CHAPTER 2

MECHANISTIC STUDIES OF ARYL-OXYGEN BOND ACTIVATION IN A NICKEL(0)
DIPHOSPHINE-ETHER COMPLEX

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Kelley, P.; Lin, S.; Edouard, G.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 5480-5483.

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 β-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 β-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 50000 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,1b]

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,1b] 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**
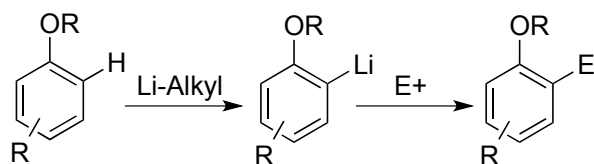
While the availability and ease of functionalization of phenolic precursors makes their advantages apparent, the implication of an aryl oxygen cleaving strategy is not simple. Aryl ether bonds are significantly stronger than their aryl halide counterparts making the direct activation of aryl-oxygen substrates challenging. Typically aryl oxygen moieties must be converted to the more reactive phosphinates, sulfunates, 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[2] or C-S[3] bonds in comparison to well-known palladium catalysts. Although cross-coupling of phenolic substrates tends to require prior conversion to the more reactive sulfonates,[2a] 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.[2b-l] 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.[2i,2j] Additionally, stoichiometric intramolecular aryl C-O activation has been reported with rhodium and palladium pincer complexes.[4] 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

challenge.[5] 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).[6] 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
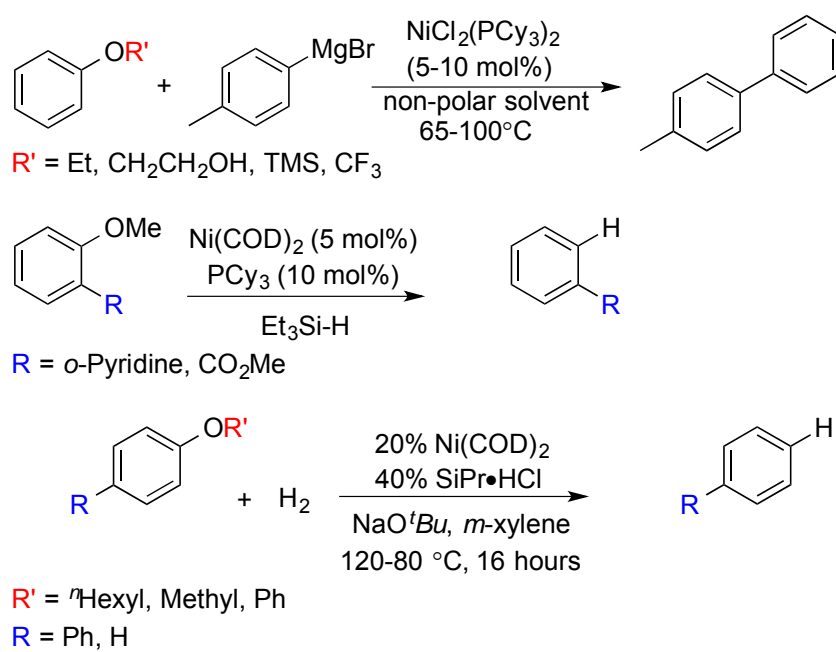

In the Agapie group several diphosphine terphenyl ligand precusors have been previously synthesized. When metallated with nickel, these scaffolds were found to support mono- and dinuclear complexes that exhibit a variety of strong nickel-arene interactions (Scheme 2.3).[7] Specifically the *meta*-terphenyl 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).[8] 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 Diphsophine Systems
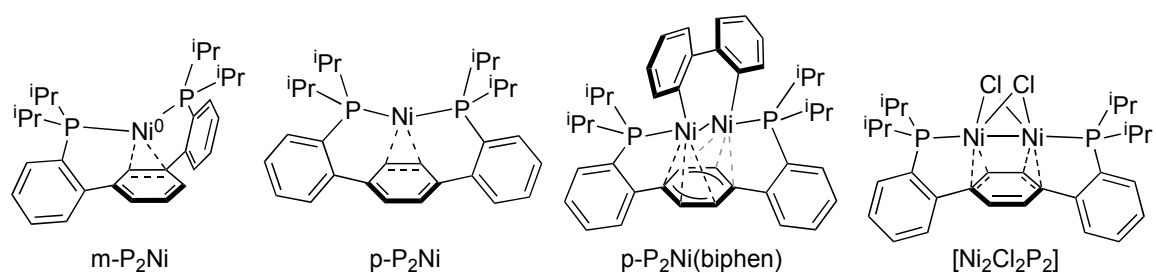
**Scheme 2.4 Design of Alkyl Ether Terphenyl Scaffold**
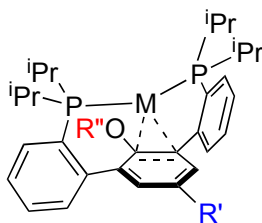
RESULTS & DISCUSSION:

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 diiodoalkoxybenzene. Treatment of the diiodo 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
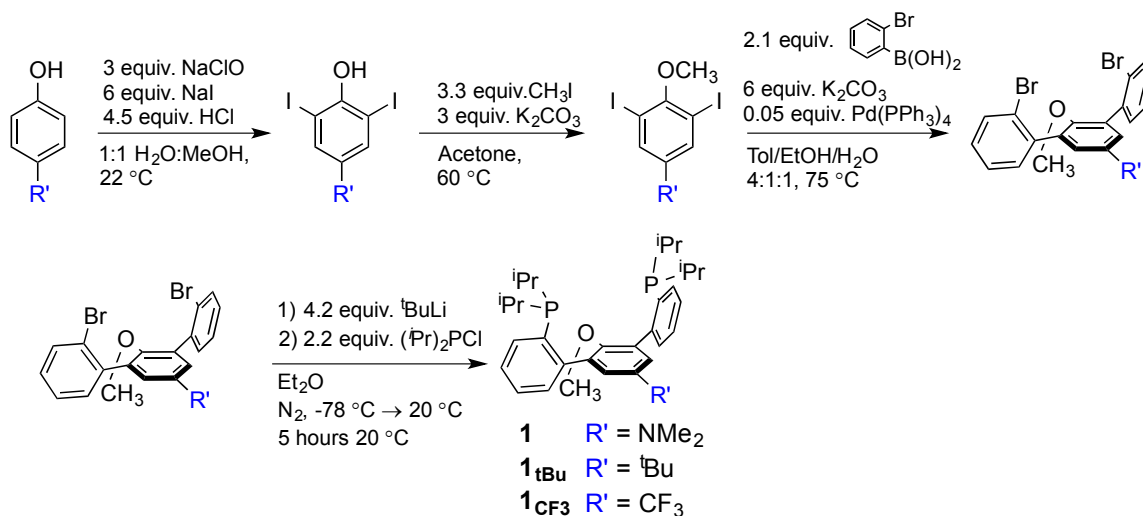
Using the general procedure outlined in Scheme 2.5 several variants of ligands were synthesized. The main diphosphine discussed in this chapter, contains a dimethylamino group in the *para*-position of the central ring and was synthesized using a modified procedure (Scheme 2.6). Starting from 4-nitrophenol, 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**
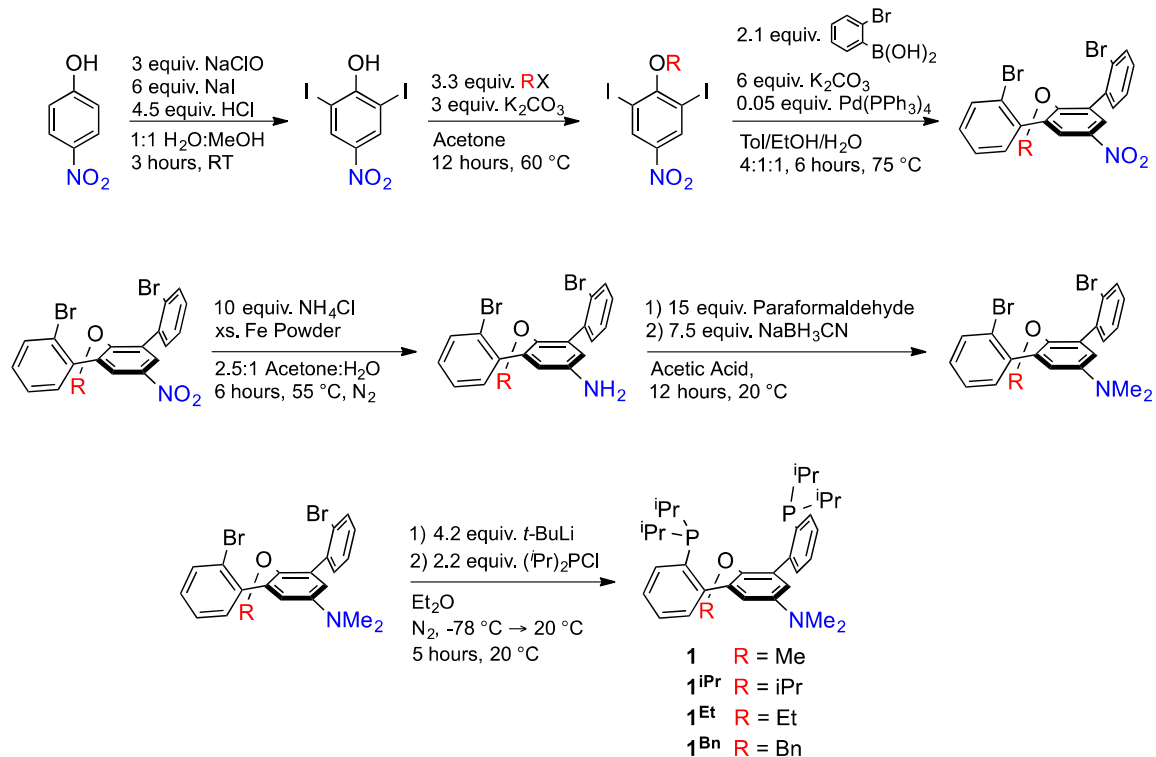
Ligands containing alkyl ethers can easily be synthesized via reaction of a diiodo phenolic precursor with the desired alkyl halide. The synthesis of a diaryl ether on this scaffold, however, requires a different approach to install the aryl group. The most promising method was found to be coupling of a phenol with a diaryl iodonium triflate salt.[9] 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). Treatment of the 2,6-diiodo-4-

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-nitrophenyoxy-2,6-diiodo-4-tertbutylbenzene cross coupling precursor (Scheme 2.7).[10] 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).

Scheme 2.7 Diphosphine terphenyl diaryl ether synthesis
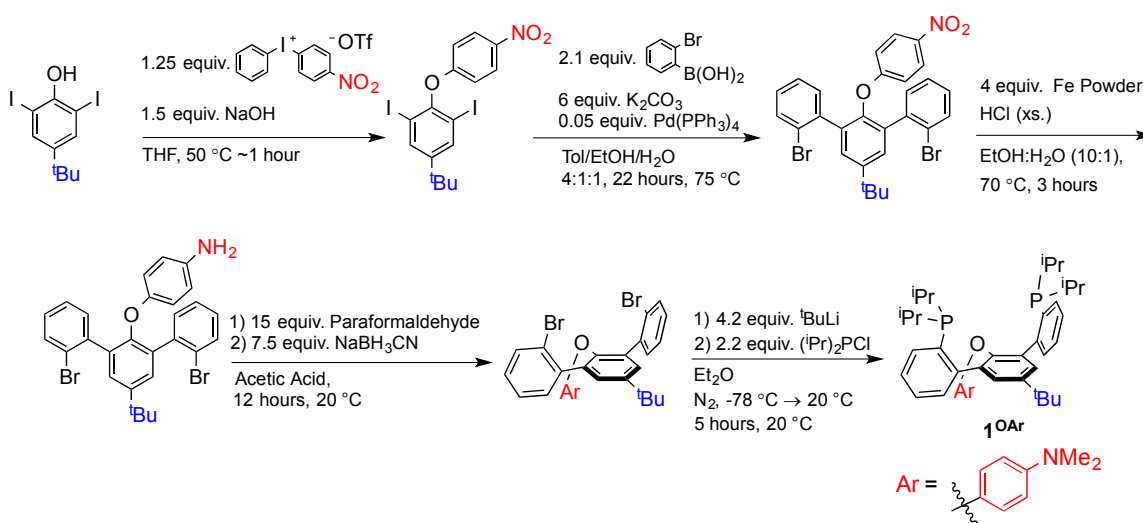
All the diphosphine ether ligands synthesized exhibit **NMR** behavior consistent with hindered rotation around the carbon-carbon bond between the central terphenyl ring and the outer terphenyl arenes (Figure 2.1). These properties arise due to the ether moiety at the *ipso*-carbon at the central terphenyl 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.
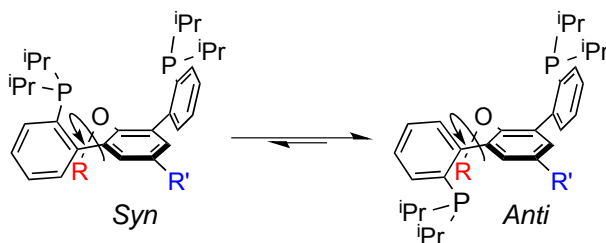

Figure 2.1. Hindered rotation around substituted terphenyl rings. *Syn* atropisomer corresponds to both phosphines on the same side of the central arene ring. The *anti* atropisomer corresponds to phosphines on either side of the central ring.

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.
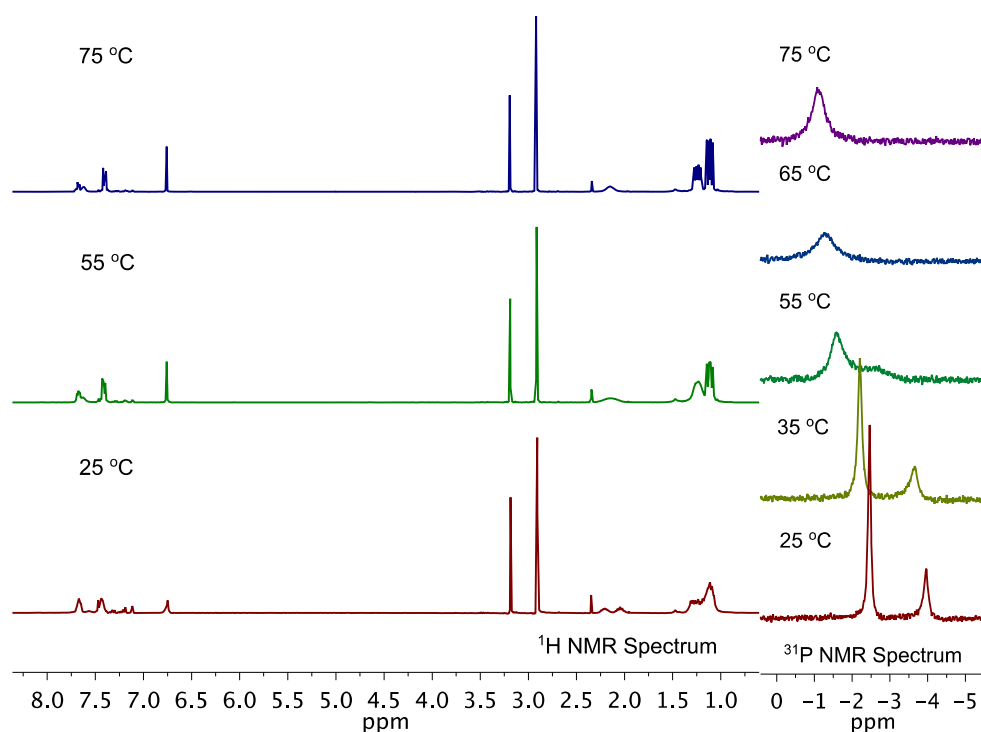
Figure 2.2. Variable temperature NMR spectra of **1**. Stacked ^{1}H NMR spectra on the left and ^{31}P NMR spectra on the right.

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).[7]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 OCH_3 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 π-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
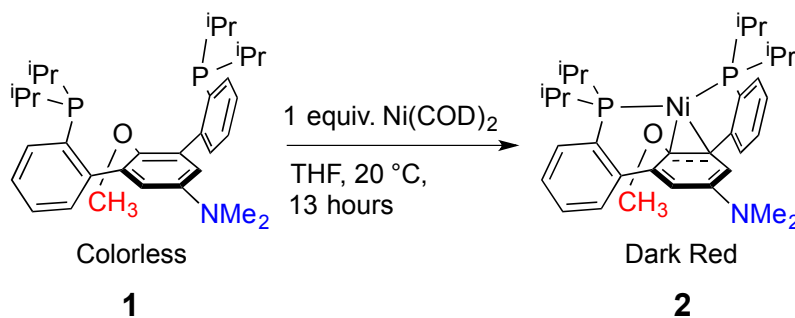
The assignment and spectroscopic findings of **2** were confirmed by a single-crystal X-ray diffraction (XRD). X-ray quality crystals of **2** were grown out of pentane at -32 °C. In the solid state the metal center is bound by two phosphines and interacts with two carbon centers of the central arene 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 sp[3] hybridization of the 2′-position of the central ring (C18, (Figure 2.3)) due to the Ni-C interaction. Notably, an intermediate displaying η[2]-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.[2g,11] Complex **2** is the only example of such an arrested intermediate characterized by crystallography, according to a Cambridge Structural Database search.[12]
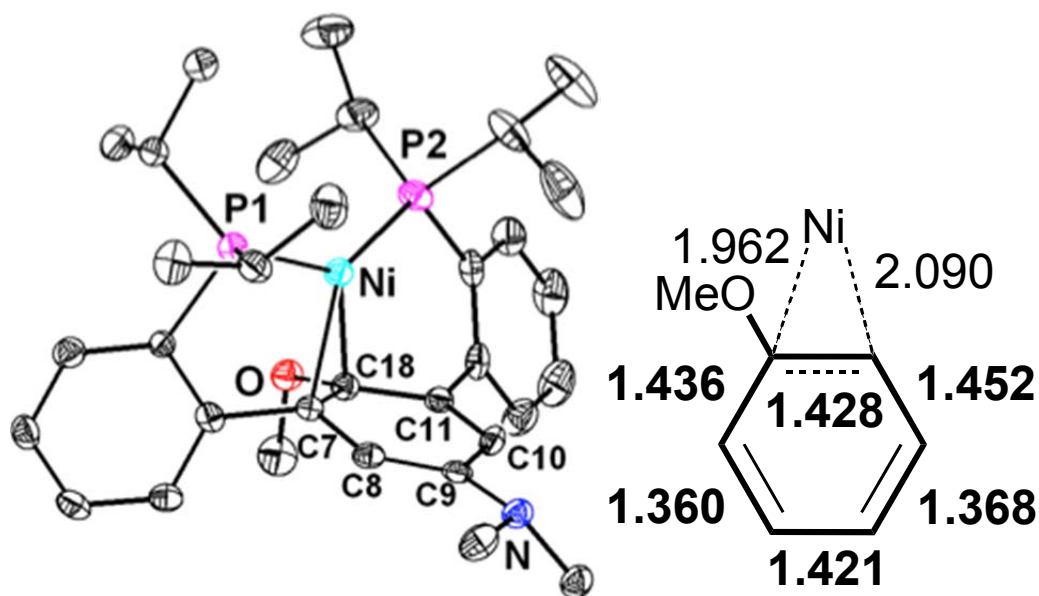

Figure 2.3 Solid-state structure of **2** (left). Solvent molecules, anions, and select hydrogen atoms not shown for clarity. Diagram of central arene bond lengths in **2** (right).

