84 (s, 2H), 6.89 (d, 2H), 1.33 (s, 9H)

**1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene**

![Reaction Diagram]

The 1,3-bis(2′-bromophenyl)-2-alkoxy-4-nitrobenzene compounds were synthesized according to the procedure for 1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene. Suzuki coupling conditions were adapted from a previously published procedure.⁶ 1,3-diiodo-2-methoxy-5-nitrobenzene (2.48 g, 6.58 mmol, 1 equiv), 2-bromo-phenylboronic acid (2.77 g, 13.80 mmol, 2.1 equiv), K₂CO₃ (5.46 g, 39.47 mmol, 6 equiv), 140 mL toluene, 40 mL ethanol, and 40 mL water were added to a 500 mL Schlenk tube fitted with a screw-in Teflon stopper. The mixture was degassed by three freeze-pump-thaw cycles, after which Pd(PPh₃)₄ (380 mg, 0.38 mmol, 0.05 equiv) was added as a solid with a counterflow of nitrogen. The reaction vessel was then placed in an oil bath pre-heated to 75°C. After stirring for 6 h, the reaction mixture was allowed to cool to room temperature, concentrated via rotary evaporation and diluted with 200 mL H₂O. The solution was extracted with three portions of CH₂Cl₂. The combined organic fractions were dried over MgSO₄, filtered and concentrated via rotary evaporation. The crude 1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene
was reduced without purification. 1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene

'H NMR (CDCl₃, 300 MHz) δ 8.17 (s, 2H, central Ar-H), 7.71 (d, 2H, Ar-H), 7.40 (m, 4H, Ar-H), 7.30 (d, 2H, Ar-H), 3.27 (s, 3H, OCH₃)

![Chemical structure image]

1,3-bis(2′-bromophenyl)-2-isopropoxy-4-nitrobenzene 'H NMR (CDCl₃, 300 MHz) δ 8.21 (s, 2H, central Ar-H), 7.72 (d, 2H, Ar-H), 7.42 (m, 4H, Ar-H), 7.29 (d, 2H, Ar-H), 3.64 (septet, 1H, OCH(CH₃)₂), 0.68 (d, 6H, OCH(CH₃)₂)

![Chemical structure image]

1,3-bis(2′-bromophenyl)-2-ethoxy-4-nitrobenzene 'H NMR (CDCl₃, 300 MHz) δ 8.18 (s, 2H, central Ar-H), 7.71 (d, 2H, Ar-H), 7.39 (m, 4H, Ar-H), 7.30 (d, 2H, Ar-H), 3.43 (m, 2H, OCH₂CH₃), 0.75 (t, 2H, OCH₂CH₃)

![Chemical structure image]

1,3-bis(2′-bromophenyl)-2-benzyl-4-nitrobenzene 'H NMR (CDCl₃, 300 MHz) δ 8.11 (s, 2H, central Ar-H), 7.38 (m, 2H, Ar-H), 6.80 (m, 9H, Ar-H), 6.57 (d, 2H, Ar-H), 4.30 (dd, 2H, OCH₂Ph)
1,3-bis(2′-bromophenyl)-2-phenoxy-4-nitrobenzene

$\text{H NMR (CDCl}_3, 300 \text{ MHz}) \delta 7.86$ (d, 2H, Ar-$H\beta$), 7.54 (d, 2H, Ar-$H\beta$), 7.44 (d, 2H, Ar-$H\beta$), 7.31 (s, 2H, Ar-$H\beta$), 7.19 (m, 2H, Ar-$H\beta$), 7.09 (m, 2H, Ar-$H\beta$), 6.61 (d, 2H, Ar-$H\beta$), 1.41 (s, 9H, C(CH$_3$)$_3$)

4-amino-1,3-bis(2′-bromophenyl)-2-methoxybenzene was synthesized using a literature procedure$^7$. The crude 4-amino-1,3-bis(2′-bromophenyl)-2-methoxybenzene was methylated without purification. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta 7.65$ (d, 2H, Ar-$H\beta$), 7.36 (m, 4H, Ar-$H\beta$), 7.20 (t, 2H, Ar-$H\beta$), 6.59 (s, 2H, central Ar-$H\beta$), 3.63 (s, 2H, NH$_2$), 3.27 (s, 3H, OCH$_3$)

4-amino-1,3-bis(2′-bromophenyl)-2-isopropoxybenzene

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.66 (d, 2H, Ar-$H\beta$), 7.41 (d, 2H, Ar-$H\beta$), 7.32 (t, 2H, Ar-$H\beta$), 7.18 (t, 2H, Ar-$H\beta$), 6.67 (s, 2H, central Ar-$H\beta$), 3.94 (s, 2H, NH$_2$), 3.38 (septet, 1H, OCH(CH$_3$)$_2$), 0.55 (d, 6H, OCH(CH$_3$)$_2$)
4-amino-1,3-bis(2'-bromophenyl)-2-ethoxybenzene \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.66 (d, 2H, Ar-H), 7.38 (m, 4H, Ar-H), 7.18 (t, 2H, Ar-H), 6.60 (s, 2H, central Ar-H), 3.63 (s, 2H, NH), 3.27 (s, 2H, OCH\(_2\)CH\(_3\)), 0.60 (s, 3H, OCH\(_2\)CH\(_3\))

![Chemical structure](image)

4-amino-1,3-bis(2'-bromophenyl)-2-benzylbenzene \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.78 (d, 2H, Ar-H), 7.52 (m, 4H, Ar-H), 7.31 (t, 2H, Ar-H), 6.90 (m, 3H, Ar-H), 6.73 (t, 1H, Ar-H), 6.31 (s, 2H, central Ar-H), 4.46 (dd, 2H, OCH\(_2\)Ph), 3.64 (br s, 2H, NH)

![Chemical structure](image)

4-amino-1,3-bis(2'-bromophenyl)-2-phenoxybenzene \( ^1 \)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.54 (d, 2H, Ar-H), 7.36 (s, 2H, central Ar-H), 7.31 (d, 2H, Ar-H), 7.18 (t, 2H, Ar-H), 7.07 (t, 2H, Ar-H), 6.28 (m, 4H, Ar-H), 3.26 (br s, 2H, NH), 1.38 (s, 9H, C(CH\(_3\))\(_3\))

![Chemical structure](image)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene was synthesized using a literature procedure\(^8\). The product was purified by Flash chromatography (dichloromethane) and isolated as a colorless solid. 1,3-bis(2'-bromophenyl)-4-
dimethylamino-2-methoxybenzene Yield: 41.9% ¹H NMR (C.D., 399.80 MHz) δ 7.57 (d, 2H, Ar-H), 7.41 (d, 2H, Ar-H), 7.01 (t, 2H, Ar-H), 6.81 (t, 2H, Ar-H), 6.68 (s, 2H, Ar-H), 3.12 (s, 3H, OCH₃), 2.48 (s, 6H, N(CH₃)₂), ¹³C NMR (C.D., 100.54 MHz) δ 146.72 (s, Ar-C), 146.66 (s, Ar-C), 141.21 (s, Ar-C), 135.74 (s, Ar-C), 132.98 (s, Ar-C), 132.31 (s, Ar-C), 128.97 (s, Ar-C), 127.09 (s, Ar-C), 124.54 (s, Ar-C), 115.73 (s, Ar-C), 60.77 (s, O-CH₃), 40.69 (N(CH₃)₂), MS (m/z): calcd, 460.9813 (M⁺); found, 460.9822 (FAB⁺, M⁺).

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-isopropoxybenzene Yield: 37.4% ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (d, 2H, Ar-H), 7.45 (d, 2H, Ar-H), 7.34 (t, 2H, Ar-H), 7.19 (t, 2H, Ar-H), 6.69 (s, 2H, Ar-H), 3.39 (septet, 1H, OCH(CH₃)₂), 2.96 (s, 6H, N(CH₃)₂), 0.59 (d, 6H, OCH(CH₃)₂)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-ethoxybenzene Yield: 41.9% ¹H NMR (CDCl₃, 300 MHz) δ 7.67 (d, 2H, Ar-H), 7.45 (d, 2H, Ar-H), 7.34 (t, 2H, Ar-H), 7.20 (t, 2H, Ar-H), 6.64 (s, 2H, Ar-H), 3.27 (br q, 3H, OCH₂CH₃), 2.95 (s, 6H, N(CH₃)₂), 0.62 (t, 3H, OCH₂CH₃)
1,3-bis(2'-bromophenyl)-4-dimethylamino-2-benzylbenzene  Yield: 41.9%  
\[ \text{H NMR (C.D., 300 MHz)} \delta 7.55 \text{ (d, 2H, Ar-} H) 7.44 \text{ (d, 2H, Ar-} H) 6.92 \text{ (t, 2H, Ar-} H) 6.77 \text{ (t, 2H, Ar-} H) 6.72 \text{ (s, 2H, Ar-} H) 4.50 \text{ (br m, 2H, OCHPh) 2.48 (s, 6H, N(CH}_3)\text{)} \]

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-phenoxybenzene  Yield: 41.9%  
\[ \text{H NMR (C.D., 300 MHz)} \delta 7.55 \text{ (s, 2H, Ar-} H) 7.38 \text{ (d, 4H, Ar-} H) 6.79 \text{ (d, 2H, Ar-} H) 6.57 \text{ (dd, 2H, Ar-} H) 6.20 \text{ (d, 2H, Ar-} H) 2.25 \text{ (s, 6H, N(CH}_3)\text{)} 1.24 \text{ (s, 9H, C(CH}_3)\text{)} \]

1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (1)

In a glovebox a 100 mL Schlenk tube was charged with a colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (50.1 mg, 0.11 mmol) in Et₂O (30 mL) and a stir bar. The Schlenk tube was removed from the glove box and cooled to -78°C in a dry ice/acetone bath. Under N₂, BuLi in pentane (1.5 M, 303.5 μL, 0.46 mmol) was added via syringe slowly to the cold solution. The resulting dark yellow mixture was stirred for one hour at -78°C. After an hour chlorodiisopropylphosphine (36.5 μL, 0.23 mmol) was added to the cold solution.
slowly via syringe. After addition the reaction mixture was allowed to warm to and stir at room temperature for 8 hours. The volatile materials were then removed under vacuum and the pale yellow/white residue was mixed in hexanes and filtered through Celite. The volatiles were removed from the filtrate in vacuo, and the resulting pale yellow/colorless oil was mixed in pentane and stirred with alumina. The mixture was filtered through a bed of alumina and the alumina was rinsed with toluene. Removal of volatile materials under vacuum yielded 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (1) as a white solid (0.68 g, 1.20 mmol) in 92.9% yield. 

Isotopic: 1H NMR (C.D., 300 MHz, 75°C) δ 7.65 (m, 2H, Ar-H), 7.48 (m, 2H, Ar-H), 7.19 (m, 4H, Ar-H), 6.73 (s, 2H, Ar-H), 3.14 (s, 3H, OCH3), 2.65 (s, 6H, N(CH3)2), 2.06 (m, 2H, CH(CH3)2), 1.92 (m, 2H, CH(CH3)2), 1.08 (m, 24H, CH(CH3)2) ppm. 

Isotopic: 13C NMR (C.D., 100.54 MHz) δ 148.52 (m, Ar-C), 147.49 (s, Ar-C), 145.61 (s, Ar-C), 136.85 (d, Ar-C), 136.44 (d, Ar-C), 132.43 (s, Ar-C), 131.68 (d, Ar-C), 128.19 (s, Ar-C), 126.68 (s, Ar-C), 117.41 (s, Ar-C), 60.18 (s, O-CH3), 41.21 (N(CH3)2), 26.79 (CH(CH3)2), 24.96 (CH(CH3)2), 20.83 (CH(CH3)2), 31P ppm. 

Isotopic: 13P NMR (C.D., 121.48 MHz) δ -2.72 (s), -4.09 (s) ppm. MS (m/z): calcd, 535.3133 (M+); found, 535.3134 (FAB+, M+). 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-isopropoxybenzene (1) (0.91 g, 1.61 mmol) in 83.1% yield. 

Isotopic: 1H NMR (C.D., 499.85 MHz, 70°C) δ 7.66 (br s, 2H, Ar-H), 7.49 (d, 2H, Ar-H), 7.20 (t, 2H, Ar-H), 7.15 (t, 2H, Ar-H), 6.70 (s, 2H, Ar-H), 3.76 (septet, 1H, OCH(CH3)2), 2.67 (s, 6H, N(CH3)2), 2.13 (m, 2H, CH(CH3)2) ppm.
1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-ethoxybenzene (1®)

(0.97 g, 1.76 mmol) in 93.9% yield. ¹H NMR (C.D.₆, 499.85 MHz, 75°C) δ 7.54 (m, 2H, Ar-H), 7.48 (m, 2H, Ar-H), 7.15 (m, 4H, Ar-H), 6.68 (s, 2H, Ar-H), 3.39 (s, 3H, OCH₂CH₃), 2.67 (s, 6H, N(CH₃)₂), 1.99 (m, 4H, CH(CH₃)₂), 1.12 (m, 12H, CH(CH₃)₂), 1.01 (m, 12H, CH(CH₃)₂), 0.57 (m, 3H, OCH₂CH₃), ¹³C [¹H] NMR (C.D.₆, 125.70 MHz) δ 148.29 (d, Ar-C), 146.39 (s, Ar-C), 145.11 (s, Ar-C), 136.90 (m, Ar-C), 136.48 (m, Ar-C), 132.04 (s, Ar-C), 131.89 (s, Ar-C), 131.39 (s, Ar-C), 130.76 (s, Ar-C), 128.17 (s, Ar-C), 126.24 (s, Ar-C), 116.96 (s, Ar-C), 116.74 (s, Ar-C), 68.79 (s, OCH₂CH₃), 68.27 (s, OCH₂CH₃), 40.85 (N(CH₃)₂), 26.44 (CH-(CH₃)₂), 25.91 (CH-(CH₃)₂), 24.47 (CH-(CH₃)₂), 20.58 (CH-(CH₃)₂), 20.28 (CH-(CH₃)₂), 19.48 (CH-(CH₃)₂), 15.20 (OCH₂CH₃), ³¹P [¹H] NMR (C.D.₆, 121.48 MHz) δ -2.84 (s), -4.30 (s)
1,3-bis(2’-diisopropylphosphino)-4-dimethylamino-2-benzylbenzene (1°n)

(0.19 g, 0.30 mmol) in 92.9% yield. ¹H NMR (C.D., 300 MHz, 20 °C) δ 7.68 (m, 1H, Ar-H), 7.48 (m, 3H, Ar-H), 7.21 (m, 4H, Ar-H), 6.93 (m, 3H, Ar-H), 6.77 (s, 2H, Ar-H), 6.62 (m, 2H, Ar-H), 4.50 (dd, 2H, OCH2Ph), 2.67 (s, 6H, N(CH3)2), 2.02 (m, 2H, CH(CH3)2), 1.91 (m, 2H, CH(CH3)2), 1.01 (m, 18H, CH(CH3)2), 0.86 (m, 6H, CH(CH3)2), 13C{¹H} NMR (C.D., 125.70 MHz) δ 148.27 (d, Ar-C10), 146.00 (s, Ar-C5), 138.41 (s, Ar-C1), 137.35 (s, Ar-C4), 137.14 (s, Ar-C5), 132.44 (s, Ar-C6-9), 131.89 (s, Ar-C6-9), 131.33 (s, Ar-C6-9), 128.33 (s, OCH2Ph), 128.16 (s, Ar-C), 127.32 (s, OCH2Ph), 126.74 (s, Ar-C), 117.16 (s, Ar-C), 75.29 (s, OCH2Ph), 75.00 (s, OCH2Ph), 41.15 (N(CH3)), 26.82 (CH(CH3)), 26.34 (CH(CH3)), 24.47 (CH(CH3)), 21.14 (CH(CH3)), 20.50 (CH(CH3)), ³¹P{¹H} NMR (C.D., 121.48 MHz) δ -2.67 (s), -4.20 (s)

1,3-bis(2’-diisopropylphosphino)-4-dimethylamino-2-phenoxybenzene (1°m)

(0.53 g, 0.83 mmol) in 92.9% yield. ¹H NMR (C.D., 300 MHz, 70 °C) δ 7.58 (br s, 2H, Ar-H), 7.44 (s, 2H, Ar-H), 7.40 (d, 2H, Ar-H), 7.01 (m, 4H, Ar-H), 6.54 (m, 2H, Ar-H), 6.23 (d, 2H, Ar-H), 2.38 (s, 6H, N(CH3)), 1.94 (br s, 2H, CH(CH3)), 1.39 (s, 3H, C(CH3)), 1.12 (br m, 18H, CH(CH3)), 1.01 (br m, 6H, CH(CH3)) ¹³C{¹H} NMR (C.D., 125.70 MHz) δ 151.82 (s, Ar-C), 150.91 (s, Ar-C), 148.23 (s, Ar-C), 147.39 (s,
Ar-C\textsubscript{6}), 147.07 (s, Ar-C), 146.83 (s, Ar-C), 145.51 (s, OAr), 145.22 (s, OAr), 145.02 (s, OAr), 144.69 (s, Ar-C), 136.60 (s, Ar-C), 136.35 (s, Ar-C), 131.83 (s, Ar-C\textsubscript{6}), 131.45 (s, Ar-C\textsubscript{6}), 130.59 (s, Ar-C\textsubscript{6}), 129.81 (s, Ar-C), 129.61 (s, Ar-C), 127.95 (s, Ar-C\textsubscript{6}), 126.40 (s, Ar-C\textsubscript{6}), 116.96 (s, OAr), 116.22 (s, OAr), 113.89 (s, OAr), 113.64 (s, OAr), 40.84 (Ar-N(CH\textsubscript{3})\textsubscript{2}), 34.24 (C(CH\textsubscript{3})\textsubscript{3}), 31.39 (C(CH\textsubscript{3})\textsubscript{3}), 26.50 (CH-(CH\textsubscript{3})\textsubscript{2}), 25.61 (CH-(CH\textsubscript{3})\textsubscript{2}), 24.43 (CH-(CH\textsubscript{3})\textsubscript{2}), 20.55 (CH-(CH\textsubscript{3})\textsubscript{2}), 19.50 (CH-(CH\textsubscript{3})\textsubscript{2}), $^{31}$P[H] NMR (C\textsubscript{6}D\textsubscript{6}, 121.48 MHz) $\delta$ -2.61 (s), -3.98 (s)

2,6-diiodo-4-trifluoromethylphenol

2,6-diiodo-4-trifluoromethylphenol was synthesized using the same procedure listed for 2,6-diiodo-4-nitrophenol. Yield: 5.32 g, 73.3% $^1$H NMR (CDCl\textsubscript{3}, 300 MHz) $\delta$ 7.92 (s, 2H, central Ar-$H$) $^19$F[H] NMR $\delta$ 61.75

1,3-diiodo-2-methoxy-5-trifluoromethylbenzene

1,3-diiodo-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-diiodo-2-methoxy-5-nitrobenzene. Yield: 4.52 g, 87.0% $^1$H NMR (CDCl\textsubscript{3}, 300 MHz) $\delta$ 8.01 (s, 2H, central Ar-$H$) 3.90 (s, 3H, OCH\textsubscript{3})
1,3-bis(2’-bromophenyl)-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2’-bromophenyl)-2-methoxy-5-nitrobenzene. Yield: 2.31 g, 53.9% \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.49 (s, 2H, central Ar-\(H\)), 7.41 (d, 2H, Ar-\(H\)), 7.00 (d, 2H, Ar-\(H\)), 6.89 (t, 2H, Ar-\(H\)), 6.73 (t, 2H, Ar-\(H\)), 2.94 (s, 3H, OCH\(_3\)) \(^19\)F{\(^1\)H} NMR \(\delta\) 61.31

1,3-bis(2’-diisopropylphosphino)-2-methoxy-5-trifluoromethylbenzene (1\(_{CF3}\))

1,3-bis(2’-2’-diisopropylphosphinophenyl)-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2’-2’-diisopropylphosphinophenyl)-2-methoxy-5-nitrobenzene. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.60 (br m, 2H, Ar-\(H\)), 7.33 (br m, 4H, Ar-\(H\)), 7.12 (br m, 4H, Ar-\(H\)), 6.89 (t, 2H, Ar-\(H\)), 6.73 (t, 2H, Ar-\(H\)), 2.94 (s, 3H, OCH\(_3\)), \(^19\)F{\(^1\)H} NMR \(\delta\) 61.31, \(^{31}\)P{\(^1\)H} NMR \(\delta\) -2.55, -4.24
1,3-diiodo-5-nitrobenzene.

A modified literature procedure was used for the synthesis of 1,3-diiodo-5-nitrobenzene. A solution of 2,6-diiodo-4-nitroaniline in ethanol (5.851 g; 15.0 mmol in 100 ml) was cooled to 0 °C using an ice bath. Upon cooling 8 ml (150 mmol) of concentrated H_2SO_4 was added drop wise over 1 hour using an addition funnel. This slurry was heated to 60 °C and 3.152 g (45.7 mmol) of sodium nitrite was added slowly to the reaction mixture. Upon addition the reaction mixture was heated to 90 °C for 24 hours. After the allocated time the reaction mixture was poured into ice water. The formed yellow solid was filtered off and extracted using water and ethyl acetate. The ethyl acetate fraction was concentrated to dryness to give the desired compound as a yellow solid. Yield 4.045g (71%) \(^1\)H NMR (300 MHz, CDCl_3) \(\delta\) 8.52 (d, 2H, metaAr-H), 8.37 (t, 1H, ipsoAr-H) ppm.

1,3-bis(2'-bromophenyl)-5-nitrobenzene.

1,3-bis(2'-bromophenyl)-5-nitrobenzene was synthesized using the same procedure listed for 1,3-bis(2'-bromophenyl)-2-methoxy-5-nitrobenzene. Yield: 2.48 g (79% yield, 5.22 mmol) of the desired terphenyl dibromide as a white solid. \(^1\)H NMR (CDCl_3, 300
MHz) δ 8.32 (d, 2H, ipso-Ar-H), 7.82 (t, 1H, meta-Ar-H), 7.72 (d, 2H, Ar-H), 7.43 (m, 2H, Ar-H), 7.30 (m, 4H, Ar-H).

1,3-bis(2′-bromophenyl)-5-dimethylaminobenzene.

1,3-bis(2′-bromophenyl)-5-dimethylaminobenzene was synthesized from 1,3-bis(2′-bromophenyl)-5-nitrobenzene using the same procedure that was used for the reduction and amination of 1,3-bis(2′-bromophenyl)-4-dimethylamino-2-methoxybenzene. 1,3-bis(2′-bromophenyl)-5-dimethylaminobenzene was purified by Flash chromatography (dichloromethane) and isolated as a colorless solid. 1H NMR (CDCl3, 300 MHz) δ 7.62 (d, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 7.35 (t, 2H, Ar-H), 7.20 (t, 2H, Ar-H), 6.78 (m, 3H, Ar-H), 3.03 (s, 6H, N(CH3)2.

1,3-bis(2′-diisopropylphosphino)-5-dimethylaminobenzene.

1,3-bis(2′-diisopropylphosphino)-5-dimethylaminobenzene was synthesized using the same procedure listed for 1,3-bis(2′-2′-diisopropyphosphinophenyl)-2-methoxy-5-nitrobenzene. 1H NMR (CDCl3, 300 MHz) δ 7.59 (br m, 2H, Ar-H), 7.47 (br m, 2H, Ar-H), 7.35 (t, 2H, Ar-H), 7.20 (t, 2H, Ar-H), 6.78 (m, 3H, Ar-H), 3.03 (s, 6H, N(CH3)).
N(CH₃)₂), 1.94 (septet, 4H, CH(CH₃)), 1.02 (m, 24H, CH(CH₃)), ¹³C{¹H} NMR (C.D., 125.70 MHz) δ 151.58 (d, Ar-C₁₀), 148.79 (s, Ar-C), 142.65 (s, Ar-C), 135.42 (d, Ar-C), 132.28 (s, Ar-C₁₂), 130.49 (s, Ar-C₁₅), 128.15 (s, Ar-C₁₁), 126.22 (d, Ar-C), 122.04 (d, Ar-C₁₃), 114.66 (d, Ar-C), 40.12 (N(CH₃)₂), 25.02 (CH-(CH₃)₂), 20.26 (CH-(CH₃)₂), 19.85 (CH-(CH₃)₂), ³¹P{¹H} NMR δ -4.62

2,6-diiodo-4-trifluoromethylaniline

A literature procedure was used for the synthesis of 2,6-diiodo-4-trifluoromethylaniline. Yield 4.734 g, 91.7% ¹H NMR (300 MHz, CDCl₃) δ 8.52 (d, 2H, metaAr-H), 4.96 (br s, 2H, NH₂) ppm

1,3-diiodo-3-trifluoromethylbenzene

A literature procedure was used for the synthesis of 1,3-diiodo-5-trifluoromethylbenzene. 0.883 g, 19.3% ¹H NMR (300 MHz, CDCl₃) δ 8.03 (br m, 1H, ipsoAr-H), 7.91 (br m, 2H, Ar-H) ppm
1,3-bis(2'-bromophenyl)-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-bromophenyl)-2-methoxy-5-nitrobenzene. Yield: 0.663 g (66.1% yield, 1.45 mmol) of the desired terphenyl dibromide as a white solid. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.59 (s, 2H, Ar-H), 7.32 (m, 3H, Ar-H), 6.87 (d, 4H, Ar-H), 6.72 (m, 2H, Ar-H). $^{19}$F{$_^1$H} NMR $\delta$ 61.99

1,3-bis(2'-diisopropylphosphinophenyl)-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-diisopropylphosphinophenyl)-2-methoxy-5-nitrobenzene. Yield: 0.710 g (92.4% yield, 1.34 mmol) of the desired terphenyl dibromide as a white solid. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.86 (s, 2H, Ar-H), 7.77 (s, 1H, Ar-H), 7.42 (m, 2H, Ar-H), 7.31 (m, 2H, Ar-H), 7.14 (m, 4H, Ar-H), 1.82 (m, 4H, CH(CH$_3$)), 1.13 (m, 12H, CH(CH$_3$)), 0.88 (m, 12H, CH(CH$_3$)). $^{13}$C{$_^1$H} NMR (C$_6$D$_6$, 125.70 MHz) $\delta$ 150.04 (d, Ar-C$_\alpha$), 143.70 (s, Ar-C), 137.66 (s, Ar-C), 136.14 (d, Ar-C), 133.60 (s, Ar-C$_\alpha$), 131.26 (s, Ar-C$_\alpha$), 129.48 (s, Ar-C$_\alpha$), 128.83 (d, Ar-C), 127.98 (d, Ar-C$_\alpha$), 127.43 (Ar-CF$_3$) 127.08 (d, Ar-C), 25.74 (CH-(CH$_3$)$_2$), 25.62 (CH-}
(CH₃)₂, 21.09 (CH-(CH₃)₂), 20.94 (CH-(CH₃)₂), 20.51 (CH-(CH₃)₂), 20.42 (CH-(CH₃)₂),

"F{¹H} NMR δ 62.03, "P{¹H} NMR δ -5.31

[1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (2)

A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-
methoxybenzene (937.2 mg, 1.74 mmol) in THF (35 ml) was mixed with a yellow
slurry of Ni(COD)₂ (477.7 mg, 1.74 mmol) in THF (5 ml) at RT. The mixture
changed color to dark red and was stirred for 11 hours. Volatiles were removed in
vacuo yielding a dark red solid. The crude solid was taken up in MeCN and filtered
through Celite to remove solids. MeCN was removed from the filtrate under vacuum.
The dark red solid was dissolved in hexanes and cooled to near freezing temperatures
in a liquid nitrogen cooled cold well and filtered through a Celite packed frit. The
hexanes were removed under vacuum yielding a dark red solid. (2) Yield: 872.9 mg,
84.4% "H NMR (C.D₆, 399.80 MHz) δ 7.70 (d, 2H, Ar-H), 7.32 (m, 2H, Ar-H), 7.24
(mm, 4H, Ar-H), 5.84 (t, 2H, Ar-H), 3.17 (s, 3H, OCH₃), 2.58 (s, 6H, N(CH₃)₂),
2.33 (m, 2H, CH(CH₃)₂), 2.04 (m, 2H, CH(CH₃)₂), 1.25 (mm, 6H, CH(CH₃)₂), 1.16
(mm, 12H, CH(CH₃)₂), 1.06 (m, 6H, CH(CH₃)₂) "C{¹H} NMR (C.D₆, 100.54 MHz) δ
151.42 (t, Ar-C), 143.50 (s, Ar-C), 140.43 (t, Ar-C), 130.82 (s, Ar-C), 129.74 (t, Ar-
C), 128.95 (s, Ar-C), 127.11 (s, Ar-C), 115.72 (t, Ar-C), 109.32 (t, Ar-C), 100.69 (t,
Ar-C), 59.55 (s, O-CH), 42.03 (N(CH₃)₂), 27.25 (CH-(CH₃)₂), 21.82 (CH-(CH₃)₂),
20.15 (CH-(CH₃)₂), 20.09 (CH-(CH₃)₂), 19.80 (CH-(CH₃)₂), 19.33 (CH-(CH₃)₂), $^{31}$P{[H]}

NMR (C.D₆, 121.48 MHz) δ 40.65 (s) Anal. Calcd. for C₃₅H₅₁NNiOP₂ (%): C, 67.54; H, 8.26; N, 2.25 Found C, 66.68; H, 8.09; N, 2.26.

