APPENDIX B

Mid- to Late- Transition Metal Complexes Supported by Terphenyl and Biphenyl Phenols Bearing Pendant Phosphines

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Abstract

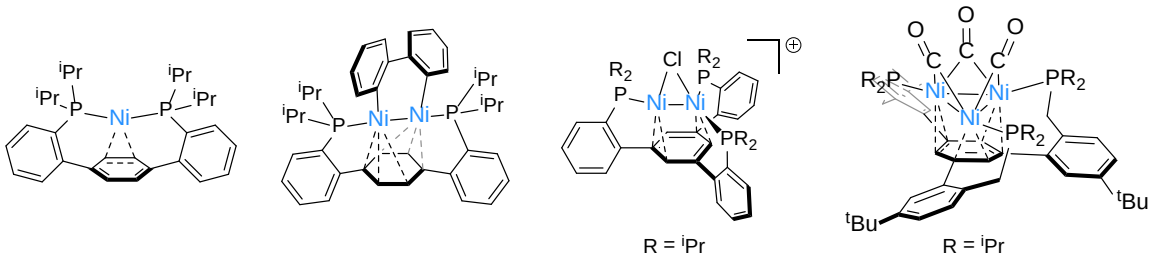
A series of low-valent, low-coordinate terphenyl diphosphine, terphenyl bisphosphinophenol, and biphenyl phosphinophenol mid- to late-transition metal compounds were prepared. Such complexes are envisioned to be suitable for small molecule (C_2H_4, CO_2. H_2, N_2) activation chemistry. The ammonia borane dehydrogenation activity of a terphenyl diphosphine molybdenum complex is noted. Phosphine ligands bearing pendant phosphines are described. Hemilable metal-arene interactions are observed upon changing oxidations states, as well as coordinately accessible transition metal complexes.

INTRODUCTION

Earth-abundant first row transition metals typically catalyze reactions in one-electron steps, often undergoing deleterious side reactions that proceed via radical mechanisms. Redox non-innocent scaffolds were identified as early as the 1960s in work with metal dithiolenes.[1] Chirik,[2] Heyduk,[3] Wieghardt[4] and others have demonstrated that redox active scaffolds can confer noble character upon base metals.[5] Bisiminopyridine Fe[6] and Co[6b] have been demonstrated to be highly active olefin oligomerization catalysts with good selectivities for α-olefins; with Fe, reduction cyclization of enynes and diynes has been reported.[7] In nature, galactose oxidase features a Cu^{II} ion coordinated to a tyrosyl radical and catalyzes the oxidation of alcohols to aldehydes;[5] evidence of protein radicals has been reported in a variety of enzymatic reactions.[8] By incorporating a redox-active phenolic moiety into phosphine ligands previously demonstrated to be capable of stabilizing mid- to late-transition metals in a variety of geometries and oxidation states, chemistry typically reserved for precious metals (e.g., Ru, Rh, Ir, Pt) is proposed to be accessible using inexpensive base metals. (e. g., Mo, Fe, Co, Ni).

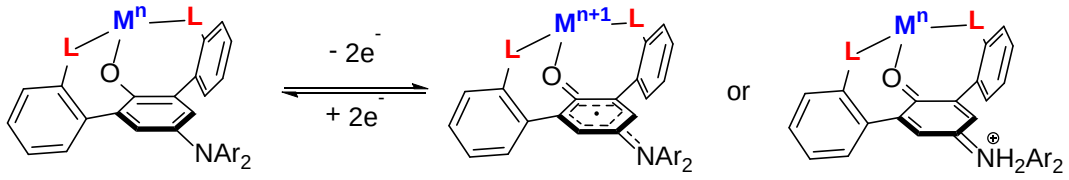
In the Agapie Group, P-arene-P diphosphine pincers and related triphosphine ligands have been used to support mid- to late-transition metals capable of a variety of organometallic transformations (Figure B.1).[9] Pincer-based metal complexes allow for precise control of stability and reactivity through systematic modification or variation of ligand donors, substituents, and transition metals. Previously, investigation of a P-arene-P pincer and ether-substituted variant demonstrated that a variety of coordination modes and oxidation states are accessible on the same ligand scaffold.[10]

Figure B.1. Terphenyl and Quaterphenyl Phosphine Mono-, Di-, and Tri-Nickel Complexes Synthesized by the Agapie Group.



Appending a phenoxide donor to previously synthesized P-arene-P pincers is envisioned to afford a ligand with a redox non-innocent moiety (Figure B.2). On such a scaffold, a two electron transformation could occur either through loss of one electron from the metal center and a second from the aminophenol moiety or through loss of two electrons from the aminophenol with no formal oxidation state change at the metal center. Earth-abundant transition metals supported by the these ligands are envisioned to catalyze a diverse set of reactions, including olefin and alkene hydrogenation, hydrosilyation, selective olefin oligomerization, intra- and intermolecular cyclizations of unsaturated olefins, and cross-couplings (Figure B.3).

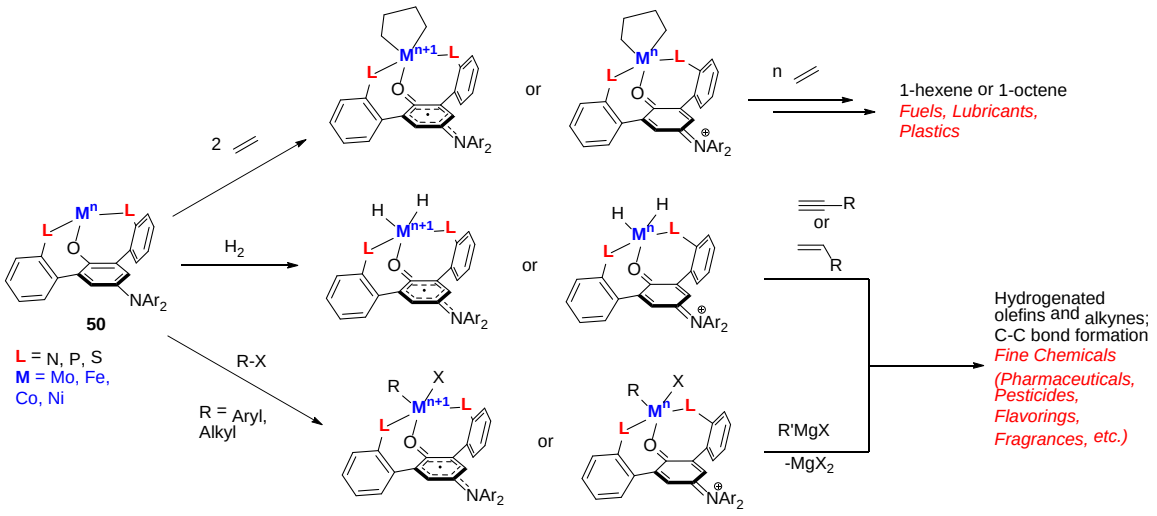
Figure B.2. Two-Electron Oxidation of Aminophenol Complex with One or No Electron Oxidation of the Metal Center.



50

L = N, P, S
M = Mo, Fe, Co, Ni

Figure B.3. Proposed Mechanisms for Olefin Oligomerization, Hydrogenation, and Cross-Coupling at Base Metals Facilitated by Redox Non-Innocent Aminophenol Scaffold.



Species such as compound **50** are envisioned to be effective catalysts for selective olefin oligomerization, hydrogenation, and cross-couplings. Hydrocarbon upgrading of light olefins affords comonomers for production of linear low-density polyethylene (LLDPE) and higher olefins desirable for fuel blends or lubricants.[11] Selective olefin oligomerization proceeds through a two-electron redox cycle involving metallacyclic intermediates.[11] Similarly, hydrogenation and cross-coupling reactions catalyzed by homogenous species, important in the context of fine chemical synthesis, are proposed to involve oxidative addition of H_2 or aryl/alkyl halide coupling partner. The proposed aminophenol ligand bearing a pendant donor is anticipated to allow for these reactions to be catalyzed by earth-abundant transition metals (Figure B.3). Bisphenoxyamine ligands coordinated to Zr^{IV} compounds have been reported to reduce O_2 in a four-electron, two-proton transformation with no formal oxidation state change at Zr, providing evidence for the potential redox-noninnocence of

aminophenol ligands.[12] Such compounds have not been well studied and may provide improvements in activity and lifetimes compared to previously reported catalysts. Pendant donors and their substituents in the proposed system are modular. Phosphines, thioethers, carbenes, amides, and amines can be used as donors to tune the reduction potential of the metal center. Changing the substitution of the amine of the aminophenol moiety will also allow for tuning the redox potential of the ligand to optimize reactivity. Progress towards the synthesis of the family of compounds of this type is described herein.

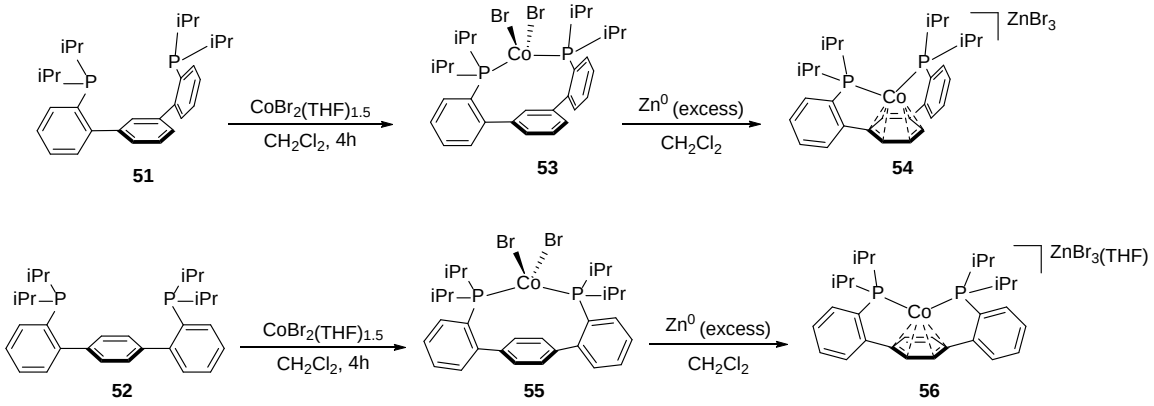
Results & Discussion

m-Terphenyl diphosphine **51** and *p*-terphenyl diphosphine **52** were metallated with Mo, Fe, and Co precursors in efforts to access an entry into mid- to late-transition metal chemistry on these and related scaffolds. New compounds were isolated with Co and Mo.

Initial attempts to isolate a cobalt complex by metallating ligand **51** with $Co_2(CO)_8$, $Co(OTf)_2$, and $CoCl(P(Ph_3)_3)$ were unsuccessful. The ^{1}H and ^{31}P spectra of **51** was unchanged after treatment with $Co(OTf)_2$, and $CoCl(PPh_3)_3$ at room temperature and with heating. In the case of $Co_2(CO)_8$, a new species was observed by ^{31}P and ^{1}H NMR. However, attempts to crystallize this complex resulted in the formation of a species insoluble in common laboratory solvents, suggesting oligomerization. $Co_2(CO)_8$ itself is thermally unstable, decomposing to Co^0 and releasing CO at room temperature and forming the tetramer $Co_4(CO)_{12}$ with mild heating.[13] $Co(OTf)_2$ may be too hard or ionic to coordinate the soft or primarily covalent bonding environment of the terphenyl diphosphine. In the case of $CoCl(PPh_3)_3$, PPh_3 seems to be too strongly donating to be exchanged with another aryl phoshpine.