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 ^{1}H 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 OCH_3 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 sp^2 aryl-oxygen bond. Compound **3** is similar to a nickel(II) PCP complex which gives similar ^{1}H 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
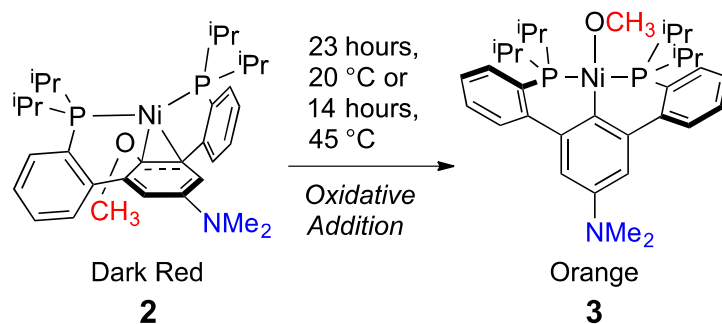
Upon further heating of **3**, a new species, **4**, is observed (Scheme 2.10). The central arene protons of this complex are also shifted relative to **2** in the aromatic region (6.79 ppm vs. 5.84 ppm) and are quite similar to the arene resonances in the nickel(II) methoxide complex **3** (6.78 ppm). Intriguingly, the OCH_3 signal is absent and upfield triplet is observed in the hydride region of the ^{1}H 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.
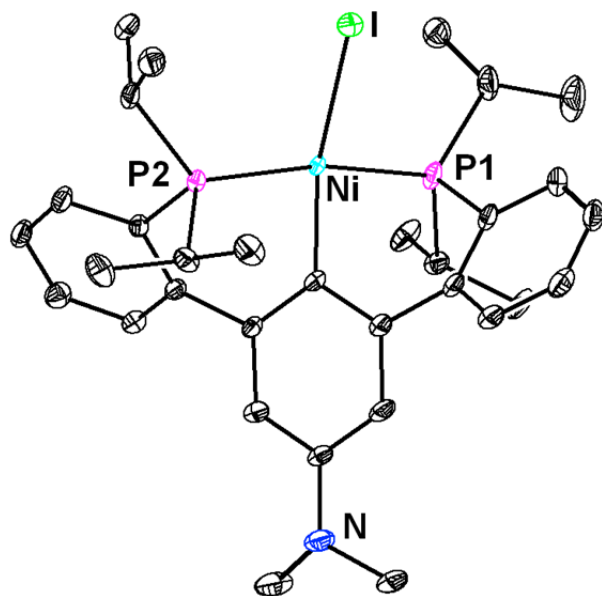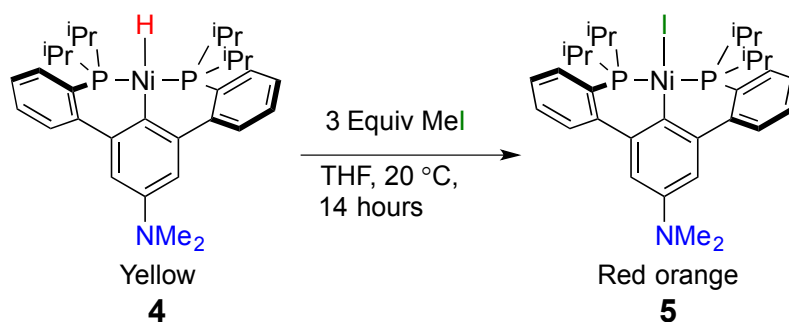
Scheme 2.10 Synthesis of nickel(II) hydride 4 from complex 2
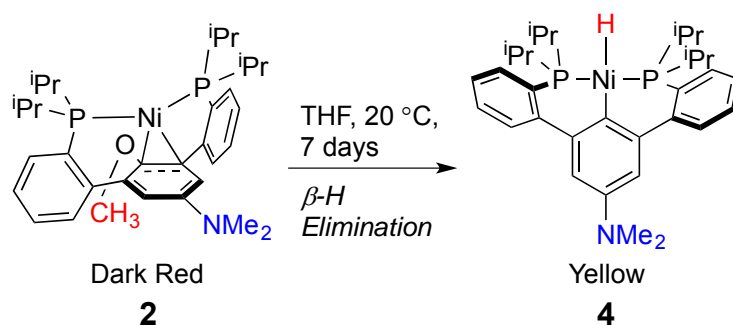
In order to obtain structural insight into compounds **3** and **4** an analog with a better crystallization profile was synthesized. Treatment of **4** with excess methyl iodide at 20 °C for 14 hours generated a new species assigned as a Ni(II) iodide, **5**; an XRD study of this species confirmed the 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.[13] The diphosphine ligand framework, bound in *pseudo-C₂* fashion, acts as a classical tridentate diphosphine-aryl pincer,[14] but with six-member chelates involving aryl-aryl linkages.[15] 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**

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).

	angles (°)
P2-Ni-P1	166.680(17)
C-Ni-I	161.06(4)
P2-Ni-I	99.972(12)
P1-Ni-I	93.156(13)
C-Ni-P2	84.30(4)
C-Ni-P1	83.98(4)

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 ^{1}H 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).[16] Similar stoichiometric reactions mediated by rhodium and palladium have been reported.[4]

**Scheme 2.12 Alternate Syntheses of 3 from 4 and 5**
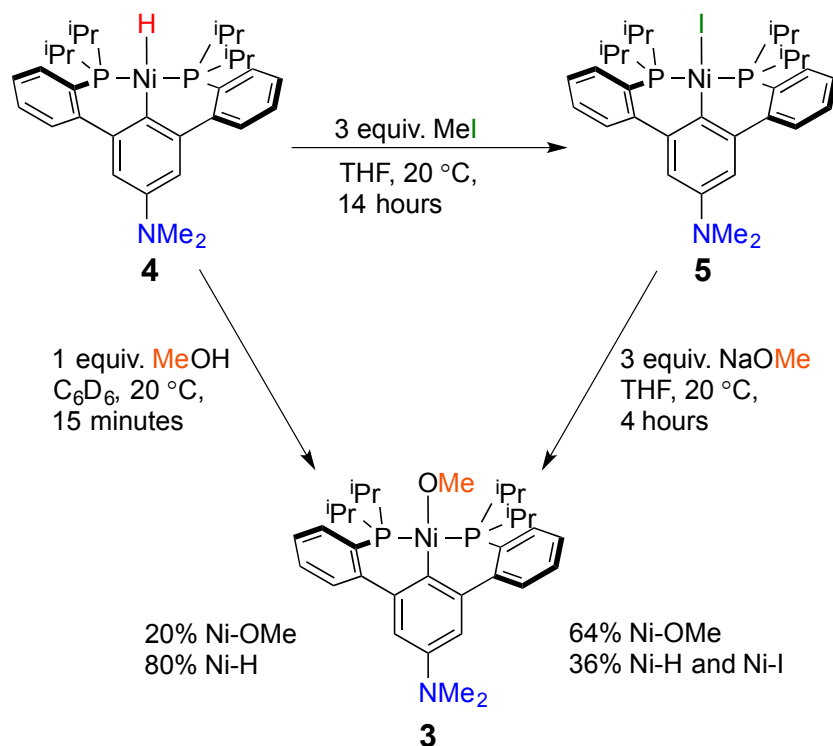
The mechanism of the hydride formation in **4** was probed through deuterium labeling studies. A ligand containing a deuterated methoxide was synthesized through the use of d_3-iodomethane in the phenol protection. **1-d_3** metallation with nickel(0) produced **2-d_3** the deuterated analog of **2**. Subjection of **2-d_3** to elevated temperatures in this complex leads to a nickel methoxide complex **3-d_3**, which is identical to **3**, albeit without resonances for the methoxy group. Further heating of **3^{d3}** leads to the formation of the nickel(II) deuteride **4-d_1**. Complex **4-d_1** 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 β-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_6-benzene. This study

confirms the methoxy group as the source of hydrogen (deuterium). *β*-hydrogen elimination could occur via a five-coordinate intermediate,[17] although, in coordinatively saturated systems it has been proposed to occur via alkoxide dissociation[18] or in bimolecular fashion.[19] Given the strain observed in the chelates in **5**, dissociation of a phosphine arm may also be possible,[17a,17b,20] 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*₁ from 2-*d*₃
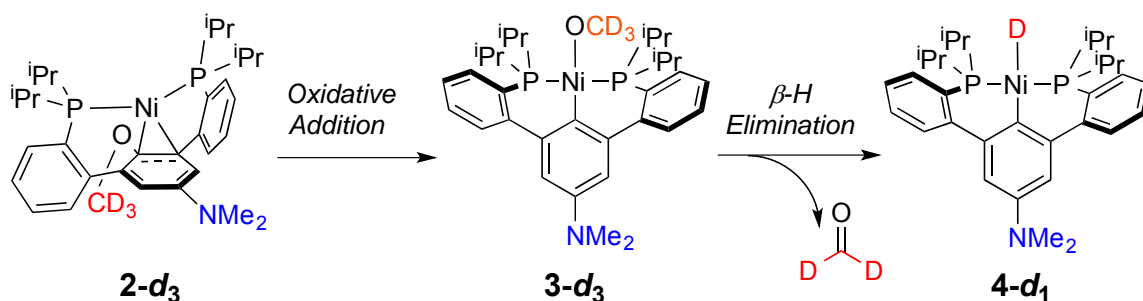
Although its generation does not require dihydrogen, hydride **4** is a potential intermediate in the hydrogenolysis of the aryl-O bond. Complex **2** was heated to 100 °C, generating new species, **6**, in over 90% yield (^{1}H NMR spectroscopy) within two hours. The Ni-*H* peak is absent from the ^{1}H 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).

Scheme 2.14 Synthesis of Ni(0) carbonyl complex 6 from 2

R'= t-Bu, NMe$_2$, CF$_3$
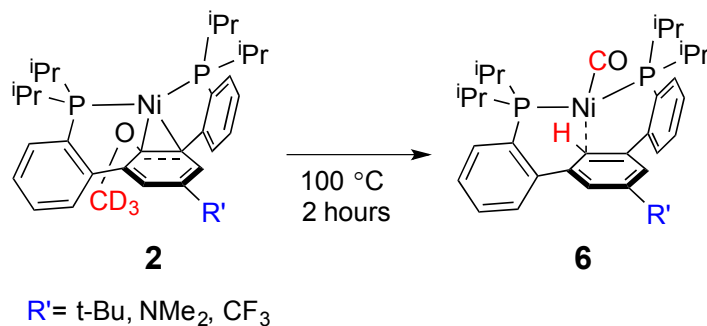
Scheme 2.15 Alternate Synthesis of 6 from 7
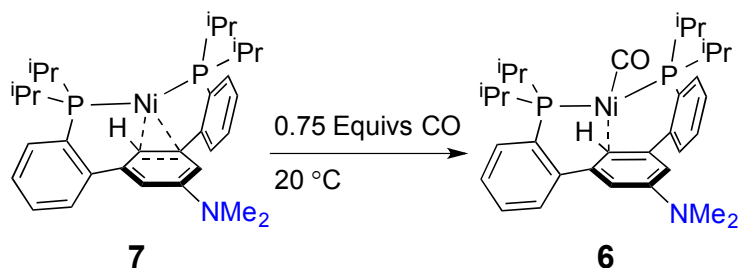
Intrigued by the presence of the *ipso*-H and the carbonyl group, we hypothesized that the *ipso*-H and carbonyl in **6** were the product of a reductive elimination and decarbonylation of formaldehyde from the previously isolated nickel(II) hydride **4**. To this end, reductive elimination in the **4** 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**.

π-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 ^{1}H and ^{31}P NMR spectroscopy revealed the quantitative formation of **6** in under 10 minutes at 20 °C. Interestingly, all the meta nickel(0) complexes (**7**, **2**, **2$_{tBu}$**, and **2$_{CF3}$**) 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).

## Scheme 2.16 Observed Model System Reactivity
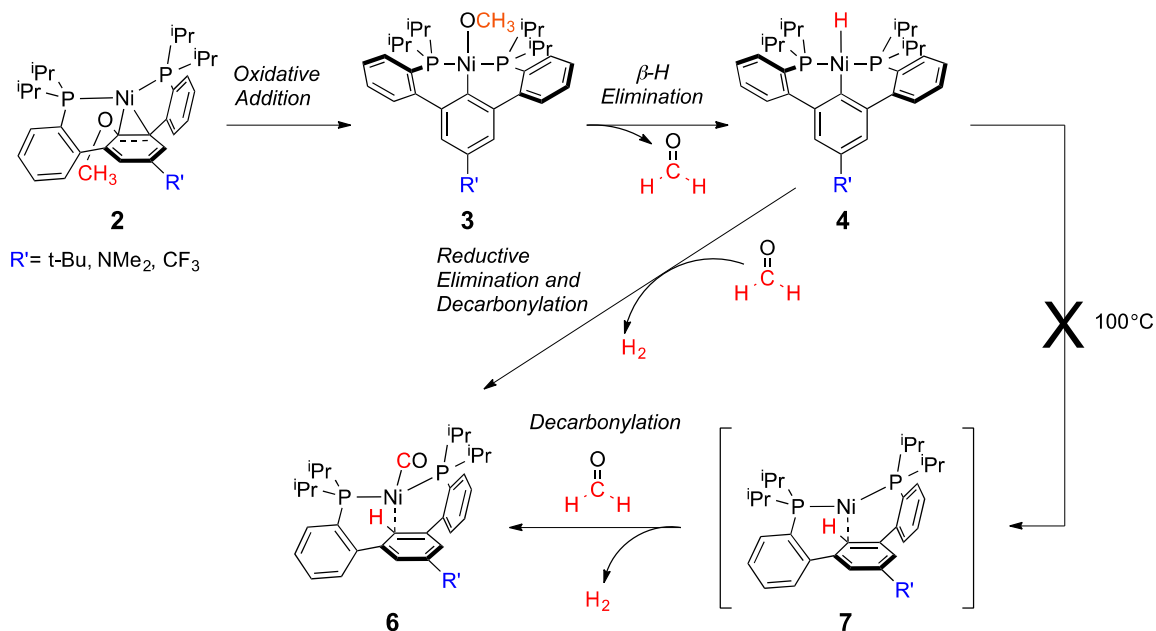
Scheme 2.17 Overall Anisole Reductive Cleavage Products
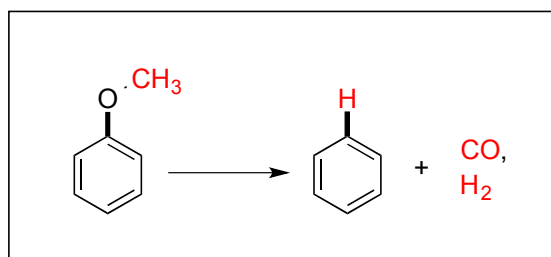
Inspired by these mechanistic results, the reactivity of the nickel model complex **2** was assessed in the presence of two prominent reductive cleavage additives, hydrogen and silanes. In a catalytic system with dihydrogen it is feasible to propose that the nickel(0) can add into the aryl oxygen bond 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-d_8** 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-d_3** and 4 atm of dihydrogen was heated to 45 °C. Under these conditions only β-hydrogen elimination was observed as only **4-d_1** was identifiable by ^{1}H 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-d_3 in the presence of H$_2$
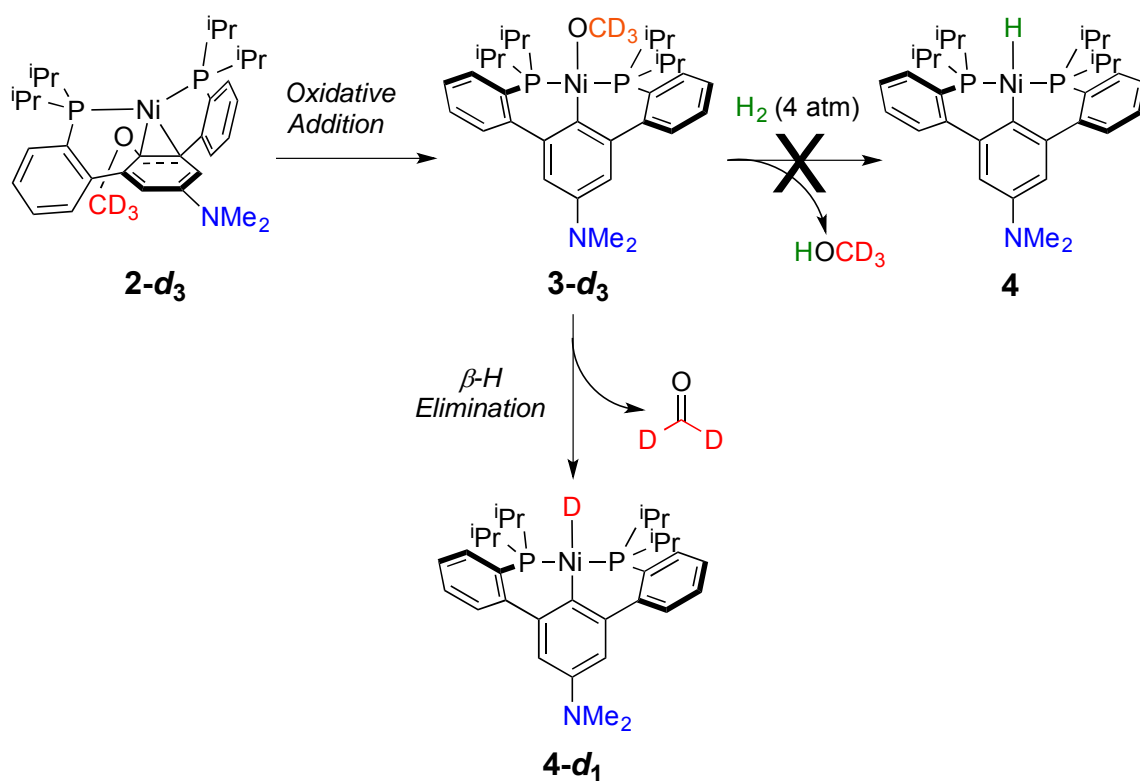
As silyl hydrides are also used as hydride sources in the reductive cleavage of aryl oxygen bonds, the reactivity of the model complex was investigated in the presence of triethylsilane (Scheme 2.19). In a catalytic system one can postulate that a

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 Et$_3$SiD for three hours generated less than 10% **6-d_1**. A larger excess of Et$_3$SiD (10 equivalents) led to more deuterium incorporation (ca 20% **6-d_1**).