$(2^*)$ Yield: 124.3 mg, 56.3% $^1$H NMR (C.D₆, 300 MHz) δ 7.72 (d, 2H, Ar-$H$), 7.31 (m, 2H, Ar-$H$), 7.23 (m, 4H, Ar-$H$), 5.78 (t, 2H, Ar-$H$), 3.89 (septet, 1H, OCH(CH₃)₂), 2.60 (s, 6H, N(CH₃)₂), 2.33 (m, 2H, CH(CH₃)₂), 1.99 (m, 2H, CH(CH₃)₂), 1.25 (mm, 6H, CH(CH₃)₂), 1.16 (mm, 12H, CH(CH₂)₂), 1.06 (m, 6H, CH(CH₃)₂), 0.67 (d, 6H, OCH(CH₃)₂). $^{13}$C{[H]} NMR (C.D₆, 100.54 MHz) δ 151.50 (t, Ar-$C$₁₀), 143.43 (s, Ar-$C$₄), 140.05 (t, Ar-$C$₅), 130.35 (s, Ar-$C$₆), 128.26 (t, Ar-$C$₉), 127.96 (s, Ar-$C$₈), 126.68 (s, Ar-$C$₇), 117.94 (t, Ar-$C$₂), 107.73 (t, Ar-$C$₃), 99.56 (t, Ar-$C$₁), 73.36 (s, O-CH(CH₃)₂), 41.59 (N(CH₃)₂), 27.04 (CH-(CH₃)₂), 23.02 (s, O-CH(CH₃)₂), 21.72 (CH-(CH₃)₂), 20.00 (CH-(CH₃)₂), 19.52 (CH-(CH₃)₂), 19.23 (CH-(CH₃)₂), 18.97 (CH-(CH₃)₂), $^{31}$P{[H]} NMR (C.D₆, 121.48 MHz) δ 39.20 (s) Anal. Calcd. for C₃₅H₅₁NNiOP₂ (%): C, 67.54; H, 8.26; N, 2.25 Found C, 66.68; H, 8.09; N, 2.26.
(2\textsuperscript{p}) Yield: 279.0 mg, 63.0% \textsuperscript{1}H NMR (C.D.\textsubscript{6}, 500 MHz) \( \delta \) 7.70 (d, 2H, Ar-H\textsubscript{2}), 7.31 (m, 2H, Ar-H\textsubscript{2}), 7.23 (mm, 4H, Ar-H\textsubscript{4}), 5.84 (t, 2H, Ar-H\textsubscript{2}), 3.57 (q, 2H, OCHCH\textsubscript{2}), 2.59 (s, 6H, N(CH\textsubscript{3})\textsubscript{2}), 2.35 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}), 2.03 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}), 1.25 (mm, 6H, CH(CH\textsubscript{3})\textsubscript{2}), 1.16 (mm, 12H, CH(CH\textsubscript{3})\textsubscript{2}), 1.06 (m, 6H, CH(CH\textsubscript{3})\textsubscript{2}), 0.50 (t, 3H, OCH\textsubscript{2}CH\textsubscript{3}), \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (C.D\textsubscript{6}, 100.54 MHz) \( \delta \) 151.05 (t, Ar-C\textsubscript{10}), 143.14 (s, Ar-C\textsubscript{4}), 140.01 (t, Ar-C\textsubscript{5}), 130.38 (s, Ar-C\textsubscript{6}), 129.31 (t, Ar-C\textsubscript{9}), 128.43 (s, Ar-C\textsubscript{8}), 126.65 (s, Ar-C\textsubscript{7}), 116.03 (t, Ar-C\textsubscript{2}), 108.57 (t, Ar-C\textsubscript{3}), 99.99 (t, Ar-C\textsubscript{1}), 67.65 (s, OCHCH\textsubscript{3}), 41.65 (N(CH\textsubscript{3})\textsubscript{2}), 26.85 (CH(CH\textsubscript{3})\textsubscript{2}), 21.57 (CH(CH\textsubscript{3})\textsubscript{2}), 19.76 (CH(CH\textsubscript{3})\textsubscript{2}), 18.96 (CH(CH\textsubscript{3})\textsubscript{2}), 15.42 (OCH\textsubscript{2}CH\textsubscript{3}), \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C.D\textsubscript{6}, 121.48 MHz) \( \delta \) 40.57 (s) Anal. Calcd. for C\textsubscript{34}H\textsubscript{49}NNiOP\textsubscript{2} (%): C, 67.12; H, 8.12; N, 2.30 Found C, 65.34; H, 8.46; N, 2.21.

(2\textsubscript{cpr}) Yield: 613.1 mg, 73.7% \textsuperscript{1}H NMR (C.D\textsubscript{6}, 499.85 MHz) \( \delta \) 7.44 (m, 2H, Ar-H\textsubscript{2}), 7.23 (m, 2H, Ar-H\textsubscript{2}), 7.18 (m, 4H, Ar-H\textsubscript{4}), 6.62 (s, 2H, Ar-H\textsubscript{2}), 3.01 (s, 3H, OCH\textsubscript{3}), 2.23 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}), 1.94 (m, 2H, CH(CH\textsubscript{3})\textsubscript{2}), 1.08 (mm, 18H, CH(CH\textsubscript{3})\textsubscript{2}), 0.91 (mm, 6H, CH(CH\textsubscript{3})\textsubscript{2}), \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (C.D\textsubscript{6}, 282.33 MHz) \( \delta \) -61.34 (s), \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C.D\textsubscript{6}, 121.48 MHz) \( \delta \) 41.12 (s) \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (C.D\textsubscript{6}, 125.70 MHz) \( \delta \) 150.14 (t, Ar-C\textsubscript{10}), 138.90 (t, Ar-
C), 130.96 (s, Ar-C), 129.75 (t, Ar-C), 129.68 (s, Ar-C), 128.35 (s, Ar-C), 127.48 (s, Ar-C), 118.89 (s, Ar-C), 117.81 (q, Ar-CF3), 111.29 (s, Ar-C), 99.40 (s, Ar-C), 58.98 (O(CH3)), 27.38 (CH(CH3)2), 21.71 (CH(CH3)2), 19.77 (CH(CH3)2), 19.60 (CH(CH3)2), 19.06 (CH(CH3)2), Anal. Calcd. for C32H41F3NiOP2 (%): C, 62.06; H, 6.67

Yield: 473.8 mg, 84.9%

1H NMR (CD6, 499.85 MHz) δ 7.65 (d, 2H, Ar-H), 7.25 (m, 2H, Ar-H), 7.15 (mm, 4H, Ar-H), 5.82 (s, 2H, Ar-H), 5.37 (s, 1H, Ar-H), 2.59 (s, 6H, N(CH3)2), 2.30 (m, 2H, CH(CH3)2), 2.04 (m, 2H, CH(CH3)2), 1.23 (mm, 6H, CH(CH3)2), 1.16 (mm, 6H, CH(CH3)2), 1.05 (m, 12H, CH(CH3)2), 31P{1H} NMR (CD6, 121.48 MHz) δ 38.55 (s)

13C{1H} NMR (CD6, 125.70 MHz) δ 153.93 (t, Ar-C10), 147.74 (s, Ar-C4), 139.81 (t, Ar-C9), 131.44 (s, Ar-C8), 129.77 (t, Ar-C7), 129.30 (s, Ar-C6), 127.81 (t, Ar-C5), 122.37 (s, Ar-C4), 107.71 (s, Ar-C3), 90.26 (s, Ar-C4), 70.33 (s, Ar-C3), 41.80 (N(CH3)2), 27.76 (CH(CH3)2), 22.32 (CH(CH3)2), 20.66 (CH(CH3)2), 20.55 (CH(CH3)2), 19.94 (CH(CH3)2), Anal. Calcd. for C32H45NNiP2 (%): C, 68.10; H, 8.04; N, 2.48 Found C, 59.35; H, 7.41; N, 2.16
(7a) Yield: 872.9 mg, 84.4% ¹H NMR (C.D., 499.85 MHz) δ 7.35 (d, 2H, Ar-H), 7.18 (m, 2H, Ar-H), 7.12 (mm, 2H, Ar-H), 7.07 (mm, 2H, Ar-H), 6.60 (s, 2H, Ar-H), 4.64 (s, 1H, Ar-H), 2.20 (m, 2H, CH(CH₃)₂), 1.95 (m, 2H, CH(CH₃)₂), 1.07 (mm, 12H, CH(CH₂)₂), 0.94 (mm, 12H, CH(CH₂)₂), ¹³P{¹H} NMR (C.D., 121.48 MHz) δ 41.93 (s) ¹⁹F{¹H} NMR (C.D., 282.33 MHz) δ -62.59 (s) ¹³C{¹H} NMR (C.D., 125.70 MHz) δ 152.33 (t, Ar-C₁₀), 137.92 (t, Ar-C₉), 131.17 (s, Ar-C₅), 129.63 (s, Ar-C₇), 128.84 (t, Ar-C₈), 127.69 (s, Ar-C₆), 125.85 (s, Ar-C₇), 121.32 (q, Ar-Ar-CF₃), 117.49 (s, Ar-C₄), 112.85 (s, Ar-C₃), 63.96 (s, Ar-C₁), 27.22 (t, CH-(CH₃)₂), 21.55 (t, CH-(CH₃)₂), 19.72 (CH-(CH₃)₂), 19.66 (CH-(CH₃)₂), 19.50 (CH-(CH₃)₂), 19.12 (CH-(CH₃)₂) Anal. Calcd. for C₃₁H₃₉F₃NiP₂ (%): C, 63.18; H, 6.67 Found C, 63.12; H, 6.74.

[1,3-bis(2′-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II) methoxide (3)

A dark red solution of purified [1,3-bis(2′-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (105.2 mg, 0.18 mmol) in C₆H₆ was warmed to 45°C in a Schlenk tube. After 14 hours the solvent was removed under vacuum. The resulting red orange solid was washed with pentane and extracted with ether. The ether was
pumped off resulting in an orange solid (3b). Yield: 82.7 mg, 78.6% \(^1\)H NMR (C,D., 399.80 MHz) \(\delta\) 7.76 (d, 2H, Ar-H), 7.44 (d, 2H, Ar-H), 7.37 (t, 2H, Ar-H), 7.17 (t, 2H, Ar-H), 6.78 (s, 2H, Ar-H), 3.67 (s, 3H, OCH), 2.56 (s, 6H, N(CH)\(_3\)), 2.52 (br, 2H, CH(CH)\(_3\)), 1.76 (br, 2H, CH(CH)\(_3\)), 1.66 (br, 6H, CH(CH)\(_3\)), 1.28 (br, 6H, CH(CH)\(_3\)), 0.96 (br, 6H, CH(CH)\(_3\)), 0.80 (br, 6H, CH(CH)\(_3\)) \(^{13}\)C\(^[1\ H]\) NMR (C,D., 100.54 MHz) \(\delta\) 153.23 (t, Ar-C), 150.95 (s, Ar-C), 147.19 (t, Ar-C), 130.26 (s, Ar-C), 129.41 (s, Ar-C), 128.40 (s, Ar-C), 128.35 (s, Ar-C), 126.99 (s, Ar-C), 126.60 (s, Ar-C), 113.59 (s, Ar-C), 54.84 (s, OCH), 40.56 (s, N(CH)\(_3\)), 23.83 (s, CH(CH)\(_3\)), 21.09 (s, CH(CH)\(_3\)), 20.45 (s, CH(CH)\(_3\)), 19.77 (s, CH(CH)\(_3\)), 18.90 (s, CH(CH)\(_3\)), 18.12 (s, CH(CH)\(_3\)). \(^{31}\)P\(^[1\ H]\) NMR (C,D., 161.85 MHz) \(\delta\) 27.26 (s) Anal. Calcd. for C\(_{30}\)H\(_{48}\)NNiOP\(_2\) (%): C, 66.68; H, 7.97; N, 2.36 Found C, 66.60; H, 8.10; N, 2.23.

[1,3-bis(2’-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)hydride (4)

\[\text{[1,3-bis(2’-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)hydride (4)}\]

A dark red solution of crude \[\text{[1,3-bis(2’-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0)}\] (100.1 mg, 0.17 mmol) in THF (10 ml) was stirred at RT for 8 days. Over the course of 8 days a yellow solid precipitated. The solid was collected on a pad of Celite. The solid was extracted from the Celite with toluene. Removal of solvent under vacuum yielded a yellow solid. Yield: 52.3 mg, 55% \(^1\)H NMR (C,D., 300 MHz) \(\delta\) 7.87 (d, 2H, Ar-H), 7.44 (t, 2H, Ar-H), 7.29 (d, 2H, Ar-H),
7.14 (t, 2H, Ar-H), 6.79 (s, 2H, Ar-H), 2.54 (t, 6H, N(CH3)2), 2.27 (br m, 2H, CH(CH3)2), 1.70 (br m, 6H, CH(CH3)2), 1.61 (br m, 2H, CH(CH3)2), 1.28 (mm, 6H, CH(CH3)2), 1.12 (mm, 6H, CH(CH3)2), 0.70 (m, 6H, CH(CH3)2), -2.80 (t, 1H, Ni-H), 13C{1H} NMR (CD2Cl2, 100.54 MHz) δ 152.69 (t, Ar-C10), 150.79 (s, Ar-C4), 147.09 (t, Ar-C5), 130.40 (s, Ar-C7), 129.13 (s, Ar-C9), 128.70 (s, Ar-C2), 128.15 (s, Ar-C6), 126.61 (s, Ar-C8), 126.41 (s, Ar-C1), 114.03 (s, Ar-C), 41.07 (s, N(CH3)2), 24.08 (s, CH(CH3)2), 20.48 (s, CH(CH3)2), 20.34 (s, CH(CH3)2), 20.08 (s, CH(CH3)2), 18.75 (s, CH(CH3)2), 18.08 (s, CH(CH3)2), 31P{1H} NMR (C6D6, 121.48 MHz) δ 30.41 (s) Anal. Calcd. for C32H45NNiP2 (%): C, 68.10; H, 8.04; N, 2.48 Found. C, 67.63; H, 7.85; N, 2.05

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)iodide (5)

A yellow solution of [1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)hydride (35.3 mg, 0.063 mmol) was made in THF (7 ml). To this solution was added dry methyl iodide (28.5 mg, 0.20 mmol) at room temperature. The solution was stirred for 14 hours at room temperature in the dark. After 14 hours the volatiles were removed under vacuum leaving a red orange residue. The residue was washed with hexanes and extracted with ether. The ether was removed under vacuum yielding a red orange solid. X-ray quality crystals were grown from a concentrated solution in ether. Yield: 27.4 mg, 63.5% 1H NMR (C6D6, 399.80 MHz)
MHz) δ 7.72 (d, 2H, Ar-H), 7.40 (d, 2H, Ar-H), 7.37 (t, 2H, Ar-H), 7.13 (t, 2H, Ar-H), 6.78 (s, 2H, Ar-H), 3.03 (m, 2H, CH(CH₃)₂), 2.52 (m, 6H, N(CH₃)₂), 1.77 (m, 2H, CH(CH₃)₂), 1.51 (q, 6H, CH(CH₃)₂), 1.31 (m, 6H, CH(CH₃)₂), 0.91 (m, 6H, CH(CH₃)₂), 0.77 (m, 6H, CH(CH₃)₂), ²³C[¹H] NMR (C₆D₆, 100.54 MHz), δ 151.38 (t, Ar-C₁₀), 151.20 (s, Ar-C₄), 146.92 (t, Ar-C₅), 130.39 (s, Ar-C₈), 129.78 (t, Ar-C₉), 127.98 (s, Ar-C₁₂), 127.95 (s, Ar-C₁₂), 127.16 (s, Ar-C₁₂), 126.19 (t, Ar-C₁₂), 113.86 (t, Ar-C₁₂), 40.28 (N(CH₃)₂), 24.29 (CH-(CH₃)₂), 23.59 (CH-(CH₃)₂), 20.55 (CH-(CH₃)₂), 20.21 (CH-(CH₃)₂), 19.39 (CH-(CH₃)₂), 18.91 (CH-(CH₃)₂), ³¹P[¹H] NMR (C₆D₆, 121.48 MHz) δ 34.35 (s) Anal. Calcd. for C₃₂H₄₄NNiP₂ (%): C, 58.01; H, 6.51; N, 1.90 Found. C, 58.23; H, 6.62; N, 2.00

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminobenzenel]nickel(0)carbonyl (6)

A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzenel]nickel(0) (96.9 mg, 0.16 mmol) in toluene was heated to 100 °C in a sealed Schlenk tube. The tube was heated for 2.5 hours. After 2.5 hours the solvent was removed under vacuum giving an orange solid. The solid was washed with hexanes and dried under vacuum yielding a red orange solid. Yield: 83.8 mg, 86.7% ¹H NMR (C₆D₆, 399.80 MHz) δ 7.49 (br m, 2H, Ar-H), 7.44 (br m, 2H, Ar-H), 7.18 (m, 4H, Ar-H), 6.56 (s, 2H, Ar-H), 6.51 (t, 1H, Ar-H), 2.65 (s, 6H, N(CH₃)₂), 2.40 (m, 2H, CH(CH₃)₂), 2.18 (m, 2H, CH(CH₃)₂), 1.24 (q, 6H, CH(CH₃)₂), 1.16 (q, 6H,
CH(CH₃)₂), 1.10 (q, 6H, CH(CH₃)₂), 1.02 (q, 6H, CH(CH₃)₂) ¹³C{¹H} NMR (C.D., 100.54 MHz) δ 195.98 (t, Ni-CO), 152.54 (s, Ar-C), 151.06 (t, Ar-C), 145.58 (s, Ar-C), 136.50 (t, Ar-C), 131.26 (s, Ar-C), 130.81 (s, Ar-C), 128.90 (s, Ar-C), 127.29 (s, Ar-C), 110.03 (s, Ar-C), 84.65 (s, Ar-C), 40.68 (N(CH₃)₂), 29.44 (CH(CH₃)₂), 26.79 (CH(CH₃)₂), 20.40 (CH(CH₃)₂), 19.62 (CH(CH₃)₂), 18.90 (CH(CH₃)₂), 18.60 (CH(CH₃)₂) ³¹P{¹H} NMR (C.D., 121.48 MHz) δ 34.17 (s) EA Calcd. C, 66.91; H, 7.66; N, 2.36 Found. C, 67.13; H, 7.67; N, 2.38 IR (C.D.): νCO = 1917 cm⁻¹.

General Synthesis of Nickel(II) Phenoxide Halide Systems (8)

To a colorless solution of 1 in THF is added a slurry of NiX₂ in THF. Upon mixing the solution develops a deep green color over time. The solution was allowed to stir overnight. After the allotted time the solvent was removed under vacuum resulting in a dark green solid. The dark green solid was rinsed with Et₂O and Hexanes resulting in pure 8 as a dark green solid. Yield: 72% ¹H NMR (C.D., 500 MHz) δ 7.22 (br m, 4H, Ar-H), 7.05 (s, 2H, Ar-H), 6.99 (m, 4H, Ar-H), 2.75 (s, 6H, N(CH₃)₂), 2.57 (m, 2H, CH(CH₃)₂), 2.12 (m, 2H, CH(CH₃)₂), 1.83 (m, 12H, Ar-C), 1.19 (m, 6H, CH(CH₃)₂), 0.66 (m, 6H, CH(CH₃)₂) ¹³C{¹H} NMR (C.D., 100.54 MHz) δ 147.15 (t, Ar-C), 134.71 (s, Ar-C), 132.85 (s, Ar-C), 130.79 (s, Ar-C), 128.19 (s, Ar-C), 124.90 (s, Ar-C), 122.73 (t, Ar-C), 119.04 (s, Ar-C), 42.22 (N(CH₃)₂), 22.85 (CH(CH₃)₂), 20.83 (CH(CH₃)₂), 19.23 (CH(CH₃)₂), 19.04 (CH(CH₃)₂), 18.55 (CH(CH₃)₂), 14.88 (CH-
(CH₃)$_2$, $^{31}$P[¹H] NMR (C.D₆, 121.48 MHz) δ 13.60 (s) Anal. Calcd. for C₃₂H₄₄ClNNiOP₂ (%): C, 62.52; H, 7.21; N, 2.28 Found C, 60.76; H, 7.10; N, 2.08.

**General Synthesis of Nickel(I) Systems (9)**

To a dark red solution of 2 in THF is added a slurry of oxidant in THF. Upon mixing the solution lightens to a yellow color over time. The solution was stirred overnight. After the allotted time the solvent was removed under vacuum resulting in a dark yellow residue. The yellow solid was rinsed with Et₂O and Hexanes resulting in 9 as a pale yellow solid. Paramagnetically broadened peaks are observed in the $^1$H and $^{31}$P NMR spectra of these compounds. Anal. Calcd. for C₃₄H₄₇ClNNiO₂P₂ (9) (%): C, 62.93; H, 7.52; N, 2.22 Found C, 62.23; H, 7.35; N, 2.12. Anal. Calcd. for C₃₄H₄₇F₃NNiO₄P₂ (9OTf) (%): C, 54.93; H, 6.37; N, 1.88 Found C, 52.54; H, 6.46; N, 1.81.
A dark red solution of crude \[1,3\text{-bis}(2'\text{-diisopropylphosphino})\text{-}4\text{-dimethylamino}\text{-}2\text{-methylbenzene}]\text{nickel}(0) (100.1 \text{ mg, 0.17 mmol}) in toluene was treated with 10 equivalents of MeMgBr and heated to 90 °C in a sealed Schlenk. The tube was heated for 36 hours. After 36 hours the solvent was removed under vacuum giving a dark red solid. The solid was triterated with pentanes and hexanes to precipitate excess Grignard reagent. The resulting slurry was filtered through Celite. 10 was obtained from the elute as a dark red solid. Yield: 52.4 mg, 53.3% \(^1\text{H} \text{NMR} \text{ (C.D}_6, 300 \text{ MHz}) \, \delta \, 7.62 \text{ (br m, 2H, Ar-}H_\text{)}, 7.24 \text{ (br m, 2H, Ar-}H_\text{)}, 7.20 \text{ (m, 4H, Ar-}H_\text{)}, 5.80 \text{ (s, 2H, Ar-}H_\text{)}, 2.60 \text{ (s, 6H, N(CH}_3)_2\text{)}, 2.26 \text{ (m, 2H, CH(CH}_3)_2\text{)}, 1.98 \text{ (m, 2H, CH(CH}_3)_2\text{)}, 1.52 \text{ (s, 3H, Ar-CH\text{)}, 1.12 \text{ (m, 24H, CH(CH}_3)_2\text{); }^{31}\text{P}[^1\text{H}] \text{NMR} \text{ (C.D}_6, 121.48 \text{ MHz}) \, \delta \, 36.83 \text{ (s)}}
[1,3-bis(2′-diisopropylphosphino)-4-dimethylamino-2-methylbenzene]nickel(0)carbonyl (11)

Method A: To a yellow solution of 4 (12.3 mg, 0.022 mmol) in benzene was added 10 equivalents of acetaldehyde. The solution was heated to 90 °C for 24 hours. After 24 hours the excess acetaldehyde was removed resulting in 11 as a red orange solid.