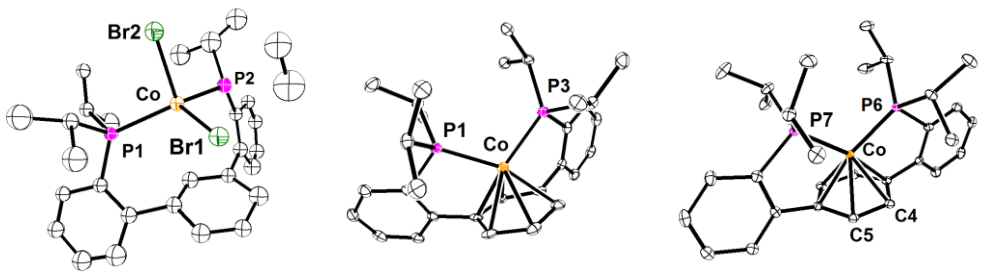
Metallation of **51** with $CoBr_2$ in CH_2Cl_2 afforded an emerald green solid (Figure B.4). This complex displayed no ^{31}P NMR resonances and a paramagnetic ^{1}H NMR spectrum. Single crystal XRD allowed for assignment of this complex as the tetrahedral dibromide **52**. Compound **52** displays no contacts to the central arene of the terphenyl diphosphine. In the presence of Zn^0, the same reaction gives rise to a diamagnetic complex (**53**) as the major product as observed by ^{1}H and ^{31}P NMR, consistent with reduction to an even electron species.

Scheme B.1. Metallation of Diphosphines *51* and *52* to afford Co^{I} and Co^{II} Compounds *53*-*56*.



A compound with similar major features in its NMR spectra can be generated from the addition of a single equivalent of cobaltocene to *53*. The solid-state structure of the product of the reaction of *51*, $CoBr_2$, and Zn^0 has been determined to be the Co^{I} complex *54* (Figure B.4). In this species, the Co^{I} center is coordinated η^6 to the central aryl ring of the ligand.

Figure B.4. Solid-State Structures of (from left to right) *53*, *54*, and *56*. Shown for connectivity. Hydrogen atoms omitted for clarity. For compound *53*, disorder is observed at the ^{i}Pr substituent of atom "P2". For *54*, 0.5 Zn_2Br_6 counteranion omitted for clarity. For *55*, $ZnBr_3(THF)$ counteranion omitted for clarity.



Using a similar strategy, a paramagnetic species putatively assigned as Co^{II} complex ***55*** was isolated by treating diphosphine ***52*** with $CoBr_2$ in CH_2Cl_2. Reduction affords Co^{I} complex ***56*** which displays η^6-coordination to the central aryl ring of the ligand. The structure of this new species was confirmed by determination of solid-state structure (Figure B.4) after single crystal X-ray diffraction (XRD). Compound ***55*** was generated in low yield (^{1}H NMR) and crystals suitable for single crystal x-ray diffraction have yet to be grown. This is consistent with the hypothesis that, relative to ligand ***52***, diphosphine ***51*** is a more effective ligand for first row transition metals whereas ***52***, which has a larger bite angle, may be better suited for coordination of second row transition metals and binuclear species.

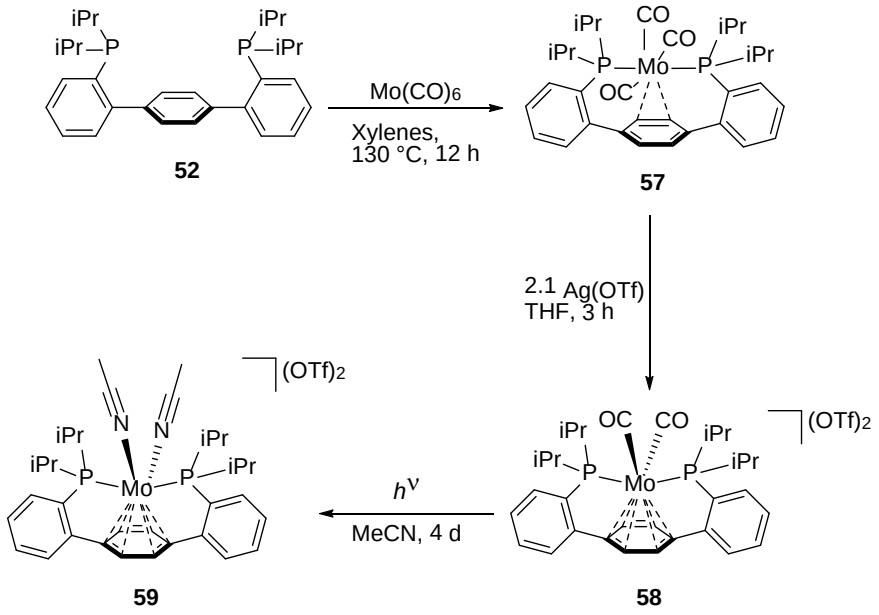
This change in geometry from ***53*** to ***54*** and from ***55*** to ***56*** can be rationalized by electron count. In the absence of coordinating solvent (e.g. THF), the d^7 Co^{II} center cannot assume a geometry which results in an electron count of 18 and assumes a tetrahedral conformation which minimizes steric interactions. The d^8 Co^{I} center with its halide ligands abstracted gains an additional 10 electrons from the ligand to achieve the favored $18e^-$ total. The ability of diphosphines ***51*** and ***52*** to accommodate $1e^-$ changes in oxidation state is promising in the context to proposed transformations (see Figure B.3) which may require one electron from a transition metal and one electron from a redox non-innocent ligand scaffold to proceed.

Use of cobaltocene as a reductant and thalium triflate (TlOTf) as a halide abstractor as opposed to Zn^0 should allow for the isolation of a Co^{I} species with halide-free counteranions and facilitate further study of reactivity with small molecules. Treatment of ***53*** with lithium triethylborohydride ($LiEt_3BH$) and *p*-tolyl magnesium bromide (MgBrTol) gave rise to new paramagnetic species by ^{1}H NMR with

overlapping signals and a notably more complicated alkyl region in the case of MgBrTol. The reduction elimination of H_2 from a transient Co^{II}-dihydride complex or 4,4'-dimethyl-1,1'-biphenyl from a transient Co^{II}-ditolyl species would constitute an interesting transformation with implications for aryl cross-coupling chemistry. Further work is necessary to purify and characterize these compounds to determine the oxidation state and identity of the products of these reactions.

Studies with diphosphine ***52*** confirm that this ligand can support a monometallic mid-transition metal species in a range of oxidation states. Mr. Jade Shi, a then-undergraduate in the group, isolated the tricarbonyl species ***57*** as a bright orange solid by heating ***52*** in xylenes at 140 °C in the presence of $Mo(CO)_6$ (Scheme B.2). $MoCO_3(MeCN)_3$[14] has since been identified as a suitable Mo precursor for this transformation.[9f]

Scheme B.2. Synthesis of Molybdenum Species *57-59* Supported by Diphosphine *52*.

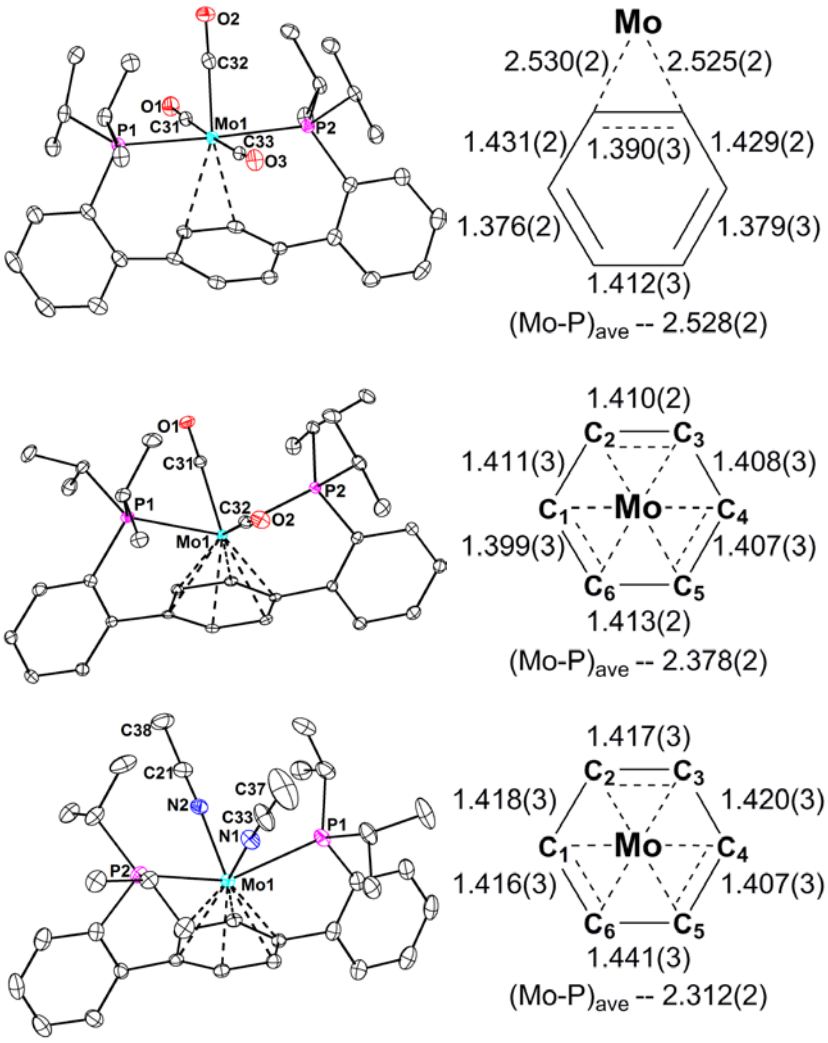


Compound **57** was characterized by ^{1}H and ^{31}P NMR, IR spectroscopy, and single crystal x-ray diffraction (XRD). Attempts were undertaken to replace the carbonyls with more labile ligands.

No change was observed in the ^{1}H or ^{31}P NMR spectrum of **57** after refluxing this species in MeCN. Oxidation of molybdenum carbonyl compounds has been reported to result in the release of CO, presumably by decreasing electron density at the molybdenum center and back-bonding into ligand CO π^* orbitals.[15] A similar strategy was employed here to displace the CO ligands of **57**. Compound **57** had been previously screened for reactivity with oxidants ferrocene and AgOTf (OTf: trifluoromethanesulfonate). Color changes were observed in both cases, and a mass consistent with a molybdenum dicarbonyl species was detected by mass spectrometry. Addition of two equivalents of AgOTf to **57** in THF afforded a single new diamagnetic species by ^{1}H and ^{31}P NMR. IR spectroscopy revealed a single strong CO stretch at 1937 cm^{-1}, consistent with the generation of a mono- or dicarbonyl species. (Compound **1** displays two CO stretches at 2030 cm^{-1} and 1976 cm^{-1}.) Single crystal XRD studies conducted on a suitable crystal of this complex revealed it to be dicarbonyl **58**. Compound **58** displays η^6-coordination to the central ring of the ligand. Comparison of solid-state structures of **57** and **58** show shorter metal-arene bond distances upon oxidation, from an average of 2.528(2) Å for **57** to 2.378(2) Å for **58**, consistent with more electron density being donated into the π^* orbitals of the central ring of the ligand with the loss of a π-accepting CO ligand.

As with **57**, compound **58** was refluxed in acetonitrile in an attempt to exchange the carbonyl ligands with more labile ligands. Again, no reaction was observed.