As there is an isotope effect favoring the formation of **6**, the effect of triethylsilane with **2-d_1** was also investigated. Treatment of **2-d_1** with Et$_3$SiH (2 equiv) generated **6-d_1** and **6** in a 1:1 ratio. The increased isotopic incorporation from Et$_3$SiH vs. Et$_3$SiD 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 ^{1}H and ^{31}P 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
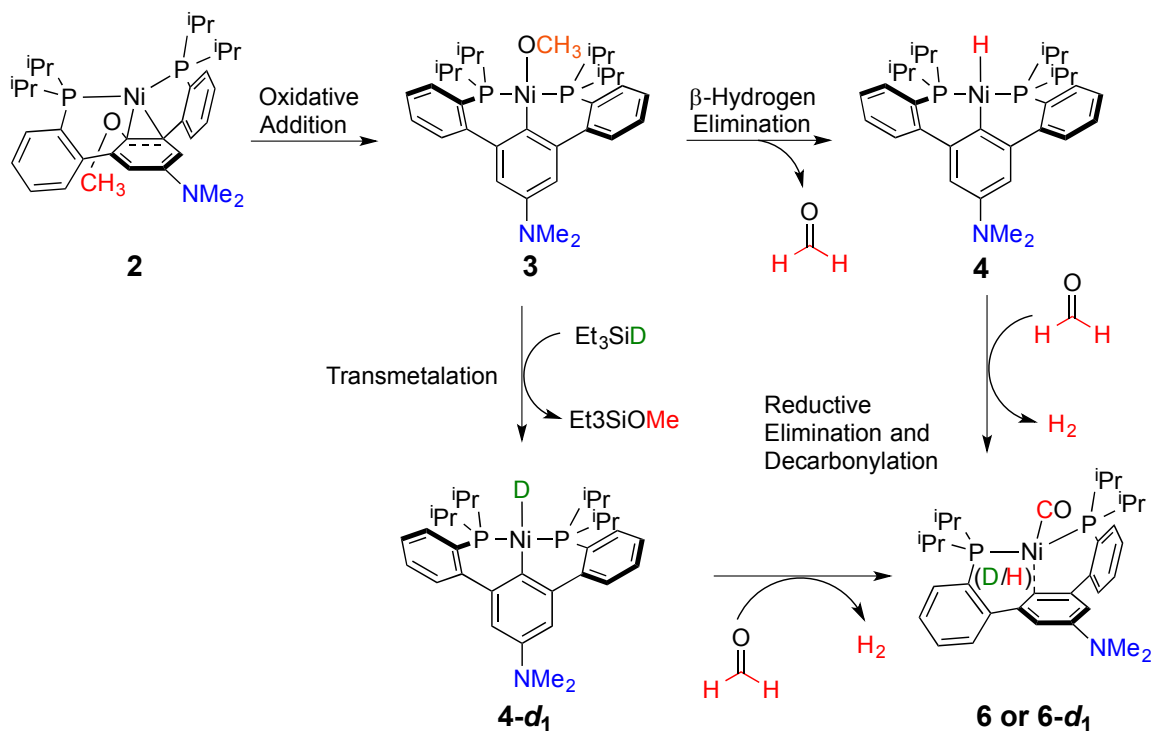
The mechanism for the reductive cleavage of the aryl-oxygen bond outlined with complex **2** was found to be the same for the other nickel(0) terphenyl diphosphine methyl ether variants. The tert-butyl variant **2**$_{tBu}$ was found to undergo a mechanism identical to the dimethyl amino variant. Interestingly the trifluoromethyl variant **2**$_{CF3}$ showed some deviation in the formation of the final nickel(0) carbonyl product. Heating of **2**$_{CF3}$ to 100 °C for 1.5 hours produces both **6**$_{CF3}$ and **7**$_{CF3}$ in a 1:1 ratio. This could be due to the lack of reactivity between **3**$_{CF3}$ and formaldehyde and formaldehyde acts like a fifth ligand promoting reductive elimination to form **4**$_{CF3}$. **7**$_{CF3}$ undergoes decarbonylation much slower (3 hours) than the more electron donating **7** (less than 10 minutes), which can explain the observed **7**$_{CF3}$, 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 ^{31}P NMR spectrum shows a shift in the phosphorous resonances of the free diphosphine to a new resonance at 13.46 ppm. The ^{1}H 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.[4] The observed reactivity appears to be limited to metal halides, treatment of the ligand with other nickel(II) salts such as Ni(II)OTf$_2$ (OTf = trifluoromethyl sulfate) does not lead to the formation of a similar phenoxide complex and only starting materials are observed by ^{1}H and ^{31}P NMR spectroscopy. The rate of the formation of the phenoxide complex is also dependent on the identity of the ether. Treatment of **1**^{Et} 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**^{OAr} does not lead to the formation of **8**.

Scheme 2.20 Reactivity of 1 with NiCl₂(DME)
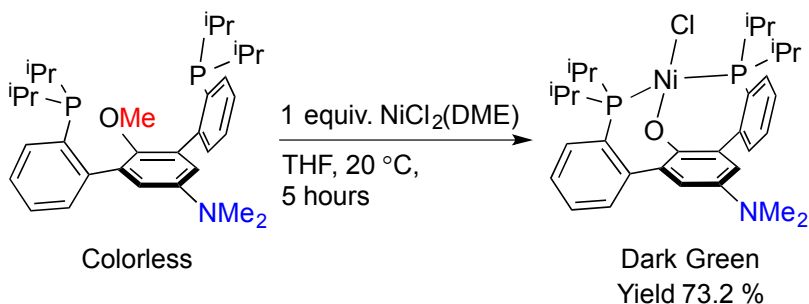
A single crystal X-ray diffraction study of a crystal of **8** grown from a concentrated solution in benzene confirmed the tentative structure (Figure 2.5). From the solid state structure we can see that the $Ni(II)Cl_2$ has activated the sp^3 C–O bond to form a nickel phenoxide species. Interestingly 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 $N–C_{Ar}$ 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.
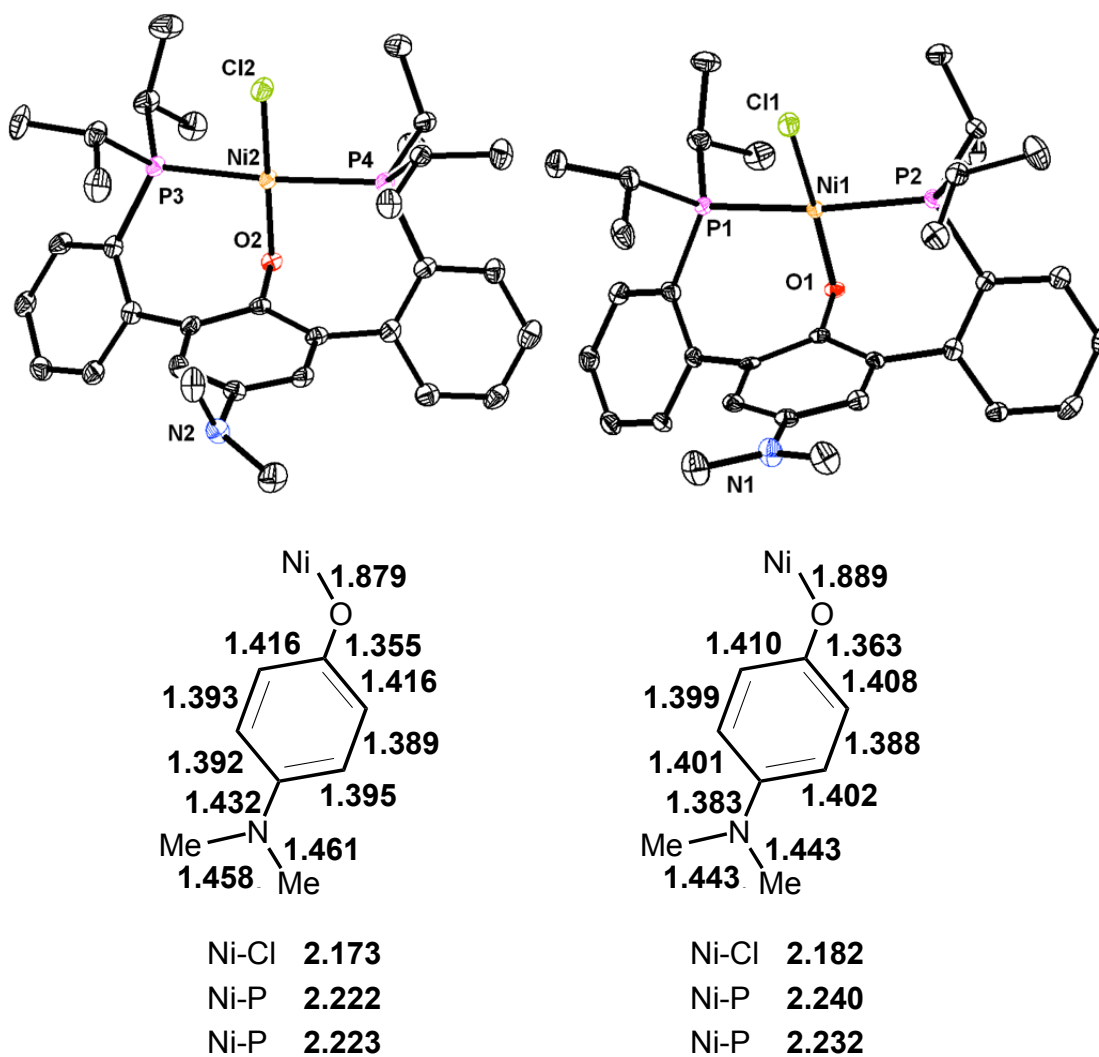
Figure 2.5 Solid-state structure of **8** (top). Solvent molecules, anions, and select hydrogen atoms not shown for clarity. Table of relevant bond lengths in **8** (bottom).

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
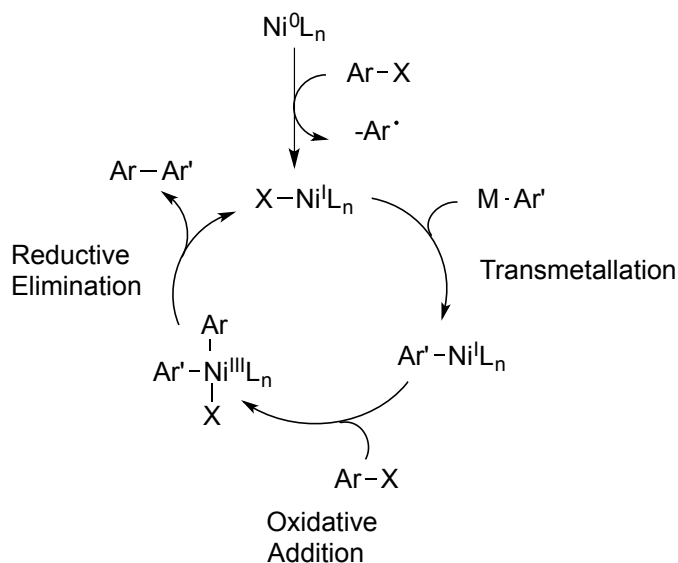
For aryl ethers, Martin et. al. developed a system for the reductive cleavage of C–O bonds based on nickel(0), tricyclohexylphosphine, and silane as the reducing agent.[2i] Using this system the reductive cleavage of aryl ethers was observed catalytically, however only when the phosphine was tricyclohexylphosphine. 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 $Ni(COD)_2$, PCy_3, and Et_3SiH through a comproportionation event. The nickel(I) diphosphine silane is the key catalytic species. The nickel(I) silane coordinates the substrate in an η^2-fashion and

undergoes a migratory insertion event and generate a benzyl nickel species. From this benzyl nickel species MeOSiR₃ 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**
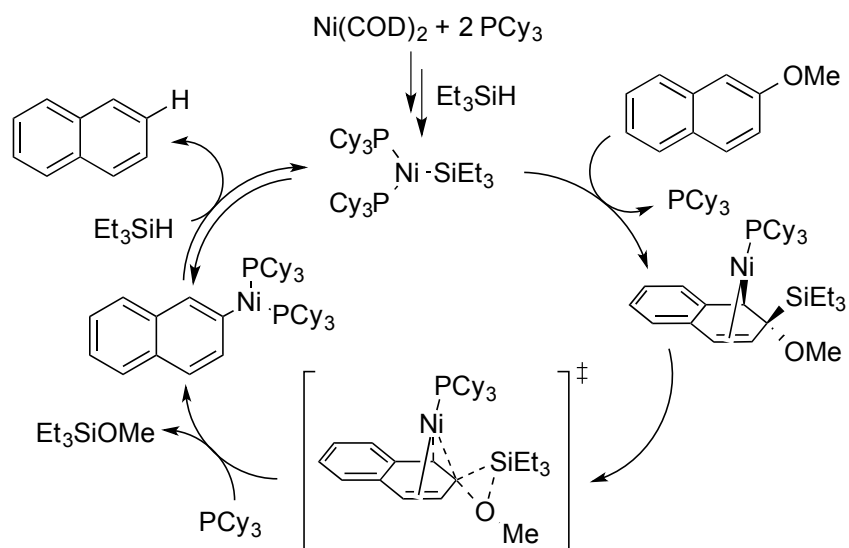
We have studied aryl–oxygen bond activation facilitated by nickel in a terphenyl diphosphine ether system. From our studies *vide supra* the activation of the aryl–oxygen bond proceeds through a nickel(0/II) mechanism in the model system. Given the evidence for nickel(I) species in activation of aryl–X 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 NiCl₂DME and NiCOD₂ 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 sp³ 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 NiCl₂DME 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)₂ and NiCl₂(DME)
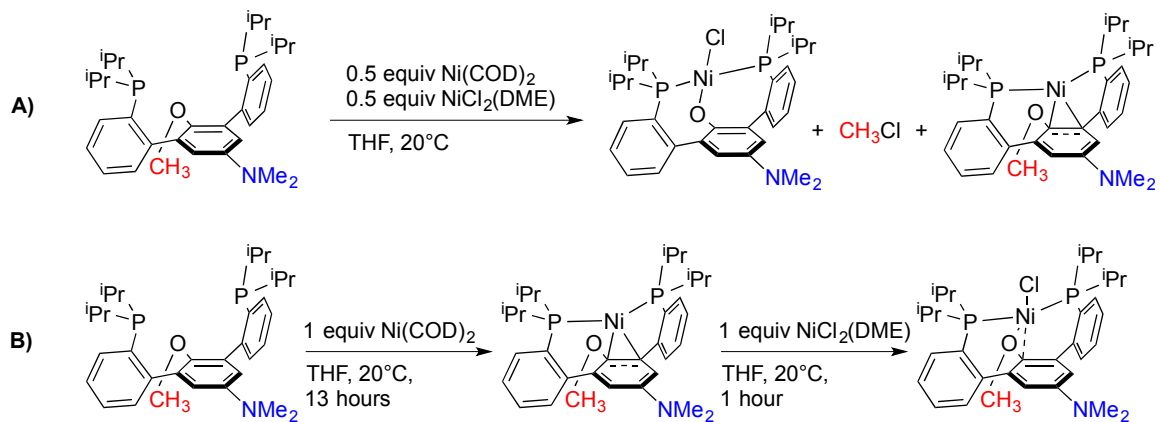
Complex **9** is paramagnetic and hence gives broad peaks ranging from -5 to 20 ppm in the ¹H NMR spectrum. No resonances are observed by ³¹P NMR spectroscopy for compound **9**. Hydrolysis of the complex with HCl and subsequent analysis by ESI mass spectrometry gives the mass of the terphenyl diphosphine **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^{OTf}**. Compound **9^{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^{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^{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
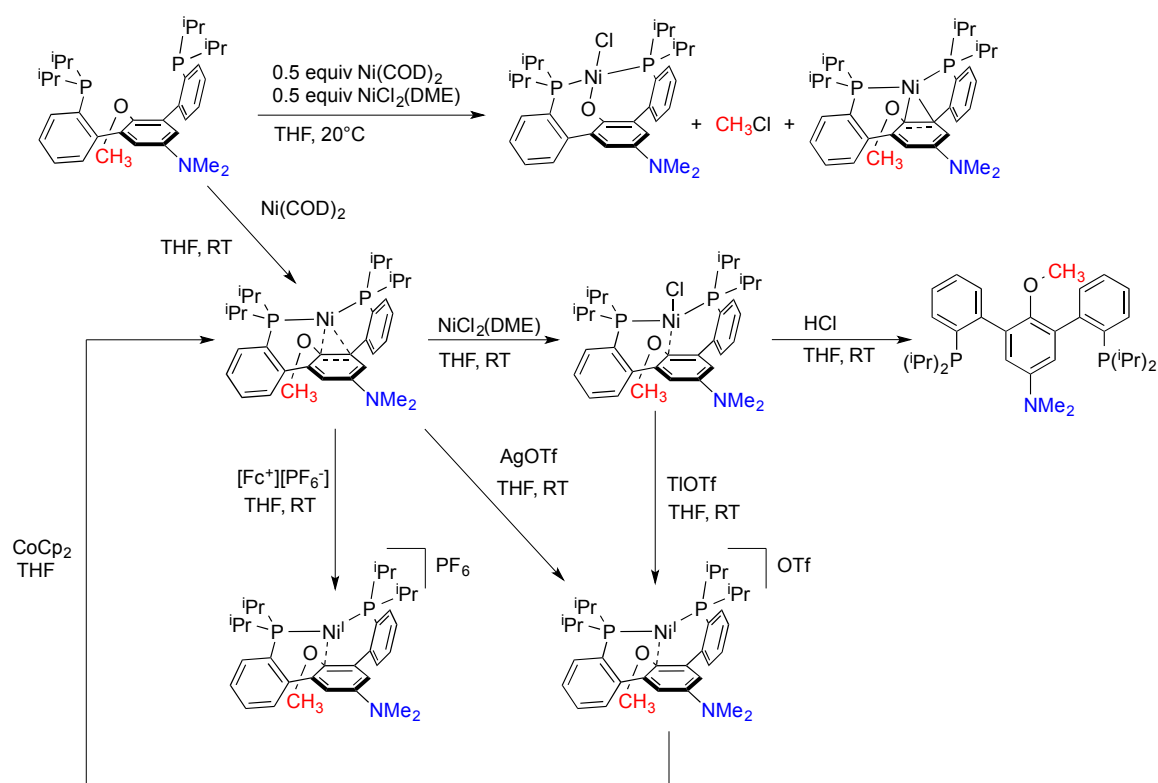
Complex **9** was found to be very robust. Heating **9** in benzene to 80 °C did not lead to any observed reactivity. Similarly heating complex **9** to 140 °C in xylenes does not result in aryl-O bond cleavage or any form of reactivity as only **9** was observed by