Method B: A dark red solution of 8 (32.9 mg, 0.057 mmol) in toluene was treated with 5 equivalents of paraformaldehyde (8.7 mg, 0.29 mmol). The solution was mixed at room temperature for 11 hours. After 11 hours the solvent was removed in vacuo and the residue was filtered through Celite with hexanes. The solvent was removed from the organic fraction yielding 11 as a red orange solid. Yield: 30.9 mg, 89.8%

\( \text{H NMR (C}_6\text{H}_6, 300 \text{ MHz)} \delta 7.44 \text{ (br m, 2H, Ar-} H\text{), } 7.37 \text{ (br m, 2H, Ar-} H\text{), } 7.20 \text{ (m, 4H, Ar-} H\text{), } 6.62 \text{ (s, 2H, Ar-} H\text{), } 2.72 \text{ (s, 6H, N(CH}_3\text{)\textsubscript{2}}\text{), } 2.42 \text{ (m, 2H, C}H\text{(CH}_3\text{)\textsubscript{2}}\text{), } 2.02 \text{ (m, 2H, C}H\text{(CH}_3\text{)\textsubscript{2}}\text{), } 1.66 \text{ (s, 3H, Ar-} C\text{H), } 1.08 \text{ (m, 24H, C}H\text{(CH}_3\text{)\textsubscript{2}}\text{), } ^{31}\text{P}\{\text{H} \text{ NMR (C}_6\text{H}_6, 121.48 \text{ MHz)} \delta 35.90 \text{ (s)} \)
A colorless solution of 1,3-bis(2’-diisopropylphosphino)-4-dimethylaminophenoxide|nickel(II)benzyl (12) benzylxybenzene (114.6 mg, 0.187 mmol) in THF (10 ml) was mixed with a yellow slurry of Ni(COD)$_2$ (48.9 mg, .178 mmol) in THF (2.5 ml) at RT. The mixture changed color to dark red and was stirred for 11 hours. Volatiles were removed in vacuo yielding a dark red purple solid. The crude solid was washed with hexanes and Et$_2$O yielding a purple red solid. Crystals were grown from a concentrated solution in Et$_2$O at 20 °C. (12) Yield: 103.9 mg, 82.9%  $^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$ 7.74 (d, 2H, Ar-H), 7.24 (m, 2H, Ar-H), 7.20 (mm, 2H, Ar-H), 7.15 (s, 2H, Ar-H), 7.04 (mm, 2H, Ar-H), 2.93 (s, 6H, N(CH$_3$)$_2$), 2.30 (m, 2H, CH(CH$_3$)$_2$), 1.88 (m, 2H, CH(CH$_3$)$_2$), 1.72 (mm, 6H, CH(CH$_3$)$_2$), 1.63 (mm, 6H, CH(CH$_3$)$_2$), 1.35 (mm, 2H, CH$_2$Ph) 0.71 (mm, 6H, CH(CH$_3$)$_2$), 0.36 (m, 6H, CH(CH$_3$)$_2$) $^{31}$C{$^1$H} NMR (C$_6$D$_6$, 100.54 MHz) $\delta$ 148.02 (t, Ar-C$_{10}$), 144.27 (s, Ar-C$_4$), 139.69 (t, Ar-C$_5$), 134.04 (s, Ar), 132.37 (s, Ar), 131.96 (s, Ar), 129.98 (s, Ar-C$_9$), 126.82 (s, Ar-C$_6$), 125.73 (t, Ar-C$_8$), 124.51 (s, Ar-C), 123.60 (s, Ar-C), 122.62 (s, Ar-C), 42.05 (N(CH$_3$)$_2$), 23.68 (CH-(CH$_3$)$_2$), 20.60 (CH-(CH$_3$)$_2$), 19.40 (CH-(CH$_3$)$_2$), 19.06 (CH-(CH$_3$)$_2$), 18.18 (CH-(CH$_3$)$_2$), 16.02 (CH-(CH$_3$)$_2$), -0.04 (t, CH$_2$-Ar), $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 121.48 MHz) $\delta$ 18.42 (s) Anal. Calcd. for C$_{39}$H$_{51}$NNiOP$_2$ (%): C, 69.86; H, 7.67; N, 2.09 Found C, 69.62; H, 7.49; N, 1.96.
[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)phenoxy (13)

A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-phenoxybenzene (110.5 mg, 0.17 mmol) in THF (5 ml) was mixed with a yellow slurry of Ni(COD)₂ (46.8 mg, .17 mmol) in THF (2.5 ml) at RT. The mixture changed color to orange and was stirred for 13 hours. Volatiles were removed in vacuo yielding an orange solid. The crude solid was washed with hexanes and Et₂O yielding an orange solid. (13) Yield: 116.3 mg, 97.8%

H NMR (C₆D₆, 300 MHz) δ 7.73 (d, 2H, Ar-H), 7.40 (m, 2H, Ar-H), 7.26 (mm, 2H, Ar-H), 7.23 (s, 2H, Ar-H), 7.14 (mm, 2H, Ar-H), 6.98 (mm, 2H, Ar-H), 6.78 (mm, 2H, Ar-H), 2.66 (s, 6H, N(CH₃)₂), 2.16 (m, 2H, CH(CH₃)₂), 1.56 (m, 2H, CH(CH₃)₂), 1.46 (mm, 6H, CH(CH₃)₂), 1.23 (mm, 9H, C(CH₃)₃), 0.85 (mm, 12H, CH(CH₃)₂) 0.68 (mm, 6H, CH(CH₃)₂), ³¹C[¹H] NMR (C-D₆, 100.54 MHz), δ 163.17 (Ar-C), 152.11 (t, Ar-C'), 149.13 (s, Ar-C), 147.01 (t, Ar-C), 140.07 (Ar-C), 130.29 (s, Ar-C), 129.52 (s, Ar-C), 127.47 (s, Ar-C), 126.54 (s, Ar-C), 126.12 (t, Ar-C), 124.07 (t, Ar-C), 119.87 (s, Ar-C), 117.16 (s, Ar-C), 43.32 (N(CH₃)₂), 33.77 (C(CH₃)₂), 31.14 (C(CH₃)₂), 22.94 (CH-(CH₃)₂), 20.50 (CH-(CH₃)₂), 20.02 (CH-(CH₃)₂), 18.77 (CH-(CH₃)₂), 18.58 (CH-(CH₃)₂), 17.54 (CH-(CH₃)₂), ³¹P[¹H] NMR (C-D₆, 121.48 MHz) δ 29.74 (s) Anal. Calcd. for C₄₂H₅₇NNiOP₂ (%): C, 70.80; H, 8.06; N, 1.97 Found C, 70.95; H, 7.98; N, 1.96.
A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (50.1 mg, 0.08 mmol) in toluene was treated with 10 equivalents of MeMgBr and heated to 90 °C in a sealed Schlenk. The tube was heated for 2 hours. After 2 hours the solvent was removed under vacuum giving a orange red solid. The solid was triterated with pentanes and hexanes to precipitate excess Grignard reagent. The resulting slurry was filtered through Celite. (12) was obtained from the elute as a yellow solid. Yield: 39.8 mg, 86.2% 

\[ ^1H \text{ NMR (C.D., 300 MHz)} \delta 7.74 \text{ (br d, 2H, Ar-}H\text{)}, 7.34 \text{ (br d, 2H, Ar-}H\text{), 7.24 \text{ (m, 2H, Ar-}H\text{), 7.10 \text{ (m, 2H, Ar-}H\text{),} 6.92 \text{ (m, 2H, Ar-}H\text{), 2.61 \text{ (s, 6H, N(CH}_3)_2\text{),} 2.46 \text{ (m, 2H, CH(CH}_3)_2\text{),} 1.92 \text{ (m, 2H, CH(CH}_3)_2\text{),} 1.05 \text{ (s, 24H, CH(CH}_3)_2\text{),} 0.36 \text{ (t, 3H, CH}_3\text{),} ^{31}C\{^1H\} \text{ NMR (CD}_2\text{Cl}_2\text,, 100.54 MHz)} \delta 152.12 \text{ (t, Ar-C}_1\text{), 150.57 \text{ (s, Ar-C}_4\text{), 147.49 \text{ (t, Ar-C}_5\text{), 129.42 \text{ (s, Ar-C}_7\text{), 128.42 \text{ (s, Ar-C}_9\text{), 127.78 \text{ (s, Ar-C}_2\text{), 126.79 \text{ (s, Ar-C}_6\text{), 125.83 \text{ (s, Ar-C}_8\text{), 126.41 \text{ (s, Ar-C}_1\text{), 112.99 \text{ (s, Ar-C}_3\text{), 40.88 \text{ (s, N(CH}_3)_2\text{), 23.13 \text{ (s, CH(CH}_3)_2\text{), 19.97 \text{ (s, CH(CH}_3)_2\text{), 18.57 \text{ (s, CH(CH}_3)_2\text{),} -18.20 \text{ (s, Ni-}CH\text{),} ^{31}P\{^1H\} \text{ NMR (C.D., 121.48 MHz)} \delta 44.51 \text{ (s)}}

\text{Anal. Calcd. for C}_{33}H_{47}NNiP_2 \text{ (%): C, 68.53; H, 8.19; N, 2.42 Found C, 68.33; H, 8.35; N, 2.15.}
Table 2.X. Crystal and refinement data for complexes 2, 5 and 8.

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*R₁ = ∑ ||Fo| - |Fc|| / ∑ |Fo|, wR₂ = [∑ [w(Fo² - Fc²)]² / ∑ [w(Fo²)]²]¹/².*
REFERENCES


Reaction of 1 with Ni(II) reagents results in stoichiometric cleavage of the ArO-CH₃ bond. Investigations of this transformation will be reported in a future manuscript.


CHAPTER 3

EXAMINATION OF THE EFFECT OF ARENE ELECTRONICS ON ARYL-OXYGEN BOND ACTIVATION IN CATALYTIC AND MODEL NICKEL(0) DIPHOSPHINE SYSTEMS
ABSTRACT

Studies of the kinetics of oxidative addition using a series of nickel(0) (diphosphine)aryl methyl ether complexes with electron donating and withdrawing groups were undertaken. The observed rates and activation parameters for aryl-oxygen bond activation were found to be independent of the electronics of the ring the metal is coordinated to. The rate was found to depend on the electronics of the leaving alkoxide. The lack of variation with electronics in the model system is believed to be due to the simultaneous stabilization of the ground state and oxidative addition transition state. Relative rates for the cross coupling of anisoles with the Ni(II)(PCy$_3$)$_2$Cl$_2$ catalytic system were obtained for para-substituted anisoles for comparison to the stoichiometric system. Anisoles containing electron-withdrawing groups were found to be cleaved faster than those containing electron-donating groups in the catalytic system. The difference in rates was attributed to the differences in the strength of the nickel arene interactions. This was corroborated with equilibrium studies with substituted arenes.
**Introduction:**

Functionalization of the aryl carbon oxygen bonds has emerged as a versatile synthetic tool in organic methodology as phenol precursors are readily available and synthetic modification of the aromatic ring is facile.\(^1\) Aryl carbon oxygen bonds, however, are strong and difficult to activate. Nickel based catalysts have been shown to be versatile in the cleavage of aryl carbon oxygen bonds in a variety of different moieties.\(^{1-8}\) The cleavage of the aryl carbon oxygen bond can be followed by the coupling of the substrate with a variety of cross-coupling partners.\(^{1,3,7,9}\) While the mechanism of palladium cross-coupling have been studied extensively, fewer mechanistic studies have been carried out on nickel catalyzed cross coupling systems.\(^{10-13}\) It is imperative to carry out such studies as nickel and palladium, while both group 10 metals have different reactivity profiles. For example, the smaller more nucleophilic nickel center more readily harnesses phenol-derived and less reactive electrophiles in cross coupling. Furthermore, nickel centers undergo such reactions using less exotic ligands than the palladium counterparts, in some cases ligand free conditions can be used.\(^1\) These factors, combined with its low cost, make nickel an ideal metal for cross coupling and activation of aryl reagents.\(^1\) Detailed mechanistic studies of nickel catalyzed aryl carbon oxygen bond activation will result in the design of better catalysts for said activation, which, as fore mentioned, is important for organic methodology and for other applications such as biomass conversion as Hartwig demonstrated.\(^11\)

Previously we reported a nickel(0) meta-terphenyl diphosphine complex containing an aryl ether functionality on the ipso carbon of the central aryl ring. Using this system it was shown that with heating the Ni center was able to undergo a subsequent oxidative addition, followed by a beta-hydrogen elimination, and an assisted reductive elimination
and decarbonylation. As this system undergoes several steps important to nickel aryl carbon oxygen bond activation relevant to cross-coupling and biomass conversion, studies of the oxidative addition were undertaken using this nickel model system. Herein is described the stoichiometric oxidative addition studies as well as the efforts to compare the model studies with data obtained from nickel catalysts.
RESULTS & DISCUSSION:

Our previously described series of nickel(0) model system, which undergoes a stoichiometric intramolecular reductive cleavage of an aryl oxygen bond, provides an ideal scaffold to study nickel facilitated oxidative addition. Variation of the electronics of the terphenyl backbone can make the observed oxidative addition similar to the activation of substrates with varying aryl electronics. To this end several nickel(0) complexes were synthesized containing different functional groups on the central arene, para to the ipso methyl ether. The functional groups were selected to cover the range of the Hammett parameters with the dimethyl amino group being the most electron donating group (EDG) and trifluoromethyl being the most electron withdrawing group (EWG) (Table 1).

Table 3.1 Hammett parameters and carbonyl stretching frequencies of 16, 16_{tBu}, and 16_{CF3}

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<th>R</th>
<th>NMe₂</th>
<th>t-Bu</th>
<th>CF₃</th>
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<td>σₚ</td>
<td>-0.83</td>
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<tr>
<td>ν_{CO} (cm⁻¹)</td>
<td>1912</td>
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The EDG and EWG on the central arene should modulate the strength of the metal arene interaction as a more electron deficient ring should have a stronger metal arene interaction. In order to probe the effect of the electronics on the central arene ring the carbonyl complexes 16, 16_{tBu}, and 16_{CF3} were synthesized. The carbonyl
stretching frequency will give a measure of the strength of the nickel arene interaction. The carbonyl complexes were synthesized through the decarbonylation of paraformaldehyde by the nickel(0) terphenyl diphosphines \( \text{2, 2}_{\text{tBu}} \) and \( \text{2}_{\text{CF3}} \) in THF. The rates of decarbonylation in \( \text{2, 2}_{\text{tBu}} \) and \( \text{2}_{\text{CF3}} \) varied with the electronics, with \( \text{NMe}_2 \) being much faster than \( \text{CF}_{3} \). Measuring the carbonyl stretching frequencies of the three nickel variants by IR spectroscopy gave the stretching frequencies listed in table 3.1.

A low carbonyl stretching frequency is indicative of backbonding between the metal and carbonyl. Backbonding occurs between the metal and the \( \pi^* \)-orbital of the C-O bond. Donation into this orbital leads to a weakening of the C-O bond and a strengthening of the M-C bond. Similarly the metal binds to the central arene through donation of electron density into the \( \pi^* \)-orbital of the central arene ring which leads to an elongation of the central arene bond the metal interacts with. As \( \sigma_p \) of the arene increases \( \nu_{\text{CO}} \) increases, which is consistent with less backbonding between the metal and the carbonyl and more backbonding to the arene. The backbonding gives an estimate of the metal arene interaction as a stronger interaction leads to a higher \( \nu_{\text{CO}} \) closer to the stretch of free CO (\( \nu_{\text{CO}} \approx 2143 \text{ cm}^{-1} \)). The stretching frequencies for the \( \text{NMe}_2 \) and t-Bu variants are quite low, indicative of a weaker nickel arene interaction. The \( \nu_{\text{CO}} \) stretching frequencies are also very similar (1912 vs. 1919 cm\(^{-1} \)) although the Hammett parameters of the two are vastly different (\( \sigma_p \Delta \approx -0.63 \)). Substitution of a trifluoromethyl group in the central ring as in \( \text{16}_{\text{CF3}} \) leads to a stronger nickel arene interaction and conversely a stronger \( \nu_{\text{CO}} \) (1943 cm\(^{-1} \)).

The kinetics of oxidative addition in these model systems was investigated. The kinetics are believed to be first order as the observed reaction is \( \text{2} \) going to \( \text{3} \) (Scheme
3.1. 2 was dissolved in d-benzene and heated to 45 °C in a J-Young tube. The decay of 2 to 3 was monitored by 1H NMR spectroscopy. Under the described conditions the oxidative addition of the nickel undergoes three half-lives in ca. 14 hours. At 45°C the observed rate of oxidative addition in 2 was found to be 2.09 ± 0.05 min⁻¹, while the $k_{obs}$ for 2tBu was 2.38 ± 0.05 min⁻¹. While the oxidative addition in 2 and 2tBu was facile at 45 °C, oxidative addition was too slow in 2CF₃. The kinetic studies for the oxidative addition in the 2 and 2tBu suggest that there is little difference between the measured rates.

Scheme 3.1 Oxidative addition in the nickel(0) model system 2

Attempts were also made to study the rate of oxidative addition at higher temperatures. At 80°C the $k_{obs}$ of oxidative addition in 2 was found to be 83 ± 2 min⁻¹ while the rates for 2tBu and 2CF₃ were found to be 72.3 ± 0.4 min⁻¹ and 18.3 ± 0.2 min⁻¹ respectively. The oxidative addition at 80°C is about 30 times faster than the determined rates at 45°C and the oxidative addition is complete after ca. 40 minutes. After collecting data on the oxidative addition at 45°C and 80°C, an attempt was made to perform a similar 1H NMR kinetic analysis at 60°C. At 60°C, however, during the course of the oxidative addition significant impurities were detected. Analysis of the 31P NMR spectrum collected after the depletion of 2 shows several phosphorus peaks of
unknown identity. In the $^{31}$P NMR spectrum peaks, are observed at 38.59, 36.26, 34.15, 30.92, and finally 27.24 ppm (Figure 1). The peaks at 34.15 and 27.24 ppm correspond to 6 and the 3 respectively. The peak at 38.59 ppm corresponds to complex 7 while the peak at 30.92 ppm is assigned to a nickel(II) chloride, which is a decomposition product of the hydride in dichloromethane. The identity of the species that produces the peak at 36.26 ppm in the $^{31}$P NMR spectrum was found to be the nickel(0)-carbonyl complex 16 by independent synthesis (Scheme 3.2).

![Figure 3.1: $^{31}$P{H} NMR spectrum of the products of 2 at 60°C. 27.23 ppm is 3, 30.92 ppm possible nickel(II) chloride impurity, 34.15 ppm 6, 36.26 ppm 16, and 38.58 ppm is the reductive elimination product of the Ni(II) hydride 7.](image-url)
Previously the only reactivity of the nickel(0) diphosphine terphenyl species observed was the described intramolecular oxidative addition. However, \( \mathbf{2} \), at room temperature, can react with formaldehyde to undergo decarbonylation to form complex \( \mathbf{16} \) (Scheme 3.2). Examination of the \(^1H\) NMR for \( \mathbf{16} \) gives a spectrum similar to \( \mathbf{6} \) albeit with an indicative peak at 2.57 ppm, which is identified as the methoxy peak by integration. Both nickel(0)-carbonyl complexes show central aryl ring resonances at similar chemical shifts (6.58 ppm for \( \mathbf{16} \) vs. 6.52 ppm for \( \mathbf{6} \)). IR spectroscopy analysis of the \( \mathbf{16} \) reveals a stretching frequency of 1912 cm\(^{-1}\), which was confirmed by independent synthesis (Table 3.1). This stretching frequency is in the range of \( \mathbf{6} \) and \( \mathbf{6}_{\text{Bu}} \) (1917 cm\(^{-1}\) and 1929 cm\(^{-1}\) respectively) albeit lower as an increase in backbonding from the Ni center to the CO is consistent with a more electron rich central arene \textit{vide supra}. \( \mathbf{16} \) is quite stable at the temperatures of the kinetic experiments (no change by \(^{31}P\) and \(^1H\) NMR spectroscopy after 9 days at 80°C). Decarbonylation of formaldehyde by \( \mathbf{2} \) is concerning, as the reaction of \( \mathbf{2} \) will increase the observed rate for the oxidative addition, as \( \mathbf{2} \) is participating in two different reactions.

Interestingly, the reaction of the Ni\(^0\) at 45°C or 80°C produces little of the \( \mathbf{16} \) impurity. Close analysis of the \(^{31}P\) NMR spectra of the reaction at 45°C reveals the
formation of a small amount of the nickel(II) hydride 4 and 16 and minuscule amounts of 7. Only 16 affects the rate of oxidative addition as it is the only impurity derived from the 2. The concentration of 16 in solution is miniscule in comparison to the remaining 1 starting material and the oxidative addition product 3. Similarly at 80°C few impurities are generated and the end product is 6. It is interesting how the interplay of the relative rates of oxidative addition and the beta-hydrogen elimination allow for the relatively clean reactions at 45°C and 80°C and a messy reaction at 60°C. At 45°C the rate of beta-hydrogen elimination is apparently slow compared to oxidative addition thus hindering the formation of 16. Increasing the temperature to 80°C drastically increases the rate of oxidative addition which becomes much faster than beta-hydrogen elimination and when formaldehyde is formed from the beta-hydrogen elimination there is no 2 remaining to react with. At 60°C however, beta-hydrogen elimination proceeds at an observable pace and oxidative addition is not fast enough resulting in the generation of significant amounts of formaldehyde which proceeds to undergo decarbonylation with 2 to form the observed complex 16 (Scheme 3.3).
The formation of 16 from formaldehyde significantly hinders the kinetic analysis of the intramolecular oxidative addition of 2. In order to inhibit the formation of 16, complex 3 was reacted with a transmetallation reagent to prevent formaldehyde formation (Scheme 3.3). The addition of Me₂MgTMEDA to a solution of 2 produced no reaction at room temperature as determined by $^{31}$P and $^1$H NMR spectroscopy. Heating this mixture to 45°C led to the exclusive formation of a new species at 44.46 ppm by $^{31}$P NMR spectroscopy. This species was identified as a nickel(II) methyl complex (14) by the upfield triplet at -0.38 ppm in the $^1$H NMR spectrum. The observed triplet is consistent with a nickel methyl with splitting from the coordinated phosphine groups. It was hypothesized that transmetallation would be fast with respect to oxidative addition and beta-hydride elimination, indeed the reaction of 2 with Me₂MgTMEDA at 80°C for one hour leads to the formation of 14 as the sole product.

Further heating of 14 at 80°C leads to the formation of a new species as identified by $^{31}$P and $^1$H NMR spectroscopy (Scheme 3.4). Heating the Ni-Me complex several hours at 80°C leads to the observation of a new resonance at 36.85 ppm in the $^{31}$P NMR spectrum. If the heating is continued for ca. 48 hours complex 14 can be
completely converted to this new species 10, which was characterized as the product of a reductive elimination of 14 by $^1$H NMR spectroscopy and ESI-MS. Analysis of the $^1$H NMR spectrum of 10 shows two indicative peaks, a peak at 1.47 ppm, consistent with the aryl methyl, and a peak for the central arene at 5.76 ppm, which is consistent with the nickel center interacting with the central arene (the central arene of 2 gives a peak at 5.85 ppm by $^1$H NMR spectroscopy).

**Scheme 3.4 Reductive elimination of 14 to form nickel(0) complex 8**

![Scheme 3.4](image)

Using Me$_2$MgTMEDA as a transmetallation agent another attempt was made to measure the kinetics of intramolecular oxidative addition of 2 at 60°C. When 1.2 eq. of Me$_2$MgTMEDA was used a rate of $k = 10.5 \times 10^{-3}$ min$^{-1}$ was obtained from observing the decay of 2 by $^1$H NMR spectroscopy (Table 3.2). To examine the possibility that the Me$_2$MgTMEDA is somehow affecting the rate of the oxidative addition, the rate was measured using different concentrations of the transmetallation agent. Using 10 and 23 eq. of Me$_2$MgTMEDA rate constants of $k = 10.2 \times 10^{-3}$ min$^{-1}$ and $k = 10.7 \times 10^{-3}$ min$^{-1}$ were obtained respectively. If the Me$_2$MgTMEDA was affecting the rate constant one would expect to observe a significant change in the rate with increasing concentration of transmetallating agent. From the rate constant data it appears that the addition of Me$_2$MgTMEDA does not affect the rate constant of oxidative addition in 2 at a given temperature.
Complex | Equivalents of Me₂MgTMEDA | Temp °C | $k_{obs}$ (min⁻¹)
--- | --- | --- | ---
2 | 1 | 60 | 10.5x10⁻³
2 | 10 | 60 | 10.2x10⁻³
2 | 23 | 60 | 10.7x10⁻³

Table 3.2: Observed rate constants for the oxidative addition of 2 in the presence of varying amounts of Me₂MgTMEDA in C₆D₆ at 60°C.

Rates of Oxidative addition from the Ni⁰ model system

As MeMgTMEDA was shown to have no effect on oxidative addition rates of oxidative addition were measured at 45, 70, and 80°C (Figure 3.2) of which the results are shown in table 3.3. The rates at 45 and 80 °C without MeMgTMEDA were found to compare well with rates observed with MeMgTMEDA (2.09 ± 0.05 and 83 ± 2 vs. 2.19 ± 0.05 and 86 ± 3 (x 10⁻³)(min⁻¹) respectively). From these rates the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated using the linear form of the Eyring correlation (Equation 3.1 B, Figure 3.3, and Table 3.4).

Equation 3.1

\[ A) \quad k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \]

\[ B) \quad \ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} \]

Analogous studies were undertaken using the previously synthesized tert-butyl variant 2tBu. The rates of oxidative addition were measured in the presence of dimethyl magnesium TMEDA at 45, 60, and 80°C the observed rates and calculated activation parameters 2tBu are listed in tables 3.3 and 3.4 respectively. In the case of the para-
trifluoromethyl substituted $2_{\text{CF3}}$ it was observed that the addition of Grignard resulted in the loss of $^1\text{H}$ and $^{31}\text{P}$ NMR resonances possibly due to the formation of a paramagnetic species. Due to this reactivity the rates of oxidative addition were obtained without the addition of a transmetallating agent. Fortunately, $2_{\text{CF3}}$ reacts much slower with formaldehyde than either $2$ or $2_{\text{tBu}}$. The rates of oxidative addition obtained from $2_{\text{CF3}}$ were found to be only three times slower than that for $2$ or $2_{\text{tBu}}$ (Table 3.3).
Figure 3.2: Kinetic plots of the first order Decay of 2 at 318, 333, 343, and 353 K.

Figure 3.3: Kinetic plots of the first order Decay of $2_{\text{tBu}}$ at 318, 333, and 353 K.
Figure 3.4: Kinetic plots of the first order Decay of $2_{\text{CF3}}$ at 333, 343, 353, and 373 K.

Figure 3.5: Eyring plots of $2$, $2_{\text{tBu}}$, and $2_{\text{CF3}}$
As can be seen from table 3.3 the rates of oxidative addition in the model systems are quite similar between the dimethylamino, tert-butyl, and trifluoromethyl groups with the trifluoromethyl group being only three times slower, despite the electronics being significantly different. Consequently the obtained activation parameters are all within error of each other. The similarities of the activation parameters could arise due to a stabilization of the nickel(0) ground state as shown in figure 3.4. This ground state stabilization arises due to the nickel arene interactions.
The nickel arene interactions could also lead to stabilization of the transition state of the aryl oxygen bond activation. But if both the ground state and transition state were stabilized similarly, overall it would appear as if there was little to no effect of electronics, which is the case in the model system. For example, 1 would form a nickel(0) complex (2) that is less stable than the trifluoromethyl complex (2\textsubscript{CF3}) due to weaker interactions with the central arene ring. From this complex the oxidative addition transition state may be destabilized by a similar energy. This trend of thought could also be applied to 2\textsubscript{CF3}, stabilization of the Ni\textsuperscript{0} and stabilization of the intermediate by similar energies and the activation parameters observed in these complexes would end up being similar (Figure 3.2).

**Figure 3.6** Hypothetical reaction coordinate diagram for oxidative addition in the studied nickel(0) model systems.
Given that the observed rate of oxidative addition was found to not be effected by the electronics of the arene that the nickel is coordinated to, an effort was made to change the electronics of the ether on the other side of the oxygen bond. To this end the kinetics of oxidative addition in the nickel(0) terphenyl diphosphine aryl ether complex 15 were investigated. 15 undergoes oxidative addition at 20 °C over the course of several hours to form 13, and hence cannot be isolated vide supra. In order to obtain rates for oxidative addition in 15 a nickel(I) system based on the terphenyl diphosphine aryl ether backbone was used 9\(^{0\alpha\omega}\) (see Chapter 2). The nickel (I) system 9\(^{0\alpha\omega}\) can be synthesizd via a comproportionation of Ni(COD)\(_2\) and NiCl\(_2\)(DME) with the diphosphine 1\(^{0\alpha\omega}\). Transmetallation of 9\(^{0\alpha\omega}\) with a Grignard leads to the formation of the reduced nickel complex 15 (presumably analogous to the reduction observed in the forementioned nickel (I) complexes (see Chapter 2)). This method of generation of 15 was used to study the kinetics of oxidative addition.