Figure B.5. Solid-State Structure of *57*-*59*. Hydrogen atoms omitted for clarity. Bond distances in Å.



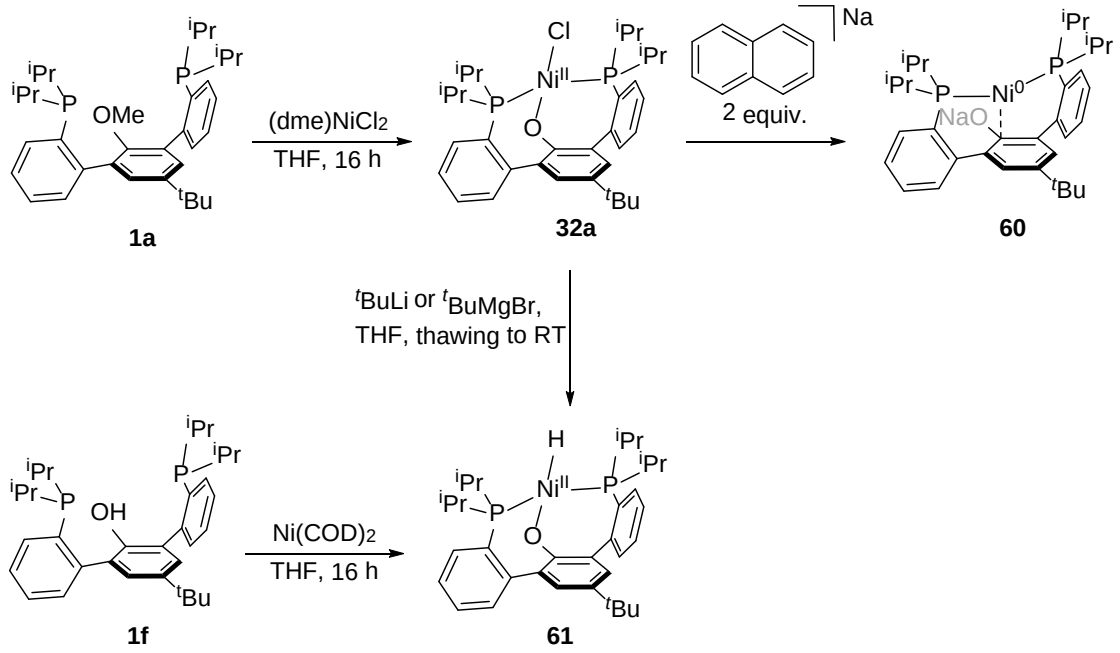
Irradiation of ***58*** in acetonitrile however, using a mercury lamp over the course of several days afforded a new diamagnetic species by ^{1}H and ^{13}C NMR. IR spectroscopy showed no stretches in the carbonyl region. A solid state structure confirmed assignment of this complex as the bisacetonitrile complex ***59*** (Figure B.5). This reaction most likely proceeds through photoexcitation of electrons from the molybdenum d-orbital manifold into the low lying π^* anti-bonding orbitals of the carbonyl ligands, facilitating ligand dissociation and coordination of acetonitrile.

Radicals have been observed through EPR studies of photoexcited single crystals of metal carbonyls.[16] Mo^{II} species **59** has been demonstrated by co-workers in our group to be a good catalyst for the dehydrogenation of ammonia borane, a molecule relevant for H_2 fuel storage.[9f] Mo species of this family display a rich and diverse chemistry with small molecules. They have been demonstrated in our group to bind N_2, reversibly bind CO_2, and form C–C bonds between the carbons of CO ligands in the presence of strong reductant.

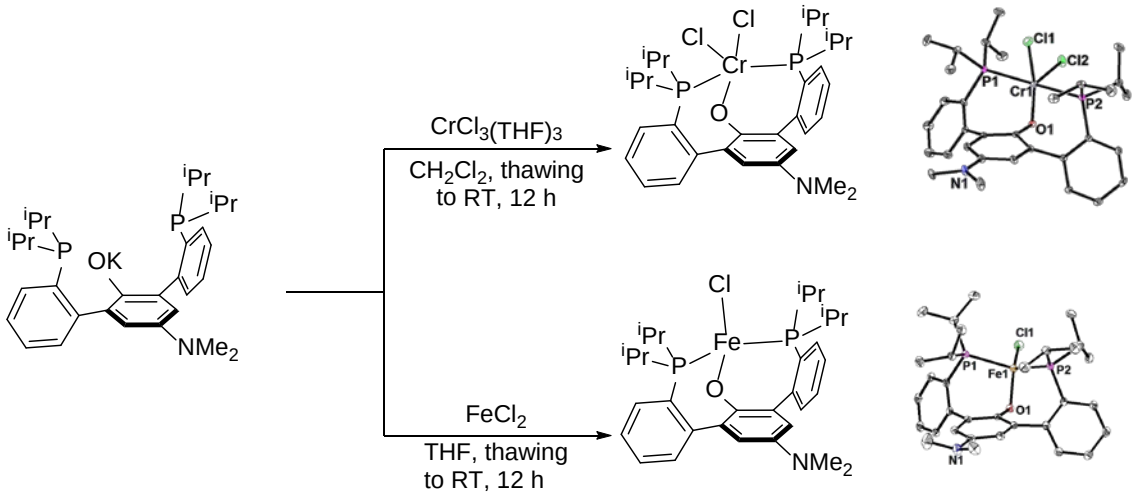
Having demonstrated that Co and Mo compounds could be isolated and characterized in several geometries and oxidation states, chemistry with more rapidly accessible alkylphosphinophenols was explored before preparation of an aminophosphinophenol. Bisphosphinophenoxide Ni^{II}–Cl **32a** was isolated during the course of studies of intramolecular aryl and alkyl C–O bond cleavage chemistry.[10b] Reduction of compound **32a** with 2 equiv. of sodium naphthalenide affords a Ni^0 complex **60** coordinated to a soft arene ligand (Scheme B.3). This result again highlights the flexibility of the terphenyl phosphine scaffolds and their ability to provide hard or soft ligand environments depending on the oxidation state of a coordinated metal. A Ni^{II}-hydride **61** could be prepared by treating **32a** with either ^{t}BuLi or ^{t}BuMgBr, presumably through alkylation, loss of LiCl of MgBrCl, and β-hydride elimination. An alternative synthesis involves treatment of bisphosphinophenol **1f** with $Ni(COD)_2$ – oxidative addition across the O–H bond affords **61**. This chemistry has been extended by Mr. Choon Heng (Marcus) Low to afford Cr^{III} and Fe^{II} analogs to **61** (Scheme B.4) with an aminophenol moiety.

With compound **60**, treatment with excess acid afforded **1f**. Oligomerization trials with bisphosphenols, C_2H_4, and methylaluminoxane (MAO) have been undertaken by Mr. Low.

Scheme B.3. Synthesis of Bisphosphinophenol Nickel Compounds 60 and 61.



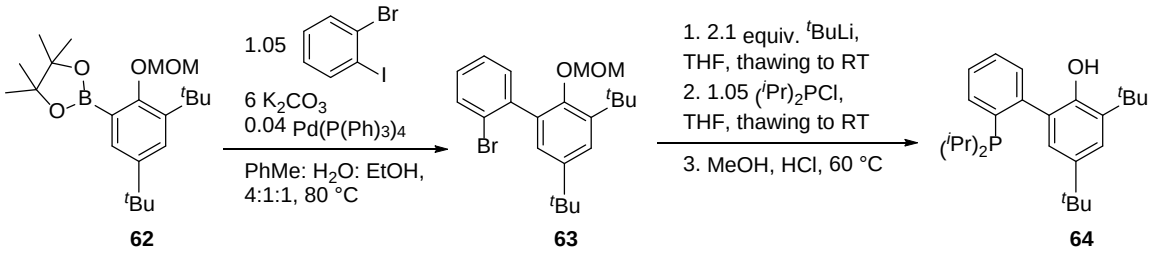
Scheme B.4. Synthesis of Bisphosphinophenoxide Cr and Fe Compounds (Marcus Low).



Removal of a pendant phosphine donor was envisioned to afford a Ni species with more accessible coordination sites. Thus, ligands bearing one pendant donor are envisioned. The flexibility and redox non-innocence of these ligands is anticipated stabilize intermediates during the rearrangements and electron transfers of a catalytic cycle.

Towards the preparation of phosphinophenol **64**, boronic ester **62** was prepared according to literature procedure (Scheme B.5). Elaboration to biphenyl bromide **63** was accomplished through Suzuki coupling of **62** with 1-bromo-2-iodobenzene. Installation of a phosphine substituent was accomplished through lithium halogen exchange and quenching with $^{i}Pr_2PCl$. Acidic work-up in MeOH results in deprotection of the methylmethoxy (-MOM) protecting group, affording the desired phosphinophenol **64**.

Scheme B.5. Synthesis of Phosphinophenol 64.



Treatment of **64** with $Ni(COD)_2$, deprotonation with base followed by treatment with $Ni(DME)Cl_2$ (DME: dimethoxyethane), and comproportionation of $Ni(COD)_2$ and $Ni(DME)Cl_2$ in the presence of **64** does not afford species consistent with coordination of Ni to the phosphinophenol (^{1}H and ^{31}P NMR). However, treatment of **64** with $Ni(TMEDA)Me_2$[17] (TMEDA: tetramethylethylenediamine) afforded Ni^{II}-Me compound **65** (Scheme B.6). A solid state structure confirmed the

initial assignment of **65** as a Ni^{II}-Me species based on NMR data and revealed η^5-coordination to the rearranged phenol moiety. The C–O bond distance of 1.253(2) Å is consistent with a double bond. Ni,[18] Pd,[18] and Ru[19] η^5-oxocyclohexadiene compounds have been previously reported. Given its similarity to the Shell Higher Olefin Process (SHOP)[20] catalyst for ethylene oligomerization, compound **65** is an attractive candidate for reactions under C_2H_4 pressure; such investigations have not yet been completed.

Scheme B.6. Synthesis of Ni^{II}-Me 65.

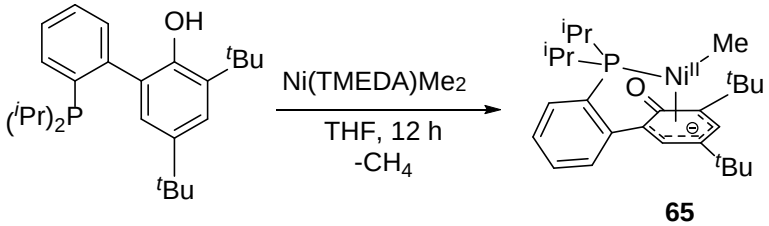
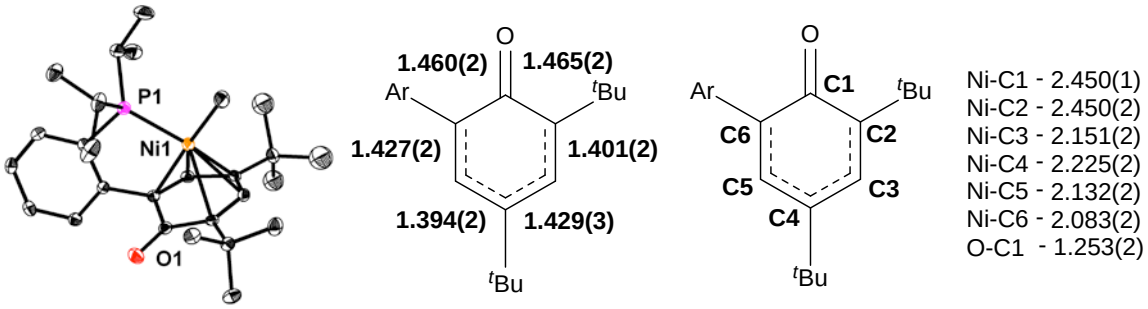


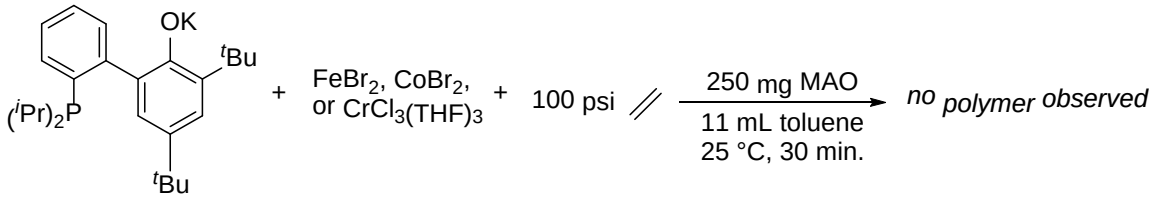
Figure B.6. Solid-State Structure of 65. Hydrogen atoms omitted for clarity. Bond distances in Å.