^{1}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
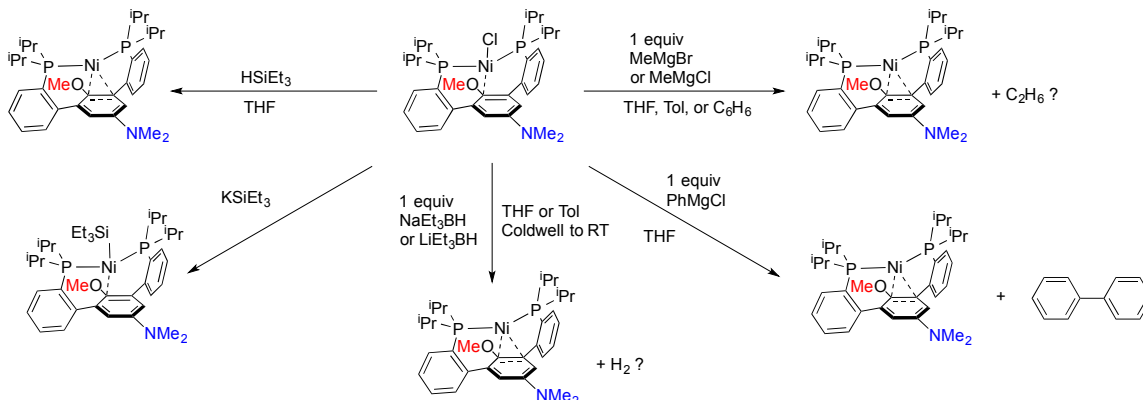
Isopropyl Ether

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^{iPr}. Treatment of 1^{iPr} with nickel(0) COD_2 at 20 °C in THF resulted in the formation of the nickel(0) diphosphine terphenyl isopropyl ether complex 2^{iPr} (Scheme 2.26). A shift is observed in the ^{31}P NMR spectrum where a single peak is observed at 39.20 ppm (vs. -2.41 and -4.54 of 1^{iPr}) for 2^{iPr}, this is comparable to the ^{31}P NMR shift of the methoxy variant 2 (40.7 ppm). By ^1H NMR spectroscopy a downfield shift in the central arene ring resonance of 2^{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^{iPr}
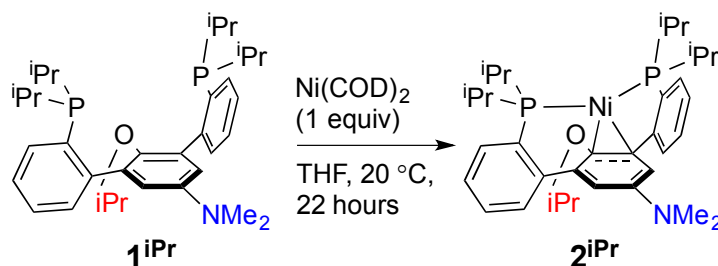
With **2^{iPr}** in hand, reactivity studies were undertaken. Unsurprisingly the nickel(0) complex **2^{iPr}** undergoes oxidative addition to form a proposed nickel(II) isopropoxide species **3^{iPr}** as identified by ^{31}P NMR spectroscopy. To date attempts to isolate complex **3^{iPr}** have resulted 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). β-H elimination quickly occurs in **3^{iPr}** 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^{iPr}**, **3^{iPr}**, **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^{iPr}** 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 β-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[iPr] Model System Reactivity
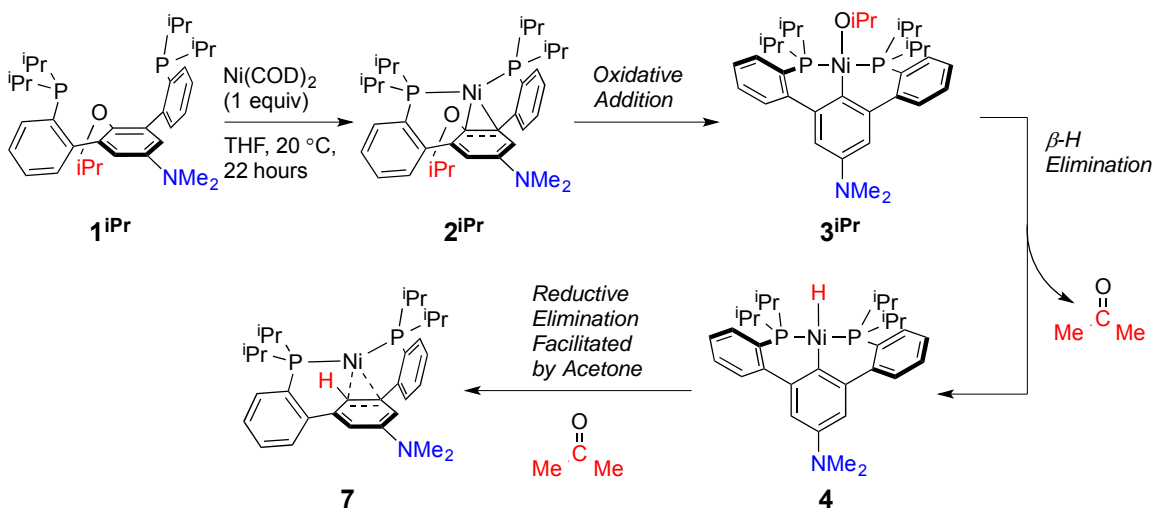
Scheme 2.28 Overall Isopropyl aryl ether Reductive Cleavage Products
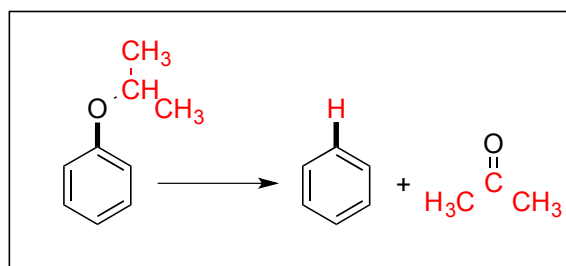

Ethyl Ether

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[Et]

was targeted. Compound **1**[Et] was synthesized via the fore mentioned synthesis route (Scheme 2.29). Mixing a solution of **1**[Et] with Ni(0)COD$_2$ at 20 °C results in the formation of a new Ni(0) terphenyl diphosphine ether complex **2**[Et]. A resonance is observed by ^{31}P NMR at an unremarkable shift of 40.56 ppm, consistent with the other synthesized terphenyl diphosphine ether complexes. ^{1}H 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**[Et] 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**[Et] (3.48 and 0.63 ppm for the methylene and methyl respectively) albeit without the isomer broadening.

Scheme 2.29 Synthesis of 2[Et]
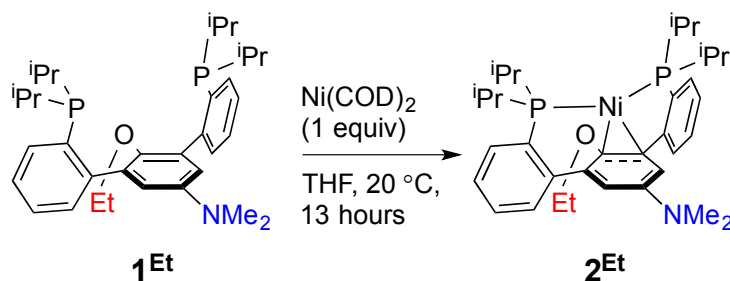
Upon heating the Ni[0] center of **2**[Et] undergoes an oxidative addition of the aryl oxygen bond resulting in a new species **3**[Et]. ^{31}P NMR spectroscopy reveals a resonance at 27.33 ppm. This new species is believed to be the nickel(II) oxidative addition product similar to **3**. Further heating 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 Ni⁰ carbonyl complex **6**, a Ni⁰ species generated from reductive elimination of a proton **7**, and a Ni⁰ 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^{Et} Model System Reactivity
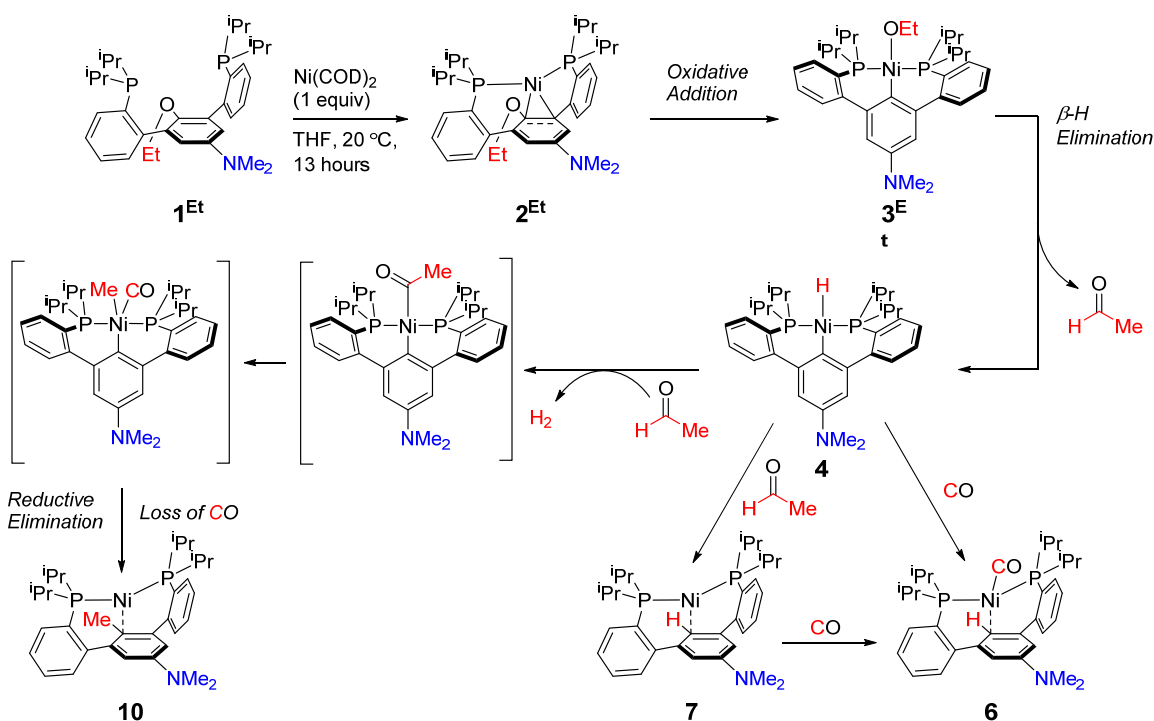
From the mixture of species formed it is probable that there are several competing processes active. For the formation of tolyl complex **10** from heating **2^{Et}** it is postulated that the nickel(II) hydride **4** reacts with the formed acetaldehyde resulting in a transient nickel(II)-acyl complex 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**
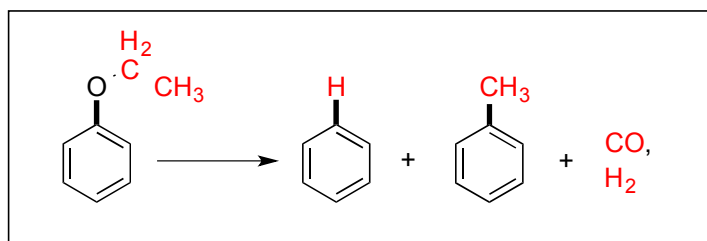
In order to probe the mechanism of **2**^{Et} further studies were carried out. If the proposed mechanism was possible, the isolable nickel hydride **4** should be able to react with acetaldehyde to form the observed ratio of products. When **4** is mixed with excess acetaldehyde little reactivity is 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**^{Et} (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 **7**$_H$ 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 ^{31}P 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
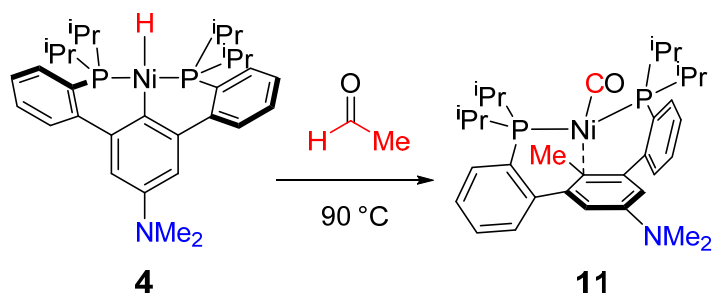
Scheme 2.33 Reactivity of nickel(0) model systems with acetaldehyde

2 R'= OMe R''= NMe$_2$
7 R'= H R''= NMe$_2$
**7$_H$** R'= H R''= H
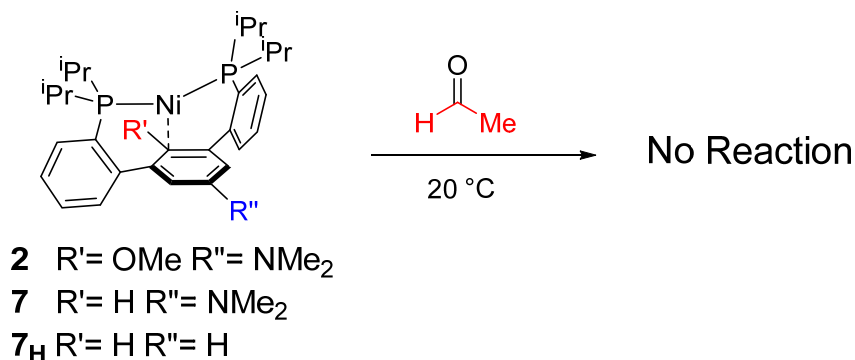
Benzyl Ether

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^{Bn}**
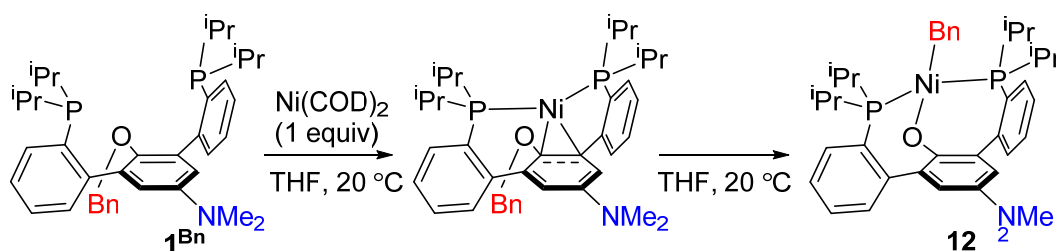
Gratifyingly, single crystals were grown from diethyl ether at room temperature, which upon preliminary analysis by single crystal x-ray diffraction resulted in the expected **12** structure. In order to further probe this system the reaction of the Benzyl ether ligand over time revealed the presence 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 *β*-hydrogen is essential for the reductive cleavage of alkyl ethers in our nickel(0) model system. The absence of a *β*-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 1^{OAr}. 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
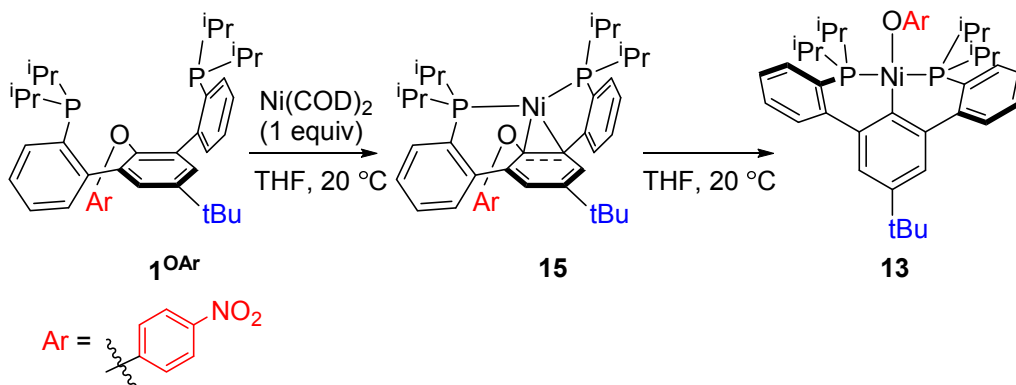
Analysis of **13** by ^{31}P NMR spectroscopy reveals a new peak at 29.73 ppm. Analysis by 1H NMR spectroscopy reveals a subtle shift in the proton resonance for the central terphenyl ring, from 7.51 ppm in the free ligand to 7.22 ppm for the nickel complex. The subtle shift in the central arene ring 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_2 a nickel(0) complex **15** is formed however this species quickly undergoes oxidative addition to form **13**. Indeed analysis of the reaction of $\mathbf{1^{OAr}}$ over time reveals a peak at 41.56 ppm by ^{31}P 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
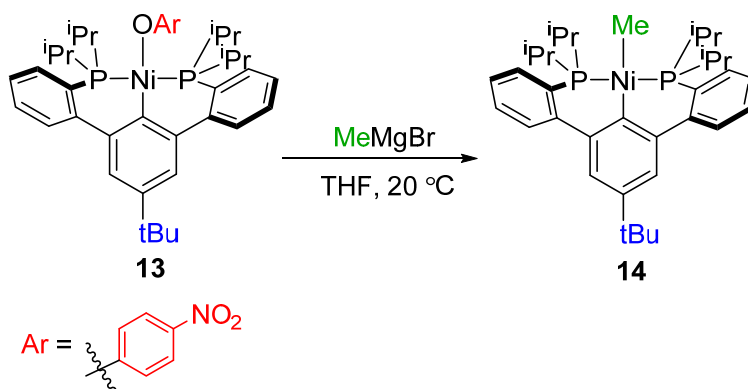
The nickel(II) complex **13** was investigated for further reactivity. Heating **13** to 100 °C does not result in any further reactivity. As predicted the lack of a β-hydrogen inhibits further reactivity in the aryl-aryl ether system. However its lack of reactivity makes it perfect for the study of 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 β-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.[21] 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.[22] 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_6D_6) and 7.26 ppm and 77.16 ppm ($CDCl_3$) 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:
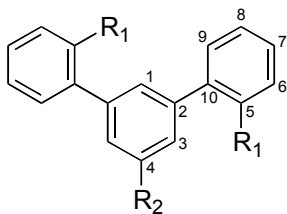
2,6-diiodo-4-nitrophenol
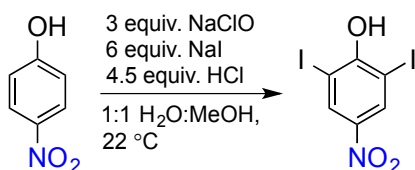
2,6-diiodo-4-nitrophenol was synthesized according to a modified literature procedure.[22b] A solution of 2,6-diiodo-4-nitrophenol (50.01 g, 359.5 mmol) in MeOH (1 L) was mixed with an aqueous solution (1 L in H_2O) of $NaClO_2$ (123.64 g, 1.09 mol) and NaI (321.04 g, 2.15 mol) in a 3 L round bottom 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 35C. 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% ^{1}H NMR (d_6-Acetone, 300 MHz) δ 8.61 (s, 2H, central Ar-*H*)