**Scheme 3.5 Synthesis of 9\(^{0\alpha\omega}\) from diphosphine 1\(^{0\alpha\omega}\)**

Oxidative addition was measured at 35, 40, 45, and 50°C of which the results are shown in table 3.5. The observed rates of oxidative addition in the aryl aryl ether were found to be about two orders of magnitude faster than the alkyl ethers (Table 3.5). Using the Eyring correlation (Equation 3.1) the activation parameters of the
oxidative addition were calculated as shown in table 3.6. The $\Delta H^\ddagger$ was found to be $19.8 \pm 0.4 \text{ (kcal/mol)}$ while $\Delta S^\ddagger$ was found to be $0.42 \pm 1 \text{ (e.u.)}$. The rate increase is believed to be in part due to the electronics of the phenoxide being a better leaving group than an alkoxide leading to faster oxidative addition. While the electronics of the nickel-coordinated arene have little effect on the observed rates the electronics of the ether greatly affect the favorability of oxidative addition.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$k_{obs} \text{ (min}^{-1}\text{)}$</th>
<th>$\Delta H^\ddagger \text{ (kcal/mol)}$</th>
<th>$\Delta S^\ddagger \text{ (e.u.)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.066</td>
<td>19.8 ± 0.4</td>
<td>0.4 ± 0.2</td>
</tr>
<tr>
<td>40</td>
<td>0.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>0.186</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.310</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5 (Left) Observed kinetics of oxidative addition in 15 at different temperatures (Right) Derived activation parameters for 15

It is known from relative rates of palladium(0) and nickel(0) catalysts that the presence of an electron withdrawing group leads to an increase in the rate of catalysis.16-19 One way of explaining this phenomenon in light of the data we observe, is that the starting points differ in each case. For our Ni$^0$ system we start with the metal center already coordinated to the substrate ligand, while in the case of the catalyst the Ni$^+$ is unbound. In the catalytic systems there is a fast pre-equilibrium which forms the nickel(0) arene adduct. This equilibrium is dependent on the electronics of the aryl substrate. The more electron deficient arenes form a stronger interaction with the
Figure 3.7: Kinetic plots of the first order Decay of 15 at 308, 313, 318, and 323 K.

Figure 3.8: Eyring plot of 15
nickel(0) center as shown with the nickel model systems *vide supra* (Table 3.1). This pre-equilibrium shifts the concentration of the nickel(0) arene species leading to an observed rate increase. In order to better understand the effect of the arene interactions in oxidative addition, studies were shifted from model systems to catalytic systems.

**Nickel Catalyst Studies**

Studies of oxidative addition in nickel catalyst systems were undertaken using two different nickel systems, the known and versatile cross coupling catalyst Ni(II)(PCy₃)₂Cl₂ (17)⁴⁻⁹, and the structurally characterized [Ni(PCy₃)₂]₂N₂ complex (18).²⁰ 17 is a known precatalyst for the Kumada coupling of aryl ethers and Grignard reagents (Scheme 3.6). It is proposed that 17 undergoes a sequential transmetallation to form a nickel(0) dialkyl species which undergoes reductive elimination leading to the formation of a nickel(0) species, which is believed to be the active catalyst. As 17 is a known catalyst for oxidative addition of anisoles, conditions similar to those found in literature were used. Initial catalysis screens yielded little to no conversion of the starting anisole. It was initially believed this limited activity could be due to the use of chloride containing Grignard reagents, however it was found that the presence of THF greatly hinders the activity of the catalyst. Removal of the THF from the Grignard reagent or the use of a Grignard containing diethyl ether resulted in catalytic activity. It was found from these initial studies that the trifluoromethyl anisole reacts faster than the dimethyl and tert-butyl variants. Similarly in 1:1 competition reactions conversion was only observed in the trifluoromethyl anisole, which indicates that the nickel
preferentially undergoes oxidative addition with the more electronegative substrate. Through competition reactions relative rates were obtained for a variety of substrates as shown in table 3.6.

Scheme 3.6 Proposed catalytic cycle for the Nickel catalyzed cross coupling of Aryl ethers with Alkyl Grignards
Table 3.6 Relative rates obtained from competition reactions. All rates are relative to 4-tertbutyl anisole.
While oxidative addition is well documented for 17 it is not as well documented in the literature for oxidative addition to anisoles. For the catalysis from the \([\text{Ni(PCy}_3\text{)}_2\text{N}_2]\) complex 18, conditions identical to those used for the \(\text{Ni(II)(PCy}_3\text{)}_2\text{Cl}_2\) system were used. Gratifyingly, 18 was found to facilitate the coupling between an anisole and an alkyl Grignard in a fashion similar to 17. In order to further probe oxidative addition in this system, attempts were made to directly observe oxidative addition via \(^1\text{H NMR spectroscopy}\) in a similar fashion to the Ni model complexes i.e. a shifting of the arene or methoxy resonances. Unfortunately, no change was observed by \(^1\text{H NMR spectroscopy}\) in a 1:1 mixture of tert-butyl anisole with 18 even when heating to 80 °C. Similarly no oxidative addition was observed to take place with trifluoromethyl anisole under similar conditions. While no oxidative addition was observed, the addition of methyl Grignard to a solution containing a catalytic amount of 18 resulted in a conversion of the tert-butyl anisole to the tert-butyl toluene. Surprisingly, one equivalent of the methyl Grignard did not result in a clean conversion of the anisole into toluene. Something similar was observed with aryl Grignards, as homo-coupled arenes were observed after the coupling reaction, when aryl Grignards were used. Although no ethane, the expected by product from methyl Grignard, was observed it is still possible homo-coupling or some other process is taking place.

The relative rates observed with the nickel systems 17 and 18 give a trend of increasing rate of reactivity with electron withdrawing substrates. This is in contrast with what was observed in our nickel model system. The observed rate of increase could be due to the nickel catalytic species having a better metal arene interaction with
the more electron withdrawing substrates as was inferred from the model complex. In
order to understand the effects of the substrate pre-equilibrium (Scheme 3.6) the
equilibrium constants of different arenes were investigated. One of the problems with
the nickel precatalysts 17 and 18, is the identity of the actual catalyst is unknown. The
actual catalyst could be a nickel diphosphine or a nickel monophosphine, which would
complicate the observed kinetics and equilibria, as phosphine dissociation/association
with the catalytic species would become relevant. As phosphine
dissociation/association could be a complicating factor a nickel(0) system containing a
chelating diphosphine was used. Nickel(II)(Cl)(dcpe) (dcpe= 1,2-
bis(dicyclohexylphosphino)ethane) can be treated with sodium naphthalene to form
nickel(0)(dcpe) naphthalene (19) where the nickel has a metal arene interaction with
the ring of the naphthalene.

**Scheme 3.7 Equilibrium reaction between 19 and Arenes**

![Scheme 3.7 Equilibrium reaction between 19 and Arenes](image)

The goal was to measure the equilibrium constants of arene exchange in the nickel
complex 19. Treatment of 19 with large amounts of substituted arenes did indeed lead
to arene exchange as observed by $^{31}$P NMR spectroscopy (Table 3.7). The more
electron withdrawing arenes were found to substitute more easily than less electron
withdrawing arenes. Comparing 4-trifluoromethyltoluene and trifluoromethylbenzene
one can see that the electron withdrawing groups shift the equilibrium in favor of the
arene binding. 4-trifluoromethylanisole was found to bind to nickel more preferentially
than 4-trifluoromethyltoluene. This could be due to interaction with the anisole or due to the anisole moiety while being $\sigma_p$ donating is actually $\sigma_m$ withdrawing in comparison to the methyl group ($\sigma_m$ 0.12 and -0.07 for OMe and Me groups respectively). This would cause the meta position of the ring to be a site of low electron density allowing the nickel to interact with the ring. 1,4-ditrifluoromethylbenzene was found to be one of the few substrates tried that easily displaced naphthalene.

<table>
<thead>
<tr>
<th>$K_m$</th>
<th>Arene$_{CF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1</td>
<td>![Arene 1]</td>
</tr>
<tr>
<td>0.003</td>
<td>![Arene 2]</td>
</tr>
<tr>
<td>0.0015</td>
<td>![Arene 3]</td>
</tr>
<tr>
<td>0.0008</td>
<td>![Arene 4]</td>
</tr>
</tbody>
</table>

**Table 3.7** Equilibrium constants for 19 with listed arenes

The equilibrium constants clearly show that the equilibrium is influenced greatly by the electron withdrawing groups. This provides support for our proposal that the substrate equilibrium plays a part in the rate acceleration observed in the catalytic systems.
**Conclusions:**

The kinetics of oxidative addition was studied using the previously studied nickel(0) terphenyl diphosphine model complexes. Formaldehyde was found to negatively affect the kinetics at certain temperatures. Kinetics were carried out in the presence of a Grignard reagent in order to prevent formaldehyde formation. The rates of oxidative addition were found to be similar amongst the three model systems. The trifluoromethyl was only three times slower than the tert-butyl and dimethylamino. Activation parameters were similar across the three complexes. The similarity of the kinetics and activation parameters was postulated to be due to stabilization of the ground state and oxidative addition transition state in the model complex. Unfortunately we were unable to determine the actual rates of oxidative addition in the catalytic systems, but using our model system in conjunction with the catalytic systems we were able to show that oxidative addition in the model system is unaffected by the electronics of the arene. While oxidative addition in the catalytic system shows a significant variance in rate depending on the electronics of the substrate arene, we were able to show that this is in part due to a shifting of the pre-equilibrium of the substrate.
EXPERIMENTAL SECTION:

General considerations: Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs’ method. Benzene-d6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. All other materials were used as received. Ni(II)Cl2(PCy3)2 was purchased from Strem Chemicals as a crystalline solid and was used as received. 1H, 13C, and 31P NMR spectra were recorded on a Varian Mercury 300 spectrometer at ambient temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C6D6) and for 1H and 13C NMR data, respectively. 31P NMR chemical shifts are reported with respect to the instrument solvent lock when a deuterated solvent was used. IR spectra were recorded on a Thermo-Fisher Scientific Nicolet 6700 FT-IR spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon filtering the sample through a plug of silica gel. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high-resolution mass spectrometer.
The synthesis of [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0)carbonyl (16) was achieved as follows: To a solution of 2 (12.3 mg, 0.021 mmol) in C6D6 was added 5 equivalents of formaldehyde (3.7 mg, 0.123 mmol). Upon addition hydrogen gas was vigorously evolved as the solution turned from dark red, to red orange in a matter of minutes. The solvent was removed in vacuo and the residue was washed with hexanes and eluted with ether. The solvent was removed from the orange ether fraction resulting in an orange residue of 16.

**16** Yield: (11.3 mg, 0.018 mmol 87.1 %) ¹H NMR (C.D., 300 MHz) δ 7.47 (br m, 4H, Ar-H), 7.22 (br m, 4H, Ar-H), 6.58 (br s, 2H, Ar-H) 2.67 (s, 6H, N(CH3)2), 2.57 (s, 3H, OCH3), 2.48 (septet, 1H, CH(CH3)2), 2.15 (septet, 1H, CH(CH3)2), 1.25 (septet, 18H, CH(CH3)2), 0.99 (septet, 6H, CH(CH3)2), ¹³C[¹H] NMR (C.D., 100.54 MHz) δ 194.01 (t, Ni-CO), 149.57 (s, Ar-C), 147.94 (t, Ar-C), 138.45 (s, Ar-C), 136.27 (t, Ar-C), 130.33 (s, Ar-C), 129.90 (s, Ar-C), 127.95 (s, Ar-C), 126.97 (s, Ar-C), 122.79 (s,
Ar-C), 113.60 (s, Ar-C), 60.59 (s, Ar-OMe), 40.91 (N(CH3)2), 29.48 (CH-(CH3)2),
26.08 (CH-(CH3)2), 19.42 (CH-(CH3)2), 19.14 (CH-(CH3)2), 18.86 (CH-(CH3)2), 18.03
(CH-(CH3)2), 31P{1H} NMR δ 36.25 Anal. Calcd. for C34H47NNiO2P2 (%): C, 65.61; H,
7.61; N, 2.25 Found C, 68.73; H, 7.41; N, 2.09.

16,16. Yield: (10.2 mg, 0.016 mmol 85.0 %) 1H NMR (C.D2, 300 MHz) δ 7.44 (br m,
4H, Ar-H), 7.21 (br m, 6H, Ar-H), 2.49 (s, 3H, OCH3) 2.46 (s, 1H, CH(CH3)2), 2.15
(s, 1H, CH(CH3)2), 1.43 (s, 6H, N(CH3)2), 1.20 (m, 18H, CH(CH3)2), 0.95 (m, 6H,
CH(CH3)2), 13C{1H} NMR (C.D2, 100.54 MHz) δ 194.80 (t, Ni-CO), 148.30 (s, Ar-C),
146.26 (t, Ar-C), 137.23 (s, Ar-C), 130.65 (t, Ar-C), 130.27 (s, Ar-C), 129.84 (s, Ar-
C), 128.67 (s, Ar-C), 126.91 (s, Ar-C), 125.88 (s, Ar-C), 60.21 (s, Ar-OMe), 34.15
(CH3), 31.36 (CH3), 29.35 (CH3), 25.55 (CH3), 19.19 (CH3), 18.89 (CH3), 18.72 (CH3),
17.77 (CH3) 31P{1H} NMR δ 35.92

16,16. Yield: (13.4 mg, 0.021 mmol 92.7 %) 1H NMR (C.D2, 300 MHz) δ 7.34 (br s,
2H, Ar-H), 7.32 (m, 2H, Ar-H), 7.23 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 2.42 (s, 3H,
OCH3) 2.39 (s, 2H, CH(CH3)2), 2.05 (s, 2H, CH(CH3)2), 1.11 (s, 12H, CH(CH3)2), 1.03
(m, 6H, CH(CH3)2), 0.82 (m, 6H, CH(CH3)2), 13C{1H} NMR (C.D2, 100.54 MHz) δ
195.52 (t, Ni-CO), 147.79 (s, Ar-C), 147.58 (t, Ar-C), 135.69 (s, Ar-C), 130.14 (t, Ar-C), 139.64 (s, Ar-C), 129.64 (s, Ar-C), 129.17 (s, Ar-C), 127.41 (s, Ar-C), 124.10 (s, Ar-C), 123.91 (Ar-CF3), 120.26 (s, Ar-C), 59.96 (s, Ar-OME), 28.78 (CH-(CH3)2), 24.78 (CH-(CH3)2), 18.82 (CH-(CH3)2), 18.52 (CH-(CH3)2), 18.42 (CH-(CH3)2), 17.44 (CH-(CH3)2), \(^1^H\)F{\(^1^H\)} NMR \(\delta -61.30\), \(^3^P{\(^1^H\)}\) NMR \(\delta 37.25\) Anal. Calcd. for C_{33}H_{41}F_{3}NiO_{2}P_{2} (%): C, 61.23; H, 6.38; Found C, 55.83; H, 6.12.

Synthesis of bis[bis(tricyclohexylphosphine)nickel] dinitrogen (18)

A modified literature procedure was used for the synthesis of 18. To a freshly thawed mixture of Ni(acac)\(_2\) (1.00 g, 3.89 mmol) and tricyclohexylphosphine (2.19 g, 7.81 mmol) in 12 ml of toluene was added a thawed solution of AlMe\(_3\) (315 mg, 4.38 mmol) in 3 ml of toluene. Upon addition of AlMe\(_3\) the blue green solution turned dark red. The reaction vessel was stoppered and the reaction mixture was stirred for 24 hours. The after 24 hours the stirring was stopped and the reaction mixture was allowed to sit for 3 hours. The slurry was filtered through Celite and the solid was eluted with toluene. The flow through of the filtration was placed in the freezer to promote crystallization/precipitation. The toluene fraction was pumped down to give a dark red solid and was used as isolated. Yield: (814 mg, 1.28 mmol 33.2 %) \(^1^H\) NMR (C.D., 300 MHz) \(\delta 1.89\) (br s, 12H, Cy-\(H\)), 1.72 (br m, 48H, Cy-\(H\)), 1.27 (br m, 72H, Cy-\(H\)) \(^3^P{\(^1^H\)}\) NMR \(\delta 45.98\)
Synthesis of 19

Naphthalene (47.5 mg, 0.37 mmol) was added to a vial containing a sodium mirror (65.3 mg, 2.84 mmol) as a solution in THF. The sodium naphthalene solution immediately turned dark forest green. The sodium naphthalene was stirred for 30 minutes. In a separate vial Ni(II)(dcpe)Cl₂ (100.2 mg, 0.18 mmol) was stirred as a slurry in THF. The dark green sodium naphthalene solution was added to the Ni(II)(dcpe)Cl₂ mixture. The solution slurry turned from dark green to yellow and finally to red orange. The mixture was stirred for 45 minutes before filtering through Celite. The solvent was removed resulting in a red orange solid. The residue was washed with pentane and eluted with benzene resulting in 18. Yield: (203.8 mg, 88.2%)

¹H NMR (C₆D₆, 300 MHz) δ 7.37 (br s, 2H, Ar-H), 7.08 (br s, 2H, Ar-H), 5.85 (br d, 4H, Ar-H), 1.62 (br d, 32H, (dcpe)-H), 1.12 (br s, 20H, (dcpe)-H), ³¹P[¹H] NMR δ 53.38 (dd, J = 717.9, 81.9 Hz)

Kinetic Studies:

Special considerations: All kinetic data over 45 °C was collected on a Varian INOVA-500 MHz NMR spectrometer and all 45°C kinetic data was collected using a Varian Mercury 300 MHz NMR spectrometer. In all experiments trimethoxybenzene was used as a standard.
Example of a Kinetic Reaction:

In a glove box a J-Young tube was charged with 11.3 mg (0.019 mmol) of 2 and 1.1 mg (0.006 mmol) of trimethoxybenzene in C.D₆ or d₈-toluene. The J-Young tube was heated to the desired temperature in either an oil bath or in an NMR spectrometer. NMR spectra were collected at regular intervals.

Catalytic Studies:

Special Considerations: All catalytic reactions were performed using 1,3,5-tritert-butylbenzene as an internal standard. All conversions listed were calculated via amounts of analytes based on gas chromatography.

Example of a Catalytic Reaction:

In a glove box a Schlenk tube containing 40.2 mg (0.244 mmol) of tert-butyl anisole, 16.4 mg (0.024 mmol) Ni(PCy₃)₂Cl₂, 12.7 mg (0.045 mmol) of PCy₃, and 61.2 mg (0.025 mmol) of 1,3,5-tritert-butylbenzene was charged with 2.7 ml of dry toluene. This solution was allowed to stir for five minutes before 300 μl of MeMgBr (3M in Et₂O) was added via syringe. The slurry immediately turned yellow. The Schlenk was sealed and heated to 80°C for 17 hours after which the reaction was quenched with water and the organics were extracted by DCM. The organic fraction was analyzed via gas chromatography.
**Example of an Equilibrium Reaction:**

In a glove box a J-Young tube containing 10.3 mg of 19 (0.017 mmol) was treated with 10 equivalents of naphthalene and one equivalent of 1,4-ditrifluorobenzene in C₆D₆. The solution was mixed by shaking. The mixture was analyzed by $^{31}$P NMR spectroscopy and the concentration of the resulting species was calculated. Using the observed concentrations of the nickel species and the added concentrations of the naphthalene and substituted benzene the equilibrium constants were calculated.
REFERENCES

CHAPTER 4

EFFECT OF LEWIS ACIDIC METALS ON ARYL-OXYGEN BOND ACTIVATION IN NICKEL(0) DIPHOSPHINE MODEL SYSTEMS
ABSTRACT

The addition of Lewis acidic metal alkyls to a nickel terphenyl diphosphine aryl ether complex led to an acceleration of the observed aryl oxygen bond activation. It was found that Grignard reagents led to an order of magnitude increase while trialkyl aluminium species led to an up to three orders of magnitude rate increase over the unaccelerated rate. Treatment with trimethyl aluminum at -80 °C led to the observation of a nickel aluminum intermediate. Through low temperature $^1$H NOESY NMR studies the intermediate was identified as a complex where the aluminum center is coordinated to the ether moiety of the terphenyl ring on the face $trans$ to the nickel center. The kinetics and activation parameters of aryl activation with trimethylaluminum are described and the proposed mechanism is discussed.
INTRODUCTION:

Aryl oxygen bonds are significantly stronger than their aryl halide counterparts making the direct activation of aryl-oxygen substrates challenging. Typically aryl oxygen moieties must be converted to the more reactive phosphinates, sulfonates, or triflates. While catalytic systems are known for the cleavage and cross coupling of aryl-oxygen bonds these systems are typically limited by low turnover numbers or poor reactivity for anisoles. Another strategy for the cleavage of aryl-X bonds is the assisted cleavage of aryl-X bonds in the presence of lewis acidic metals.

Currently there are several different nickel systems for the cross coupling of aryl oxygen bonds. Most of these systems use high temperatures and long reaction times for homogeneous systems. The most common of these systems contain basic phosphines such as tricyclohexylphosphine or carbenes. The common catalytic systems for these activations are Ni(COD), with 2 equivalents of PCy₃, NiCl₂(PCy₃)₃, or Ni(COD), with 2 equivalents of SIPr-HCl or a N-heterocyclic carbene. Others systems also use less basic phosphines. While the phosphines vary, the presence of the Lewis acid does not. The transmetallation species in these reactions is typically either a Grignard reagent or an alkyl borane both of which are Lewis acidic species which can aid in aryl oxygen bond activation.

Lewis acids have been used in conjunction with nickel catalysts for the activation of nitrile groups. In 1984, Tolman et. al. observed that the catalytic hydrocyanation of olefins by Ni(0) phosphite complexes was changed in the presence of Lewis acids. This concept was later carried out in the carbocyanation of alkynes by nickel system by Nakao et al. in 2007. What the researchers observed was a large effect of the Lewis
acid on the activation of the arene nitrile bond where the increase in the rate of activation varied with the strength of the Lewis acidity of the additive. Using aluminum based Lewis acids they were able to determine the crystal structure of one of the intermediate species which among other things, revealed an aluminum center coordinated directly to the nitrogen of the nitrile group while the nickel center coordinated to the pi bond of the nitrile group, showing that the metal centers do indeed react in concert for the activation of the nitrile groups.

There is also precedence for the use of a secondary Lewis acidic metal center to assist the activation of aryl oxygen bonds in the literature. While the studies are not numerous, there are some reports, such as the catalytic system reported by Hartwig being able to cleave aryl oxygen bonds at lower temperatures with an equivalent of added trimethylaluminum. More extensive studies in this area have been done by Shi et al. who found the presence of a Lewis acidic Grignard reagent allowed for cleavage of the aryl oxygen bond in naphthanol and benzylic alcohols. They proposed that the naphtholate interacts with multiple Lewis acidic Grignards to form a regular framework. In these frameworks they hypothesized that the coordination would induce reorganization of the electronic structure of the phenolic aryl-oxygen bond (Figure 1).
This reorganization of electron density would activate the aryl oxygen bond for cleavage. Essentially, the metals would act both as electron withdrawing groups, simultaneously weakening the oxygen carbon bond and making the oxygen moiety a better leaving group. However, they noted that phenol derivatives did not successfully undergo this transformation.

More recently the Shi group extended this research to non-metallic Lewis acids. Using aryl boronic reagents the Shi group could observe a similar effect on the activation of phenolates. The addition of excess boronic reagents and triethyl borane leads to a similar effect as the Grignards on the phenolates. It is postulated that there is a double Lewis acid effect on the phenolate as they propose that both the boronic
acid and the triethyl borane contribute Lewis acidic effects on the phenolic aryl oxygen bond.

**Figure 4.2:** Palladium magnesium bimetallic system for the directed activation of aryl halide bonds

Some bimetallic systems have been developed where the Lewis acidic metal center has been used to impart selectivity on the activation of aryl heteroatom bonds. For example Manabe et. al. explored the use of a Lewis acid to guide the reactivity of a palladium center in oligoarene and terphenyl systems. Their terphenyl system contains a phosphine arm and a phenolic arm. The phosphine arm is envisioned to bind a palladium(0) metal center for arene heteroatom bond activation while the phenolic arm is envisioned to bind a Lewis acidic Grignard reagent (Figure 5).

Using this system, Manabe et al. they were able to activate ortho arene heteroatom bonds on phenolate substrates preferentially to any other ortho arene
bonds. They proposed that substrate binds to the magnesium coordinated to the phenolic arm of the ligand allowing for the ortho positions of the substrate to be accessible to the palladium(0) center.\textsuperscript{44} Substitution of both sides of the phenol arm led to an increase in the bond selectivity providing more support for their proposed mechanism and reactivity.\textsuperscript{74}

As these examples have shown the cleavage of aryl oxygen bonds can be activated through the use of a bimetallic system containing an electron-rich nickel center to coordinate the arene and a Lewis acidic metal to help activate the substrate. However systematic studies on the effect of the Lewis acid and the acceleration of the rate have not been undertaken. Such studies as described would allow for the development of better heterometallic catalysts for the cleavage of aryl oxygen bonds. As our group has recently developed a nickel(0) model system. In this model system the nickel readily undergoes oxidative addition giving us a unique platform from which to probe oxidative addition facilitated by nickel mechanistically and kinetically. With this in mind we extended our studies to aryl oxygen bond activation in the presence of Lewis acids. Herein is described the studies of Lewis acidic accelerated aryl oxygen bond activation in a nickel(0) model system.
RESULTS & DISCUSSION:

In our investigations of the rate of aryl-oxygen bond activation in nickel(0) diphosphine aryl ether complexes we have observed a rate acceleration in the presence of Grignard reagents. The treatment of 2 with ten equivalents of MeMgBr in toluene leads to an order of magnitude rate increase in the aryl-oxygen bond activation (Scheme 4.1, Table 4.1, and Figure 4.3). Interestingly, the addition of one to twenty three equivalents of MeMgTMEDA does not lead to a rate increase in aryl-oxygen bond activation *vide supra*. This is postulated to be due to the Lewis acidity of the metal as has been observed in other systems. The less Lewis acidic MeMgTMEDA does not lead to acceleration due to the bidentate ligand TMEDA, which effectively quenches the Lewis acidity of the metal center. Indeed the treatment of 2 with ten equivalents of MeMgBr in the presence of THF does not lead to an increase in the rate of oxidative addition. This is consistent with the coordinating solvent THF binding to the Grignard reagent, resulting in a less Lewis acidic metal center. It is possible that the MeMgBr is coordinating to the methoxy moiety of the terphenyl backbone weakening the oxygen arene oxygen bond and simultaneously making the methoxy a better leaving group leading to an accelerated oxidative addition forming a nickel(II) species. This nickel(II) can either be transmetallated by the coordinated Grignard reagent (a concerted process between the methoxy Grignard adduct) or transmetallated via another equivalent of the Grignard.
Figure 4.3: Rate acceleration of aryl-oxygen bond activation in 2 with 1 and 10 equivalents of MeMgBr.