With structural evidence that phosphinophenol **64** could accommodate a first row transition metal with an sterically accessible face, C_2H_4 oligomerization and polymerization trials were attempted on conditions of C_2H_4 pressure (100 PSI) and MAO (360 equiv.) for 30 min. at 25 °C (Scheme B.7). Phosphinophenol **64** was

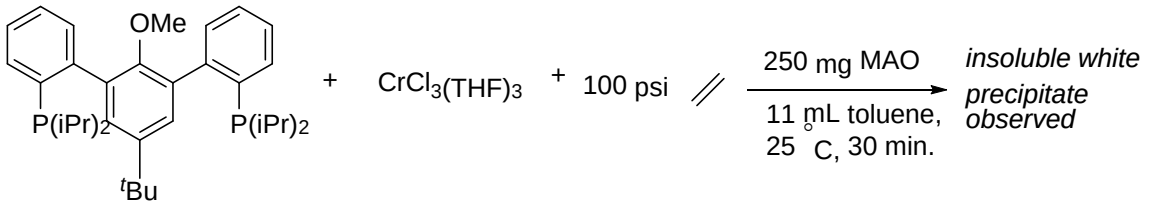
treated with benzyl potassium (BnK) and loss of the resonance assigned to phenol was observed by ^{1}H NMR to afford potassium phenoxide compound **66**.

Scheme B.7. Oligomerization/Polymerization Reactions with 66 and Fe, Co, and Cr Halide Precursors.



66
ca. 12 μmol

Scheme B.8. Oligomerization/Polymerization Reaction with 1a and $CrCl_3(THF)_3$.



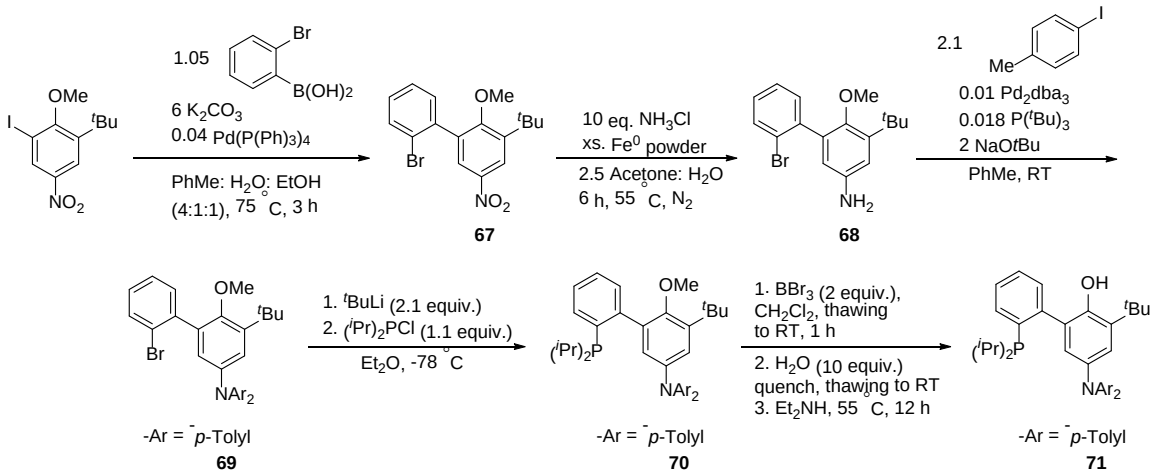
1a
ca. 12 μmol

In separate reactions, phenoxide **66** was treated with $FeBr_2$, $CoBr_2$, or $CrCl_3(THF)_3$ in toluene before being loaded in a Fischer-Porter apparatus and place under oligomerization/polymerization conditions. No insoluble polymer was observed and no C_2H_4 was observed in an aliquot of the reaction mixture analyzed by GC.

At this time, **1a** was tested under the above conditions for a possible effect on C_2H_4 oligomerization/polymerization activity (Scheme B.8). "PSP" and "PNP" ligands have been reported to selective afford α-olefins in the presence of Cr precursors, methylaluminoxane activator, and C_2H_4. In the absence of **1a**, *ca.* 0.5 g of insoluble

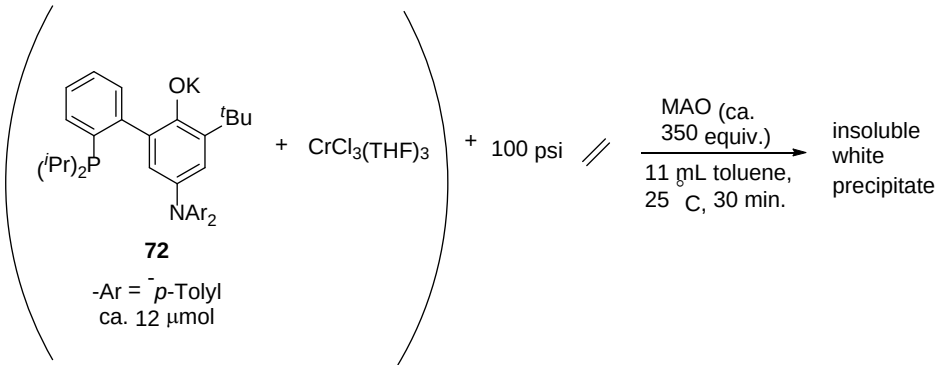
polymer was observed. In the presence of **1a**, a similar amount of insoluble polymer was observed. No oligomers were detected by GC in an aliquot from the reaction mixture.

Scheme B.9. Synthesis of Aminophosphinophenol 71.



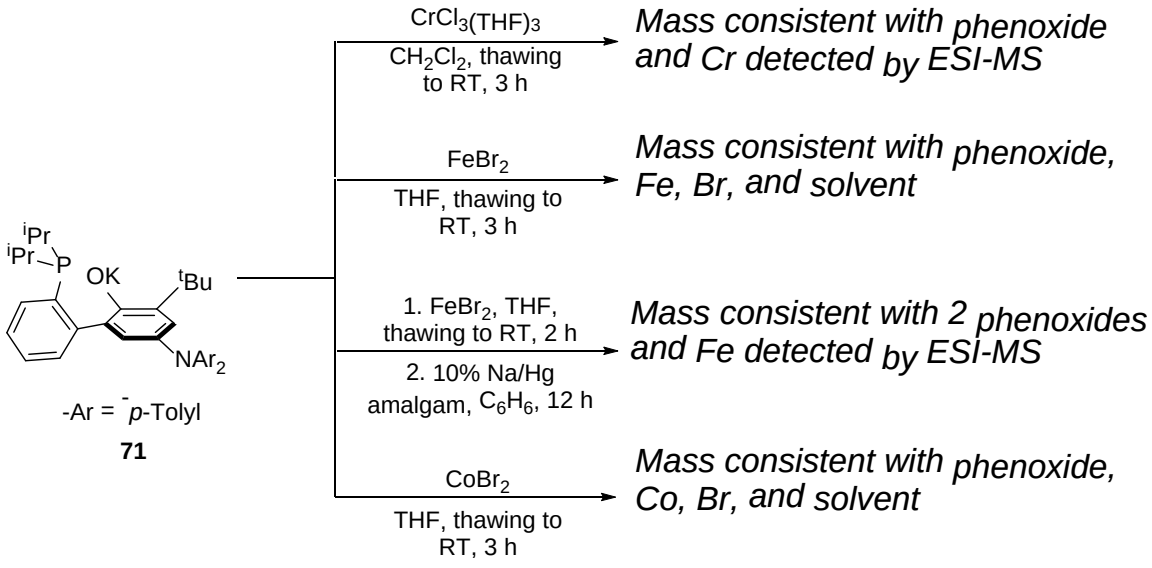
Given the lack of oligomer observed in reactions with C_2H_4 with **1a** or **66**, aminophosphinophenol **71** was prepared. The aminophenol moiety was envisioned to facilitate two electron processes, specifically transformations necessary for selective C_2H_4 oligomerization through a metallocyclic mechanism. 1-(tert-Butyl)-3-iodo-2-methoxy-5-nitrobenzene was prepared according to a reported literature procedure[21]. Suzuki coupling with (2-bromophenyl)boronic acid affords biphenyl bromide **67**. Reduction of compound **67** affords biphenyl amine **68**.[22] Use of Buchwald-Hartwig technology for amine arylation allows for preparation of di-*para*-tolyl amine **69** from **68**. Installation of phosphine is achieved by treatment of aryl amine bromide **69** with ^{t}BuLi followed by quenching with $(^i\text{Pr})_2\text{PCl}$ to afford **70**. Deprotection of methyl aryl ether **70** is achieved by treatment of the phosphine with BBr_3 followed by heating in Et_2NH to quench boron reagent affords the desired aminophosphinophenol **71**.

Scheme B.10. Oligomerization/Polymerization Reactions with 71 and $CrCl_3(THF)_3$.



Compound **71** was treated with BnK to afford phenoxide **72**. Loss of the resonance assigned to the phenolic proton of **71** observed by ^{1}H NMR after treatment with BnK was consistent with the assignment. Compound **71** was treated with $CrCl_3(THF)_3$ in CH_2Cl_2, then used as a precatalyst under previously described oligomerization/polymerization conditions. An insoluble white precipitate was observed and no oligomers were detected from an aliquot of the reaction mixture analyzed by GC.

Scheme B.11. Metallation of 72 with $CrCl_3(THF)_3$, $FeBr_2$, and $CoBr_2$.



Metallations with Fe, Co, and Cr halides were attempted using **72** (Scheme B.11). Treatment of **72** with $CrCl_3(THF)_3$ allowed for observation of a mass consistent with phenoxide and Cr by ESI-MS. Treatment of **72** with $FeBr_2$ allowed for observation of a mass consistent with phenoxide and Fe by ESI-MS. Treatment of this material with Na/Hg resulted in observation of a new signal consistent with 2 phenoxide ligands and one Fe center. With $CoBr_2$ and **72** a mass which could be assigned to phenoxide, Co, Br, and THF solvent was observed. To date, a solid-state structure of a transition metal complex supported by phosphine **71** or its derivatives has not been obtained. Structural characterization of such compounds should facilitate screening for reactivity and design of new proligands to facilitate the desired $2e^-$ chemical transformations (Scheme B.3) proposed herein.