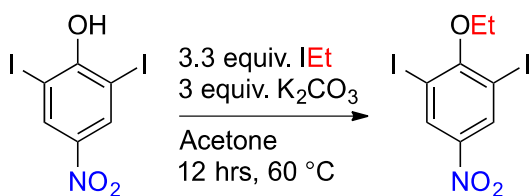### 1,3-diiodo-2-alkoxy-5-nitrobenzene
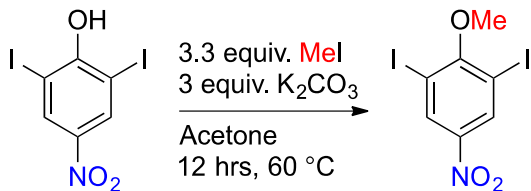
The 1,3-diiodo-2-alkoxy-5-nitrobenzene compounds were synthesized using a modified literature procedure for the synthesis of 1,3-diiodo-2-methoxy-5-nitrobenzene.[22a] In a 500 ml round bottom flask potassium carbonate (21.69 g, 156.9 mmol) was mixed with 20.13 g (51.5 mmol) 2,6-diiodo-4-nitrophenol in 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% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.64 (s, 2H), 3.94 (s, 3H)
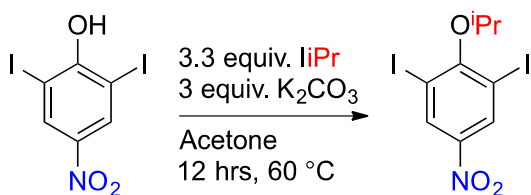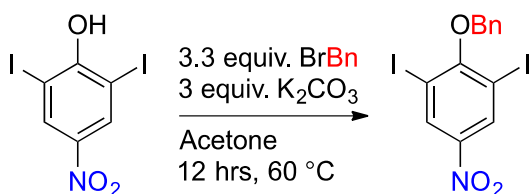

1,3-diiodo-2-isopropoxy-5-nitrobenzene Yield: 4.13 g, 52.3% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.66 (s, 2H), 4.96 (septet, 1H), 1.46 (d, 6H)

1,3-diiodo-2-ethoxy-5-nitrobenzene Yield: 6.23 g, 62.7% ^{1}H NMR (CDCl₃, 300 MHz) δ
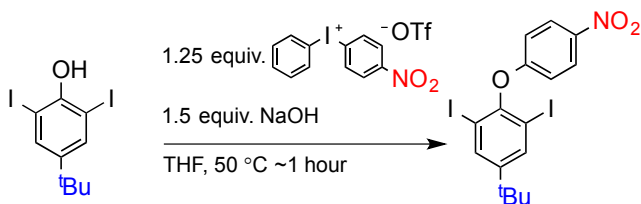
8.66 (s, 2H), 4.04 (quartet, 2H), 1.20 (t, 3H)

1,3-diiodo-2-benzyl-5-nitrobenzene Yield: 19.08 g, 91.5% ^{1}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.[9d] In a

round bottom flask 0.75 g NaOH (18.6 mmol) and 5.00 g 2,6-diiodo-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:Et₂O 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% ^{1}H NMR (CDCl[3], 300 MHz) δ 8.22 (d, 2H), 7.84 (s, 2H), 6.89 (d, 2H), 1.33 (s, 9H)

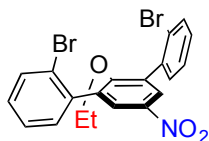## 1,3-bis(2´-bromophenyl)-2-methoxy-4-nitrobenzene
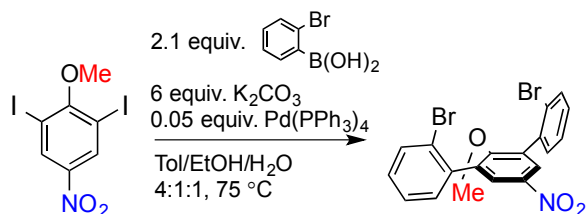
The 1,3-bis(2´-bromophenyl)-2-alkoxy-4-nitrobenzene compounds were synthesized according to the procedure for 1,3-bis(2'-bromophenyl)-2-methoxy-4-nitrobenzene. Suzuki coupling conditions were adapted from a previously published procedure.[6] 1,3-diiodo-2-methoxy-5-nitrobenzene (2.48 g, 6.58 mmol, 1 equiv), 2-bromo-phenylboronic acid (2.77 g, 13.80 mmol, 2.1 equiv), K[2]CO[3] (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(PPh[3])[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 H[2]O. The solution was extracted with three portions of CH[2]Cl[2]. The combined organic fractions were dried over MgSO[4], 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

^{1}H NMR (CDCl$_3$, 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, OC*H*$_3$)
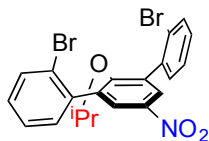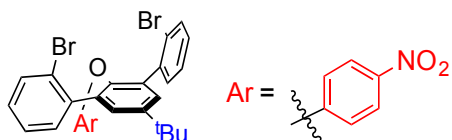

1,3-bis(2'-bromophenyl)-2-isopropoxy-4-nitrobenzene ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.21 (s, 2H, central Ar-*H*), 7.72 (d, 2H, Ar-*H*), 7.42 (m, 4H, Ar-*H*), 7.29 (d, 2H, Ar-*H*), 3.64 (septet, 1H, OC*H*(CH$_3$)$_2$), 0.68 (d, 6H, OCH(C*H*$_3$)$_2$)

1,3-bis(2'-bromophenyl)-2-ethoxy-4-nitrobenzene ^{1}H NMR (CDCl$_3$, 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, OC*H*$_2$CH$_3$), 0.75 (t, 2H, OCH$_2$C*H*$_3$)
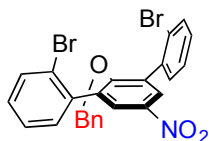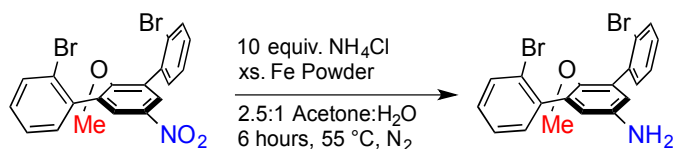

1,3-bis(2'-bromophenyl)-2-benzyl-4-nitrobenzene ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.11 (s, 2H, central Ar-*H*), 7.38 (m, 2H, Ar-*H*), 6.80 (m, 9H, Ar-*H*), 6.57 (d, 2H, Ar-*H*), 4.30 (dd, 2H, OC*H*$_2$Ph)

1,3-bis(2'-bromophenyl)-2-phenoxy-4-nitrobenzene ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.86 (d, 2H, Ar-*H*), 7.54 (d, 2H, Ar-*H*), 7.44 (d, 2H, Ar-*H*), 7.31 (s, 2H, Ar-*H*), 7.19 (m, 2H, Ar-*H*), 7.09 (m, 2H, Ar-*H*), 6.61 (d, 2H, Ar-*H*), 1.41 (s, 9H, C(C*H*$_3$)$_3$)
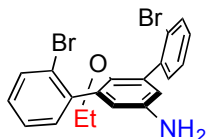
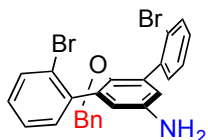**4-amino-1,3-bis(2'-bromophenyl)-2-methoxybenzene**

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) δ 7.65 (d, 2H, Ar-*H*), 7.36 (m, 4H, Ar-*H*), 7.20 (t, 2H, Ar-*H*), 6.59 (s, 2H, central Ar-*H*), 3.63 (s, 2H, N*H*$_2$), 3.27 (s, 3H, OC*H*$_3$)
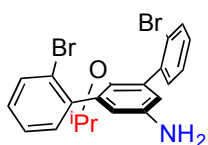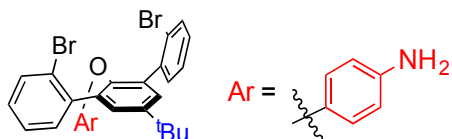

4-amino-1,3-bis(2'-bromophenyl)-2-isopropoxybenzene ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.66 (d, 2H, Ar-*H*), 7.41 (d, 2H, Ar-*H*), 7.32 (t, 2H, Ar-*H*), 7.18 (t, 2H, Ar-*H*), 6.67 (s, 2H, central Ar-*H*), 3.94 (s, 2H, N*H*$_2$), 3.38 (septet, 1H, OC*H*(CH$_3$)$_2$), 0.55 (d, 6H, OCH(C*H*$_3$)$_2$)

4-amino-1,3-bis(2'-bromophenyl)-2-ethoxybenzene ^{1}H NMR (CDCl₃, 300 MHz) δ 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, N*H₂*), 3.27 (s, 2H, OC*H₂*CH₃), 0.60 (s, 3H, OC*H₂*CH₃)

4-amino-1,3-bis(2'-bromophenyl)-2-benzylbenzene ^{1}H NMR (CDCl₃, 300 MHz) δ 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, OC*H₂*Ph), 3.64 (br s, 2H, N*H₂*)

4-amino-1,3-bis(2'-bromophenyl)-2-phenoxybenzene ^{1}H NMR (CDCl₃, 300 MHz) δ 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, N*H₂*), 1.38 (s, 9H, C(C*H₃*)₃)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene
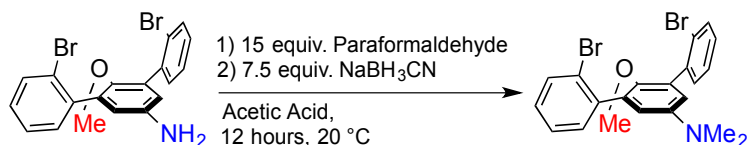
1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene was synthesized using a literature procedure[8]. The product was purified by Flash chromatography (dichloromethane) and isolated as a colorless solid. 1,3-bis(2'-bromophenyl)-4-

dimethylamino-2-methoxybenzene Yield: 41.9% ^{1}H NMR (C$_6$D$_6$, 399.80 MHz) δ 7.57 (d, 2H, Ar-H_6), 7.41 (d, 2H, Ar-H_9), 7.01 (t, 2H, Ar-H_7), 6.81 (t, 2H, Ar-H_8), 6.68 (s, 2H, Ar-H_3), 3.12 (s, 3H, OCH_3), 2.48 (s, 6H, N(CH_3)$_2$), ^{13}C NMR (C$_6$D$_6$, 100.54 MHz) δ 146.72 (s, Ar-C_1), 146.66 (s, Ar-C_4), 141.21 (s, Ar-C_{10}), 135.74 (s, Ar-C_2), 132.98 (s, Ar-C_9), 132.31 (s, Ar-C_6), 128.97 (s, A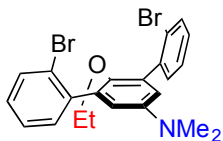r-C_7), 127.09 (s, Ar-C_8), 124.54 (s, Ar-C_5), 115.73 (s, Ar-C_3), 60.77 (s, O-CH$_3$), 40.69 (N(CH$_3$)$_2$), MS (m/z): calcd, 460.9813 (M+); found, 460.9822 (FAB+, M+).
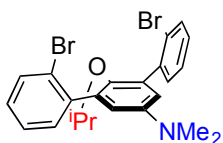
1,3-bis(2'-bromophenyl)-4-dimethylamino-2-isopropoxybenzene Yield: 37.4% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.66 (d, 2H, Ar-H_6), 7.45 (d, 2H, Ar-H_9), 7.34 (t, 2H, Ar-H_7), 7.19 (t, 2H, Ar-H_8), 6.69 (s, 2H, Ar-H_3), 3.39 (septet, 1H, OCH(CH$_3$)$_2$), 2.96 (s, 6H, N(CH_3)$_2$), 0.59 (d, 6H, OCH(CH_3)$_2$)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-ethoxybenzene Yield: 41.9% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.67 (d, 2H, Ar-H_6), 7.45 (d, 2H, Ar-H_9), 7.34 (t, 2H, Ar-H_7), 7.20 (t, 2H, Ar-H_8), 6.64 (s, 2H, Ar-H_3), 3.27 (br q, 3H, OCH_2CH$_3$), 2.95 (s, 6H, N(CH_3)$_2$), 0.62 (t, 3H, OCH_2CH$_3$)
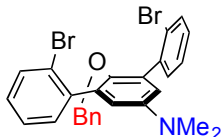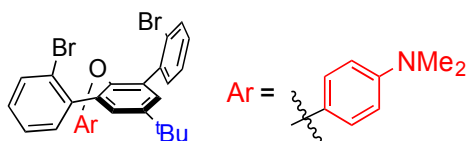
1,3-bis(2'-bromophenyl)-4-dimethylamino-2-benzylbenzene Yield: 41.9% ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.55 (d, 2H, Ar-H_6), 7.44 (d, 2H, Ar-H_9), 6.92 (t, 2H, Ar-H_7), 6.77 (t, 2H, Ar-H_8), 6.72 (s, 2H, Ar-H_3), 4.50 (br m, 2H, OCH_2Ph), 2.48 (s, 6H, N(CH_3)$_2$)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-phenoxybenzene Yield: 41.9% ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.55 (s, 2H, Ar-H), 7.38 (d, 4H, Ar-H), 6.79 (d, 2H, Ar-H), 6.57 (dd, 2H, Ar-H), 6.20 (d, 2H, Ar-H), 2.25 (s, 6H, N(CH_3)$_2$), 1.24 (s, 9H, C(CH_3)$_3$)

1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (1)
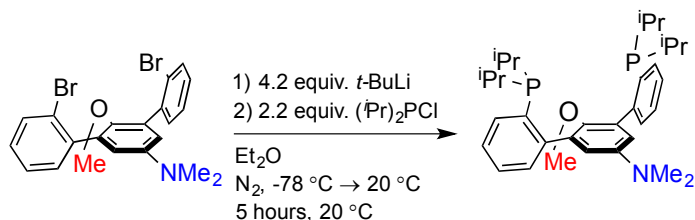
In a glovebox a 100 mL Schlenk tube was charged with a colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (50.1 mg, 0.11 mmol) in Et$_2$O (30 mL) and a stir bar. The Schlenk tube was removed from the glove box and cooled to -78°C in a dry ice/acetone bath. Under N2, tBuLi 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. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 75°C) δ 7.65 (m, 2H, Ar-H_6), 7.48 (m, 2H, Ar-H_9), 7.19 (m, 4H, Ar-H_{7-8}), 6.73 (s, 2H, Ar-H_3), 3.14 (s, 3H, OC$H_3$), 2.65 (s, 6H, N(C$H_3$)$_2$), 2.06 (m, 2H, C$H$(CH$_3$)$_2$) , 1.92 (m, 2H, C$H$(CH$_3$)$_2$) , 1.08 (m, 24H, CH(C$H_3$)$_2$) ^{13}C{^{1}H} NMR (C$_6D_6$, 100.54 MHz) δ 148.52 (m, Ar-C_{10}), 147.49 (s, Ar-C_1), 145.61 (s, Ar-C_4), 136.85 (d, Ar-C_5), 136.44 (d, Ar-C_2), 132.43 (s, Ar-C_9), 131.68 (d, Ar-C_6), 128.19 (s, Ar-C_8), 126.68 (s, Ar-C_7), 117.41 (s, Ar-C_3), 60.18 (s, O-CH$_3$), 41.21 (N(CH$_3$)$_2$), 26.79 (CH-(CH$_3$)$_2$), 24.96 (CH-(CH$_3$)$_2$), 20.83 (CH-(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ -2.72 (s), -4.09 (s) MS (m/z): calcd, 535.3133 (M+); found, 535.3134 (FAB+, M+). 1,3-
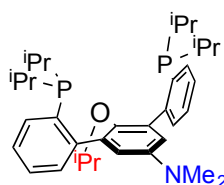
bis(2'-diisopropylphosphino)-4-dimethylamino-2-isopropoxybenzene (1^{iPr})

(0.91 g, 1.61 mmol) in 83.1% yield. ^{1}H NMR (C$_6$D$_6$, 499.85 MHz, 70°C) δ 7.66 (br s, 2H, Ar-H_6), 7.49 (d, 2H, Ar-H_9), 7.20 (t, 2H, Ar-H_{7-8}), 7.15 (t, 2H, Ar-H_8), 6.70 (s, 2H, Ar-H_3), 3.76 (septet, 1H, OCH(CH$_3$)$_2$), 2.67 (s, 6H, N(CH_3)$_2$), 2.13 (m, 2H, CH(CH$_3$)$_2$)

, 1.91 (m, 2H, C*H*(CH₃)₂) , 1.08 (m, 24H, CH(C*H*₃)₂), 0.59 (d, 6H, OCH(C*H*₃)₂), ¹³C{¹H} NMR (C₆D₆, 125.70 MHz) δ 149.04 (d, Ar-*C*₁₀), 145.41 (s, Ar-*C*₁), 145.20 (s, Ar-*C*₁), 137.24 (d, Ar-*C*₅), 137.03 (d, Ar-*C*₂), 132.18 (s, Ar-*C*₆₋₉), 132.06 (d, Ar-*C*₆₋₉), 128.12 (s, Ar-*C*₇₋₈), 126.55 (s, Ar-*C*₇₋₈), 117.48 (d, Ar-*C*₃), 74.61 (s, O*C*H-(CH₃)₂), 41.32 (N(*C*H₃)₂), 27.08 (*C*H-(CH₃)₂), 24.53 (*C*H-(CH₃)₂), 22.86 (OCH-(*C*H₃)₂), 22.27 (OCH-(*C*H₃)₂), 21.32 (CH-(*C*H₃)₂), 20.86 (CH-(*C*H₃)₂), 20.64 (CH-(*C*H₃)₂), 20.53 (CH-(*C*H₃)₂), ³¹P{¹H} NMR (C₆D₆, 121.48 MHz) δ -2.41 (s), -4.53 (s)
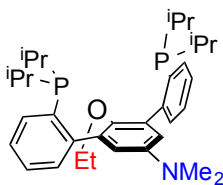
1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-ethoxybenzene (1ᴱᵗ)