<table>
<thead>
<tr>
<th></th>
<th>T(°C)</th>
<th>kobs (min⁻¹) (x10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni° w/1 Equiv MeMgBr</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>Ni° w/1.25 Equiv Me₂MgTMEDA</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Ni° w/10 Equiv MeMgBr</td>
<td>80</td>
<td>774</td>
</tr>
</tbody>
</table>

Table 4.1: Rate acceleration of aryl-oxygen bond activation in 2

Scheme 4.1: Reactivity of 2 with excess Grignard reagent

Intrigued by the results with MeMgBr the effect of other Grignard reagents were investigated. It was found that other alkyl and aryl Grignard reagents also accelerate the rate of oxidative addition in 2. Ethyl, phenyl, benzyl, and mesityl
Grignards all resulted in rate increases. It was quite surprising that the bulkier Grignards (mesityl and phenyl) still resulted in an observed increase in rate.

Emboldened by the effect of Grignard reagents on aryl oxygen bond activation, other Lewis acids were tested for similar effects. The addition of MeLi lead to an increase in rate similar to what was observed with Grignard reagents. Surprisingly diethyl, dimethyl, and dipentafluorobenzyl zinc species did not result in an increase in aryl oxygen bond activation. Similarly metal tert-butoxides (Li, Na, and K) did not result in an increase in rate. It was proposed that the solubility of the metal tert-butoxides might inhibit their effect on the reactivity of the nickel complex, however, while changing the solvent to difluorobenzene did increase the amount of solubilized tert-butoxide the rate of aryl-oxygen bond activation was not found to increase. Even when a more soluble metal alkoxide was used (potassium 2-methylbutan-2-olate) no effect was observed. Several Lewis acidic metal salts were tried (MgX₂, FeX₃, FeX₂, AlCl₃, and CrX₃) however the salts were found to be insoluble under the reaction conditions and while difluorobenzene did seem to increase the amount of the metal salt solubilized the rate of aryl-oxygen bond cleavage was found to be the same as the rate without additive. Although no rate acceleration was observed, the addition of AlCl₃ did result in the formation and precipitation of a dark solid, which did not change upon heating. Hydrolysis of this solid with HCl and investigation of the organics by ESI mass spectrometry revealed the mass of the free diphosphine terphenyl anisole showing that the aryl-oxygen bond had not been cleaved.

Unexpectedly, the addition of alkyl boranes did not lead to increased reactivity in 2. Alkyl boranes have been shown to increase oxidative addition in nickel catalytic systems for the activation of cyano groups and other catalytic systems. Fortunately, the
addition of alkyl aluminum reagents led to increased rate of oxidative addition in 2. Addition of one equivalent of AlMe₃ lead to complete conversion of 2 into the previously characterized 14 (oxidative addition followed by a subsequent transmetallation) within minutes (Scheme 4.2). Without any additive the 2 undergoes complete conversion to the 3 within approximately seven days at 20 °C. This leads to an estimate of a three order of magnitude rate increase for the addition of AlMe₃.

Scheme 4.2: Addition of AlMe₃ to 2 leads to a room temperature aryl oxygen bond activation

The addition of other alkyl aluminum reagents also leads to an observed rate increase. AliBu₃, AlEt₃, and AlPh₃ all lead to a rate acceleration for the formation of a nickel(II) species. The AlPh₃ lead to significantly slower rates than that observed for the aluminum alkyls (AlMe₃, AliBu₃, and AlEt₃), possibly due to the steric bulk of the triphenyl species.

In order to better understand the observed effect of Lewis acidic additives, studies were undertaken to better understand the binding of AlR₃ to the nickel(0) system and the method of aryl-oxygen bond activation. To test if nickel was required for the aryl-oxygen bond activation the diphosphine terphenyl anisole (1) was treated with ten equivalents of AlMe₃. Upon mixing a new species formed as observed by NMR spectroscopy. 'H NMR shows shifts in the isopropyl methyls and methine
protons, where one methine shows a large shift upfield from 1.87 ppm to 1.18 ppm. Upfield shifts are also observed for the -NMe₂ and -OMe functional groups from 2.60 to 2.25 ppm and 3.10 to 2.63 ppm respectively. ³¹P NMR shows two broad peaks at 18.25 and -4.82 ppm. The spectroscopic data is consistent with the aluminum coordinating to the diphosphine terphenyl anisole. There are multiple points where the AlMe₃ could coordinate, either through the methoxy group, the dimethyl amine, or through the phosphines. Coordination through the methoxy or dimethyl amine would not account for the large phosphorous shift in the ³¹P NMR. It is likely that the AlMe₃ is coordinating through the phosphine, although coordination of multiple equivalents of AlMe₃ could be possible. Regardless, hydrolysis of this adduct results in the recovery of 1. Trimethylaluminum does not cleave the aryl oxygen bond in the absence of nickel (Scheme 4.3).

Scheme 4.3: Reactivity of AlMe₃ with 1

As nickel is required to cleave the aryl-oxygen bond it is possible that AlR₃ coordinates through nickel and the adduct cleaves the aryl-oxygen bond. To this end a nickel(0) diphosphine meta-terphenyl containing no ipso- or para-functionalities (7h) was treated with AlMe₃. The addition of AlMe₃ leads to no change in the nickel complex as observed by NMR spectroscopy (Scheme 4.4). This suggests that the nickel does not interact with an added AlR₃ in the absence of the ligand functionalities.
Scheme 4.4: Reactivity of AlMe₃ with 7ₜ

Introduction of a –NMe₂ group in the para-position of the ligand backbone (7ₜ) leads to the observed coordination of AlMe₃ by spectroscopy. An upfield shift is observed for the –NMe₂ group resonance from 2.58 ppm to 2.36 ppm upon coordination. A similar shift is observed in the resonance of the ipso-proton from 5.37 to 4.85 ppm, while the while the central arene resonance shifts downfield from 5.83 to 6.04. There is a small shift of 2.8 ppm by ³¹P NMR spectroscopy (38.55 to 41.33 ppm upon AlMe₃) indicating there is not much interaction of AlMe₃ with the phosphines in the nickel(0) model complexes. The shifts observed upon AlMe₃ coordination are mainly localized to the central arene ring of the terphenyl backbone in 7, which leads to the proposal that the added aluminum is interacting with the free lone pair on the –NMe₂ group (Scheme 4.5).
Scheme 4.5: Coordination of AlMe₃ to 7 through the NMe₂ moiety

When the backbone contains a –NMe₂ group the AlR₃ coordinates to the –NMe₂ group, however it is not clear how that will accelerate the aryl-oxygen bond activation. Changing the para- group to a tBu should prevent para-coordination. As a tBu group should eliminate para coordination and binding is not observed in the absence of any groups, complex 2₉aₕ should allow us to test for coordination of AlR₃ to the methoxy moiety of the terphenyl backbone. Treatment of 2₉aₕ with ten equivalents of AlMe₃ leads to the formation of 13₉aₕ. As the methoxy group is the only group capable of binding AlMe₃ (vide supra) this provides evidence that the AlMe₃ (and other AlR₃ or Lewis acidic reagents) is coordinating to the methoxy group when accelerating the rate of oxidative addition (Scheme 4.6).

Scheme 4.6: Addition of AlMe₃ to 2₉aₕ

Low temperature NMR spectroscopy studies were carried out in an attempt to observe intermediates in the Lewis acid accelerated aryl oxygen bond activation. At -80 °C, 2₉aₕ gives a broad ‘H NMR spectrum with –OMe and central arene resonances at
3.19 and 6.44 ppm respectively. The addition of one equivalent of AlMe₃ leads to a downfield shift in the methoxy resonance to 3.39 ppm and an upfield shift in the central arene resonances to 6.15 ppm. A curious downfield shift is observed for the ortho protons of the outer terphenyl rings from 7.73 to 8.00 ppm upon AlMe₃ coordination (Figure 4.4). This intermediate is stable surprisingly stable at low temperatures, at -80 °C no decomposition was observed after eight hours. Warming leads to aryl-oxygen bond activation and formation of 14tBu. No other intermediates are observed by 1H NMR for the conversion of the nickel aluminum intermediate to 14tBu.

Figure 4.4: Addition of AlMe₃ to 2tBu at -80 °C

NOE experiments were used to provide further insight into structure of the intermediate. Homonuclear 2D NOESY spectra collected at -80 °C gratifyingly reveal interaction between the AlMe₃ methyl groups and the ipso methoxy group as observed as a cross peak at -0.5 and 3.5 ppm (Figure 4.5). Interestingly there is also an interaction between the aluminum alkyl and the ortho protons of the outer terphenyl
rings as shown by the cross peak at -0.5 and 8.0 ppm (Figure 4.5). The low temperature NOE data suggests that the AlMe₃ is coordinated to the methoxy on the face of the central arene ring opposite that of the nickel center. The methoxy group shows correlations to the isopropyl groups relating their close proximity in space (cross peak between 1 and 3.5 ppm, Figure 4.5). No methyl correlations were observed between the isopropyl groups of the phosphine and AlMe₃, which would be present if the aluminum center resided on the same side as the nickel center.

![Figure 4.5: NOESY spectra of 2tBu•AlMe₃ collected at -80 °C](image)

Figure 4.5: NOESY spectra of 2tBu•AlMe₃ collected at -80 °C

With a better understanding of where and how the aluminum alkyl is accelerating the rate of aryl oxygen bond activation in depth studies of the rate were undertaken. The decay of the nickel(0) trimethyl aluminum intermediate (2ₜBu•AlMe₃)
was observed over time for three reaction half lives using 10 to 100 equivalents of AlMe₃ (Figure 4.6). As one can see from the rate data there is an increase in the rate of the aryl oxygen bond activation with increasing concentrations of AlMe₃. It should be noted that a similar rate increase is observed with increasing concentration with Grignard reagents. This rate increase is consistent with a bimolecular mechanism. However there is also a significant increase with just one equivalent of AlMe₃.

Determination of the activation parameters for the aryl oxygen bond assisted cleavage were undertaken with two and ten equivalents of AlMe₃. Surprisingly both two and ten equivalents gave similar values for ΔS‡ (-4.83 and -2.23 cal K⁻¹ respectively) and ΔH‡ (14.78 and 14.92 kcal mol⁻¹ respectively) of activation (Table 4.2). The small negative ΔS‡ suggests that the mechanism is intramolecular, which is not consistent with the effect of AlMe₃ concentration on the rate that is observed. It is possible that there are two alternate mechanisms for the activation of the aryl oxygen bond. The first mechanism would only require a single equivalent of AlMe₃ coordinated to the oxygen bond. This single equivalent leads to a large rate increase (about three orders of magnitude) over what is observed in the absence of any additive. The second mechanism would involve several equivalents of AlMe₃, possibly to further activate the aryl-oxygen bond or form a lower energy transition state. Calculations performed by Sibo Lin suggest that the aryl oxygen bond activation in the presence of AlMe₃ proceeds through an intermediate where the AlMe₃ and Ni metal center are on the same side. While this is not observed by NOE studies, it does provide a possible explanation of how the presence of excess AlMe₃ could accelerate the rate of the assisted oxidative addition. Upon addition of one equivalent of AlMe₃, the aluminum
center coordinates to the face opposite of the metal center, possibly due to sterics (Scheme 4.7).

**Scheme 4.7: Possible Mechanism for rate acceleration with excess AlMe₃**

From here since the activation energy for oxidative addition in this intermediate is large the AlMe₃ must rearrange somehow from the local minimum to the active transition state. Another equivalent of AlMe₃ could coordinate to the methoxy from the top face of the ring causing dissociation of the first AlMe₃ equivalent leading to the calculated more favorable transition state for oxidative addition (Scheme 4.7). Increases in the concentration of AlMe₃ would lead to greater concentrations of this unstable intermediate leading to a faster rate, which coincides with what is observed. However, the rate increase by the additional equivalents of AlMe₃ is not as substantial as the first. Increasing the AlMe₃ from 2 to 10 equivalents only results in a 2.5x increase in rate. Similarly increasing the rate from 10 to 100 equivalents affords only a 5 fold increase.
Table 4.2: Observed activation parameters of aryl oxygen bond activation in $2_{\text{a}}$ with 2 and 10 equivalents of AlMe$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger$ (kcal mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (cal K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(0) with No Additive</td>
<td>20 ± 2</td>
<td>-6 ± 1</td>
</tr>
<tr>
<td>Ni(0) with 2 Equivs of AlMe$_3$</td>
<td>15 ± 1</td>
<td>-5 ± 2</td>
</tr>
<tr>
<td>Ni(0) with 10 Equivs of AlMe$_3$</td>
<td>14.9 ± 0.7</td>
<td>-2 ± 1</td>
</tr>
</tbody>
</table>

Figure 4.6: Rate of aryl oxygen bond activation in $2_{\text{a}}\cdot$AlMe$_3$ with varying concentration of AlMe$_3$ at -40 °C.
CONCLUSIONS:

The rate of oxidative addition observed in the nickel(0) diphosphine terphenyl ether model system was found to increase in the presence of Lewis acidic metals. Grignard reagents were found to increase the rate an order of magnitude while trimethylaluminum increases the rate about three orders of magnitude. At -80 °C an intermediate was identified by NOE coorelations where the AlMe₃ is coordinated to the ether moiety of the terphenyl ether trans to the nickel metal center. Warming this intermediate lead to the activation of the aryl ether bond. Increases in the concentration of AlMe₃ or MeMgBr leads to an increase in the observed rate. Although the rate increase is not as substantial as the increase from 0 to 1 equivalents of AlMe₃. This leads to the possibility two different mechanisms, one which requires only one equivalent and another, which requires multiple AlMe₃ centers.
EXPERIMENTAL SECTION:

General considerations: Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs’ method. Benzene-d6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. All other materials were used as received. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Varian Mercury 300 spectrometer at ambient temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C.D.) and for $^1$H and $^{13}$C NMR data, respectively. $^{31}$P NMR chemical shifts are reported with respect to the instrument solvent lock when a deuterated solvent was used. IR spectra were recorded on a Thermo-Fisher Scientific Nicolet 6700 FT-IR spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon filtering the sample through a plug of silica gel. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high-resolution mass spectrometer.

Kinetic Studies:

Special considerations: All kinetic data was collected on a Varian INOVA-500 MHz NMR spectrometer. In all experiments tri-tert-butylbenzene was used as a standard.

Example of a Kinetic Reaction:

In a glove box a J-Young tube was charged with 7.3 mg (0.012 mmol) of 2a, and 1.1 mg (0.004 mmol) of trimethoxybenzene in 200 μL d-toluene. This mixture in the J-Young tube was frozen in a liquid N₂ cooled cold well. After the solution was frozen a 100 μL d-toluene buffer layer was added to the tube and the frozen. On top of this layer was
added a solution of AlMe₃ in d₉-toluene. The J-Young tube was frozen and transferred to a dry ice acetone bath. The tube was transferred to the NMR at the desired temperature. NMR spectra were collected at regular intervals.
REFERENCES


CHAPTER 5

METALLOMACROCycles AS Ligands: Synthesis and Characterization of Aluminium-Bridged Bisglyoximato Complexes of Iron

The text for this chapter was taken in part from:
Abstract

Dialuminiummacrocycles based on bisglyoximato moieties were prepared and their coordination chemistry with FeII was investigated. The nature of the ancillary ligands bound to aluminum affect the overall geometry of the metallomacrocycles. Additionally, remote substituents on aluminium-bound ligands affect the binding mode, electrochemistry, and electronic properties of the central iron.
INTRODUCTION:

Metallomacrocycles have been studied for a variety of applications including the synthesis of extended solids, catalysis, selective binding of ions and sensing.\textsuperscript{1-18} Rational selection of metal precursors and ligands has afforded metallomacrocycles with diverse shape and size. Incorporation of binding sites for additional metals into the metallomacrocycles typically relies on the ability of coordinating atoms to bridge between the macrocycle metals and the incoming metals. Such systems, known as metallacrowns, have been extensively studied.\textsuperscript{2, 3, 19} An alternative approach to coordinating additional metals involves orthogonal metal-binding atoms on the organic units of the macrocycles. Systems with monodentate phosphines, phenanthroline, phenols or diimines donors capable of binding diverse transition metals are known.\textsuperscript{20-24}

Transition metal complexes supported by bisglyoximato moieties exhibit the interesting ability to bind metal centres in a coordination environment similar to biologically relevant macrocycles. Iron bisglyoximato complexes have chemistry reminiscent of heme species.\textsuperscript{25, 26} The reactivity of cobalt bisglyoximato complexes was investigated in the context of vitamin B12 chemistry\textsuperscript{27, 28} and, recently, in the context of catalytic proton reduction to dihydrogen.\textsuperscript{29-34} The large majority of these species display proton or boron bridges between the oxygen atoms. Boron-bridged variants are generally constructed from the preformed, proton-bridged, metal-bisglyoximate species.\textsuperscript{35-38} Metallomacrocycles consisting of two glyoximato ligands and bridges other than hydrogen or boron are rare, but examples are known with aluminium, gallium, indium or copper moities.\textsuperscript{39, 40} Additionally there are several examples of cryptands consisting of tris-glyoximato moieties with the oxygen donors bound to antimony, tin,
iron, manganese, and chromium. We report herein on the synthesis of metallomacrocycles based on aluminium bridged bisglyoximato frameworks and their coordination chemistry with iron.
RESULTS & DISCUSSION:

In order to assemble metallomacrocycles capable of chelating a variety of metals, a strategy to link two dioximato ligands was employed. Aluminium precursors supported by tetradeinate ligands capable of affording two open cis-coordination sites were selected. Diphenoxide diamines have been used as ancillary ligands for olefin polymerization precisely due to the availability of two cis coordination sites.\(^{46-50}\) Furthermore, the synthesis of these ligands is modular and allows for steric and electronic variation as well as changes in the linkages between the donor atoms. Methylaluminium species were prepared \textit{in situ} by a modification of literature procedures and used as precursors for protonolysis reactions with glyoximes (Scheme 5.1).\(^{31-32}\)

**Scheme 5.1: Synthesis of metal complexes supported by aluminum macrocycles.**

Treatment of diphenylglyoxime (Scheme 5.1), which is sparingly soluble in THF, with 21 led to a homogeneous mixture indicating that a reaction occurred. The
'H NMR spectrum in C.6D6 contains signals corresponding to both the phenoxide ligand and the dioximato backbone. Additionally, a peak slightly downfield of 14 ppm indicated protonation of two of the nitrogen atoms of the glyoximato moiety. To investigate the binding mode of the aluminium macrocycle to metal centres that can access six-coordinate geometry, Fe(II) complexes were synthesized. Via synthetic route B, previously reported iron diglyoximato complex (24)26,53 was treated with methylaluminium species 3a in THF. Precursor 24 is sparingly soluble in THF, but slowly dissolved as the reaction proceeded to generate a bright purple solution. Purification by fractional precipitation afforded the isolation of a red-purple solid. Using route A, treatment of 23 with base followed by FeCl₃ and pyridine allows the isolation of a red-purple solid with spectroscopic properties identical to the product obtained from route B. The 'H NMR spectrum of the red-purple residue in C.6D6 shows a single major peak for each of the three types of methyl groups, NMe₂, para-CH₃ and ortho-CH₃. Additionally, two coordinated pyridines are present (by integration of 1H NMR peaks). Similar to previously synthesized palladium complexes in the group, these spectroscopic data suggest a C₂h structure (or fast exchange) with two pyridines bound along the C₂ axis. ESI-MS data shows a peak at m/z = 1452.7 that is consistent with assignment of the product as 25.

Attempts of growing X-ray quality single crystals of 25 resulted in yellow crystals from a red-purple solution in THF layered with hexanes. An XRD study of this material revealed an unexpected binding for the macrocycle (26, Figure 5.1 and Scheme 5.2). The iron centre is six-coordinate, with a trigonal prismatic geometry. The iron ligands are two phenoxide oxygens bridging between iron and aluminium and the four oxime moieties. The conformation of the metallomacrocycle bound to iron
has the two dioximato planes departing from coplanarity with a dihedral angle of 63°.

Compound 26 was prepared free of pyridine by trituration of 25 with toluene several times. 26 shows a paramagnetic 1H NMR spectrum with broad peaks between 1 and 14 ppm. Further studies were performed to elucidate the behaviour of 25 and 26 in solution. An NMR sample of 25 in CD₂Cl₂ displayed the diamagnetic peaks as described above, but also some paramagnetic peaks consistent with the presence of 26. Addition of excess pyridine led to an increase of the diamagnetic peaks assigned to 25.

Figure 5.1. Solid-state structure of 26. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.
Scheme 5.2: Ancillary and Axial Ligand effects on Fe Coordination

Compound 25 was dissolved in benzene and analyzed by UV-Vis spectroscopy (Figure 5.2). Two absorptions, at 461 and 548 nm were observed. Addition of pyridine led to an increase in the intensity of the band at 548 nm and decrease of the band at 461 nm. The 548 nm band is in the range previously reported for iron bisglyoximato complexes, with coplanar oximes.\textsuperscript{25,34,55} The observed spectral shift in the presence of pyridine is consistent with an equilibrium between 25 and 26 plus free pyridine.
Figure 5.2. UV-Vis spectra at 70 μM of complexes 26 (black), 25 (blue), 25<sup>6-tBu</sup> (green) and 25 plus excess pyridine (2 mM, red).

The structural change from 25 and 26 is accompanied by a spin change from diamagnetic to paramagnetic and a change in the electronic absorption spectrum (Figure 5.2). The change in the iron coordination geometry from square bipyramid to trigonal prism is expected to lead to a smaller d-d splitting because none of the d orbitals have all lobes pointing to ligands. Consequently a high-spin species was generated. The band at 548 nm (25) is consistent with a d-π* charge transfer, as previously assigned. The observed shift to higher energy is likely due to an increase in the energy of the glyoxime π* orbital due to more direct interactions with d orbitals.

Analysis of the solid-state structure of 26 shows that the two bridging phenoxides are spatially close to each other. In order to disfavour phenoxide bridges and facilitate intermolecular binding of ligands, a bulkier phenoxide was utilized. A
variant with tert-butyl instead of methyl groups in the para position vs. the phenoxide oxygens was employed. Species $25^\text{tBu}$ was prepared analogously to $25$ and investigated by UV-Vis spectroscopy (Figure 5.2). Without added pyridine the peak at 548 nm, corresponding to the d-$\pi^*$ transition in $25^\text{tBu}$, is almost as intense as the 548 nm peak of $25$ upon addition of excess pyridine. This indicates that the increased steric bulk on the ligand periphery affects the coordination environment at the iron center, disfavouring the formation of phenoxide bridges (Scheme 5.2).

The geometry of the ancillary ligand bound to the aluminum center affects the overall symmetry of the metallomacrocycle. A tripodal N(O,N) ligand generates an aluminium precursor of pseudo-$C$ symmetry (21, Scheme 5.1). Since two aluminium centres are part of the metallomacrocycle, the symmetry can be pseudo-$C_6$ or pseudo-$C_{2v}$ (approximating the macrocycle as planar) dependent on the relative orientation of the Al[N(O,N)] moiety (Scheme 5.3). If the four donors of the diphenoxide diamines ligands are linked in a linear fashion (NO), the resulting aluminium complexes display pseudo-$C_2$-symmetry rendering the metal centres chiral. Again, depending on the stereochemistry at aluminium, two types of macrocycles are possible, with pseudo-$D_2$ or pseudo-$C_{2v}$ symmetry. It was envisioned that the stereochemistry at aluminium could be set by a chiral centre in the ligand backbone, such as defined by a trans-1,2-diaminocyclohexane moiety. Control of the stereochemistry by the ancillary ligand was expected to favour the chiral, pseudo-$D_2$ structure.

To examine the stereochemistry of complexes with $C_i$ symmetric ancillary ligands on aluminium, precursors$^7,10$ supported by linear diphenoxide diamine ligands were prepared using 1,2-ethylenediamine or ($R,R$)-trans-1,2-diaminocyclohexane backbones (Scheme 5.3). Attempts to prepare iron complexes ligated by
aluminium macrocycles with ethylenediamine backbones resulted in a mixture of diamagnetic products likely due to the formation of both pseudo-D₄ and pseudo-C₄₅₄ structures. Nevertheless, one isomer can be enriched by precipitation. Since NMR spectroscopy does not allow for determination of the symmetry of the isolated product, an XRD study was performed and showed a pseudo-D₄ structure in the solid-state (29ᵗBu). The iron coordination environment is pseudo-octahedral, with the phenoxide oxygens coordinated only to aluminium. This geometry at iron is consistent with the sharp, diamagnetic NMR spectra, and the vibrant purple colour. Since a variant with methyl groups in the position para to the phenoxide oxygen was not prepared, it is not clear if the macrocycle binding mode is a consequence of the bulky substituent or the steric demands of the linear ligand set bound to aluminium. The metallomacrocycle appears to be larger than boron or hydrogen linked versions.⁵⁹,⁶⁰ The O1-O3 and O2-O4 distances in 29ᵗBu are ca. 0.4 Å larger than the corresponding ones in difluoroborate and proton linked iron diglyoximato species (average 2.90 vs. 2.57 and 2.52 Å respectively).⁵⁹,⁶⁰ This ring expansion is due to the larger aluminium centre. Ruffling of the metallacycle is observed and contrasts with the flat geometry observed for bisglyoximato complexes bridged by protons or boron moieties. This distortion could be due to C-twists caused by the aluminium centres or the larger size of the macrocycle.
Scheme 5.3. Effect of the ancillary ligand of aluminum on the symmetry of the metallomacrocycle.
Figure 5.3. Solid state structures of $29^{\text{tBu}}$ and $32^{\text{NO2}}$. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.
Utilization of enantiopure \((R,R)\text{-}trans\)-1,2-diaminocyclohexane backbones results in significantly cleaner reactions for the synthesis of iron complexes ligated by aluminium macrocycles, \(32^{\text{tn}}\) and \(32^{\text{NO}_2}\) (1H NMR spectroscopy). Analysis of \(31^{\text{tn}}\) by \(^{27}\text{Al}\) NMR gives a broad peak ca. 74 ppm consistent with a five coordinate aluminium center as described in literature.\(^{52,61-63}\) Mixing \(31^{\text{tn}}\) with diphenyl glyoxime forms the \(31^{\text{tn}}\) macrocycle, which gives a broad \(^{27}\text{Al}\) NMR peak ca. 14 ppm consistent with aluminium coordination to the glyoxime oxygens. Subsequent metallation and carbonyl coordination to form \(32^{\text{tn}}\) and \(33^{\text{tn}}\) does not substantionally change the shift in the \(^{27}\text{Al}\) NMR (14 and 12 ppm respectively).\(^{61-63}\) Ligand variants with \(\text{para-NO}_2\) and \(\text{para-tert-butyl}\) substitution were employed for the phenoxides. An XRD study of complex \(32^{\text{NO}_2}\) revealed a \(\text{pseudo-}\text{D}\)\(_2\) structure. Similar to complex \(29^{\text{tn}}\) supported by the ethylenediamine backbone, \(32^{\text{NO}_2}\) shows ruffling of the macrocycle departing from an idealized \(D\)\(_2\) structure. The control of the overall symmetry of the metallomacrocycle by the ancillary ligand on aluminium is notable as it affords enantiopure macrocycles.\(^{18,64}\)

Remote substituents on the phenoxide rings were found to affect the coordination environment around the central iron, likely due to steric interactions (vide supra). To complement those findings, complexes \(32^{\text{tn}}\) and \(32^{\text{NO}_2}\) allow for studies of the electronic effect of remote groups on aluminium-bound phenoxide on chemistry at the iron centre. Cyclic voltammetry of \(32^{\text{tn}}\) shows waves between 0.5 and 1 V vs. [FeCp\(_2\)]\(^+\) / FeCp\(_2\), which are assigned to phenoxide based redox events (Figure 5.4). Metal-bound trialkyl phenoxides were reported previously to have reduction potentials in the above range.\(^{63,66}\) Complex \(32^{\text{NO}_2}\) displays a positive shift of these potentials consistent with the presence of electron withdrawing nitro groups that
disfavouring ligand oxidation. A large peak is seen close to 1 V in \(32^{\text{NO}_2}\), which is assigned to the oxidation of the nitro substituted phenoxides on the ancillary aluminium centers as the \(31^{\text{NO}_2}\) diphenylglyoxime macrocycle also contains a large oxidation wave in that region (Figure 5.5). The redox event at -0.34 V for \(32^{\text{tBu}}\) was assigned to the Fe\(^{\text{III}}/\text{Fe}^{\text{II}}\) couple. This is 0.32 V more negative compared to proton-bridged iron diglyoximato species (-0.02 V vs. \([\text{FeCp}^i]^+ / \text{FeCp}^j\)). It is not clear if this a consequence of increasing electron density at iron when six-coordinate aluminium bridges are present or of the larger macrocycle size with aluminium. The presence of four para-NO\(_2\) groups in \(32^{\text{NO}_2}\) led to a Fe\(^{\text{III}}/\text{Fe}^{\text{II}}\) couple at -0.07 V. The significant 0.27 V shift of the Fe\(^{\text{III}}/\text{Fe}^{\text{II}}\) reduction potential compared to \(32^{\text{tBu}}\) supports the notion that the redox properties of the central atom can be affected by remote substituents at the periphery of the macrocycle.
Figure 5.4. Cyclic voltammograms of complexes $32^{tBu}$ (red) and $32^{NO2}$ (blue) (1 mM in 1:1 DCM:MeCN solution, 0.1 M nBuClO$_4$, 0.01 M AgNO$_3$ reference electrode, platinum working electrode, Pt wire counter electrode, referenced to FeCp$^+$/[FeCp]$^-$).