CONCLUSIONS:

Hemilabile ligands are ideal for stabilizing transition metals over a range of oxidation states. Low-valent mononuclear molybdenum, iron, cobalt and copper compounds supported by para- and meta- terphenyl diphosphine ligands were targeted. The metal-arene interactions were analyzed by single-crystal X-ray diffraction and solution-state nuclear magnetic resonance. Other investigators in our research group have demonstrated that, upon reduction of an isolated Mo^{II} precursor, a Mo^{0} complex is formed. This Mo^{0} complex can bind N_2 and CO_2 and oxidatively add H_2 to form a Mo^{II} dihydride. Compounds of this family are also effective ammonia borane dehydrogenation catalysts. This study was extended to the investigation of phenols bearing pendant phosphines, as A Ni^{II} compound supported by such a ligand has been demonstrated to be stabilized by the phenoxide donor whereas the corresponding reduced Ni^{0} complex is instead stabilized by a metal-arene interaction.

Experimental Section

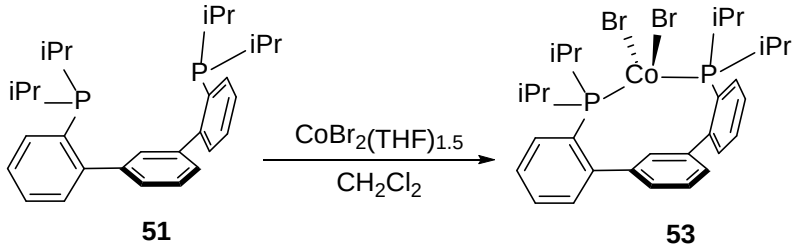
General Considerations

Unless otherwise indicated, reactions performed under inert atmosphere were carried out in oven-dried glassware in a glovebox under a nitrogen atmosphere purified by circulation through RCI-DRI 13X-0408 Molecular Sieves 13X, 4x8 Mesh Beads and BASF PuriStar® Catalyst R3-11G, 5x3 mm (Research Catalysts, Inc.). Solvents for all reactions were dried by Grubbs' method.[23] Acetonitrile-d_3, benzene-d_6, chloroform-d_1, and dichloromethane-d_2 were purchased from Cambridge Isotope Laboratories. Benzene-d_6 was vacuum distilled from sodium benzophenone ketyl. Acetonitrile-d_3 and dichloromethane-d_2 were vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 °C for 24 h. 1,3,-bis(2'-diisopropylphosphino)phenyl)benzene[9b] (**51**), 1,4,-bis(2'-diisopropylphosphino)phenyl)benzene[9c] (**52**), [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]nickel(II)-chloride[10b] (**32a**), $Mo(CO)_3(MeCN)_3$,[14] 2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenol[10b] (**1f**), 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene (**1a**),[10a] 2-(3,5-di-tert-butyl-2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[24] benzyl potassium,[25] and 1-(tert-Butyl)-3-iodo-2-methoxy-5-nitrobenzene[21] were prepared according to previously reported literature procedures. $Ni(TMEDA)Me_2$[17] (TMEDA: tetramethylenediamine) was synthesized from $Ni(acac)_2(TMEDA)$[26] (acac: acetylacetone) and $Mg(TMEDA)Me_2$.[27] All other materials were used as received. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian or Bruker spectrometers at ambient temperature unless denoted otherwise. Chemical shifts are reported with respect to internal solvent for ^1H and ^{13}C NMR data, respectively: 1.94 ppm and 118.26 and 1.32 ppm (CD_3CN); 7.16 ppm and 128.06 ppm

(C_6D_6); 7.26 ppm and 77.16 ppm ($CDCl_3$); 5.32 ppm and 53.84 ppm (CD_2Cl_2).[28] ^{19}F and ^{31}P NMR chemical shifts are reported with respect to an external standard of C_6F_6 (-164.9 ppm) and 85% H_3PO_4 (0.0 ppm), respectively, unless denoted otherwise. IR measurements were obtained on a Bruker Alpha spectrometer equipped with a diamond ATR probe.

Experimental Details

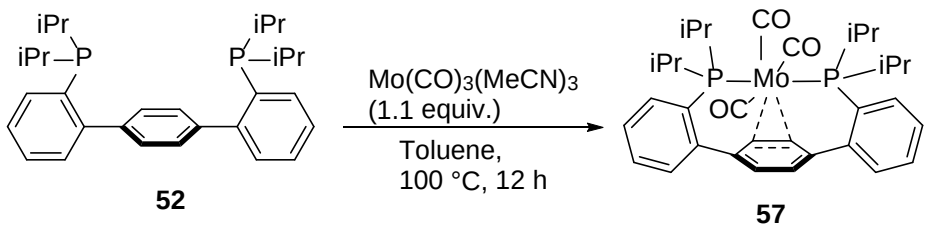
Synthesis of [1,3,-bis(2'-diisopropylphosphino)phenyl)benzene]cobalt(II) bromide (53).



51 **53**

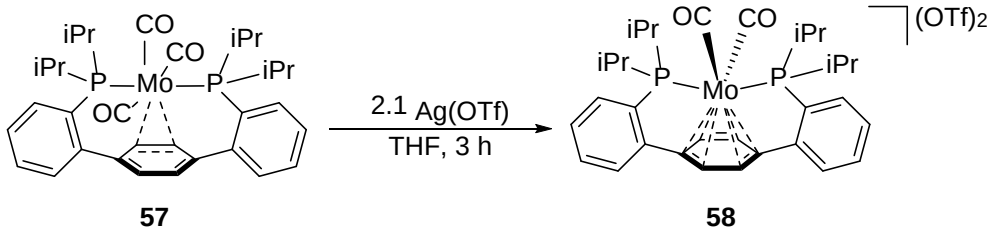
A 20 mL scintillation vial was charged with a magnetic stir bar, $CoBr_2$ (0.02 g, 0.09 mmol), and THF (3 mL). A colorless solution of **51** (0.04 g, 0.09 mmol) in THF (2 mL) was added and the reaction mixture stirred at room temperature. After 1 h, a color change from dark blue to emerald green was observed. After 2 h, solvent was removed *en vacuo*. DCM (3 mL) was added to the green residue and the reaction mixture was allowed to stir for 5 min. before the solvent was removed under reduced pressure. This process was repeated three times. The resulting powder was dissolved in DCM (3 mL) once more, filtered through Celite, and the solvent removed under reduced pressure to afford **53**. ^1H NMR (300 MHz, CD_2Cl_2). δ 26.41 (s, br), 23.12 (s, br), 21.23 (s, br), 17.15 (s, br), 13.93 (s, br), 8.17 (s, br), 3.63 (s, br), 0.15 (s), -1.67 (s, br), -5.06 (s, br), -13.16 (s, br). No ^{31}P NMR signal observed (121 MHz, CD_2Cl_2).

Synthesis of [1,4-bis(2'-diisopropylphosphino)phenyl)benzene]molybdenum(0)tricarbonyl (*57*).



Addition of $Mo(CO)_3(MeCN)_3$[14] (1.43 g, 4.75 mmol, 1.1 equiv.) to a clear solution of ***52*** (2.05 g, 4.32 mmol, 1.0 equiv.) in toluene (50 mL) resulted in a yellow/green heterogeneous mixture. Following heating to 100 °C and stirring for 12 h, the mixture became a deep orange homogenous solution. The volatiles were removed under reduced pressure. The resulting orange solids were collected and washed with cold hexanes (2 x 15 mL). Residual volatiles were removed under reduced pressure to yield ***57*** (2.54 g, 3.81 mmol, 88 %). X-ray quality crystals were grown from vapor diffusion of pentane into a saturated THF solution of ***57***. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) δ 7.86 (m, 2H, aryl-*H*), 7.53 (m, 6H, aryl-*H*), 6.52 (br s, 4H, central arene-*H*), 2.75 (br s, 4H, C*H*$(CH_3)_2$), and 1.09-1.23 (br s, 24H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ: 221.15 (t, *J* = 10.19 Hz, Mo-*C*O), 213.75 (t, *J* = 8.87 Hz, Mo-*C*O), 148.80 (t, *J* = 6.90 Hz, aryl-*C*), 139.99 (t, *J* = 2.74, central arene-*C*), 131.23 (s, aryl-*C*H), 131.02 (t, *J* = 9.41 Hz, aryl-*C*), 129.90 (s, aryl-*C*H), 129.35 (s, aryl-*C*H), 128.34 (s, aryl-*C*H), 33.83 (br s, *C*H$(CH_3)_2$), 19.88 (s, CH(*C*H$_3)_2$), and 19.43 (s, CH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 25 °C) δ: 51.01. IR (CaF_2 window, C_6H_6, cm^{-1}) ν_{CO}: 2298.5, 2192.8. Anal. Calcd. for ***57*** $C_{33}H_{40}MoO_3P_2$ (%): C, 61.68; H, 6.27. Found: C, 61.43; H, 5.99.

Synthesis of [(1,4-bis(2'-diisopropylphosphino)phenyl)benzene)molybdenum(II)dicarbonyl][bistrifluoromethylsulfonate] (58).

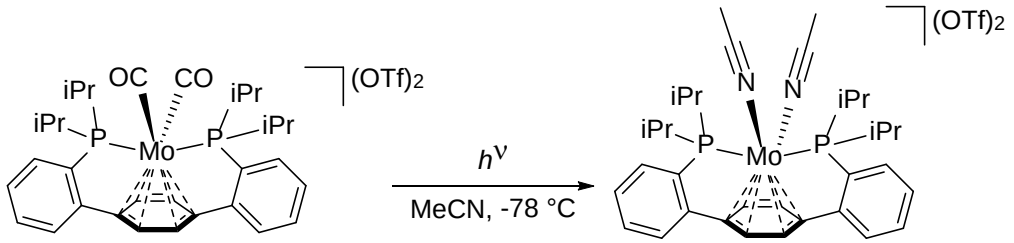


57 **58**

To a rapidly stirring solution of ***57*** (1.17 g, 1.82 mmol) in THF (50 mL), a solution of AgOTf (1.00 g, 3.83 mmol) in THF (35 mL) was added dropwise. With each drop, an darkening of the solution was observed. Complete addition of the silver solution led to a persistent purple/brown mixture, which was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure to yield green/brown solids. These solids were collected on a fritted glass funnel and washed with THF (3 x 10 mL). The solid residue was extracted into MeCN (30 mL), filtered through Celite, and the resulting yellow solution was dried under reduced pressure. The yellow solids were dissolved in minimal MeCN and filtered through Celite once more. Et_2O was added to the filtrate which was then cooled to -35 °C. The precipitate was collected via vacuum filtration, providing ***58*** (1.16 g, 1.26 mmol, 69 %) as yellow microcrystals. X-ray quality crystals were obtained from vapor diffusion of diethyl ether into a saturated MeCN solution of ***58***. ^{1}H NMR (300 MHz, CD_3CN, 25 °C) δ: 7.93 (m, 2H, aryl-*H*), 7.83 (m, 6H, aryl-*H*), 7.15 (s, 4H, central arene-*H*), 3.35 (m, 4H, C*H*$(CH_3)_2$), and 1.29-1.44 (m, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 25 °C) δ: 219.03 (s, Mo-*C*O), 141.32 (dd, *J* = 7.58, 5.79, aryl-*C*), 137.69 (t, *J* = 3.93 Hz, central arene-*C*), 134.64 (s, aryl-*C*H), 133.93 (dd, *J* = 47.74, 8.22, aryl-*C*), 133.83 (s, aryl-*C*H), 132.12 (t, *J* = 3.07 Hz, aryl-*C*H), 128.58 (t, *J* = 5.70 Hz, aryl-*C*H), 122.07 (q, *J* = 320.73 Hz, $F_3CSO_3^-$),

104.72 (s, central arene-*C*H), 28.97 (q, *J* = 11.67 Hz, *C*H(CH$_3$)$_2$), 18.47 (s, CH(*C*H$_3$)$_2$), and 18.07 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121 MHz, CD$_3$CN, 25 °C) δ: 75.05. IR (CaF$_2$ window, C$_6$H$_6$, cm^{-1}) ν_{CO}: 2025.2, 1986.4. Anal. Calcd. for 3 $C_{34}H_{40}F_6MoO_8P_2S_2$ (%): C, 44.74; H, 4.42. Found: C, 44.65; H, 4.49.