(0.97 g, 1.76 mmol) in 93.9% yield. ¹H NMR (C₆D₆, 499.85 MHz, 75°C) δ 7.54 (m, 2H, Ar-*H*₆), 7.48 (m, 2H, Ar-*H*₅), 7.15 (m, 4H, Ar-*H*₇₋₈), 6.68 (s, 2H, Ar-*H*₃), 3.39 (s, 3H, OC*H*₂CH₃), 2.67 (s, 6H, N(C*H*₃)₂), 1.99 (m, 4H, C*H*(CH₃)₂), 1.12 (m, 12H, CH(C*H*₃)₂), 1.01 (m, 12H, CH(C*H*₃)₂), 0.57 (m, 3H, OCH₂C*H*₃), ¹³C{¹H} NMR (C₆D₆, 125.70 MHz) δ 148.29 (d, Ar-*C*₁₀), 146.39 (s, Ar-*C*₁), 145.11 (s, Ar-*C*₁), 136.90 (m, Ar-*C*₅), 136.48 (m, Ar-*C*₂), 132.04 (s, Ar-*C*₆₋₉), 131.89 (s, Ar-*C*₆₋₉), 131.39 (s, Ar-*C*₆₋₉), 130.76 (s, Ar-*C*₆₋₉), 128.17 (s, Ar-*C*₇₋₈), 126.24 (s, Ar-*C*₇₋₈), 116.96 (s, Ar-*C*₃), 116.74 (s, Ar-*C*₃), 68.79 (s, O*C*H₂CH₃), 68.27 (s, O*C*H₂CH₃), 40.85 (N(*C*H₃)₂), 26.44 (*C*H-(CH₃)₂), 25.91 (*C*H-(CH₃)₂), 24.47 (*C*H-(CH₃)₂), 20.58 (CH-(*C*H₃)₂), 20.28 (CH-(*C*H₃)₂), 19.48 (CH-(*C*H₃)₂), 15.20 (OCH₂*C*H₃), ³¹P{¹H} NMR (C₆D₆, 121.48 MHz) δ -2.84 (s), -4.30 (s)
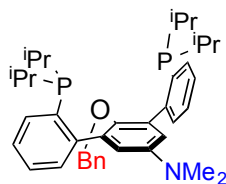
1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-benzylbenzene (1^{Bn})

(0.19 g, 0.30 mmol) in 92.9% yield. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 20 °C) δ 7.68 (m, 1H, Ar-H_6), 7.48 (m, 3H, Ar-H_6), 7.21 (m, 4H, Ar-H_{7-8}), 6.93 (m, 3H, Ar-H_3), 6.77 (s, 2H, Ar-H_3), 6.62 (m, 2H, Ar-H_3), 4.50 (dd, 2H, OCH_2Ph), 2.67 (s, 6H, N(CH_3)$_2$), 2.02 (m, 2H, CH(CH$_3$)$_2$) , 1.91 (m, 2H, CH(CH$_3$)$_2$) , 1.01 (m, 18H, CH(CH_3)$_2$), 0.86 (m, 6H, CH(CH_3)$_2$), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 148.27 (d, Ar-C_{10}), 146.00 (s, Ar-C_5), 138.41 (s, Ar-C_1), 137.35 (s, Ar-C_4), 137.14 (s, Ar-C_5), 132.44 (s, Ar-C_{6-9}), 131.89 (s, Ar-C_{6-9}), 131.33 (s, Ar-C_{6-9}), 128.33 (s, OCH$_2$$Ph$), 128.16 (s, Ar-$C_{7-8}$), 127.32 (s, OCH$_2$$Ph$), 126.74 (s, Ar-$C_{7-8}$), 117.16 (s, Ar-$C_3$), 75.29 (s, O$CH_2$Ph), 75.00 (s, O$CH_2$Ph), 41.15 (N($CH_3$)$_2$), 26.82 ($C$H-(CH$_3$)$_2$), 26.34 ($C$H-(CH$_3$)$_2$), 24.47 ($C$H-(CH$_3$)$_2$), 21.14 (CH-($CH_3$)$_2$), 20.50 (CH-($CH_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6D_6$, 121.48 MHz) δ -2.67 (s), -4.20 (s)
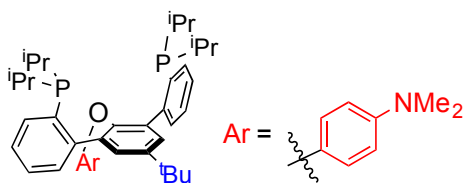
1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-phenoxybenzene (1^{OAr})

(0.53 g, 0.83 mmol) in 92.9% yield. ^{1}H NMR (C$_6$D$_6$, 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(CH_3)$_2$), 1.94 (br s, 2H, CH(CH$_3$)$_2$), 1.39 (s, 3H, C(CH_3)$_3$), 1.12 (br m, 18H, CH(CH_3)$_2$), 1.01 (br m, 6H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 151.82 (s, Ar-C_1), 150.91 (s, Ar-C_1), 148.23 (s, Ar-C_{10}), 147.39 (s,

Ar-C_{10}), 147.07 (s, Ar-C_2), 146.83 (s, Ar-C_2), 145.51 (s, OAr), 145.22 (s, OAr), 145.02 (s, OAr), 144.69 (s, Ar-C_1), 136.60 (s, Ar-C_5), 136.35 (s, Ar-C_5), 131.83 (s, Ar-C_{6-9}), 131.45 (s, Ar-C_{6-9}), 130.59 (s, Ar-C_{6-9}), 129.81 (s, Ar-C_3), 129.61 (s, Ar-C_3), 127.95 (s, Ar-C_{7-8}), 126.40 (s, Ar-C_{7-8}), 116.96 (s, OAr), 116.22 (s, OAr), 113.89 (s, OAr), 113.64 (s, OAr), 40.84 (Ar-N(CH$_3$)$_2$), 34.24 (C(CH$_3$)$_3$), 31.39 (C(CH$_3$)$_3$), 26.50 (CH-(CH$_3$)$_2$), 25.61 (CH-(CH$_3$)$_2$), 24.43 (CH-(CH$_3$)$_2$), 20.55 (CH-(CH$_3$)$_2$), 19.50 (CH-(CH$_3$)$_2$), ^{31}P$\{^1$H$\}$ NMR (C$_6$D$_6$, 121.48 MHz) δ -2.61 (s), -3.98 (s)

2,6-diiodo-4-trifluoromethylphenol
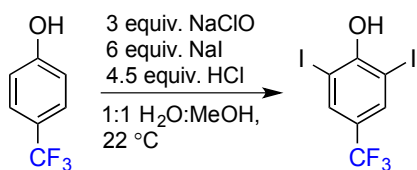
2,6-diiodo-4-trifluoromethylphenol was synthesized using the same procedure listed for 2,6-diiodo-4-nitrophenol. Yield: 5.32 g, 73.3% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.92 (s, 2H, central Ar-H) ^{19}F$\{^1$H$\}$ NMR δ 61.75

1,3-diiodo-2-methoxy-5-trifluoromethylbenzene
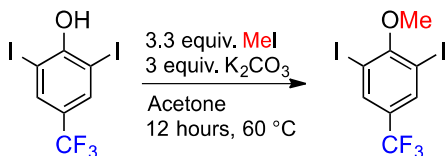
1,3-diiodo-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-diiodo-2-methoxy-5-nitrobenzene. Yield: 4.52 g, 87.0% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.01 (s, 2H, central Ar-H) 3.90 (s, 3H, OCH_3)

1,3-bis(2´-bromophenyl)-2-methoxy-5-trifluoromethylbenzene
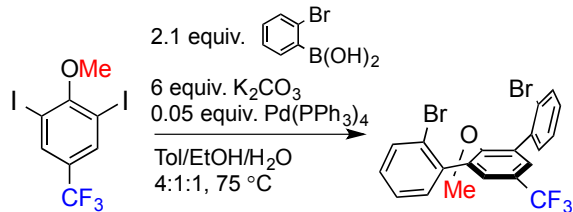
1,3-bis(2'-bromophenyl)-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-bromophenyl)-2-methoxy-5-nitrobenzene. Yield: 2.31 g, 53.9% ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.49 (s, 2H, central Ar-*H*), 7.41 (d, 2H, Ar-*H*), 7.00 (d, 2H, Ar-*H*), 6.89 (t, 2H, Ar-*H*), 6.73 (t, 2H, Ar-*H*), 2.94 (s, 3H, OC*H*$_3$) ^{19}F{^{1}H} NMR δ 61.31

1,3-bis(2'-diisopropylphosphino)-2-methoxy-5-trifluoromethylbenzene (1$_{CF3}$)
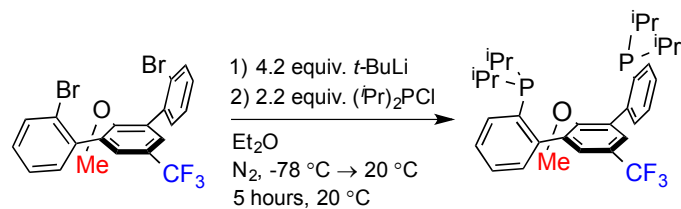
1,3-bis(2'-2'-diisopropyphosphinophenyl)-2-methoxy-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-2'-diisopropyphosphinophenyl)-2-methoxy-5-nitrobenzene. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.60 (br m, 2H, Ar-*H*), 7.33 (br m, 4H, Ar-*H*), 7.12 (br m, 4H, Ar-*H*), 3.00 (m, 3H, OC*H*$_3$), 1.93 (septet, 2H, C*H*(CH$_3$)), 1.71 (septet, 2H, C*H*(CH$_3$)), 1.01 (m, 6H, CH(C*H*$_3$)), 0.87 (m, 18H, CH(C*H*$_3$)), ^{19}F{^{1}H} NMR δ 61.31, ^{31}P{^{1}H} NMR δ -2.55, -4.24

1,3-diiodo-5-nitrobenzene.
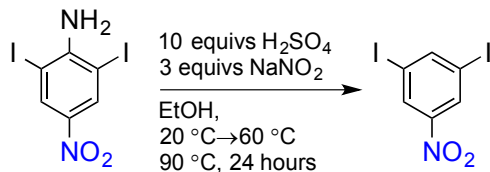
A modified literature procedure was used for the synthesis of 1,3-diiodo-5-nitrobenzene.[23] A solution of 2,6-diiodo-4-nitroaniline in ethanol (5.851 g; 15.0 mmol in 100 ml) was cooled to 0 °C using an ice bath. Upon cooling 8 ml (150 mmol) of concentrated H_2SO_4 was added drop wise over 1 hour using 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$_3$) δ 8.52 (d, 2H, *meta*Ar-*H*), 8.37 (t, 1H, *ipso*Ar-*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.
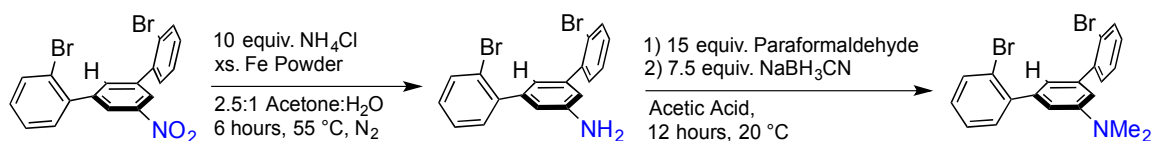
1,3-bis(2'-bromophenyl)-*5*-dimethylaminobenzene was synthesized from 1,3-bis(2'-bromophenyl)-*5*-nitrobenzene using the same procedure that was used for the reduction and amination of 1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene. 1,3-bis(2'-bromophenyl)-*5*-dimethylaminobenzene was purified by Flash chromatography (dichloromethane) and isolated as a colorless solid. ^{1}H 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(C*H*₃)₂.

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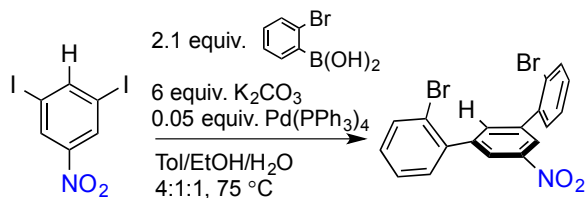

1,3-bis(2'-diisopropyphosphinophenyl)-*5*-dimethylaminobenzene was synthesized using the same procedure listed for 1,3-bis(2'-2'-diisopropyphosphinophenyl)-2-methoxy-*5*-nitrobenzene. ^{1}H NMR (CDCl₃, 300 MHz) δ 7.59 (br m, 2H, Ar-*H*), 7.47 (br m, 2H, Ar-*H*), 7.18 (br m, 4H, Ar-*H*), 7.03 (s, 1H, Ar-*H*), 6.91 (s, 2H, Ar-*H*), 2.68 (s, 6H,

N(C*H*₃)₂), 1.94 (septet, 4H, C*H*(CH₃)), 1.02 (m, 24H, CH(C*H*₃)), ¹³C{¹H} NMR (C₆D₆, 125.70 MHz) δ 151.58 (d, Ar-*C*₁₀), 148.79 (s, Ar-*C*₄), 142.65 (s, Ar-*C*₁), 135.42 (d, Ar-*C*₅), 132.28 (s, Ar-*C*₇₋₈), 130.49 (s, Ar-*C*₇₋₈), 128.15 (s, Ar-*C*₆₋₉), 126.22 (d, Ar-*C*₂), 122.04 (d, Ar-*C*₆₋₉), 114.66 (d, Ar-*C*₃), 40.12 (N(*C*H₃)₂), 25.02 (CH-(*C*H₃)₂), 20.26 (*C*H-(CH₃)₂), 19.85 (CH-(*C*H₃)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.[24] Yield 4.734 g, 91.7% ¹H NMR (300 MHz, CDCl₃) δ 8.52 (d, 2H, *meta*Ar-*H*), 4.96(br s, 2H, N*H*₂) ppm

1,3-diiodo-3-trifluoromethylbenzene
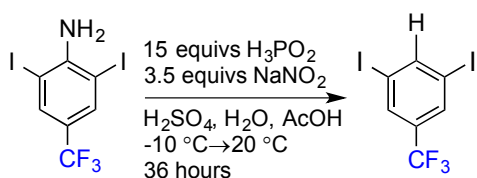
A literature procedure was used for the synthesis of 1,3-diiodo-5-trifluoromethylbenzene.[25] 0.883 g, 19.3% ¹H NMR (300 MHz, CDCl₃) δ 8.03 (br m, 1H, *ipso*Ar-*H*), 7.91(br m, 2H, Ar-*H*) ppm

1,3-bis(2´-bromophenyl)-5-trifluoromethylbenzene
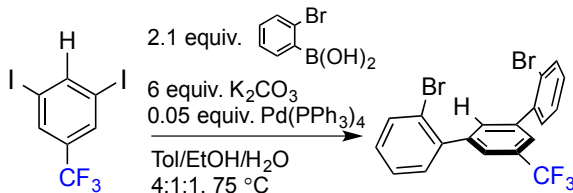
1,3-bis(2'-bromophenyl)-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-bromophenyl)-2-methoxy-5-nitrobenzene. Yield: 0.663 g (66.1% yield, 1.45 mmol) of the desired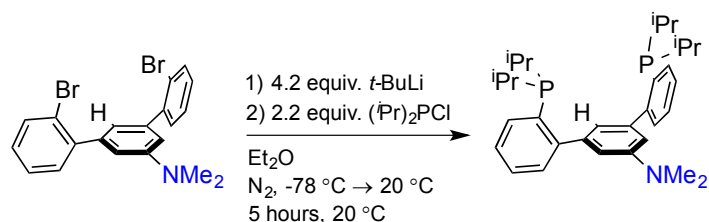 terphenyl dibromide as a white solid. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.59 (s, 2H, Ar-*H*), 7.32 (m, 3H, Ar-*H*), 6.87 (d, 4H, Ar-*H*), 6.72 (m, 2H, Ar-*H*) ^{19}F{^{1}H} NMR δ 61.99
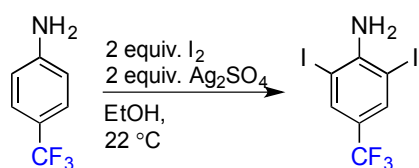
1,3-bis(2'-diisopropylphosphino)-5-trifluoromethylbenzene.