Figure 5.5. Cyclic voltammograms of complexes $31^{NO2}$ (blue) and $31^{tBu}$ (red), 1 mM solutions of each using a 100 mV/s scan rate, both referenced to Fe/Fe$^+$. 
Scheme 5.4. Synthesis of iron complexes supported by aluminium macrocycles with C2-symmetric ancillary ligands.

Treatment of complexes 32\textsuperscript{\textit{tBu}} and 32\textsuperscript{\textit{NO2}} with CO generated new species cleanly by 1H NMR spectroscopy (Scheme 5.4). The number of peaks corresponding to the diphenoxide diamine ligands is doubled, consistent with a decrease in molecular symmetry. For example, the methyl groups ortho to the phenoxide oxygen display two singlets rather than one in 32\textsuperscript{\textit{tBu}} or 32\textsuperscript{\textit{NO2}}. Displacement of one pyridine with CO leads to a pseudo-$C_2$ structure. The two different ligands located on the $C_i$ axis, CO and pyridine, render chemically different the two halves of the molecule delimited by the Fe-diglyoximato moiety.\textsuperscript{26} The carbonyl C–O stretch for complexes 33\textsuperscript{\textit{tBu}} and 33\textsuperscript{\textit{NO2}} (Scheme 5.4) appears at 2019 and 2020 cm$^{-1}$, respectively. The carbon monoxide adduct of the proton-bridged iron diglyoximato species (24) shows a C–O stretch at 2004 cm$^{-1}$ in THF.\textsuperscript{26} The cyclic voltammograms of the CO adducts 33\textsuperscript{\textit{NO2}} and 33\textsuperscript{\textit{tBu}} show a large shift in the Fe$^{II}$/Fe$^{III}$ couple in comparison with the dipyridine complexes 32\textsuperscript{\textit{NO2}} and 32\textsuperscript{\textit{tBu}}. The Fe$^{II}$/Fe$^{III}$ couple in 33\textsuperscript{\textit{NO2}} shows up as an irreversible oxidation at 0.71 V, which is ca. 700 mV more positive than that observed in 32\textsuperscript{\textit{NO2}}. Similarly, the Fe$^{II}$/Fe$^{III}$ couple in the 33\textsuperscript{\textit{tBu}} complex is shifted, albeit obscured by the phenoxide oxidation peaks. The shift in the Fe$^{II}$/Fe$^{III}$ couple is similar to what is seen in a boron-bridged...
iron bisdimethylglyoxime system and metal porphyrin systems upon the binding of carbon monoxide. The similar values for \(33^{tBu}\) and \(33^{NO2}\) suggest that although the iron reduction potential is affected by the substituents, the electron density of the metal is affected to a greater extent by interactions with the carbonyl ligand. Compared to proton bridged system, \(33^{tBu}\) and \(33^{NO2}\) both appear less electron rich on the central metal based on the C–O stretch.
**CONCLUSIONS:**

In summary, metallomacrocycles consisting of dialuminium diglyoximato frameworks were synthesized and utilized as ligands for iron. These iron complexes were also prepared independently by first binding two glyoximato units to a central metal followed by reaction with alkyl aluminium precursors. The overall symmetry of the products is affected by the ancillary ligands bound to aluminium. Utilization of enatiopure, $C$-symmetric backbones facilitates the formation of a single, chiral isomer. The steric bulk of remote substituents was found to affect the conformation of the free metallomacrocycles as well as the coordination geometry around the central metal. For iron, complexes with trigonal prismatic and square bipyramidal coordination modes were characterized. Additionally, the electronic properties of the substituents on ligands bound to aluminium significantly influence the reduction potentials of the central metal. The present synthetic strategies and properties suggest that metallomacrocycles with a variety of ancillary ligands can be prepared and designed to affect chemistry at the central atom both sterically and electronically.
EXPERIMENTAL SECTION:

General Considerations. Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs’ method. Benzene-d₆ was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. Chloroform-d and dichloromethane-d₂ were also purchased from Cambridge Isotope Laboratories and vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 °C for 12 h. Tetradentate salan ligands (21ᵗBu), methyl aluminum complexes (22, 22ᵗBu, and 27ᵗBu), and metal glyoxime precursors (24) were all synthesized according to literature procedures. All other materials were used as received. All ¹H, ¹³C, and 2D NMR spectra were recorded on Varian Mercury 300 MHz, Varian 400 MHz, or Varian INOVA-500 or 600 MHz spectrometers at room temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C₆D₆), 7.26 ppm and 77.16 ppm (CDCl₃), and 5.32 ppm and 53.84 ppm (CD₂Cl₂) for ¹H and ¹³C NMR data, respectively. The chemical shifts in the ²⁷Al NMR data were referenced to a 1.1 M solution of Al(NO₃)₃ in D₂O. Electrochemical measurements were recorded in a glovebox under a N₂ atmosphere using a Pine Instrument Company Bipotentiostat, at 1mM of the complex of interest, in DCM containing 0.1 M nBu₄N(ClO₄) as the supporting electrolyte. For the electrochemistry a platinum working electrode, a platinum wire auxiliary electrode, and a 0.01M Ag/AgNO₃ nonaqueous reference electrode were used for all measurements. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN).
Synthesis of 23

A stirring solution of 2 (0.158 g, 0.387 mmol) in THF was treated with a slurry of diphenylglyoxime (0.096 g, 0.398 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. The macrocycle 22 was used as isolated without any further purification. Yield 0.211 g, 88 %.

^1H NMR (300 MHz, C6D6) \(\delta\) 14.41 (2H, s, NH), 7.86 (8H, m, k) 6.98 (4H, t, \(J = 7.6\) Hz, i), 6.83 (8H, m, j), 6.76 (4H, s, l,l'), 6.69 (4H, s, l,l'), 4.89 (4H, d, \(J = 12.9\) Hz, b,b'), 2.79 (4H, d, \(J = 13.1\) Hz, b,b'), 2.38 (12H, s, e), 2.32 (4H, m, a,a'), 2.18 (12H, s, c), 2.15 (12H, s, d), 1.75 (4H, m, a,a') ppm. Anal. Calcd for C72H82Al2N8O8: C, 69.66; H, 6.66; N, 9.03; Found: C, 69.07; H, 6.69; N, 8.69 %.
Synthesis of 25

Route B: In a 20 ml vial (0.043 g, 0.062 mmol) of 24 was stirred in about 2 ml of THF. To this was added (0.050 g, 0.126 mmol) of 22 as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 3 days. Over the reaction time the solid 24 became soluble. The volatiles were removed under vacuum and the resulting purple solid was washed with Et₂O and benzene. The benzene was removed from the benzene fraction via vacuum and the resulting solid was dissolved in minimal amounts of THF. Small amounts of hexanes were added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.033 g, 36 %.

Route A: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of 23 (0.100 g, 0.081 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a solution of FeCl₂ (0.010 g, 0.079 mmol) in THF. The solution immediately turned a dark purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding the a
purple red solid which was washed with ether. Yield 0.060 g, 52 %, about 90 % pure. To date, an analytically pure sample has yet to be obtained due to contamination of what is believed to be another isomer of the desired complex. ¹H NMR (500 MHz, C.D.) δ 9.30 (4H, d, J=5.6 Hz, h), 7.33 (4H, m, J=5.8 Hz, i), 6.98 (16H, m, j,l), 6.95 (4H, s, l’), 6.79 (2H, t, J=8.2 Hz, f), 6.63 (4H, m, g), 6.61 (4H, s, l), 4.61 (4H, d, J=13.0 Hz, b’), 2.61 (4H, d, J=12.9 Hz, b), 2.36 (6H, s, d), 2.15 (4H, m, a’), 1.97 (6H, s, e), 1.80 (6H, s, c), 1.64 (4H, m, a) ppm. ¹³C{¹H} (126 MHz, C.D.) δ 159.08 (4), 158.35 (6), 156.67 (h), 135.70 (7), 134.57 (f), 131.41 (f’), 130.49 (6), 130.43 (k), 127.63 (j), 127.25 (l), 126.01 (5), 122.59 (g), 122.15 (3), 121.80 (2), 64.97 (b,b’), 58.18 (a,a’), 50.11 (a,a’), 47.68 (c), 20.89 (d), 16.74 (e) ppm. MS ESI (m/z): calcd, 1453.46 (M+); found 1452.7 (M+) (dipyridine) and 1390.2 (M+) (monopyridine with an oxygen)

Synthesis of 26

A solution of 23 (0.248 g, 0.200 mmol) in THF was treated with a solution of Sodium hexamethyldisilazide (0.073 g, 0.400 mmol) also in THF. The solution was stirred for 3 hours over which the solution lost some of its color. After 3 hours the solvent was removed in vacuo resulting in a pale yellow white solid. The solid was washed with pentane resulting in a white THF soluble solid (0.116 g, 0.090 mmol, 23-Na). To a THF solution of this disodium salt was added a slurry of FeCl₃ in THF (0.0115 g,
0.091 mmol). Upon addition the solution immediately became a dark black with an orange hue. The solution was stirred for 4 hours and the THF was removed \textit{in vacuo}. The resulting dark brown solid was washed with diethyl ether resulting in an orange solid which was extracted using DCM. The DCM was removed \textit{in vacuo} resulting in a dark orange solid paramagnetic material. Alternatively, 26 can be synthesized by removing the pyridines from 25, by dissolving 25 in a high boiling solvent and removing the solvent \textit{in vacuo}. Crystals were grown from a concentrated solution of 25 in THF layered with hexanes. Yield 0.066 g, 57%. $^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ 18.46, 15.23, 12.84, 11.02, 10.67, 9.82, 8.97, 7.13, 6.68, 5.26, 4.96, 4.27 ppm.

\textbf{Synthesis of 23$^{th}$}

The macrocycle was synthesized following the synthesis procedure for 23. A stirring solution of 22$^{th}$ (0.100 g, 0.021 mmol) in THF was treated with a slurry of diphenylglyoxime (0.050 g, 0.021 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed \textit{in vacuo} to yield a pale yellow solid. The Al(salan)(diphenylglyoxime)$_2$ macrocycle was used as isolated without any further purification. $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 14.10 (2H, s, NH), 7.85 (4H, d, J = 6.7 Hz, l,l'), 7.61 (4H, t, J = 7.6 Hz, l,l'), 6.92 (8H, m, j), 6.82 (8H, m, j),
6.65 (4H, m, i), 4.82 (4H, d, J = 12.7 Hz, b,b’), 2.81 (4H, d, J = 12.9 Hz, b,b’), 2.32 (12H, s, e), 2.23 (4H, m, a,a’), 2.02 (12H, s, c), 1.78 (4H, m, a,a’), 1.48 (36H, s, d) ppm.

**Synthesis of 25**

25 was synthesized and purified according to the synthesis procedures of 25.

**Route A:** In a 20 ml vial 0.072 g (0.010 mmol) of 24 was stirred in about 2 ml of THF. To this was added 0.110 g (0.023 mmol) of the 22 complex as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 16 days. Over the reaction time the solid 24 glyoxime became soluble. The volatiles were removed under vacuum and the resulting purple red solid was washed with hexanes, pentane, diethyl ether, and toluene. The toluene fraction was concentrated via vacuum and a small amount of hexanes was added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.071 g, 44%.

**Route B:** Sodium hexamethyldisilazide 0.036 g (0.200 mmol) was added to a solution of 23 (0.141 g, 0.100 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane.
to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.126 g, 0.090 mmol) was taken up in THF and mixed with a solution of Fe(II)Cl₂ (0.011 g, 0.090 mmol) in THF. The solution immediately turned a dark purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple red solid, which was washed with pentane and hexanes and extracted with diethyl ether. Yield 0.098 g, 67%

¹H NMR (300 MHz, C.D.): δ 9.26 (4H, d, J=5.5 Hz, h), 7.41 (4H, d, J=8.4 Hz, g), 7.21 (8H, s, k), 6.97 (8H, s, j), 6.89 (8H, s, l), 6.83 (4H, t, J=6.7 Hz, i), 6.58 (2H, t, J=6.7 Hz, f), 4.65 (4H, d, J=12.9 Hz, b,b'), 2.71 (4H, d, J=13.3 Hz, b,b'), 2.15 (4H, m, a,a'), 2.08 (6H, s, e), 1.81 (6H, s, c), 1.63 (4H, m, a,a'), 1.44 (36H, s, d) ppm. ¹³C[¹H] NMR (126 MHz, C.D.) δ 159.02 (4), 158.88 (6), 156.46 (h), 153.80 (7), 134.24 (2), 130.62 (f), 130.37 (k), 127.66 (j), 127.53 (i), 127.44 (l,l'), 125.67 (5), 123.18 (l,l'), 122.52 (g), 121.53 (3), 65.65 (b,b'), 58.10 (a,a'), 50.33 (a,a'), 47.64 (c), 33.90 (1), 32.33 (d), 17.12 (e) ppm. Anal. Calcd for C₄₆H₅₆Al₆Fe₇N₁₅O₆: C, 69.62; H, 7.09; N, 8.64; Found C, 69.36; H, 7.33; N, 8.63
**Synthesis of 29**

In a round bottom flask 24 (0.692 g, 0.98 mmol) was stirred in 10 ml of toluene at ambient temperature. To this purple slurry was added a solution of the 28 (0.999 g, 2.08 mmol) in toluene. The solution was stirred for 14 hours. After 14 hours toluene was removed in vacuo yielding a purple solid. The solid was washed with hexanes, Et2O, and toluene. The toluene washed was pumped down to a solid yielding clean 6. Yield: 0.688 g, 43 %

**H NMR (500 MHz, C6D6)** \[\delta 9.21 (4H, d, J = 4.9 Hz, b), 7.31 (8H, d, J = 7.3 Hz, k), 7.21 (4H, d, J = 2.4 Hz, l'), 7.01 (8H, t, J = 7.5 Hz, j), 6.91 (4H, m, i), 6.75 (2H, t, J = 7.6 Hz, f), 6.74 (4H, d, J = 2.5 Hz, l), 6.30 (4H, t, J = 7.0 Hz, g), 4.49 (4H, d, J = 12.8 Hz, b,b'), 2.69 (4H, d, J = 9.0 Hz, a,a'), 2.57 (4H, d, J = 13.1 Hz, b,b'), 2.14 (12H, s, e), 1.90 (12H, s, c), 1.38 (36H, s, d), 0.89 (4H, d, J = 9.1 Hz, a,a') ppm.

**^{13}C{[^1}H] NMR (126 MHz, C6D6)** \[\delta 158.90 (4), 157.44 (6), 156.83 (h), 135.99 (2), 135.87 (7), 134.16 (f), 130.58 (k), 127.75 (j), 127.43 (i), 126.90 (l'), 126.68 (5), 123.14 (l), 122.65 (g), 120.89 (3), 63.73 (b,b'), 49.97 (a,a'), 46.85 (c), 33.88 (1), 32.30 (d), 17.62 (e) ppm.

Anal. Calcd for C_{94}H_{114}Al_{2}FeN_{10}O_{8}: C, 69.62; H, 7.09; N, 8.64; Found, C, 69.49; H, 6.96; N, 8.44;
Synthesis of $30^{\text{NO}_2}$

This ligand variant was synthesized using a modified literature procedure. A solution of N,N'-dimethylcyclohexane-1,2-diamine (0.233 g, 1.63 mmol) and diisopropylethylamine (0.424 g, 3.28 mmol) in THF (7.5 ml) at 0°C (ice bath) was treated with a cold solution (ice bath) of 2-(chloromethyl)-6-methyl-4-nitrophenol (0.661 g, 3.28 mmol) in THF (5 ml). The solution was stirred for 16 hours during which a yellow precipitate formed. The resulting slurry was filtered using a medium glass frit and washed with 3x 20 ml of cold MeOH. The resulting off white solid was dried under vacuum. Yield 0.298 g, 38 %. 1H NMR (300 MHz, CDCl3), $\delta$ 11.99 (2H, br s, OH) 8.01 (2H, d, J = 2.8 Hz, l,l'), 7.84 (2H, d, J = 2.4 Hz, l,l'), 3.91 (4H, d, J = 13.2 Hz, b,b'), 3.59 (2H, br s, b,b'), 2.83 (2H, m, a), 2.29 (6H, s, c), 2.14 (6H, s, c), 2.11 (2H, m, a"), 1.91 (2H, s, a'), 1.27 (4H, br m, a",a") ppm. 13C[1H] NMR (from 2D spectra, 126 MHz, (CD₃)₂SO) $\delta$ 166.98 (4), 135.7 (2), 126.12 (5), 125.8 (l'), 127.3 (l), 122.58 (3), 62.56 (b,b'), 25.54 (c), 22.78 (a), 16.68 (a), 16.53 (c) ppm from . ESI-MS Calc. (M) 472.2322 Found. 473.2 (MH+)
The synthesis of $^{31}$NO$_2$ was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes. A freshly thawed slurry of $^{30}$NO$_2$ (0.024 g, 0.052 mmol) in toluene (5 ml) was treated with a thawed solution of trimethylaluminum (0.004 g, 5.2 μl, 0.053 mmol). Upon mixing the solid particulates dissolved and the solution became a dark orange color which faded after a few minutes resulting in a light yellow solution. The solution was allowed to stir for 18 hours. During this time the solution became a slurry. The solvent was removed *in vacuo* resulting in a light yellow powder which was used without further purification. Yield 0.026 g, 99 % 1H NMR (300 MHz, CD$_2$Cl$_2$), δ 8.04 (2H, m, l,l’), 7.85 (2H, m, l,l’), 4.00 (2H, J = 13.4 Hz, b,b’), 3.50 (2H, J = 13.0 Hz, b,b’), 2.95 (2H, m, a), 2.32 (3H, s, e), 2.28 (6H, m, e’,c’), 2.18 (2H, m, a”), 2.10 (3H, s, c), 1.97 (2H, m, a’), 1.51(2H, m, a”), 1.25(2H, m, a’), -0.69 (3H, s, AlCH$_3$) ppm.
Synthesis of $31^{\text{NO}_2}$ Macrocycle

The macrocycle was synthesized following the synthesis procedure for $23$. A stirring solution of $31^{\text{NO}_2}$ (0.100 g, 0.019 mmol) in THF was treated with a slurry of diphenylglyoxime (0.046 g, 0.019 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed in vacuo to yield a pale yellow solid. $31^{\text{NO}_2}$ macrocycle was used as isolated without any further purification. Yield 0.139 g, 97 %. $^1$H NMR (300 MHz, C$_6$D$_6$) δ 13.98 (2H, s, NH), 7.77 (4H, d, $J = 2.9$ Hz, l,l’), 7.59 (12H, m, i and j), 7.29 (12H, m, k and l,l’), 4.41 (4H, d, $J = 13.5$ Hz, b,b’), 3.25 (4H, d, $J = 13.6$ Hz, b,b’), 2.44 (4H, m, a), 2.06 (12H, s, e), 1.92 (12H, s, c), 1.72 (4H, m, a’), 1.59 (4H, m, a’’), 1.03 (4H, m, a’’), 0.80 (4H, m, a’’) ppm. $^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$) δ 165.86 (4), 149.36 (6), 136.44 (2), 130.11 (k), 128.28 (j), 127.97 (5), 127.40 (7), 126.39 (l’), 123.49 (l), 120.79 (3), 58.45 (b,b’), 56.39 (a), 39.97 (c), 24.01 (a’’), 21.89 (a’), 16.18 (e) ppm. Anal. Calcd for C$_{76}$H$_{82}$Al$_2$FeN$_{12}$O$_{16}$: C, 61.95; H, 5.61; N, 11.41; Found: C, 61.91; H, 5.74; N, 11.29 %.
Synthesis of $\text{32}^{\text{NO}_2}$

Route A: To a slurry of $\text{31}^{\text{NO}_2}$ (0.150 g, 0.302 mmol) in toluene (5 ml) was added 24 (0.101 g, 0.146 mmol) with THF (3 ml). The slurry was stirred for a total of 3 days, during which the solution took on a purple orange hue. From this colored solution a solid precipitated on the walls of the vial. After the allotted time the solvent was removed in vacuo. The solid was washed three times with hexanes to remove the excess toluene. The solid was fractioned with hexanes, diethylether, toluene, and THF. The desired product was found in the THF fraction. Yield 0.129 g, 52%.

Route B: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of $\text{31}^{\text{NO}_2}$ macrocycle (0.236 g, 0.160 mmol) in THF. The solution was stirred for 12 hours and the solvent was removed via vacuum. The resulting residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.217 g, 0.143 mmol) was taken up in THF and mixed with a solution of Fe(II)Cl$_2$ (0.019 g, 0.146 mmol) in THF. The solution immediately turned a dark purple. The dark purple solution was stirred for 3 hours after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple solid which was washed with benzene and extracted with THF. Yield 0.174 g, 72%.
'H NMR (500 MHz, CD₂Cl₂), δ 8.61 (4H, s, h), δ 7.83 (4H, l'), δ 7.63 (4H, l'), δ 7.28 (m, 20H), δ 7.02 (dd, 4H), δ 6.37 (m, 2H), δ 4.15 (d, 4H), δ 2.89 (d, 4H), δ 1.80 (s, 12H), δ 1.75 (s, 12H) ¹³C[¹H] NMR (126 MHz, CD₂Cl₂) δ 166.85 (4), 159.75 (6), 155.16 (h), 135.81 (2), 134.82 (k), 129.75 (j), 128.35 (5) 128.25 (7) 127.76 (f), 126.35 (l'), 123.88 (l), 123.05 (g), 121.54 (3), 58.48 (b,b'), 56.27 (a), 40.97 (c), 24.40 (a''), 22.06 (a'), 16.69 (e) ppm. Anal. Calcd for C₈₆H₉₀Al₂FeN₁₄O₁₆: C, 61.28; H, 5.38; N, 11.63; Found: C, 61.13; H, 5.46; N, 11.43 %

**Synthesis of 30**

This compound was synthesized via a manich condensation of the (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and 2-methyl-4-tert-butylphenol using a previously published procedure. The amines were methylated following the same procedure resulting in the compound 30. ¹H NMR (300 MHz, CDCl₃), δ 10.01 (2H, br s, OH), 7.05 (2H, d, J = 2.1 Hz, l,l'), 6.82 (2H, d, J = 2.4 Hz, l,l'), 3.77 (2H, d, J = 13.2 Hz, b,b'), 3.66 (2H, d, J = 13.3 Hz, b,b'), 2.70 (2H, m, a), 2.20 (6H, s, e), 2.17 (6H, s, e), 2.01 (2H, m, a''), 1.81 (2H, d, a'), 1.27 (18H, s, d), 1.17 (4H, m, a',a'') ppm. ¹³C[¹H] NMR (126 MHz, CD₃D₃) δ 154.06 (4), 140.74 (2), 127.17 (l'), 124.73 (5), 123.32 (l), 121.26 (3), 61.65 (b,b'), 33.66 (l), 31.60 (d), 25.05 (c), 21.99 (a,a',a''), 16.23 (e) ppm. ESI-MS Calc. (M) 494.3872 Found. 495.3 (MH⁺)
Synthesis of 31<sub>tBu</sub>

Compound 31<sub>tBu</sub> was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes. A slurry of 30<sub>tBu</sub> (0.956 g, 1.93 mmol) in toluene was frozen in a coldwell. Upon freezing the solution was allowed to thaw upon which a freshly thawed solution of trimethylaluminum (0.139 g, 1.93 mmol) in toluene (3 ml) was added slowly. This mixture was allowed to warm to room temperature and left stirring for 12 hours. After 12 hours the solvent was removed in vacuo, yielding an off white solid which was used without further purification. Yield: 0.900 g, 87 % 1H NMR (300 MHz, C6D6) δ 7.32, 7.29, 6.90, 6.82, and 6.78 (l,l'), 3.61, 3.54, 3.32, 3.27, 2.79, 2.75, and 2.70 (b,b'), 2.63 and 2.43 (e), 2.29 and 1.99 (a), 1.88, 1.68, and 1.66 (c), 1.41, 1.39, and 1.39 (d), 1.21, 0.60, and 0.48 (a',a''), -0.40 (AlCH3) ppm. 13C{1H} NMR (126 MHz, CD2Cl2) δ 156.06 (4), 155.89 (4), 138.33 (2), 137.68 (2), 127.43 (l'), 127.29 (l'), 126.93 (l'), 126.68 (5), 126.55 (5), 126.01 (5), 123.04 (l), 122.84 (l), 120.03 (3), 118.54 (3), 63.81 (b,b'), 60.73 (b,b'), 60.26 (b,b'), 59.48 (b,b'), 42.67, 36.77, 33.57 (l), 31.51 (d), 24.79 (a''), 24.54 (a''), 23.13(a'), 22.89
187

(a’), 22.72 (a’), 16.21 (e), 16.08 (e), 15.72 (Al CH₃) ppm multiple diastereomers in
solution. ²⁷Al NMR (104.7 MHz, 25 °C, CD₂Cl₂) δ 74.21 ppm, ω₁/₂ 6500 Hz.