Synthesis of [(1,4-bis(2'-diisopropylphosphino)phenyl)benzene)molybdenum(II)di-acetonitrile][bistrifluoromethylsulfonate] (59).

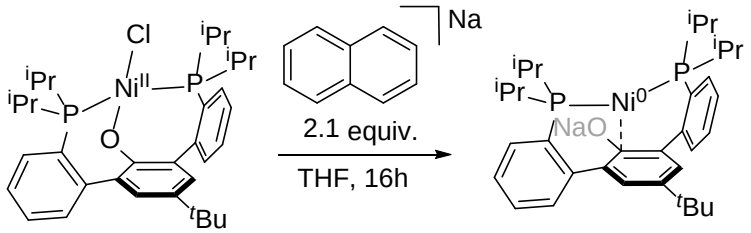


58 **59**

A bright yellow acetonitrile (20 mL) solution of **58** (533 mg, 0.583 mmol) was transferred to a quartz Schlenk tube, charged with a stir bar. The tube was degassed via three freeze-pump-thaw cycles and then, while stirring, irradiated with a 200 W Hg/Xe lamp at -78 °C for 2 h. The evolution of bubbles was observed and the solution steadily darkened to deep red. The flask was degassed as above and photolysis continued. With continued irradiation, the solution darkened to a deep purple color that glowed intensely under the UV light. This degas/irradiation process was continued until aliquots of the solution showed no presence of **58** or the putative monocarbonyl species by ^{31}P NMR (75.05 and 68.62 ppm, respectively). The total irradiation time was dependent on lamp age, frequency of degassing, and solution concentration, varying from 12 h to several days. Upon complete conversion, volatiles were removed under reduced pressure, providing deep purple solids. These solids were collected on a fritted funnel and washed with THF until the filtrate was colorless. The purple

microcrystalline product was collected (528 mg, 0.565 mmol, 97 %). Crystals suitable for X-ray diffraction were obtained from vapor diffusion of Et_2O into a saturated MeCN solution of **59**. ^{1}H NMR (300 MHz, CD_3CN, 25 °C) δ: 7.62-7.72 (m, 6H, aryl-*H*), 7.51-7.52 (m, 2H, aryl-*H*), 5.59 (t, 4H, *J* = 2.2 Hz, central arene-*H*), 2.86-2.93 (m, 4H, C*H*(CH_3)$_2$), 2.72 (m, 6H, NC(C*H*$_3$)), and 1.25-1.31 (m, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, CD_3CN, 25 °C) δ: 145.36 (t, *J* = 10.51 Hz, aryl-*C*), 143.35 (s, N*C*CH_3), 133.44 (s, aryl-*C*H), 132.35 (s, aryl-*C*H), 130.60 (dd, *J* = 62.25, 23.73, aryl-*C*), 130.57 (s, aryl-*C*H), 127.48 (s, aryl-*C*H), 123.39 (s, Mo- *C*NCH_3), 122.15 (q, *J* = 318.51, $F_3CSO_3^-$), 120.50 (s, central arene-*C*), 88.90 (s, central arene-*C*H), 25.74 (t, *J* = 9.77 Hz, *C*H(CH_3)$_2$), 18.67 (s, CH(*C*H_3)$_2$), 17.86 (s, CH(*C*H_3)$_2$), 7.03 (s, Mo-NC*C*H_3) and 6.52 (m, Mo-NC*C*H_3). ^{31}P{^{1}H} NMR (121 MHz, CD_3CN, 25 °C) δ: 63.35. Anal. Calcd. for **4**: $C_{36}H_{46}F_6MoN_2O_6P_2S_2$ (%): C, 46.06; H, 4.94; N, 2.98. Found: C, 45.09; H, 4.77; N, 3.25.

Synthesis of [sodium][(2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide)nickel(0)] (60).

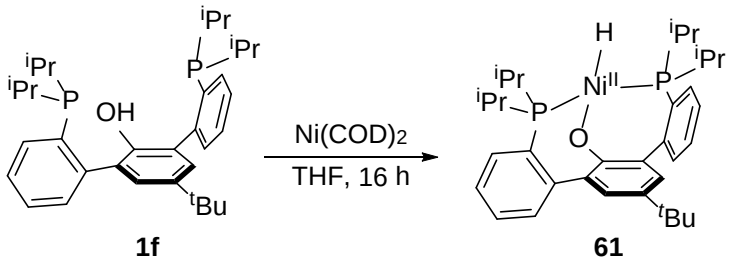


32a **60**

A 20 mL scintillation vial coating with a mirror of Na and charged with a stir bar was charged with naphthalene (0.021 g, 0.17 mmol, 2.1 equiv.) as a solution in THF (2 mL). The solution was stirred vigorously for 1 h. A dark green color, consistent with the formation of sodium naphthalenide[29] was observed. A separate 20 mL scintillation vial was charged with phenoxide Ni^{II}Cl compound **32** (0.050 g, 0.08 mmol, 1.0 equiv.),

THF (1 mL), and a stir bar. A dark purple solution was observed. The dark green solution was added and the vial of sodium napthalenide solution was rinsed with two portions of THF (1 mL) which was combined with the reaction mixture. A dark red solution was observed. After 1 h, volatiles were removed under reduced pressure. A dark red residue was observed. Pentane (1 mL) was added, the residue was triturated, and volatiles were removed under reduced pressure. The resulting residue was washed three times with pentane (1 mL) then extracted with three portions of C_6H_6 (1 mL). The combined C_6H_6 solution was filtered through Celite and volatiles were removed from the filtrate to afford **60**. Crystals suitable for X-ray diffraction were grown from a saturated solution of pentane. ^{1}H NMR (400 MHz, C_6D_6) δ 7.36 (m, 2H, Ar-*H*$_6$), 7.05 (m, 2H, Ar-*H*$_8$), 7.01 – 6.93 (m, 4H, Ar-*H*$_9$ & Ar-*H*$_7$), 6.40 (t, 2H, Ar-*H*$_3$, J_{PC} = 2.0 Hz), 2.15 (m, 2H, -C*H*(CH$_3$)$_2$), 1.88 (m, 2H, -C*H*(CH$_3$)$_2$), 1.39 (s, 9H, -C(C*H*$_3$)$_3$), 1.24 (dd, 6H, -CH(C*H*$_3$)$_2$), 1.04 (m, 12H, -CH(C*H*$_3$)$_2$), 0.68 (m, 6H, -CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 152.24 (app t, Ar-*C*, J_{PC} = 14.7 Hz), 142.04 (app t, Ar-*C*, J_{PC} = 14.7 Hz), 132.71 (s, Ar-*C*$_1$), 130.29 (app t, Ar-*C*$_6$, J_{PC} = 2.5 Hz), 129.73 (s, Ar-*C*$_9$), 128.21 (obscured by solvent residual, detected by HSQC, Ar-*C*$_7$), 127.31 (s, Ar-*C*$_8$), 118.12 (s, Ar-*C*$_3$), 33.89 (s, -*C*(CH$_3$)$_3$, 32.18 (s, -C(*C*H$_3$)$_3$), 27.84 (app t, -*C*H(CH$_3$)$_2$, J_{PC} = 7.1 Hz), 20.55 (app t, -CH(*C*H$_3$)$_2$, J_{PC} = 6.1 Hz), 20.24 (s, br, -CH(*C*H$_3$)$_2$, 20.07 (app t, -*C*H(CH$_3$)$_2$, J_{PC} = 7.1 Hz), 19.77 (s, br, -CH(*C*H$_3$)$_2$), 19.16 (app t, -CH(*C*H$_3$)$_2$, J_{PC} = 6.1 Hz). Two Ar-*C* not detected. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 38.31 (s).

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]nickel(II)-hydride (61).

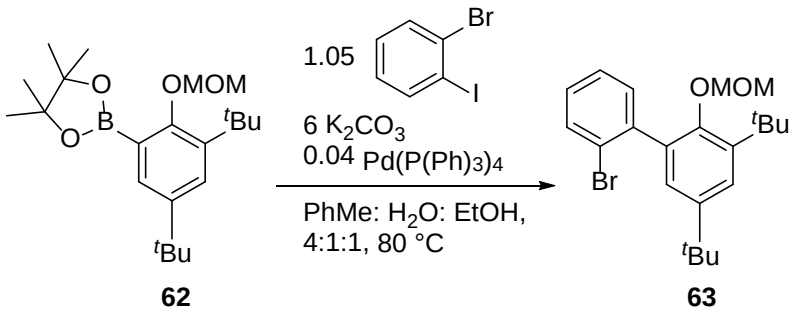


1f **61**

A 20 mL scintillation vial was charged with $Ni(COD)_2$ (0.052 g, 0.191 mmol), THF (2 mL), and a stir bar. A slurry of a yellow solid in THF was observed. Bisphosphinophenol **1f** (0.102 g, 0.19 mmol) was added as a colorless solution in THF (2 mL). After 16 h, a yellow solution was observed. Volatiles were removed under reduced pressure. Pentane (2 mL) was added and the mixture was triturated. The resulting yellow solid was washed with pentane (3 x 2 mL), hexanes (3 x 2 mL), and Et_2O (3 x 2 mL). The residue was then extracted with C_6H_6 (2 x 3 mL). The combined C_6H_6 solution was filtered through Celite and volatiles removed under reduced pressure to afford **61** (0.088 g, 0.15 mmol, 78.9%). ^{1}H NMR (300 MHz, C_6D_6) δ 7.38 (s, 2H, Ar-H_3), 7.34 - 7.30 (m, 2H, Ar-H_6), 7.22 – 7.15 (m, 4H, Ar-H_7 & Ar-H_9), 7.05 (m, 2H, Ar-H_8), 2.15 (m, 2H, -CH(CH_3)$_2$), 1.68 (m, 2H, -CH(CH_3)$_2$), 1.57 (dd, 6H, -CH(CH_3)$_2$), 1.50 (s, 9H, -C(CH_3)$_3$), 1.30 (dd, 6H, -CH(CH_3)$_2$), 1.04 (dd, 6H, -CH(CH_3)$_2$, 0.72 (dd, 6H, -CH(CH_3)$_2$), -25.62 (t, 1H, Ni-H, J_{PH} = 78.0 Hz). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 150.75 (app t, Ar-C_5, J_{PC} = 8.6 Hz), 145.75 (s, Ar-C_1), 138.14 (s, Ar-C_4), 134.48 (s, Ar-C_2), 133.27 (app t, Ar-C_6, J_{PC} = 4.5 Hz), 130.75 (s, Ar-C_7 or Ar-C_9), 130.59 (s, Ar-C_7 or Ar-C_9), 129.98 (s, Ar-C_3), 125.92 (td, Ar-C_{10}, J_{PC} = 34.8 Hz, J_{HC} = 2.0 Hz), 125.13 (app t, Ar-C_8, J_{PC} = 4.5 Hz), 34.23 (s, -C(CH_3)$_3$), 32.19 (s, -C(CH$_3$)$_3$), 29.61 (td, -CH(CH_3)$_2$, J_{PC} = 14.6 Hz, J_{HC} = 3.7 Hz),

22.77 (t, -*C*H(CH$_3$)$_2$, J_{PC} = 12.1 Hz), 19.98 – 19.45 (m, -CH(*C*H$_3$)$_2$), 16.48 (s, -CH(*C*H$_3$)$_2$). ^{31}P NMR (121 MHz, C_6D_6) δ 39.37 (m).