1,3-bis(2'-diisopropylphosphinophenyl)-5-trifluoromethylbenzene was synthesized using the same procedure listed for 1,3-bis(2'-diisopropyphosphinophenyl)-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) δ 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, C*H*(CH$_3$)), 1.13 (m, 12H, CH(C*H$_3$*)), 0.88 (m, 12H, CH(C*H$_3$*)), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 150.04 (d, Ar-*C*$_{10}$), 143.70 (s, Ar-*C*$_4$), 137.66 (s, Ar-*C*$_1$), 136.14 (d, Ar-*C*$_5$), 133.60 (s, Ar-*C*$_{7-8}$), 131.26 (s, Ar-*C*$_{7-8}$), 129.48 (s, Ar-*C*$_{6-9}$), 128.83 (d, Ar-*C*$_2$), 127.98 (d, Ar-*C*$_{6-9}$), 127.43 (Ar-*C*F$_3$) 127.08 (d, Ar-*C*$_3$), 25.74 (CH-(*C*H$_3$)$_2$), 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),

¹⁹F{¹H} NMR δ 62.03, ³¹P{¹H} NMR δ -5.31

[1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (2)
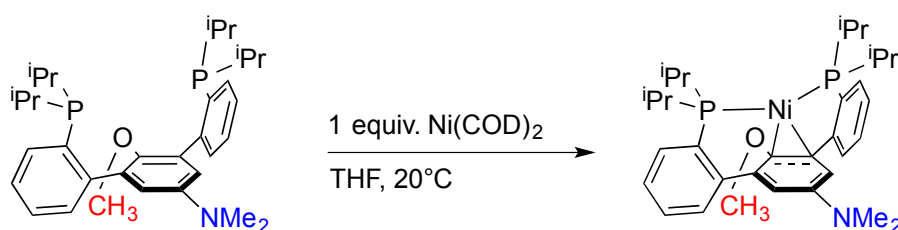
A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (937.2mg, 1.74 mmol) in THF (35 ml) was mixed with a yellow slurry of Ni(COD)₂ (477.7 mg, 1.74 mmol) in THF (5 ml) at RT. The mixture changed color to dark red and was stirred for 11 hours. Volatiles were removed *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 neigh 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% ¹H NMR (C₆D₆, 399.80 MHz) δ 7.70 (d, 2H, Ar-H_6), 7.32 (m, 2H, Ar-H_9), 7.24 (mm, 4H, Ar-H_{7-8}), 5.84 (t, 2H, Ar-H_3), 3.17 (s, 3H, OCH_3), 2.58 (s, 6H, N(CH_3)₂), 2.33 (m, 2H, CH(CH₃)₂), 2.04 (m, 2H, CH(CH₃)₂), 1.25 (mm, 6H, CH(CH_3)₂), 1.16 (mm, 12H, CH(CH_3)₂), 1.06 (m, 6H, CH(CH_3)₂) ¹³C{¹H} NMR (C₆D₆, 100.54 MHz) δ 151.42 (t, Ar-C_{10}), 143.50 (s, Ar-C_4), 140.43 (t, Ar-C_5), 130.82 (s, Ar-C_6), 129.74 (t, Ar-C_9), 128.95 (s, Ar-C_8), 127.11 (s, Ar-C_7), 115.72 (t, Ar-C_2), 109.32 (t, Ar-C_3), 100.69 (t, Ar-C_1), 59.55 (s, O-CH₃), 42.03 (N(CH₃)₂), 27.25 (CH-(CH₃)₂), 21.82 (CH-(CH₃)₂),

20.15 (CH-(CH$_3$)$_2$), 20.09 (CH-(CH$_3$)$_2$), 19.80 (CH-(CH$_3$)$_2$), 19.33 (CH-(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 40.65 (s) Anal. Calcd. for C$_{33}$H$_{47}$NNiOP$_2$ (%): C, 66.68; H, 7.97; N, 2.36 Found C, 66.45; H, 7.94; N, 2.11.
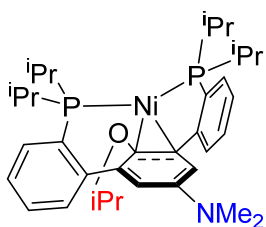
(**2^{iPr}**) Yield: 124.3 mg, 56.3% ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.72 (d, 2H, Ar-H), 7.31 (m, 2H, Ar-H), 7.23 (mm, 4H, Ar-H), 5.78 (t, 2H, Ar-H), 3.89 (septet, 1H, OCH(CH$_3$)$_2$), 2.60 (s, 6H, N(C$H$$_3$)$_2$), 2.331(m, 2H, C$H$(CH$_3$)$_2$), 1.99 (m, 2H, C$H$(CH$_3$)$_2$), 1.25 (mm, 6H, CH(C$H$$_3$)$_2$), 1.16 (mm, 12H, CH(C$H$$_3$)$_2$), 1.06 (m, 6H, CH(C$H$$_3$)$_2$), 0.67 (d, 6H, OCH(CH$_3$)$_2$), ^{13}C{^{1}H} NMR (C$_6D_6$, 100.54 MHz) δ 151.50 (t, Ar-C_{10}), 143.43 (s, Ar-C_4), 140.05 (t, Ar-C_5), 130.35 (s, Ar-C_6), 128.26 (t, Ar-C_9), 127.96 (s, Ar-C_8), 126.68 (s, Ar-C_7), 117.94 (t, Ar-C_2), 107.73 (t, Ar-C_3), 99.56 (t, Ar-C_1), 73.36 (s, O-CH(CH$_3$)$_2$), 41.59 (N(CH$_3$)$_2$), 27.04 (CH-(CH$_3$)$_2$), 23.02 (s, O-CH(CH$_3$)$_2$), 21.72 (CH-(CH$_3$)$_2$), 20.00 (CH-(CH$_3$)$_2$), 19.52 (CH-(CH$_3$)$_2$), 19.23 (CH-(CH$_3$)$_2$), 18.97 (CH-(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 39.20 (s) Anal. Calcd. for C$_{35}$H$_{51}$NNiOP$_2$ (%): C, 67.54; H, 8.26; N, 2.25 Found C, 66.68; H, 8.09; N, 2.26.
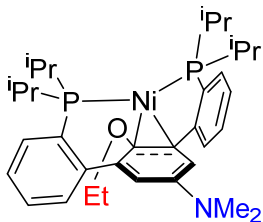
(**2^{Et}**) Yield: 279.0 mg, 63.0% ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.70 (d, 2H, Ar-*H*), 7.31 (m, 2H, Ar-*H*), 7.23 (mm, 4H, Ar-*H*), 5.84 (t, 2H, Ar-*H$_3$*), 3.57 (q, 2H, OC*H$_2$*CH$_3$), 2.59 (s, 6H, N(C*H$_3$*)$_2$), 2.35 (m, 2H, C*H*(CH$_3$)$_2$), 2.03 (m, 2H, C*H*(CH$_3$)$_2$), 1.25 (mm, 6H, CH(C*H$_3$*)$_2$), 1.16 (mm, 12H, CH(C*H$_3$*)$_2$), 1.06 (m, 6H, CH(C*H$_3$*)$_2$), 0.50 (t, 3H, OCH$_2$C*H$_3$*), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz) δ 151.05 (t, Ar-*C$_{10}$*), 143.14 (s, Ar-*C$_4$*), 140.01 (t, Ar-*C$_5$*), 130.38 (s, Ar-*C$_6$*), 129.31 (t, Ar-*C$_9$*), 128.43 (s, Ar-*C$_8$*), 126.65 (s, Ar-*C$_7$*), 116.03 (t, Ar-*C$_2$*), 108.57 (t, Ar-*C$_3$*), 99.99 (t, Ar-*C$_1$*), 67.65 (s, O*C*H$_2$CH$_3$), 41.65 (N(*C*H$_3$)$_2$), 26.85 (*C*H-(CH$_3$)$_2$), 21.57 (*C*H-(CH$_3$)$_2$), 19.76 (CH-(*C*H$_3$)$_2$), 18.96 (CH-(*C*H$_3$)$_2$), 15.42 (OCH$_2$*C*H$_3$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 40.57 (s) Anal. Calcd. for C$_{34}$H$_{49}$NNiOP$_2$ (%): C, 67.12; H, 8.12; N, 2.30 Found C, 65.34; H, 8.46; N, 2.21.
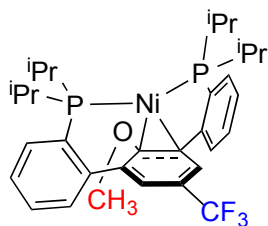
(**2$_{CF3}$**) Yield: 613.1 mg, 73.7% ^{1}H NMR (C$_6$D$_6$, 499.85 MHz) δ 7.44 (m, 2H, Ar-*H*), 7.23 (m, 2H, Ar-*H*), 7.18 (m, 4H, Ar-*H*), 6.62 (s, 2H, Ar-*H*), 3.01 (s, 3H, OC*H$_3$*), 2.23 (m, 2H, C*H*(CH$_3$)$_2$), 1.94 (m, 2H, C*H*(CH$_3$)$_2$), 1.08 (mm, 18H, CH(C*H$_3$*)$_2$), 0.91 (mm, 6H, CH(C*H$_3$*)$_2$), ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282.33 MHz) δ -61.34 (s), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 41.12 (s) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 150.14 (t, Ar-*C$_{10}$*), 138.90 (t, Ar-

C_5), 130.96 (s, Ar-C_9), 129.75 (t, Ar-C_6), 129.68 (s, Ar-$C_{7\text{-}8}$), 128.35 (s, Ar-C_2), 127.48 (s, Ar-$C_{7\text{-}8}$), 118.89 (s, Ar-C_3), 117.81 (q, Ar-CF$_3$), 111.29 (s, Ar-C_1), 99.40 (s, Ar-C_4), 58.98 (O(CH$_3$)), 27.38 (CH-(CH$_3$)$_2$), 21.71 (CH-(CH$_3$)$_2$), 19.77 (CH-(CH$_3$)$_2$), 19.60 (CH-(CH$_3$)$_2$), 19.06 (CH-(CH$_3$)$_2$), Anal. Calcd. for C$_{32}$H$_{41}$F$_3$NiOP$_2$ (%): C, 62.06; H, 6.67 Found C, 61.77; H, 6.60.
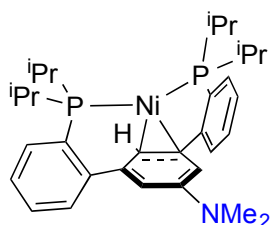
(7) Yield: 473.8 mg, 84.9% ^{1}H NMR (C$_6$D$_6$, 499.85 MHz) δ 7.65 (d, 2H, Ar-H), 7.25 (m, 2H, Ar-H), 7.15 (mm, 4H, Ar-H), 5.82 (s, 2H, Ar-H), 5.37 (s, 1H, Ar-H), 2.59 (s, 6H, N(CH_3)$_2$), 2.30 (m, 2H, CH(CH$_3$)$_2$), 2.04 (m, 2H, CH(CH$_3$)$_2$), 1.23 (mm, 6H, CH(CH_3)$_2$), 1.16 (mm, 6H, CH(CH_3)$_2$), 1.05 (m, 12H, CH(CH_3)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 38.55 (s) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 153.93 (t, Ar-C_{10}), 147.74 (s, Ar-C_4), 139.81 (t, Ar-C_9), 131.44 (s, Ar-C_8), 129.77 (t, Ar-C_5), 129.30 (s, Ar-C_6), 127.81 (t, Ar-C_7), 122.37 (s, Ar-C_{10}), 107.71 (s, Ar-C_3), 90.26 (s, Ar-C_4), 70.33 (s, Ar-C_1), 41.80 (N(CH$_3$)$_2$), 27.76 (CH-(CH$_3$)$_2$), 22.32 (CH-(CH$_3$)$_2$), 20.66 (CH-(CH$_3$)$_2$), 20.55 (CH-(CH$_3$)$_2$), 20.37 (CH-(CH$_3$)$_2$), 19.94 (CH-(CH$_3$)$_2$), Anal. Calcd. for C$_{32}$H$_{45}$NNiP$_2$ (%): C, 68.10; H, 8.04; N, 2.48 Found C, 59.35; H, 7.41; N, 2.16
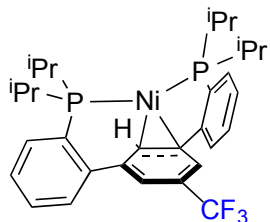
(7$_{CF3}$) Yield: 872.9 mg, 84.4% ^{1}H NMR (C$_6$D$_6$, 499.85 MHz) δ 7.35 (d, 2H, Ar-*H*), 7.18 (m, 2H, Ar-*H*), 7.12 (mm, 2H, Ar-*H*), 7.07 (mm, 2H, Ar-*H*), 6.60 (s, 2H, Ar-*H*), 4.64 (s, 1H, Ar-*H*), 2.20 (m, 2H, C*H*(CH$_3$)$_2$), 1.95 (m, 2H, C*H*(CH$_3$)$_2$), 1.07 (mm, 12H, CH(C*H*$_3$)$_2$), 0.94 (mm, 12H, CH(C*H*$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 41.93 (s) ^{19}F{^{1}H} NMR (C$_6$D$_6$, 282.33 MHz) δ -62.59 (s) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.70 MHz) δ 152.33 (t, Ar-*C*$_{10}$), 137.92 (t, Ar-*C*$_9$), 131.17 (s, Ar-*C*$_5$), 129.63 (s, Ar-*C*$_7$), 128.84 (t, Ar-*C*$_8$), 127.69 (s, Ar-*C*$_6$), 125.85 (s, Ar-*C*$_2$), 121.32 (q, Ar-Ar-*C*F$_3$), 117.49 (s, Ar-*C*$_3$), 112.85 (s, Ar-*C*$_4$), 63.96 (s, Ar-*C*$_1$), 27.22 (t, *C*H-(CH$_3$)$_2$), 21.55 (t, *C*H-(CH$_3$)$_2$), 19.72 (CH-(*C*H$_3$)$_2$), 19.66 (CH-(*C*H$_3$)$_2$), 19.50 (CH-(*C*H$_3$)$_2$), 19.12 (CH-(*C*H$_3$)$_2$) Anal. Calcd. for C$_{31}$H$_{39}$F$_3$NiP$_2$ (%): C, 63.18; H, 6.67 Found C, 63.12; H, 6.74.

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)methoxide (3)
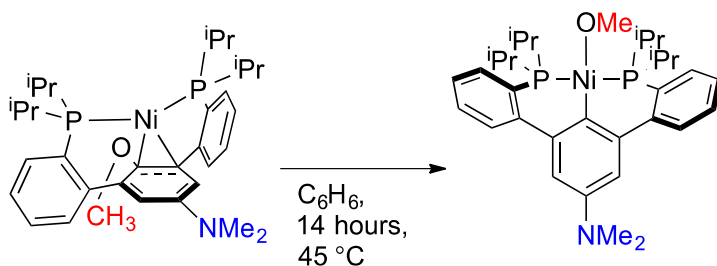
A dark red solution of purified [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (105.2 mg, 0.18 mmol) in C$_6$H$_6$ was warmed to 45°C in a Schlenk tube. After 14 hours the solvent was removed under vacuum. The resulting red orange solid was washed with pentane and extracted with ether. The ether was

pumped off resulting in an orange solid (**3b**). Yield: 82.7 mg, 78.6% ^{1}H NMR (C$_6$D$_6$, 399.80 MHz) δ 7.76 (d, 2H, Ar-H_6), 7.44 (d, 2H, Ar-H_9), 7.37 (t, 2H, Ar-H_7), 7.17 (t, 2H, Ar-H_8), 6.78 (s, 2H, Ar-H_3), 3.67 (s, 3H, OCH_3), 2.56 (s, 6H, N(CH_3)$_2$), 2.52 (br, 2H, CH(CH$_3$)$_2$), 1.76 (br, 2H, CH(CH$_3$)$_2$), 1.66 (br, 6H, CH(CH_3)$_2$), 1.28 (br, 6H, CH(CH_3)$_2$), 0.96 (br, 6H, CH(CH_3)$_2$), 0.80 (br, 6H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz) δ 153.23 (t, Ar-C_{10}), 150.95 (s, Ar-C_1), 147.19 (t, Ar-C_5), 130.26 (s, Ar-C_7), 129.41 (s, Ar-C_9), 128.40 (s, Ar-C_2), 128.35 (s, Ar-C_6), 126.99 (s, Ar-C_4), 126.60 (s, Ar-C_8), 113.59 (s, Ar-C_3), 54.84 (s, OCH$_3$), 40.56 (s, N(CH$_3$)$_2$), 23.83 (s, CH(CH$_3$)$_2$), 21.09 (s, CH(CH$_3$)$_2$), 20.45 (s, CH(CH$_3$)$_2$), 19.77 (s, CH(CH$_3$)$_2$), 18.90 (s, CH(CH$_3$)$_2$), 18.12 (s, CH(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.85 MHz) δ 27.26 (s) Anal. Calcd. for C$_{33}$H$_{47}$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)

A dark red solution of crude [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$_6$D$_6$, 300 MHz) δ 7.87 (d, 2H, Ar-H_6), 7.44 (t, 2H, Ar-H_7), 7.29 (d, 2H, Ar-H_9),

7.14 (t, 2H, Ar-H_8), 6.79 (s, 2H, Ar-H_4), 2.54 (t, 6H, N(CH_3)$_2$), 2.27 (br m, 2H, CH(CH$_3$)$_2$), 1.70 (br m, 6H, CH(CH_3)$_2$), 1.61 (br m, 2H, CH(CH$_3$)$_2$), 1.28 (mm, 6H, CH(CH_3)$_2$), 1.12 (mm, 6H, CH(CH_3)$_2$), 0.70 (m, 6H, CH(CH_3)$_2$), -2.80 (t, 1H, Ni-H), ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.54 MHz) δ 152.69 (t, Ar-C_{10}), 150.79 (s, Ar-C_4), 147.09 (t, Ar-C_5), 130.40 (s, Ar-C_7), 129.13 (s, Ar-C_9), 128.70 (s, Ar-C_2), 128.15 (s, Ar-C_6), 126.61 (s, Ar-C_8), 126.41 (s, Ar-C_1), 114.03 (s, Ar-C_3), 41.07 (s, N(CH$_3$)$_2$), 24.08 (s, CH(CH$_3$)$_2$), 20.48 (s, CH(CH$_3$)$_2$), 20.34 (s, CH(CH$_3$)$_2$), 20.08 (s, CH(CH$_3$)$_2$), 18.75 (s, CH(CH$_3$)$_2$), 18.08 (s, CH(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 30.41 (s) Anal. Calcd. for C$_{32}$H$_{45}$NNiP$_2$ (%): C, 68.10; H, 8.04; N, 2.48 Found. C, 67.63; H, 7.85; N, 2.05
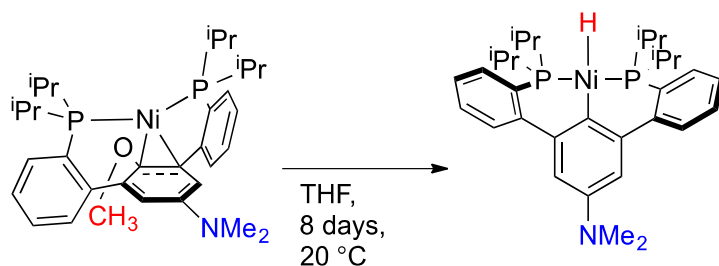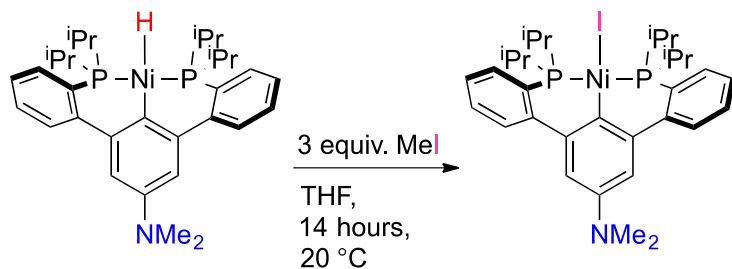
[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)iodide (5)

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% ^{1}H NMR (C$_6$D$_6$, 399.80