Synthesis of 3¹ᵗBu macrocycle

The macrocycle was synthesized following the synthesis procedure for 3a. A stirring
solution of 3¹ᵗBu (0.105 g, 0.197 mmol) in THF was treated with a slurry of
diphenylglyoxime (0.047 g, 0.196 mmol) in THF. The solution was stirred for 3 hours
over which the solution became yellow. The solvent was removed in vacuo to yield a
pale yellow solid. 3¹ᵗBu macrocycle was used as isolated without any further purification.
It can also be purified through precipitation from pentane. Yield 0.145 g, 98 %. 1H
NMR (300 MHz, C6D6) δ 14.20 (2H, s, NH), 7.67 (8H, d, J = 7.1 Hz, k), 7.29 (4H, s,
l,l’), 6.91 (12H, m, j,i), 6.78 (4H, m, l,l’), 4.54 (4H, d, J = 13.0 Hz, b,b’), 2.88 (4H, d, J
- 13.1 Hz, b,b’), 2.57 (4H, m, a), 2.34 (12H, s, e), 2.06 (12H, s, c), 1.45 (36H, s, d),
1.25 (8H, m, a’, a’’), 0.38 (8H, m, a’,a’’), ppm. 13C{1H} NMR (126 MHz, CD₂Cl₂) δ
156.69 (4), 148.27 (6), 136.31 (7), 131.56 (2), 130.12 (k), 128.76 (j), 127.53 (i), 126.99
(l’), 125.54 (5), 123.17 (l), 120.29 (3), 59.40 (b,b’), 55.56 (a), 39.89 (c), 33.49 (1),
31.67 (d), 24.31 (a”), 21.83 (a’), 16.05 (e). 27Al NMR (104.7 MHz, 25 °C, CD₂Cl₂) δ
14.40 ppm, $\delta_{1/2}$ 4150 Hz. Anal. Calcd for C$_{92}$H$_{118}$Al$_2$FeN$_8$O$_8$: C, 72.80; H, 7.84; N, 7.38; Found: C, 72.68; H, 7.60; N, 7.12 %

**Synthesis of 32$^{30}$$^{30}$**

Route B: In a 100 mL round bottom, a solution of 30$^{30}$ (2.167 g, 4.05 mmol) was treated with a slurry of Fe(DPG)$_2$(Py)$_2$ (1.334 g, 1.93 mmol) in benzene at room temperature. The solution was stirred allowing for the produced methane to escape. After 24 hours the solvent was removed in vacuo. The crude solid was taken up in hexanes and filtered. The recovered solid was washed with diethyl ether and extracted with toluene. Purified 12$^{30}$ was precipitated from toluene by adding hexanes to the toluene mixture and cooling the mixture to -35°C overnight. Another crop of purified solid can be obtained from the hexane fraction via cooling to -35°C overnight. Yield 2.197 g, 66%

Route A: Sodium hexamethyldisilazide (0.013 g, 0.069 mol) was added to a solution of 31$^{30}$ macrocycle (0.503 g, 0.033 mol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting residue was triterated with THF to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a slurry of Fe(II)Cl$_2$ (0.005 g, 0.039 mmol) in THF. The
solution immediately turned a dark purple. The dark purple solution was stirred for one hour after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple solid. The solid was washed with hexanes and a small amount of diethylether before it was extracted with toluene. The solvent was removed in vacuo yielding the same product as Route A. Yield 0.414 g, 72 %

\(^1\)H NMR (500 MHz, C6D6) \(\delta\) 9.35 (4H, d, \(J = 5.5\) Hz, h), 7.33 (8H, d, \(J = 7.4\) Hz, k), 7.20 (4H, s, l'), 7.06 (8H, t, \(J = 7.4\) Hz, j), 7.00 (4H, m, \(J = 7.1\) Hz, i), 6.77 (2H, t, \(J = 7.6\) Hz, f), 6.74 (4H, s, l), 6.34 (4H, t, \(J = 6.7\) Hz, g), 4.54 (4H, d, \(J = 13.2\) Hz, b'), 2.80 (4H, d, \(J = 13.4\) Hz, b), 2.52 (4H, s, a), 2.17 (12H, s, c), 1.93 (12H, s, e), 1.35 (36H, s, d), 1.22 (4H, m, a'), 1.02 (4H, s, a''), 0.46 (4H, m, a''), 0.28 (4H, m, a'') ppm; \(^{13}\)C NMR (125.70 MHz, C6D6) \(\delta\) 158.77 (6), 157.80 (4), 157.01 (h), 136.14 (7), 135.90 (2), 134.17 (f), 130.62 (k), 127.78 (j), 127.41 (i), 127.08 (l'), 126.17 (5), 122.82 (l), 122.56 (g), 121.27 (3), 59.90 (b,b'), 55.45 (a), 40.90 (c), 33.86 (l), 32.29 (d), 24.26 (a''), 21.78 (a'), 17.51 (e) ppm; \(^{27}\)Al NMR (104.7 MHz, 25 °C, C6D6) \(\delta\) 14.19 ppm, \(\omega_{1/2}\) 9000 Hz.

Anal. Calcd for C\(_{102}\)H\(_{126}\)AlFeN\(_{10}\)O\(_{8}\): C, 70.82; H, 7.34; 8.10; Found C, 69.90; H, 7.24; N, 7.44 %
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<tr>
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\(^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad ^b wR_2 = \frac{\sum [w(F_o^2-F_c^2)]/\sum w(F_o^2)]^{0.5}}{wR_2 = \frac{\sum [w(F_o^2-F_c^2)]/\sum w(F_o^2)]^{0.5}}.\)
REFERENCES


CHAPTER 6

Aluminum-Bridged Bisglyoximato Cobalt Complexes: Synthesis and Electrochemical Proton Reduction Properties

The text for this chapter was taken in part from:
ABSTRACT

The syntheses of several cobalt diglyoximato complexes connected by one or two aluminum bridges are described. The aluminum centers are supported by tunable tetradeinate diamine bisphenoxide ligands. Electrochemical investigations revealed that the number of aluminum bridges and the nature of the substituents on the phenoxide ligands significantly affect the cobalt reduction potentials. The present aluminium-cobalt compounds are electrocatalysts for proton reduction to dihydrogen at potentials negative of boron-and proton-bridged analogs. The reported synthetic strategies allow for modulation of reduction potentials and secondary coordination sphere interactions by tuning the ancillary ligands bound to aluminum.
INTRODUCTION:

The reduction of protons to dihydrogen is of interest in the context of solar energy conversion and storage in chemical bonds.\textsuperscript{[1]} In biological systems, this reaction is catalyzed at near thermodynamic potentials by [FeNi] and [FeFe] hydrogenases.\textsuperscript{[2]} Although useful models for mechanistic studies, synthetic complexes based on hydrogenase active sites display large overpotentials and low turnover numbers.\textsuperscript{[3]} Systems based on nickel tetraphosphine catalysts show high activity.\textsuperscript{[4]} Several promising cobalt-based catalysts have been reported, supported by multidentate nitrogen ligands.\textsuperscript{[4c, 1d, 3]} Bisglyoximato cobalt complexes, Co(dpgX)\textsubscript{2}(L)\textsubscript{2} (dpg = diphenylglyoximato, X = H, BF\textsubscript{2}), were reported to catalyze the reduction of protons both chemically and electrochemically.\textsuperscript{[5a-h, 6]} Substitution of the protons bridging the two glyoximato groups (see complex 3, Scheme 1) with BF\textsubscript{2} groups was found to affect the reduction potential of the cobalt complexes resulting in electrocatalysts active at low overpotentials.\textsuperscript{[4d-4a]} The BF\textsubscript{2} moiety also imparts a greater stability towards acid in contrast to the proton-bridged species.\textsuperscript{[4d, 6a]} Optimization of these catalysts has been focused either on varying the axial ligand of cobalt or the glyoxime backbone.\textsuperscript{[4d, 6a-b, 7]} Herein, we report on the synthesis of bisglyoximato cobalt complexes supported by one or two aluminum-based linkers and their electrochemical properties.
**RESULTS & DISCUSSION:**

In analogy to the tetracoordinate boron bridges, saturated, six-coordinate aluminum linkers were targeted. Aluminum precursors having varied electronic properties were prepared, with ancillary ligands (30^tBu and 30^NO2) based on enantiopure tetradentate diamine bisphenoxide salan frameworks, starting from (R,R)-trans-1,2-diaminocyclohexane.\[^8\] Reaction of diphenols 30^NO2 and 30^tBu with AlMe3 generated monoalkylaluminum diphenoxide species (31^NO2 and 31^tBu, Scheme 1) as indicated by the peaks upfield of 0 ppm in the ^1H NMR spectrum assigned to the Al-CH3 group. Monoalkylaluminum species supported by closely related ancillary ligands are formed as mixtures of inseparable isomers some of which interconvert at room temperature.\[^8c\] Similarly, two Al-CH3 singlets were observed for 31^NO2, but since the subsequent step could involve isomerizations, the mixture was used without separation.

Reaction of two equivalents of $31^{\text{Bu}}$ or $31^{\text{NO}_2}$, with cobalt diglyoximato complex $34$ led to the generation of new species according to $^1\text{H}$ NMR spectroscopy. The absence of the upfield shifted singlets diagnostic of the Al-$\text{CH}_3$ moiety supports alkane elimination. Integrals for the ortho pyridine protons and the NCH$_2$ protons are consistent with the incorporation of two salan-supported aluminum moieties for each cobalt. The presence of four diastereotopic proton signals for the NCH$_2$ moieties indicates a $C$-symmetric structure, with the $C_3$ axis containing the cobalt center and its axial ligands. The distinct axial ligands (chloride vs pyridine) differentiate the top and bottom of the molecule, as depicted in Scheme 1. Employing the analog of $34$
displaying the dimethyl glyoxime backbone resulted in similar species (1H NMR), however isolation of analytically pure samples was unsuccessful to date due to their solubility properties.

Single crystal X-ray diffraction (XRD) studies confirmed the above structural assignment (Figure 1). The aluminum-bound glyoxime oxygen atoms are found at average O-O distances of 2.84 Å for 36\textsubscript{tBu}, 2.83 Å for 36\textsubscript{NO2}, which are significantly larger than those in H- (3, 2.47 Å)\textsuperscript{[9]} or BF\textsubscript{2}-linked (2.50 Å) analogs.\textsuperscript{[5e, 9b]} The average Co-N distances were found to be 1.91 Å for both 36\textsubscript{tBu} and 36\textsubscript{NO2}, which are similar to those found in the H- (1.91 Å) and BF\textsubscript{2}-linked species (1.89 Å). These structural characteristics suggest that although the macrocycles containing aluminum are larger, the effect on the Co-N distances is small. In contrast to proton- or boron-linked diglyoximato complexes that are typically planar, the cobalt-bound N,O\textsubscript{2}Al\textsubscript{2} macrocycle displays significant ruffling and doming distortions. The ruffling may be due to the C-steric strain imposed by the salan ligands found on opposite sides of the macrocycle or, as observed for porphyrins,\textsuperscript{[10]} to the larger macrocycle which requires distortion to allow for binding to a central metal. The doming is likely caused by repulsive steric interaction between the pyridine and the proximal phenoxide ortho-methyl groups. Indeed, the methyl C-C distances are 7.60 and 6.86 Å on the chloride side vs 10.15 and 10.08 Å on the pyridine side, for 36\textsubscript{tBu} and 36\textsubscript{NO2}, respectively.
Figure 6.1. Solid state structures of 36\textsuperscript{th} and 36\textsuperscript{NO2}. Hydrogen atoms and cocry stallization solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50\% probability.
Reaction of 34 with one equivalent of 31\textsuperscript{th} led to the generation of a new species with NMR spectroscopic features consistent with a bimetallic cobalt-aluminum complex of $C_1$ symmetry (35, Scheme 1). A downfield singlet, at 20 ppm, is indicative of the proton bridging two glyoximato units. An XRD study confirms this structural assignment and highlights the effect of bridging proton and aluminum in the same cobalt diglyoximato unit. The O-O distance is 2.38 Å on the protonated side and 2.85 Å on the aluminum side. The average Co-N distances are similar on the H- and Al-sides of the macrocycle. These are in agreement with the structural parameters observed in compounds 34 and 36.

**Figure 6.2.** Solid state structure of 35. Hydrogen atoms and cocrystallization solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.
A dialuminum zinc analog of $36^{tBu}$ was targeted via a complementary synthetic protocol for comparison (Scheme 2). Reaction of $31^{tBu}$ with diphenylglyoxime led to a species ($31^{tBu}$ macrocycle) that displays a singlet at 14 ppm (H NMR spectrum) assigned to protonated oxime nitrogens. Treatment with diethylzinc generates a new species without any signals downfield of 8 ppm, again consistent with alkane elimination. Only two doublets are observed for the NCH$_5$ protons consistent with the pseudo-$D_2$ structure assigned to the $31^{tBu}$ macrocycle.

**Scheme 6.2. Synthesis of dialuminum-bridged bisglyoximato zinc complex via dialuminum templation of bisglyoximato macrocycle.**

The electrochemistry of the present complexes was investigated by cyclic voltammetry (CV). In dimethylformamide (DMF), the Co$^{II}$/Co$^I$ couple was observed for $35$ at -1.34 V vs Fc/Fc, $36^{tBu}$ at -1.59 V, and $36^{NO_2}$ at -1.35 V (Figure 6.3 and 6.4). These are the potentials at which increase in current was observed upon addition of acid (vide infra). These couples are more negative than for boron- and proton-bridged analogs. Several redox events were also observed between 0.2 and 1 V and were assigned to ligand-based processes (Figure 6.3). These waves are in the range of previously
reported electrochemical oxidations of phenoxides coordinated to redox inactive metals.\[12\] As expected, compound 37, containing Zn\textsuperscript{II} instead of Co\textsuperscript{III}, shows redox events at similar potentials and no events between -2 and 0 V, consistent with lack of redox chemistry at the central atom.

**Figure 6.3.** Cyclic voltammograms in 1:1 MeCN:DCM of 35 (black), \(36^\text{tBu}\) (blue), \(36^\text{NO}_2\) (red), 37 (green), 34 (turquoise), and \(34^\text{NNO}_2\) (orange) referenced to Fc/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu\textsubscript{4}ClO\textsubscript{4} in MeCN:DCM.
Figure 6.4. Cyclic voltammograms of the Co$^{II}$/Co$^I$ couples of 36$^{tBu}$ (blue), 36$^{NO_2}$ (turquoise), 35 (purple), 34$^H$ (green), and 34$^{BF_2}$ (red) (1 mM) recorded in a 1:1 MeCN:DCM solution of [nBu$_4$N][ClO$_4$] (0.1 M) at a glassy carbon working electrode using a Ag/AgNO$_3$ (0.01 M) reference electrode using a scan rate of 100 mV/s. Potentials referenced to the Fc$^-$/Fc couple.

Addition of trichloroacetic acid (pKa 3.5 in DMF) under electrochemical conditions resulted in catalytic waves for complexes 35, 36$^{tBu}$, and 36$^{NO_2}$ at the potentials assigned as the Co$^{II}$/Co$^I$ couples (Figures 6.4-6.7). Subsequent additions of trichloroacetic acid caused cathodic shift and increase in the catalytic wave. Overpotentials were determined by comparison of the measured potential value for cobalt catalyzed proton reduction to the experimentally determined thermodynamic potential for proton reduction of trichloroacetate in DMF. Overpotentials are 680, 650, and 860 mV for the aluminum linked glyoxime complexes 35, 36$^{tBu}$, and 36$^{NO_2}$, respectively, and 520 and 110 mV for 34$^H$ and 34$^{BF_2}$, respectively with trichloroacetic acid. Bulk electrolysis experiments were performed with complexes 35 and 36$^{tBu}$ in a
MeCN/DCM solvent mixture, in the presence of para-cyanoanilinium triflate at a potential of -1.62 and -1.83 V, respectively, for two hours. Formation of \( \text{H}_2 \) was confirmed and quantified by GC analysis of the headspace. Faradaic yields of 90% and 70% were calculated for 35 and 36\textsuperscript{tBu}, respectively.

**Figure 6.5.** Addition of trichloroacetic acid to 35 at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (green), 11 mM acid (purple), 15 mM acid (turquoise). All waves referenced to Fc/\(^{+}\)Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu\(_4\)ClO\(_4\) in DMF.
Figure 6.6. Addition of trichloroacetic acid to 36\textsuperscript{th} at (1 mM) in DMF, No acid (blue), 3 mM acid (red), 6 mM acid (purple), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc/Fc. Cyclic voltammograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the positive direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu\textsubscript{4}ClO\textsubscript{4} in DMF.
Figure 6.7. Addition of trichloroacetic acid to 36\textsuperscript{NO2} at (1 mM) in DMF. No acid (blue), 3 mM acid (red), 6 mM acid (green), 10 mM acid (turquoise), 15 mM acid (orange). All waves referenced to Fc/Fc. Cyclic voltamograms taken using a glassy carbon electrode with a scan rate was 100 mV/s initially in the negative direction. The analyte concentration was 1 mM. The electrolyte was 0.1 M NBu\textsubscript{4}ClO\textsubscript{4} in DMF.

Table 6.1. Potentials (V) of Synthesized Complexes in DMF (0.1 M NBu\textsubscript{4}ClO\textsubscript{4}). Reported potentials are referenced to Fc/Fc

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### Table 6.2. Summary of Bulk Electrolysis Studies$^\text{[a]}$

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<td>2</td>
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[a] All bulk electrolysis experiments carried out with 0.1 mM catalyst and 9 mM acid in a MeCN:DCM 1:1 solution of [nBu₄N][ClO₄] (0.1 M) using glassy carbon plate working and counter electrodes with a Ag/AgNO₃ (0.01 M) reference electrode. [b] All values corrected for background proton reduction on the glassy carbon plate at the listed potentials. [c] TON calculated from the amount of hydrogen produced during the duration of the bulk electrolysis experiment vs catalyst in solution.

Comparison of 35 and 34 (Co$^{\text{II}}$/Co$^{\text{I}}$ at -1.25 V) indicates that substitution of a proton linker with aluminum leads to a 0.14 V negative shift of the Co$^{\text{II}}$/Co$^{\text{I}}$ reduction potential and onset of catalysis. Substitution of the second proton with aluminum in 36$^{\text{tBu}}$ led to further cathodic shift by 0.32 V. In contrast, complex 36$^{\text{NO₂}}$ shows an anodic shift by 0.27 V compared to 36$^{\text{tBu}}$. The negative shift of the Co$^{\text{II}}$/Co$^{\text{I}}$ reduction potential upon incorporation of aluminum centers vs protons may be a consequence of the electron rich, multidentate diamine bisphenoxide framework coordinated to aluminum. In agreement, the analog with electron withdrawing nitro substituents shows a significant positive potential shift.
**Conclusions:**

In summary, the synthesis and characterization of several aluminum-bridged bisglyoximato cobalt and zinc complexes are reported. The ligands supporting the aluminum centers were found to affect the reduction potentials of cobalt and consequently the potential for proton reduction catalysis. Electrocatalytic proton reduction occurs at potentials more negative than the boron- and proton-bridged analogs. Nevertheless, the synthetic protocols presented here may be extended to other metal bridges or ancillary ligands toward tuning the reduction potential of the central metal, improving the stability, attaching photosynthesizers or affecting the second coordination sphere.
EXPERIMENTAL SECTION:

**General:** All air sensitive reactions were carried out in a glovebox under a nitrogen atmosphere using oven-dried glassware cooled in vacuo. Anhydrous solvents were dried by the method of Grubbs.\textsuperscript{[14]} All non-dried solvents used were of reagent grade or better and were used as is. NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. C6D6 was dried over sodium/benzophenone ketyl while CD2Cl2 was dried over calcium hydride, both were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. CDCl3 was used as purchased. All proton NMR spectra were recorded on either a Varian Mercury 300MHz or a Varian INOVA-500 spectrometer with chemical shifts reported in ppm relative to the pertinent solvent peaks (7.16 ppm for C6D6, 7.26 ppm for CDCl3, and 5.32 ppm for CD2Cl2). (R,R)-1,2-diaminocyclohexane was purified from a racemic mixture of 1,2-diaminocyclohexane using a literature procedure.\textsuperscript{[15]} 2-(chloromethyl)-6-methyl-4-nitrophenol,\textsuperscript{[16a]} N,N'-dimethylcyclohexane-1,2-diamine,\textsuperscript{[16b]} 30\textsuperscript{NO2},\textsuperscript{[11]} 30\textsuperscript{NO2},\textsuperscript{[11]} 32\textsuperscript{NO2},\textsuperscript{[11]} 32\textsuperscript{NO2},\textsuperscript{[11]} 34,\textsuperscript{[11]} and 31 macrocycle\textsuperscript{[11]} were synthesized according to literature procedures. All other starting materials were used as purchased.

Electrochemical measurements were recorded in a glovebox under a N2 atmosphere using a Pine Instrument Company Bipotentiostat, at 1mM of the complex of interest unless otherwise stated, in a mixture of 1:1 DCM:MeCN or DMF containing 0.1 M nBu4N(ClO4) as the supporting electrolyte, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a 0.01M Ag/AgNO3 nonaqueous reference electrode. For proton reduction trichloroacetic acid and p-cyanoanilinium triflate were used as the proton sources. Bulk electrolysis experiments were conducted in a sealed two-chambered cell where the first chamber held the working and reference electrodes and the second chamber contained the auxiliary electrode. The two chambers were separated by a fine frit.
Glassy carbon plates (12 cm x 3 cm x 1 cm) were used as the working and auxiliary electrodes and submerged such that ca. 64 cm$^2$ of the plate was in the 0.1 M nBu$_4$N(ClO$_4$)$_2$ MeCN:DCM solution. For the bulk electrolysis studies para-cyanoanilinium trillate was used as the proton source. The amount of H$_2$ evolved was quantified from an analysis of the headspace of the cell with an Agilent 7890A gas chromatograph using a thermal conductivity detector. The overpotentials were determined by comparing the derivative of the catalytic wave observed with the stated catalyst in 3 mM trichloroacetic acid with the determined thermodynamic half wave potential of trichloroacetic acid in DMF. The thermodynamic half wave potential of trichloroacetic was determined to be -710 ± 20 mV by analysis of the catalytic wave for proton reduction in a 1M solution of trichloroacetic acid in a hydrogen (1 atm) saturated DMF solution.

Position labels for listed nuclear magnetic resonance spectroscopy characterization.

[Diagram of a molecule with labels a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z, A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z.]

**Synthesis of 35:** Cobalt(III) diphenylglyoximato precursor 34 (0.127 g, 0.195 mmol) was treated with one equivalent of 31* (0.102 g, 0.192 mmol) in toluene (10 mL) at room temperature for 16 hours. Over time the solution became a homogeneous dark brown. The solvent was removed in vacuo resulting in a brown solid. The solid was washed with diethyl ether and extracted with benzene. The benzene solution was concentrated until solid precipitated was and filtered through celite. The filtrate was concentrated under
vacuum. To the resulting brown powder was added a small amount of benzene to barely
dissolve the solid and the solution was filtered. The solvent was removed and the resulting
solid was washed three times with pentane resulting in a light brown powder. Yield: 0.177 g,
79%. 1H NMR (300 MHz, CD2Cl2) δ 19.20 (1H, s, OH), 9.13 (2H, d, J = 5.0 Hz, h), 7.75
(1H, t, J = 7.6 Hz, f), 7.29 (8H, m, j), 7.24 (2H, m, l) 7.26 (8H, m, k), 7.21 (2H, m, g), 7.16
(2H, m, i), 7.05 (2H, m, i), 6.97 (2H, d, J = 2.6 Hz, l,l'), 6.77 (2H, d, J = 2.5 Hz, l,l'), 6.50
(2H, d, J = 2.5 Hz, l,l'), 4.32 (1H, d, J = 13.4 Hz, b,b'), 3.89 (1H, d, J = 13.3 Hz, b,b'), 2.94
(1H, d, J = 13.6 Hz, b,b'), 2.75 (1H, d, J = 13.5 Hz, b,b'), 2.49 (2H, m, a), 2.12 (3H, s, e,e'),
2.07 (3H, s, e,e'), 1.85 (3H, s, e,e'), 1.66 (3H, s, c,c'), 1.63 (2H, m, a'), 1.52 (2H, m, a''),
1.35 (9H, s, d,d'), 1.25 (9H, s, d,d'), 0.96 (2H, m, a'), 0.75 (2H, m, a'') ppm. 13C{1H} NMR
(126 MHz, CD2Cl2) δ 157.16 (4,4'), 157.07 (4,4'), 155.40 (6,6'), 154.31 (6,6'), 153.27 (h),
139.22 (g), 136.96 (2,2'), 135.62 (2,2'), 132.56 (6,i'), 132.36 (6,i'), 130.93 (6,i'), 130.80 (6,i'),
130.03 (k,k'), 129.97 (k,k'), 129.52 (7,7'), 129.43 (7,7'), 129.11 (7,7'), 129.02 (7,7'), 128.32
(l'), 128.17 (j), 127.54 (5,5'), 126.91 (l'), 125.87 (f), 124.98 (5,5'), 123.69 (l), 123.04 (l),
121.24 (3,3'), 119.64 (3,3'), 59.86 (b,b'), 59.57 (b,b'), 55.93 (a), 55.75 (a), 40.56 (c,c'),
40.44 (c,c'), 33.97 (l), 33.76 (l), 31.96 (d), 24.62 (a''), 22.02 (a'), 17.94 (e,e'), 17.32 (c,c')
ppm. Anal. Calcd. for C60H69AlClCoN6O6 (%): C, 66.69; H, 6.37; N, 8.38; Found: C, 67.04;
H, 6.77; N, 7.99.
**Synthesis of 36**: A slurry of 34 (0.453 g, 0.695 mmol) in toluene (10 mL) was treated with a solution of 31 (0.750 g, 1.40 mmol) in toluene (10 mL) at room temperature. After 36 hours of stirring volatile materials were removed in vacuo. The crude solid was washed with hexanes. The desired product was extracted with diethyl ether and toluene. The desired product was isolated as a brown orange powder upon removing volatile material from the diethyl ether fraction. Yield: 0.437 g, 37%.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 9.64 (2H, d, J = 5.7 Hz, h), 7.56 (1H, t, J = 7.6 Hz, f), 7.30 (8H, m, k), 7.19 (8H, q, J = 7.8, 6.3 Hz, j), 7.13 (2H, d, J = 2.6 Hz, l'), 6.97 (2H, d, J = 2.7 Hz, l), 6.88 (4H, d, i), 6.82 (2H, m, g), 6.64 (4H, dd, J = 12.3, 2.7 Hz, l), 4.23 (2H, d, J = 13.3 Hz, b,b'), 4.06 (2H, d, J = 13.3 Hz, b,b'), 2.90 (2H, d, J = 13.5 Hz, b,b'), 2.80 (2H, d, J = 13.5 Hz, b,b'), 2.61 (2H, m, a), 2.52 (2H, m, a), 2.26 (6H, s, e,e'), 2.21 (6H, s, e,e'), 1.84 (6H, s, c,c'), 1.66 (6H, s, c,c'), 1.60 (2H, m, a'), 1.52 (2H, m, a''), 1.29 (18H, s, d,d'), 1.28 (18H, s, d,d'), 0.96 (2H, m, a'), 0.76 (2H, m, a'') ppm. $^{13}$C{H} NMR (126 MHz, CD$_2$Cl$_2$) δ 157.62 (4,4'), 157.10 (4,4'), 156.05 (6,6'), 154.89 (h), 154.38 (6,6'), 138.80 (g), 136.55 (2,2'), 135.00 (2,2'), 133.66 (7,7'), 133.12 (7,7'), 130.31 (k), 130.00 (i), 128.57 (l',l'), 128.49 (l',l'), 128.04 (j,j'), 127.90 (j,j'), 127.24 (5,5'), 126.91 (l,l), 125.16 (5,5'), 124.65 (l), 123.42 (l,l), 121.05 (3,3'), 119.30 (3,3'), 60.29 (b,b'), 59.39 (b,b'), 55.88 (a), 40.57 (c,c'), 33.90 (l), 32.01 (d), 24.69 (a''), 22.08 (a'), 18.14 (e,e').
215