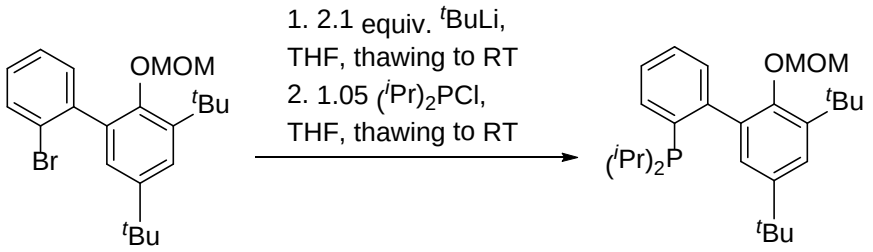
Synthesis of 1-(2'-bromo)phenyl-2-methoxymethoxy-3,5-di-tert-butyl-benzene (63).



In the fume hood, a 500 mL Schlenk tube fitted with a Teflon screw cap was charged with 2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[24] (1.950 g, 5.15 mmol, 1.1 equiv.), 1-bromo-2-iodobenzene (1.333 g, 4.71 mmol, 1.0 equiv.), K_2CO_3 (3.906 g, 28.26 mmol, 6.0 equiv.), toluene (100 mL), EtOH (30 mL), and H_2O (30 mL). On the Schlenk line, the reaction mixture was degassed via three freeze-pump-thaw cycles. With N_2 backflow, Pd(PPh$_3$)$_4$ (0.272 g, 0.24 mmol, 0.05 equiv.) was added, providing a yellow biphasic solution. The reaction was stirred at 80 °C for 23 h at which time the reaction mixture was transferred to a round bottom flask and concentrated under reduced pressure to a total volume of *ca.* 100 mL. This mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (*ca.* 75 mL) three times. The combined organics were washed with brine and dried over Mg(SO$_4$)$_2$. The volatiles were removed under reduced pressure, providing **63** as a brown oil. Material of this purity was heated under vacuum on the Schlenk line and used in a subsequent phosphination without further purification. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.70 (m, 1H, Ar-*H*), 7.52 – 7.43 (m, 2H, Ar-*H*), 7.24 – 7.16 (m, 2H, Ar-*H*), 7.09 (d, 1H, Ar-

H), 4.52 (d, 1H, -OC*H*$_2$OCH$_3$), 4.42 (d, 1H, -OC*H*$_2$OCH$_3$), 3.15 (s, 1H, -OCH$_2$OC*H*$_3$), 1.47 (s, 9H, -C(C*H*$_3$)$_3$, 1.33 (s, 9H, -C(C*H*$_3$)$_3$.

Synthesis of 1-(2'-diisopropylphosphino)phenyl-2-methoxymethoxy-3,5-di-tert-butyl-benzene.

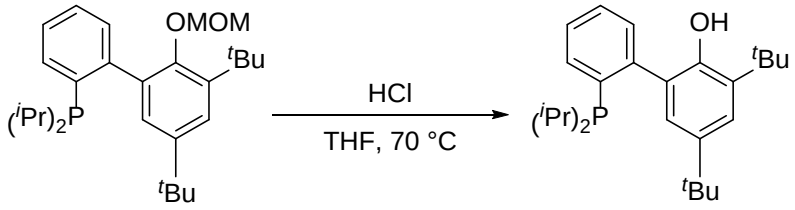


63

In the glovebox, a 250 mL round bottom flask charged with biphenyl bromide **63** (3.321 g, 6.59 mmol, 1.0 equiv.), THF (80 mL), and a stir bar. Separately, a 20 mL scintillation vial was charged with ^{t}BuLi (16.3 mL, 27.66 mmol, 1.7 M solution in heptane). The solutions were frozen in a liquid N_2-chilled cold well. The just-thawed solution of ^{t}BuLi was added to the thawing solution of **63**. The mixture was allowed to warm to room temperature. A separate 20 mL scintillation vial was charged with (^{i}Pr$_2$)PCl (2.111 g, 2.20 mL, 13.83 mmol, 2.1 equiv.). The reaction mixture and (^{i}Pr$_2$)PCl were frozen in a liquid N_2-chilled cold well. The just-thawed solution of (^{i}Pr$_2$)PCl was added to the thawing reaction mixture. The mixture was allowed to warm to room temperature and stir for 12 h. After 12 h, volatiles were removed under reduced pressure to afford a brown residue. Hexanes (10 mL) was added and the residue was triturated. Volatiles were removed under reduced pressure. The resulting powder was extracted with 3 portions of C_6H_6 (20 mL each). The combined organic layer was filtered through alumina. Volatiles were removed under reduced pressure. The resulting solid was precipitated from hexanes to afford the desired –MOM

protected phosphinophenol as a pale yellow solid which was used in a subsequent deprotection step without further purification. ^{1}H NMR (400 MHz, C_6D_6) δ 7.59 (d, 1H, Ar-*H*$_3$), 7.41 – 7.31 (m, 2H, Ar-*H*$_6$ & Ar-*H*$_9$), 7.14 – 7.12 (m, 2H, Ar-*H*$_{12}$ & Ar-*H*$_7$ or Ar-*H*$_8$), 7.04 (m, 1H, Ar-*H*$_7$ or Ar-*H*$_8$), 4.70 (d, 1H, -O*C*H$_2$OCH$_3$), 4.42 (d, 1H, -O*C*H$_2$OCH$_3$), 3.12 (s, 3H, -OCH$_2$OC*H*$_3$), 2.05 (m, 1H, -C*H*(CH$_3$)$_2$), 1.67 (s, 9H, -C(C*H*$_3$)$_3$; m, 1H, -C*H*(CH$_3$)$_2$), 1.35 (s, 9H, -C(C*H*$_3$)$_3$, 1.10 (m, 6H, -CH(C*H*$_3$)$_2$), 0.85 (m, 6H, -CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 152.79 (d, Ar-*C*$_1$, J_{PC} = 1.0 Hz), 149.22 (d, Ar-*C*$_{10}$, J_{PC} = 31.3 Hz), 144.49 (s, -*C*(CH$_3$)$_3$), 141.53 (s, -*C*(CH$_3$)$_3$), 137.15 (d, Ar-*C*$_5$, J_{PC} = 23.2 Hz), 136.10 (d, Ar-*C*$_2$, J_{PC} = 6.1 Hz), 132.70 (d, Ar-*C*$_6$ or Ar-*C*$_9$, J_{PC} = 4.0 Hz), 131.21 (d, Ar-*C*$_6$ or Ar-*C*$_9$, J_{PC} = 6.1 Hz), 128.88 (d, Ar-*C*$_7$ or Ar-*C*$_8$, J_{PC} = 1.0 Hz), 128.80 (s, Ar-*C*$_7$ or Ar-*C*$_8$), 126.76 (s, Ar-*C*$_{12}$), 123.26 (s, Ar-*C*$_3$), 99.65 (s, -O*C*H$_2$OCH$_3$), 56.90 (s, -OCH$_2$O*C*H$_3$), 35.56 (s, -*C*(CH$_3$)$_3$), 34.64 (s, -*C*(CH$_3$)$_3$), 31.83 (s, -C(*C*H$_3$)$_3$), 31.11 (s, -C(*C*H$_3$)$_3$), 26.58 (d, -*C*H(CH$_3$)$_2$, J_{PC} = 18.1 Hz), 23.36 (d, -*C*H(CH$_3$)$_2$, J_{PC} = 15.2 Hz), 20.95 (d, -CH(*C*H$_3$)$_2$, J_{PC} = 16.2 Hz), 20.59 (d, -CH(*C*H$_3$)$_2$, J_{PC} = 11.1 Hz), 20.39 (d, -CH(*C*H$_3$)$_2$, J_{PC} = 19.2 Hz), 19.27 (d, -CH(*C*H$_3$)$_2$, J_{PC} = 8.1 Hz). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ -0.99 (s).

Synthesis of 2-(2'-diisopropylphosphino)phenyl-4,6-di-tert-butyl-phenol (64).

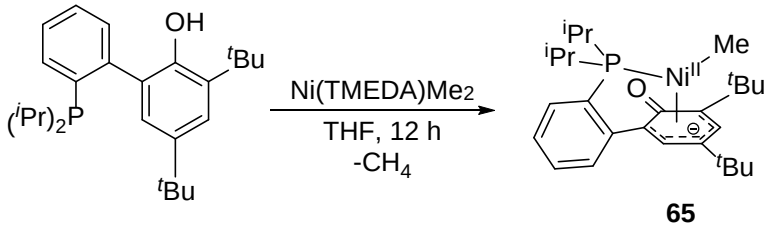


64

In a N_2-filled glovebox containing protic solvents, a 100 mL Schlenk tube fitted with a Teflon screw cap was charged with –MOM protected phosphinophenol (1.60 g, 3.61

mmol, 1.0 equiv.), aqueous HCl (9.0 mol, 10.83 mL, conc. HCl *ca.* 12 M, *ca.* 3.0 equiv.), THF (70 mL), a stir bar. The resulting mixture was place in an oil bath pre-heated to 70 °C for *ca.* 12 h, providing a homogenous orange solution. Volatiles were removed under reduced pressure. In a N_2-filled glovebox containing protic solvents, the resulting orange residue was taken up in CH_2Cl_2 (50 mL) and washed with saturated aqueous solutions of K_2CO_3 (50 mL x 2) and NH_4Cl (50 mL x 1). The volatiles were removed under reduced pressure, Et_2O was added, and the precipitate was isolated to afford phenol **64**. Material of this purity was used in a subsequent deprotonation with BnK without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (m, 1H, Ar-*H*), 7.35 (m, 1H, Ar-*H*), 7.20 (m, 1H, Ar-*H*), 7.14 (m, 1H, Ar-*H*), 7.09 (m, 2H, Ar-*H*), 5.09 (d, 1H, -O*H*), 1.89 (m, 1H, -C*H*(CH_3)$_2$), 1.66 (s, 9H, -C(C*H*$_3$)$_3$), 1.54 (m, 1H, -C*H*(CH_3)$_2$), 1.37 (s, 9H, -C(C*H*$_3$)$_2$), 1.01 - 0.79 (m, 12, -CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ -0.45.