MHz) δ 7.72 (d, 2H, Ar-H_6), 7.40 (d, 2H, Ar-H_9), 7.37 (t, 2H, Ar-H_8), 7.13 (t, 2H, Ar-H_7), 6.78 (s, 2H, Ar-H_3), 3.03 (m, 2H, CH(CH$_3$)$_2$), 2.52 (m, 6H, N(CH_3)$_2$), 1.77 (m, 2H, CH(CH$_3$)$_2$), 1.51 (q, 6H, CH(CH_3)$_2$), 1.31 (m, 6H, CH(CH_3)$_2$), 0.91 (m, 6H, CH(CH_3)$_2$), 0.77 (m, 6H, CH(CH_3)$_2$), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz), δ 151.38 (t, Ar-C_{10}), 151.20 (s, Ar-C_4), 146.92 (t, Ar-C_5), 130.39 (s, Ar-C_8), 129.78 (t, Ar-C_9), 127.98 (s, Ar-C_2), 127.95 (s, Ar-C_6), 127.16 (s, Ar-C_7), 126.19 (t, Ar-C_1), 113.86 (t, Ar-C_3), 40.28 (N(CH$_3$)$_2$), 24.29 (CH-(CH$_3$)$_2$), 23.59 (CH-(CH$_3$)$_2$), 20.55 (CH-(CH$_3$)$_2$), 20.21 (CH-(CH$_3$)$_2$), 19.39 (CH-(CH$_3$)$_2$), 18.91 (CH-(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 34.35 (s) Anal. Calcd. for C$_{32}$H$_{44}$NNiP$_2$ (%): 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)
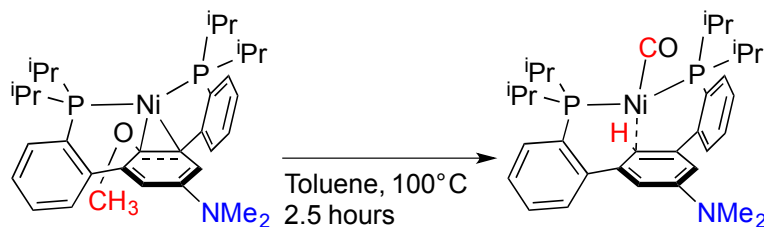
A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (96.9 mg, 0.16 mmol) in toluene was heated to 100 °C in a sealed Schlenk tube. The tube was heated for 2.5 hours. After 2.5 hours the solvent was removed under vacuum giving an orange solid. The solid was washed with hexanes and dried under vacuum yielding a red orange solid. Yield: 83.8 mg, 86.7% ^{1}H NMR (C$_6$D$_6$, 399.80 MHz) δ 7.49 (br m, 2H, Ar-H_6), 7.44 (br m, 2H, Ar-H_9), 7.18 (m, 4H, Ar-H_{7-8}), 6.56 (s, 2H, Ar-H_3), 6.51 (t, 1H, Ar-H_1), 2.65 (s, 6H, N(CH_3)$_2$), 2.40 (m, 2H, CH(CH$_3$)$_2$), 2.18 (m, 2H, CH(CH$_3$)$_2$), 1.24 (q, 6H, CH(CH_3)$_2$), 1.16 (q, 6H,

CH(C*H*₃)₂), 1.10 (q, 6H, CH(C*H*₃)₂), 1.02 (q, 6H, CH(C*H*₃)₂) ¹³C{¹H} NMR (C₆D₆, 100.54 MHz) δ 195.98 (t, Ni-*C*O), 152.54 (s, Ar-*C*₄), 151.06 (t, Ar-*C*₁₀), 145.58 (s, Ar-*C*₂), 136.50 (t, Ar-*C*₅), 131.26 (s, Ar-*C*₉), 130.81 (s, Ar-*C*₆), 128.90 (s, Ar-*C*₈), 127.29 (s, Ar-*C*₇), 110.03 (s, Ar-*C*₃), 84.65 (s, Ar-*C*₁), 40.68 (N(*C*H₃)₂), 29.44 (*C*H-(CH₃)₂), 26.79 (*C*H-(CH₃)₂), 20.40 (CH-(*C*H₃)₂), 19.62 (CH-(*C*H₃)₂), 18.90 (CH-(*C*H₃)₂), 18.60 (CH-(*C*H₃)₂) ³¹P{¹H} NMR (C₆D₆, 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 (C₆D₆): ν꜀ₒ = 1917 cm⁻¹.

General Synthesis of Nickel(II) Phenoxide Halide Systems (8)
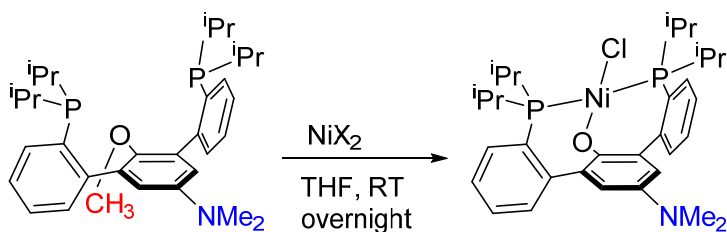
To a colorless solution of **1** in THF is added a slurry of NiX₂ in THF. Upon mixing the solution develops a deep green color overtime. The solution was allowed to stir overnight. After the allotted time the solvent was removed under vacuum resulting in a dark green solid. The dark green solid was rinsed with Et₂O and Hexanes resulting in pure **8** as a dark green solid. Yield: 72% ¹H NMR (C₆D₆, 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(C*H*₃)₂), 2.57 (m, 2H, C*H*(CH₃)₂), 2.12 (m, 2H, C*H*(CH₃)₂), 1.83 (m, 12H, Ar-C*H*₃), 1.19 (m, 6H, CH(C*H*₃)₂), 0.66 (m, 6H, CH(C*H*₃)₂), ¹³C{¹H} NMR (C₆D₆, 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(*C*H₃)₂), 22.85 (*C*H-(CH₃)₂), 20.83 (*C*H-(CH₃)₂), 19.23 (CH-(*C*H₃)₂), 19.04 (CH-(*C*H₃)₂), 18.55 (CH-(*C*H₃)₂), 14.88 (CH-

(CH_3)$_2$), ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ 13.60 (s) Anal. Calcd. for $C_{32}H_{44}ClNNiOP_2$ (%): 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)
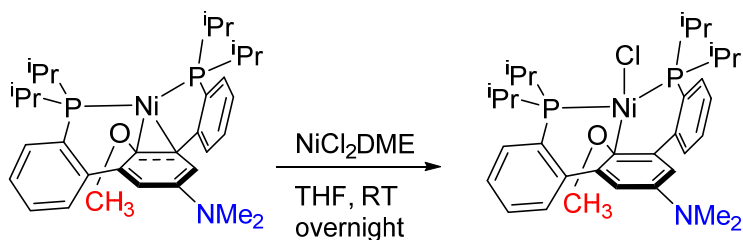
To a dark red solution of **2** in THF is added a slurry of oxidant in THF. Upon mixing the solution lightens to a yellow color overtime. The solution was stirred overnight. After the allotted time the solvent was removed under vacuum resulting in a dark yellow residue. The yellow solid was rinsed with Et_2O 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 $C_{34}H_{47}ClNNiOP_2$ (**9**) (%): C, 62.93; H, 7.52; N, 2.22 Found C, 62.23; H, 7.35; N, 2.12. Anal. Calcd. for $C_{34}H_{47}F_3NNiO_4P_2S$ (**9**^{OTf}) (%): C, 54.93; H, 6.37; N, 1.88 Found C, 52.54; H, 6.46; N, 1.81.

[1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methylbenzene]nickel(0) (10)
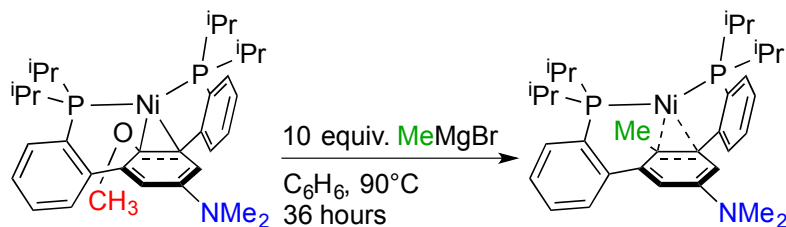
A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (100.1 mg, 0.17 mmol) in toluene was treated with 10 equivalents of MeMgBr and heated to 90 °C in a sealed Schlenk. The tube was heated for 36 hours. After 36 hours the solvent was removed under 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}H NMR (C$_6$D$_6$, 300 MHz) δ 7.62 (br m, 2H, Ar-*H*), 7.24 (br m, 2H, Ar-*H*), 7.20 (m, 4H, Ar-*H*), 5.80 (s, 2H, Ar-*H*), 2.60 (s, 6H, N(C*H*$_3$)$_2$), 2.26 (m, 2H, C*H*(CH$_3$)$_2$), 1.98 (m, 2H, C*H*(CH$_3$)$_2$), 1.52 (s, 3H, Ar-C*H*$_3$), 1.12 (m, 24H, CH(C*H*$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 36.83 (s)

[1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methylbenzene]nickel(0)carbonyl (11)
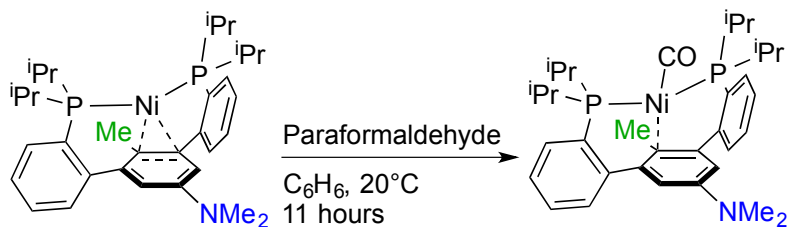
Method A: To a yellow solution of **4** (12.3 mg, 0.022 mmol) in benzene was added 10 equivalents of acetaldehyde. The solution was heated to 90 °C for 24 hours. After 24 hours the excess acetaldehyde was removed resulting in **11** as a red orange solid.

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% ^{1}H NMR (C_6D_6, 300 MHz) δ 7.44 (br m, 2H, Ar-*H*), 7.37 (br m, 2H, Ar-*H*), 7.20 (m, 4H, Ar-*H*), 6.62 (s, 2H, Ar-*H*), 2.72 (s, 6H, N(C*H*$_3$)$_2$), 2.42 (m, 2H, C*H*(CH$_3$)$_2$), 2.02 (m, 2H, C*H*(CH$_3$)$_2$), 1.66 (s, 3H, Ar-C*H*$_3$), 1.08 (m, 24H, CH(C*H*$_3$)$_2$), ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ 35.90 (s)

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenoxide]nickel(II)benzyl (12)
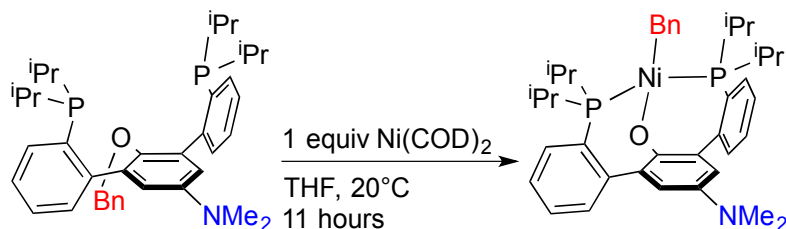
A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-benzyloxybenzene (114.6 mg, 0.187 mmol) in THF (10 ml) was mixed with a yellow slurry of Ni(COD)$_2$ (48.9 mg, .178 mmol) in THF (2.5 ml) at RT. The mixture changed color to dark red and was stirred for 11 hours. Volatiles were 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) δ 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(C*H*$_3$)$_2$), 2.30 (m, 2H, C*H*(CH$_3$)$_2$), 1.88 (m, 2H, C*H*(CH$_3$)$_2$), 1.72 (mm, 6H, CH(C*H*$_3$)$_2$), 1.63 (mm, 6H, CH(C*H*$_3$)$_2$), 1.35 (mm, 2H, CH$_2$Ph) 0.71 (mm, 6H, CH(C*H*$_3$)$_2$), 0.36 (m, 6H, CH(C*H*$_3$)$_2$) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz) δ 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*$_6$), 129.64 (t, Ar-*C*$_9$), 126.82 (s, Ar-*C*$_8$), 125.73 (t, Ar-*C*$_2$), 124.51 (s, Ar-*C*$_7$), 123.60 (s, Ar-*C*$_3$), 118.25 (s, Ar-*C*$_1$), 42.05 (N(*C*H$_3$)$_2$), 23.68 (*C*H-(CH$_3$)$_2$), 20.60 (*C*H-(CH$_3$)$_2$), 19.40 (CH-(*C*H$_3$)$_2$), 19.06 (CH-(*C*H$_3$)$_2$), 18.18 (CH-(*C*H$_3$)$_2$), 16.02 (CH-(*C*H$_3$)$_2$), -0.04 (t, *C*H$_2$-Ar), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 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.

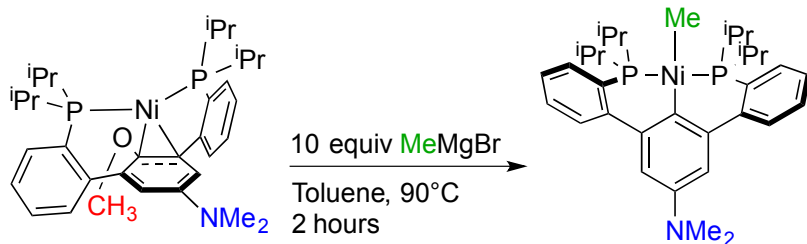## [1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)phenoxide (13)
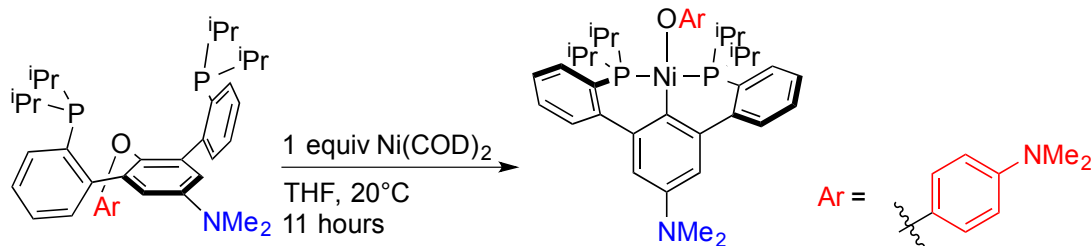
A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-phenoxybenzene (110.5 mg, 0.17 mmol) in THF (5 ml) was mixed with a yellow slurry of Ni(COD)$_2$ (46.8 mg, .17 mmol) in THF (2.5 ml) at RT. The mixture changed color to orange and was stirred for 13 hours. Volatiles were removed *in vacuo* yielding a orange solid. The crude solid was washed with hexanes and Et$_2$O yielding a orange solid. (13) Yield: 116.3 mg, 97.8% ^{1}H NMR (C$_6$D$_6$, 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(C*H*$_3$)$_2$), 2.16 (m, 2H, C*H*(CH$_3$)$_2$), 1.56 (m, 2H, C*H*(CH$_3$)$_2$), 1.46 (mm, 6H, CH(C*H*$_3$)$_2$), 1.23 (mm, 9H, C(C*H*$_3$)$_3$), 0.85 (mm, 12H, CH(C*H*$_3$)$_2$) 0.68 (mm, 6H, CH(C*H*$_3$)$_2$), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz), δ 163.17 (Ar-*C*), 152.11 (t, Ar-*C*$_{10}$), 149.13 (s, Ar-*C*$_4$), 147.01 (t, Ar-*C*$_5$), 140.07 (Ar-*C*), 130.29 (s, Ar-*C*$_8$), 129.52 (s, Ar-*C*$_9$), 127.47 (s, Ar-*C*$_2$), 126.54 (s, Ar-*C*$_6$), 126.12 (t, Ar-*C*$_7$), 124.07 (t, Ar-*C*$_1$), 119.87 (s, Ar-*C*), 117.16 (s, Ar-*C*$_3$), 43.32 (N(*C*H$_3$)$_2$), 33.77 (*C*(CH$_3$)$_3$), 31.14 (*C*(CH$_3$)$_3$), 22.94 (*C*H-(CH$_3$)$_2$), 20.50 (*C*H-(CH$_3$)$_2$), 20.02 (CH-(*C*H$_3$)$_2$), 18.77 (CH-(*C*H$_3$)$_2$), 18.58 (CH-(*C*H$_3$)$_2$), 17.54 (CH-(*C*H$_3$)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 29.74 (s) Anal. Calcd. for C$_{42}$H$_{57}$NNiOP$_2$ (%): C, 70.80; H, 8.06; N, 1.97 Found C, 70.95; H, 7.98; N, 1.96.

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)methyl (14)

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% ^{1}H NMR (C_6D_6, 300 MHz) δ 7.74 (br d, 2H, Ar-H), 7.34 (br d, 2H, Ar-H), 7.24 (m, 2H, Ar-H), 7.10 (m, 2H, Ar-H), 6.92 (m, 2H, Ar-H), 2.61 (s, 6H, N(CH_3)$_2$), 2.46 (m, 2H, CH(CH$_3$)$_2$), 1.92 (m, 2H, CH(CH$_3$)$_2$), 1.05 (s, 24H, CH(CH_3)$_2$), 0.36 (t, 3H, CH_3), ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.54 MHz) δ 152.12 (t, Ar-C_{10}), 150.57 (s, Ar-C_4), 147.49 (t, Ar-C_5), 129.42 (s, Ar-C_7), 128.42 (s, Ar-C_9), 127.78 (s, Ar-C_2), 126.79 (s, Ar-C_6), 125.83 (s, Ar-C_8), 126.41 (s, Ar-C_1), 112.99 (s, Ar-C_3), 40.88 (s, N(CH$_3$)$_2$), 23.13 (s, CH(CH$_3$)$_2$), 19.97 (s, CH(CH$_3$)$_2$), 18.57 (s, CH(CH$_3$)$_2$), -18.20 (s, Ni-CH$_3$), ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ 44.51 (s) Anal. Calcd. for $C_{33}H_{47}$NNiP$_2$ (%): 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**.

	2	5	8
CCDC Number	859840	859841	
Empirical formula	$C_{33}H_{47}NOP_2Ni$	$C_{32}H_{44}NP_2INi \cdot$ $C_4H_{10}O$	$C_{32}H_{44}ClNNiOP_2$
Formula weight	594.37	764.35	614.78
T (K)	100(2)	100(2)	100(2)
a, Å	10.6162(4)	9.0551(6)	17.0566(7)
b, Å	19.6007(8)	17.5696(12)	10.9300(4)
c, Å	15.6192(6)	11.5133(8)	33.5079(14)
, deg	90	90	90
, deg	103.887(2)	102.374(3)	97.838(2)
, deg	90	90	90
Volume, Å^3	3155.1(2)	1789.2(2)	6188.5(4)
Z	4	2	8
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2/n	P 2$_1$	P2(1)/n
d_{calc}, g/cm^3	1.251	1.419	1.320
range, deg	2.08 to 33.20	1.81 to 36.41	0.92 to 25.00
μ, mm^{-1}	0.742	1.522	0.842
Abs. Correction	None	Semi-empirical from equivalents	None
GOF	1.604	1.924	1.050
R_1,^{a} wR_2^{b} [I>2 (I)]	R1 = 0.0489, wR2 = 0.0501	R1 = 0.0266, wR2 = 0.0483	R1 = 0.0570, wR2 = 0.1043

^{a} $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$. ^{b} $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

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