17.42 (e,e’) ppm. Elemental Analysis C_{97}H_{121}AlClCoN_{9}O_{8} (%): Calc. C, 68.96; H, 7.22; N, 7.46; Found. C, 69.41; H, 7.09; N, 7.15

Synthesis of 36\textsuperscript{NO2}: A solution of 31\textsuperscript{NO2} (0.111 g, 0.217 mmol) in THF (5 mL) was mixed with a solution of 3 (0.063 g, 0.090 mmol) in THF (5 mL). The mixture was sealed in a Schlenk tube and heated to 66 °C for 12 hours. After the allocated time the solvent was removed in vacuo. The recovered solid was washed with diethyl ether, benzene, and extracted with THF. The product of the THF fraction was recrystallized from a vapor diffusion of diethyl ether into THF at room temperature as brown orange crystals. The \textsuperscript{1}H NMR spectrum indicates the presence of an impurity that was assigned as a isomer based on its spectroscopic features. Yield: 0.063 g, 43% \textsuperscript{1}H NMR (500 MHz, CD$_2$Cl$_2$) \(\delta\) 9.23 (2H, d, J = 5.1 Hz, h), 8.12 (2H, d, J = 2.9 Hz, l,l’), 7.94 (2H, d, J = 2.9 Hz, l,l’), 7.76 (4H, dd, J = 4.7, 3.0 Hz, j), 7.69 (1H, m, f), 7.41 (4H, m, j), 7.29 (2H, m, i), 7.22 (4H, dd, J = 8.3, 7.2 Hz, k), 7.17 (4H, m, k), 6.86 (2H, m, i), 6.76 (4H, d, J = 7.6 Hz, l,l’), 4.31 (2H, d, J = 13.7 Hz, b,b’), 4.17 (2H, d, J = 13.8 Hz, b,b’), 3.11 (2H, d, J = 13.9 Hz, b,b’), 3.00 (2H, d, J = 14.1 Hz, b,b’), 2.45 (2H, m, a), 2.25 (6H, s, e), 2.17 (6H, s, e), 1.80 (6H, s, c,c’), 1.70 (4H, m, a’), 1.61 (4H, m, a’), 1.54 (6H, s, c,c’), 0.95 (4H, m, a’), 0.80 (4H, m, a’) ppm. \textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CD$_2$Cl$_2$) \(\delta\) 166.95 (4,4’), 166.24 (4,4’), 157.45 (6,6’), 156.34 (6,6’), 153.55 (h), 139.68 (i), 136.68 (2,2’), 135.82 (2,2’), 133.03 (7,7’), 131.54 (7,7’), 129.62 (k), 129.42
(i,i'), 129.33 (5,5'), 129.06 (i,i'), 128.69 (l,l'), 128.22 (l,l'), 127.29 (l,l'), 126.85 (l,l'), 126.26 (5,5'), 125.21 (g), 124.15 (j), 121.59 (3,3'), 120.09 (3,3'), 58.99 (b,b'), 58.30 (b,b'), 56.69 (a), 40.58 (c,c'), 24.41 (a''), 22.12 (a'), 17.74 (e,e') ppm. Anal. Calc. C₈₁H₈₅Al₂ClCoN₁₃O₁₆ (%): C, 59.14; H, 5.21; N, 11.07; Found. C, 60.03; H, 5.56; N, 10.82.

**Synthesis of 37:** To a just thawed solution of 31<sup>th</sup> macrocycle (0.424 g, 0.28 mmol) in THF (10 mL) was added a freshly thawed solution of diethylzinc (0.034 g, 28.6 μl, 0.28 mmol) in THF (5 mL). The solution was allowed to warm to room temperature. After 3 hours of stirring volatile materials were removed in vacuo. The crude solid was triturated with Et₂O. The resulting solid was fractionated into hexanes and THF. Removal of volatile materials from the hexanes fraction under vacuum resulted in the desired product as an off white solid. Yield 0.305 g, 69%. <sup>1</sup>H NMR (300 MHz, C₆D₆) δ 7.51 (8H, d, J = 7.0 Hz, k), 6.96 (16H, m, i, j, l,l'), 6.66 (4H, d, J = 2.3 Hz, l,l'), 4.59 (4H, d, J = 12.7 Hz, b,b'), 2.72 (4H, d, J = 12.7 Hz, b,b'), 2.37 (4H, m, a), 2.31 (12H, s, e), 1.91 (12H, s, c), 1.35 (36H, s, d), 1.18 (4H, m, a''), 1.04 (4H, m, a'), 0.35 (4H, m, a''), 0.26 (4H, m, a') ppm. <sup>13</sup>C<sup>{1}H</sup> NMR (126 MHz, C₆D₆) δ 157.80 (4), 150.92 (6), 137.65 (7), 132.79 (2), 130.97 (k), 127.61 (i), 127.32 (j), 126.95 (5), 123.75 (l), 121.90 (3), 59.94 (b,b'), 55.92 (a), 39.63 (c), 33.91 (1), 32.30 (d), 24.41 (a), 22.33 (a'), 17.78 (e) ppm. Elemental Analysis C₉₂H₁₁₆Al₂ZnN₈O₈ (%): Calc. C, 69.88; H, 7.39; N, 7.09; Found. C, 69.90; H, 7.24; N, 7.44.
**Acid stability test of 35:** A solution of 35 (0.012 g, 0.010 mmol) in C₆D₆ was mixed with (0.040 g, 0.149 mmol) trichloroacetic acid in a J-Young tube. The tube was sealed under N₂. The degradation of 35 was observed over time by ¹H NMR spectroscopy. The amount of degradation of complex was estimated from the comparison of the benzylic protons with peaks from the degradation product in the benzylic region.
Table 6.X. Crystal and refinement data for complexes 35, 36$^{\text{tBu}}$, and 36$^{\text{NO2}}$.

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$^{a}$ R$_1$ = $\sum| |F_o| - |F_c| |\sum| F_o|$.  
$^{b}$ wR$^2$ = [$\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]$]$^{1/2}$.
REFERENCES


APPENDIX A

RELEVANT SPECTROSCOPIC DATA
Figure A.1: $^1$H NMR Spectrum ($CD_6$, 25°C, 399.80 MHz) of 1

Figure A.2: $^1$H NMR Spectrum ($CD_6$, 75°C, 300.08 MHz) of 1

Figure A.3: $^{13}$C($^1$H) NMR Spectrum ($CD_6$, 25°C, 100.54 MHz) of 1
Figure A.4: $^{31}\text{P}('\text{H})$ NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 1

Figure A.5: $^{31}\text{P}('\text{H})$ NMR Spectrum (C$_6$D$_6$, 75°C, 121.48 MHz) of 1
Figure A.6: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_6$D$_6$, 25°C, 399.80, 100.54 MHz) of 1

Figure A.7: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_6$D$_6$, 25°C, 399.80, 100.54 MHz) of 1
Figure A.8: $^1$H NMR Spectrum of 1$_{CF3}$

Figure A.9: $^{19}$F($^1$H) NMR Spectrum of 1$_{CF3}$

Figure A.10: $^{31}$P($^1$H) NMR Spectrum of 1$_{CF3}$
Figure A.11: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 1

Figure A.12: $^1$H NMR Spectrum (CD$_6$, 70°C, 499.85 MHz) of 1

Figure A.13: $^{13}$C{^1}H NMR Spectrum (CD$_6$, 25°C, 125.70 MHz) of 1
Figure A.14: $^3$P[$^1$H] NMR Spectrum (CD$_6$, 25°C, 121.48 MHz) of 1$^{13}$
Figure A.15: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1$^{iv}$

Figure A.16: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1$^{iv}$
Figure A.17: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 1$^a$

Figure A.18: $^1$H NMR Spectrum (CD$_6$, 75°C, 499.85 MHz) of 1$^b$

Figure A.19: $^{13}$C NMR Spectrum (CD$_6$, 25°C, 125.70 MHz) of 1$^c$
Figure A.20: $^3P[H]$ NMR Spectrum (CD$_2$Cl$_2$, 25°C, 121.48 MHz) of $1^\text{st}$
Figure A.21: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of $^1$Et

Figure A.22: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of $^1$Et
Figure A.23: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 1$^{3a}$

Figure A.24: $^{13}$C($^1$H) NMR Spectrum (CD$_6$, 25°C, 125.70 MHz) of 1$^{3a}$

Figure A.25: $^{31}$P($^1$H) NMR Spectrum (CD$_6$, 25°C, 121.48 MHz) of 1$^{3a}$
Figure A.26: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1$^a$ 

Figure A.27: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1$^a$
Figure A.28: $^1$H NMR Spectrum (C$_6$D$_6$, 25°C, 499.85 MHz) of $^{10}$Ar

Figure A.29: $^1$H NMR Spectrum (C$_6$D$_6$, 70°C, 499.85 MHz) of $^{10}$Ar

Figure A.30: $^{13}$C($^1$H) NMR Spectrum (C$_6$D$_6$, 25°C, 125.70 MHz) of $^{10}$Ar
Figure A.31: $^31$P{H} NMR Spectrum (CD$_6$, 25°C, 121.48 MHz) of $1^{0ax}$

Figure A.32: $^31$P{H} NMR Spectrum (CD$_6$, 70°C, 202.36 MHz) of $1^{0ax}$
Figure A.33: $^1$H-$^1$C HSQC NMR Spectrum (CD$_2$C, 25°C, 499.85, 125.70 MHz) of 1$_{\text{OAr}}$

Figure A.34: $^1$H-$^1$C HMBC NMR Spectrum (CD$_2$C, 25°C, 499.85, 125.70 MHz) of 1$_{\text{OAr}}$
Figure A.35: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-dimethylaminobenzene.

Figure A.36: $^{13}$C($^1$H) NMR Spectrum (CD$_6$, 25°C, 125.70 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-dimethylaminobenzene.

Figure A.37: $^{31}$P($^1$H) NMR Spectrum (CD$_6$, 121.48 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-dimethylaminobenzene.
Figure A.38: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_2$F, 25°C, 499.85, 125.70 MHz) of 1,3-bis($^{2'}$-diisopropylphosphino)-5-dimethylaminobenzene.

Figure A.39: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_2$F, 25°C, 499.85, 125.70 MHz) of 1,3-bis($^{2'}$-diisopropylphosphino)-5-dimethylaminobenzene.
Figure A.40: $^1$H NMR Spectrum (C$_2$D$_6$, 25°C, 499.85 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.

Figure A.41: $^{13}$C{$^1$H} NMR Spectrum (C$_2$D$_6$, 25°C, 125.70 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.

Figure A.42: $^{31}$P{$^1$H} NMR Spectrum (C$_2$D$_6$, 121.48 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.
Figure A.43: $^{19}$F{H} NMR Spectrum (C.D$_2$, 121.48 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.
Figure A.44: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.

Figure A.45: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.
Figure A.46: $^1$H NMR Spectrum (CD$_3$, 399.80 MHz) of 2

Figure A.47: $^{13}$C{$^1$H} NMR Spectrum (CD$_3$, 100.54 MHz) of 2

Figure A.48: $^{31}$P{$^1$H} NMR Spectrum (CD$_3$, 121.48 MHz) of 2
Figure A.49: $^1$H-$^{13}$C H2BC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 2.

Figure A.50: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 25°C, 499.85, 125.70 MHz) of 2.
Figure A.51: $^1$H NMR Spectrum (C.D$_6$, 399.80 MHz) of 2$^\nu$

Figure A.52: $^{13}$C NMR Spectrum (C.D$_6$, 100.54 MHz) of 2$^\nu$

Figure A.53: $^{31}$P{$^1$H} NMR Spectrum (C.D$_6$, 121.48 MHz) of 2$^\nu$
Figure A.54: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_6$D$_6$, 25°C, 499.85, 125.70 MHz) of 2iPr.

Figure A.55: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_6$D$_6$, 25°C, 499.85, 125.70 MHz) of 2iPr.
Figure A.56: $^1$H NMR Spectrum (C$_6$D$_6$, 399.80 MHz) of 2$^e$

Figure A.57: $^{13}$C NMR Spectrum (C$_6$D$_6$, 100.54 MHz) of 2$^e$

Figure A.58: $^{31}$P{[^1]H} NMR Spectrum (C$_6$D$_6$, 121.48 MHz) of 2$^e$
Figure A.59: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_2$D$_2$, 25°C, 499.85, 125.70 MHz) of 2$^a$.

Figure A.60: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_2$D$_2$, 25°C, 499.85, 125.70 MHz) of 2$^a$. 
Figure A.61: $^1$H NMR Spectrum (CD$_3$, 499.85 MHz) of 2$_{cns}$

Figure A.62: $^{13}$C{H} NMR Spectrum (CD$_3$, 125.70 MHz) of 2$_{cns}$

Figure A.63: $^{19}$F{H} NMR Spectrum (CD$_3$, 282.33 MHz) of 2$_{cns}$
Figure A.64: $^3\text{P}[\text{H}]$ NMR Spectrum (CD$_2$Cl$_2$, 121.48 MHz) of 2cns
Figure A.65: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_2$, 499.85, 125.70 MHz) of 2$_{cn}$

Figure A.66: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_2$, 499.85, 125.70 MHz) of 2$_{cn}$
Figure A.67: $^1$H NMR Spectrum (CD$_3$, 399.80 MHz) of 3

Figure A.68: $^{13}$C NMR Spectrum (CD$_3$, 100.54 MHz) of 3

Figure A.69: $^{31}$P{$^1$H} NMR Spectrum (CD$_3$, 121.48 MHz) of 3
Figure A.70: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 3

Figure A.71: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 3
Figure A.72: $^1$H NMR Spectrum (CD$_3$, 399.80 MHz) of 4

Figure A.73: $^{13}$C NMR Spectrum (CD$_3$, 100.54 MHz) of 4

Figure A.74: $^{31}$P{$^1$H} NMR Spectrum (CD$_3$, 121.48 MHz) of 4
Figure A.75: $^1$H-$^{13}$C HSQC NMR Spectrum (C.D$_2$, 499.85, 125.70 MHz) of 4

Figure A.76: $^1$H-$^{13}$C HMBC NMR Spectrum (C.D$_2$, 499.85, 125.70 MHz) of 4
Figure A.77: $^1$H NMR Spectrum (CD$_6$, 399.80 MHz) of 5

Figure A.78: $^{13}$C NMR Spectrum (CD$_6$, 100.54 MHz) of 5

Figure A.79: $^{31}$P{$^1$H} NMR Spectrum (CD$_6$, 121.48 MHz) of 5
Figure A.80: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 5

Figure A.81: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 5
Figure A.82: $^1$H NMR Spectrum (C.D$_6$, 399.80 MHz) of 6

Figure A.83: $^{13}$C NMR Spectrum (C.D$_6$, 100.54 MHz) of 6

Figure A.84: $^{31}$P{$^1$H} NMR Spectrum (C.D$_6$, 121.48 MHz) of 6
Figure A.85: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 6

Figure A.86: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 6
Figure A.87: $^1$H NMR Spectrum (C6D6, 399.80 MHz) of 7

Figure A.88: $^{13}$C NMR Spectrum (C6D6, 100.54 MHz) of 7

Figure A.89: $^{31}$P{$^1$H} NMR Spectrum (C6D6, 121.48 MHz) of 7
Figure A.90: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 7

Figure A.91: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 7
Figure A.92: $^1$H NMR Spectrum (CD$_6$, 399.80 MHz) of 7$_{crs}$

Figure A.93: $^{13}$C NMR Spectrum (CD$_6$, 100.54 MHz) of 7$_{crs}$

Figure A.94: $^{31}$P{$^1$H} NMR Spectrum (CD$_6$, 25°C, 121.48 MHz) of 7$_{crs}$
Figure A.95: $^{19}$F{H} NMR Spectrum (C$_6$D$_6$, 282.33 MHz) of 7$_{crs}$
Figure A.96: $^1$H-$^{13}$C HSQC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 7_{CF3}

Figure A.97: $^1$H-$^{13}$C HMBC NMR Spectrum (C$_6$D$_6$, 499.85, 125.70 MHz) of 7_{CF3}
Figure A.98: $^1$H NMR Spectrum (C$_6$D$_6$, 399.80 MHz) of 8

Figure A.99: $^{13}$C{$^1$H} NMR Spectrum (C$_6$D$_6$, 100.54 MHz) of 8

Figure A.100: $^{31}$P{$^1$H} NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 8
Figure A.101: $^1$H-$^{13}$C HSQC NMR Spectrum (C:D$_6$, 499.85, 125.70 MHz) of 8

Figure A.102: $^1$H-$^{13}$C HMBC NMR Spectrum (C:D$_6$, 499.85, 125.70 MHz) of 8
Figure A.103: $^1$H NMR Spectrum (C$_6$D$_6$, 300 MHz) of 9

Figure A.104: $^{31}$P($^1$H) NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 9

Figure A.105: $^1$H NMR Spectrum (C$_6$D$_6$, 300 MHz) of 9$^{OTf}$
Figure A.106: $^{31}\text{P}[^1\text{H}]$ NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 9

Figure A.107: $^1\text{H}$ NMR Spectrum (C$_6$D$_6$, 25°C, 499.85 MHz) of 10

Figure A.108: $^{31}\text{P}[^1\text{H}]$ NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 10
Figure A.109: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 11

Figure A.110: $^{31}$P($^1$H) NMR Spectrum (CD$_6$, 25°C, 121.48 MHz) of 11

Figure A.111: $^1$H NMR Spectrum (CD$_6$, 25°C, 499.85 MHz) of 12
Figure D.112: $^{13}$C{\( ^1H \)} NMR Spectrum (C\( _6 \)D\( _6 \), 25°C, 125.70 MHz) of 12

Figure A.113: $^{31}$P{\( ^1H \)} NMR Spectrum (C\( _6 \)D\( _6 \), 25°C, 121.48 MHz) of 12
Figure A.114: $^1$H-$^{13}$C HSQC NMR Spectrum (C,D$_6$, 499.85, 125.70 MHz) of 12

Figure A.115: $^1$H-$^{13}$C HMBC NMR Spectrum (C,D$_6$, 499.85, 125.70 MHz) of 12
Figure A.116: $^1$H NMR Spectrum (C6D6, 25°C, 499.85 MHz) of 13

Figure A.117: $^{13}$C{H} NMR Spectrum (C6D6, 25°C, 125.70 MHz) of 13

Figure A.118: $^{31}$P{H} NMR Spectrum (C6D6, 25°C, 121.48 MHz) of 13
Figure A.119: $^1$H-$^{13}$C HSQC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 13

Figure A.120: $^1$H-$^{13}$C HMBC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 13
Figure A.121: $^1$H NMR Spectrum (C$_6$D$_6$, 25°C, 499.85 MHz) of 14

Figure A.122: $^{13}$C($^1$H) NMR Spectrum (C$_6$D$_6$, 25°C, 125.70 MHz) of 14

Figure A.123: $^{31}$P($^1$H) NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 14
Figure A.124: $^1$H-$^{13}$C HSQC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 14

Figure A.125: $^1$H-$^{13}$C HMBC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 14
Figure A.126: $^1\text{H}$ NMR Spectrum (C$_6$D$_6$, 25°C, 499.85 MHz) of 16

Figure A.127: $^{13}\text{C}(^1\text{H})$ NMR Spectrum (C$_6$D$_6$, 25°C, 125.70 MHz) of 16

Figure A.128: $^{31}\text{P}(^1\text{H})$ NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 16
Figure A.129: $^1$H-$^{13}$C HSQC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 16

Figure A.130: $^1$H-$^{13}$C HMBC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 16
Figure A.131: $^1$H NMR Spectrum (C.D$_x$, 25°C, 499.85 MHz) of 16$_{\text{th}}$

Figure A.132: $^{13}$C{$^1$H} NMR Spectrum (C.D$_x$, 25°C, 125.70 MHz) of 16$_{\text{th}}$

Figure A.133: $^{31}$P{$^1$H} NMR Spectrum (C.D$_x$, 25°C, 121.48 MHz) of 16$_{\text{th}}$
Figure A.134: $^1$H-$^{13}$C HSQC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 16$_{\text{thr}}$

Figure A.135: $^1$H-$^{13}$C HMBC NMR Spectrum (CD$_6$, 499.85, 125.70 MHz) of 16$_{\text{thr}}$
Figure A.136: $^1$H NMR Spectrum (C$_6$D$_6$, 25°C, 499.85 MHz) of 16$_{crs}$

Figure A.137: $^{13}$C NMR Spectrum (C$_6$D$_6$, 25°C, 125.70 MHz) of 16$_{crs}$

Figure A.138: $^{31}$P($^1$H) NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 16$_{crs}$
Figure A.139: $^{19}$F{H} NMR Spectrum (C₆D₆, 282.33 MHz) of 16CF₃
Figure A.140: $^1$H-$^{13}$C HSQC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 16CF$_3$

Figure A.141: $^1$H-$^{13}$C HMBC NMR Spectrum (C.D$_6$, 499.85, 125.70 MHz) of 16CF$_3$
Figure A.142: $^1$H NMR Spectrum (C$_2$D$_2$, 25°C, 300 MHz) of 18

Figure A.143: $^{31}$P($^1$H) NMR Spectrum (C$_2$D$_2$, 25°C, 121.48 MHz) of 18

Figure A.144: $^1$H NMR Spectrum (C$_2$D$_2$, 25°C, 300 MHz) of 19
Figure A.145: $^{31}\text{P}('\text{H})$ NMR Spectrum (C$_6$D$_6$, 25°C, 121.48 MHz) of 19

Figure A.146. $^1\text{H}$ NMR spectrum of 23 in C$_6$D$_6$.

Figure A.147. $^1\text{H}$ NMR spectrum of 25 in C$_6$D$_6$. 
Figure A.148. $^{13}$C NMR spectrum of 25 in C$_6$D$_6$.

Figure A.149. $^1$H NMR spectrum of 26 in CD$_2$Cl$_2$.

Figure A.150. $^1$H NMR spectrum of 23$^{^tBu}$ in C$_6$D$_6$. 
Figure A.151. $^1$H NMR spectrum of 25$^{th}$ in C$_6$D$_6$.

Figure A.152. $^{13}$C({H}) NMR spectrum of 25$^{th}$ in C$_6$D$_6$.

Figure A.153. $^1$H NMR spectrum of 29$^{th}$ in C$_6$D$_6$. 
Figure A.154. $^{13}$C["H"] NMR spectrum of 29 in C6D6.

Figure A.155. 'H NMR spectrum of 30 in CDCl₃.
Figure A.156. $^1$H-$^{13}$C gHMBCAD NMR spectrum of 30$^{NO_2}$ in (CD$_3$)$_2$SO.

Figure A.157. $^1$H NMR spectrum of 31$^{NO_2}$ in CD$_2$Cl$_2$. 
Figure A.158. $^1$H NMR spectrum of $32^\text{NO}_2$ in CD$_2$Cl$_2$.

Figure A.159. $^{13}$C($^1$H) NMR spectrum of $32^\text{NO}_2$ in CD$_2$Cl$_2$.

Figure A.160. $^1$H NMR spectrum of $33^\text{NO}_2$ in CD$_2$Cl$_2$. 
Figure A.161. $^{13}$C($^1$H) NMR spectrum of 33$^{\text{NO}_2}$ in CD$_2$Cl$_2$.

Figure A.162. $^1$H NMR spectrum of 30$^{\text{tBu}}$ in CDCl$_3$.

Figure A.163. $^1$C($^1$H) NMR spectrum of 30$^{\text{tBu}}$ in C$_6$D$_6$. 
Figure A.164. $^1$H NMR spectrum of $31^{th}$ in C$_6$D$_6$

Figure A.165. $^{13}$C{$^1$H} NMR spectrum of $31^{th}$ in CD$_2$Cl$_2$

Figure A.166. $^{27}$Al NMR spectrum of $31^{th}$ in CD$_2$Cl$_2$
Figure A.167. $^1$H NMR spectrum of 32$^{ts}$ in CD$_2$Cl$_2$.

Figure A.168. $^{13}$C($^1$H) NMR spectrum of 32$^{ts}$ in CD$_2$Cl$_2$.

Figure A.169. $^{27}$Al NMR spectrum of 32$^{ts}$ in CD$_2$Cl$_2$. 
Figure A.170. $^1$H NMR spectrum of 33$^{tBu}$ in C$_6$D$_6$.

Figure A.171. $^{13}$C($^1$H) NMR spectrum of 33$^{tBu}$ in C$_6$D$_6$.

Figure A.172. $^{27}$Al NMR spectrum of 33$^{tBu}$ diphenylglyoxime macrocycle in C$_6$D$_6$. 
Figure A.173. $^1$H NMR spectrum of 35 in CD$_2$Cl$_2$.

Figure A.174. $^{13}$C{$^1$H} NMR spectrum of 35 in CD$_2$Cl$_2$.

Figure A.175. $^1$H NMR spectrum of 36$_{th}$ in CD$_2$Cl$_2$. 
Figure A.176. $^1$H NMR spectrum of $36$ in CD$_2$Cl$_2$.

Figure A.177. $^1$H NMR spectrum of crystals of $36$ in CD$_2$Cl$_2$ (contains THF and Et$_2$O).

Figure A.178. $^{13}$C($^1$H) NMR spectrum of crystals of $36$ in CD$_2$Cl$_2$ (contains THF and Et$_2$O).
Figure A.179. $^1$H NMR spectrum of 37 in C$_6$D$_6$.

Figure A.180. $^{13}$C($^1$H) NMR spectrum of 37 in C$_6$D$_6$ (contains pentane and THF).