Synthesis of [2-(2'-diisopropylphosphino)phenyl-4,6-di-tert-butyl-oxocyclohexa-diene]nickel(II) methyl .(65)

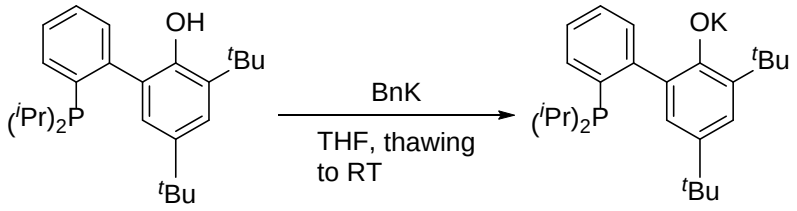


64 **65**

A 20 mL scintillation vial was charged with Ni(TMEDA)Me_2[17] (0.052 g, 0.25 mmol), THF (1 mL), and a stir bar. A yellow-brown solution was observed. A solution of phenol **64** (0.101 g, 0.25 mmol) in THF (1 mL) was added. A dark red solution was observed. After 4 h, the volatiles were removed under reduced pressure. Hexanes (1 mL) was added and the dark red residue was triturated. Volatiles were removed under

reduced pressure. The resulting residue was extracted with three portions of hexanes (*ca.* 2 mL each) and the combined hexanes solution was filtered through Celite. Volatiles were removed under reduced pressure to afford crude **65**. Crystals suitable for X-ray diffraction were grown from a concentrated hexanes solution. ^{1}H NMR (300 MHz, C_6D_6) δ 7.74 (m, 1H, Ar-*H*), 7.14 (m, 1H, Ar-*H*), 6.97 (m, 1H, Ar-*H*), 6.89 (m, 1H, Ar-*H*), 6.21 (m, 1H, oxocyclohexadienyl-*H*), 6.10 (d, 1H, oxocyclohexadienyl-*H*), 1.99 – 1.84 (m, 2H, -C*H*(CH_3)$_2$), 1.78 (s, 9H, -C(C*H*$_3$)$_3$), 1.24 (s, 9H, -C(C*H*$_3$)$_3$), 1.07 (dd, 3H, -CH(C*H*$_3$)$_2$), 0.99 – 0.78 (m, 9H, -CH(C*H*$_3$)$_2$), -0.37 (d, 3H, Ni-C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 169.96 (s), 149.58 (d, Ar-*C*, J_{PC} =20.2 Hz), 140.46 (d, Ar-*C*, J_{PC} = 40.4 Hz), 130.99 (d, J_{PC} = 12.1 Hz), 130.55 (d, Ar-*C*H, J_{PC} = 2.0 Hz), 129.74 (s, Ar-*C*H), 128.16 (obscured by solvent residual, detected by HMBC, oxocyclohexadienyl-*C*-C(CH_3)$_3$), 126.73 (d, Ar-*C*H, J_{PC} = 6.1 Hz), 109.03 (d, oxocyclohexadienyl-*C*-C(CH_3)$_3$, J_{PC}= 5.1 Hz), 107.35 (s, Ar-*C*H, oxocyclohexadienyl-*C*H), 106.09 (d, Ar-*C*H, oxocyclohexadienyl-*C*H, J_{PC} = 6.1), 105.22 (d, J_{PC} = 5.1 Hz), 35.66 (s, -*C*(CH_3)$_3$), 34.05 (s, -*C*(CH_3)$_3$), 30.99 (s, -C(*C*H$_3$)$_3$), 30.12 (s, -C(*C*H$_3$)$_3$), 27.04 (d, -*C*H(CH_3)$_2$, J_{PC} = 24.2 Hz), 25.26 (d, -*C*H(CH_3)$_2$, J_{PC} = 26.3 Hz), 18.84 (d, -CH(C*H*$_3$)$_2$, J_{PC} = 3.0 Hz), 18.76 (d, -CH(C*H*$_3$)$_2$, J_{PC} = 3.0 Hz), 18.54 (s, -CH(C*H*$_3$)$_2$), 18.31 (s, -CH(C*H*$_3$)$_2$), -30.82 (d, Ni–*C*H$_3$, J_{PC} = 27.3 Hz). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 64.33 (s).

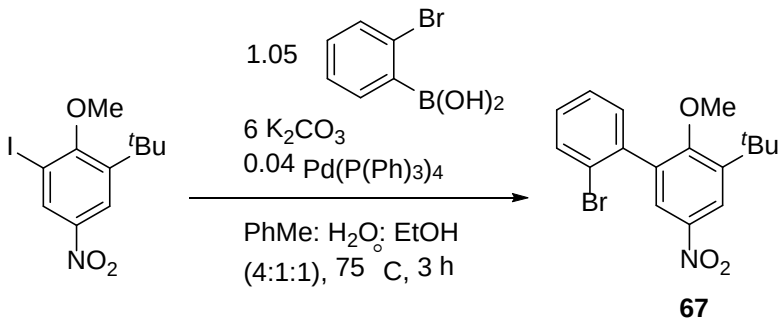
Synthesis of [potassium][2-(2'-diisopropylphosphino)phenyl-4,6-di-tert-butyl-phenoxide] (66).



64 **66**

In the glovebox, a 20 mL scintillation vial was charged with phenol **64** (0.100 g, 0.25 mmol, 1.0 equiv.), THF (2 mL), and a stir bar. A separate 20 mL vial was charged with BnK (0.036 g, 0.28 mmol, 1.1 equiv.) and THF (2 mL). Both solution were frozen in a liquid N_2-chilled cold well. The just-thawed solution of BnK was added dropwise to a thawing solution of phenol **64**. A dark red color was observed upon completion of addition. Volatiles were removed under reduced pressure. Hexanes (2 mL) was added and the resulting dark red residue was titurated. Volatiles were removed under reduced pressure. The resulting residue was extracted with C_6H_6 (3 times, 2 mL). The combined C_6H_6 solution was filtered through Celite and volatiles were removed to afford an orange powder which was used for metallation with metal halides without further purification. ^{1}H NMR (300 MHz, C_6D_6) δ 7.52 (d, 1H, Ar-*H*), 7.24 (m, 1H, Ar-*H*), 7.11 (obscured by solvent residual), 7.05 (d, 1H, Ar-*H*), 6.99 (m, 2H, Ar-*H*), 1.95 (m, 2H, -C*H*(CH_3)$_2$), 1.54 (s, 9H, -C(C*H*$_3$)$_3$), 1.48 (s, 9H, -C(C*H*$_3$)$_3$), 0.99 – 0.78 (m, 12H, -CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 2.92 (s, br), -0.03 (s).

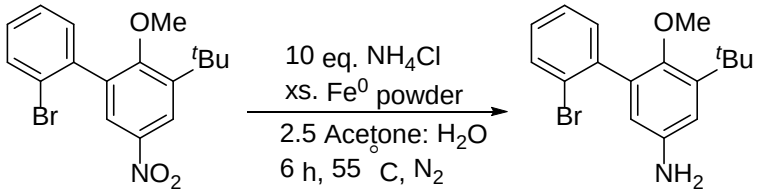
Synthesis of 1-(2'-bromophenyl)-4-nitro-5-tert-butyl-6-methoxybenzene (67).



67

1-(2'-bromophenyl)-4-nitro-5-tert-butyl-6-methoxybenzene (**67**) was synthesized using a modification of the procedure reported by Albrecht and co-workers for the Suzuki coupling of aryl halides with boronic acids.[30] In the fume hood, a 500 mL Schlenk tube fitted with a Teflon screw cap was charged with 1-iodo-3-nitro-5-*tert*-butyl-6-methoxybenzene (4.000 g, 11.94 mmol, 1.00 equiv.), 2-bromophenylboronic acid (1.727 g, 12.53 mmol, 1.05 equiv.), K_2CO_3 (7.191 g, 35.81 mmol, 6.00 equiv.), toluene (160 mL), EtOH, (40 mL), deionized H_2O (40 mL), and a stir bar. On the Schlenk line, the reaction mixture was degassed via three freeze-pump-thaw cycles. With N_2 backflow, $Pd(PPh_3)_4$ (0.055 g, 0.48 mmol, 0.05 equiv.) was added, providing a yellow biphasic solution. The reaction was stirred at 75 °C for 3 h at which time the reaction mixture was transferred to a round bottom flask and concentrated under reduced pressure to a total volume of *ca.* 100 mL. This mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (*ca.* 75 mL) three times. The combined organics were washed with brine and dried over $Mg(SO_4)_2$. The volatiles were removed under reduced pressure, providing **67** as a yellow-brown oil. Material of this purity was used in a subsequent reduction without further purification.

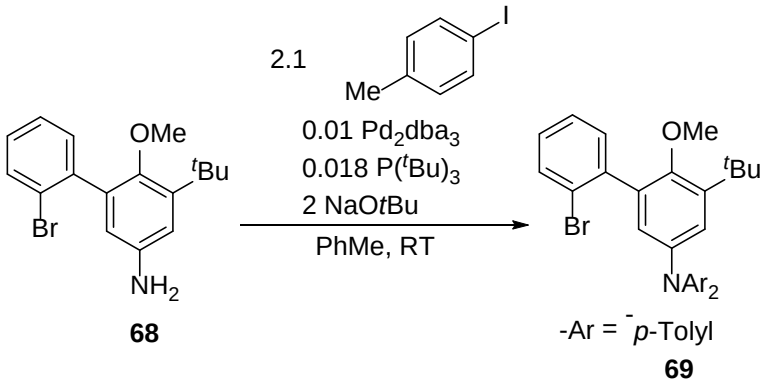
Synthesis of 1-(2'-bromophenyl)-4-amino-5-tert-butyl-6-methoxybenzene (68).



67 **68**

Biphenyl **67** was reduced according to a literature procedure.[31] A 500 mL round bottom was charged with **67** (4.170 g, 11.45 mmol, 1.0 equiv.), iron powder (2.557 g, 45.79 mmol, 4.0 equiv.), NH_4Cl (6.124 g, 114.49 mmol, 10.0 equiv.), acetone (100 mL), 50 mL (H_2O), and a stir bar. A reflux condenser was affixed to the round bottom and the reaction mixture was heated at 55 °C for 6 h under N_2. After 6 h, the reaction mixture was filtered through Celite and volatiles were evaporated from the filtrate. The dark residue was dissolved in 100 mL CH_2Cl_2. The organic layer was washed twice with H_2O (100 mL) and once with brine (100 mL). The organic layer was dried with $Mg(SO_4)_2$, filtered, and volatiles were removed from the filtrate. Column chromatography using 4:1 hexanes:EtOAc as eluent afforded biphenyl amine **68**. Amine of this purity was used in a subsequent Buchwald-Hartwing arylation without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 1H, Ar-*H*), 7.40 – 7.30 (m, 2H, Ar-*H*), 7.19 (m, 1H, Ar-*H*), 6.71 (d, 1H, Ar-*H*, J_{HH} = 3.0 Hz), 6.44 (d, 1H, Ar-*H*, J_{HH} = 3.0 Hz), 3.52 (s, br, 2H, -NH_2), 3.20 (s, 3H, -OCH_3), 1.39 (s, 9H, -C(CH_3)$_3$).

Synthesis of 1-(2'-bromophenyl)-4-ditolylamino-5-tert-butyl-6-methoxybenzene (68).

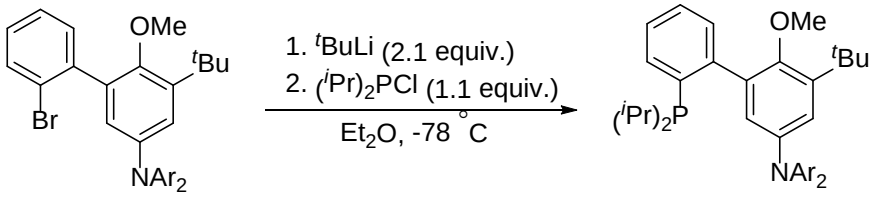


68 **69**

A 100 mL Schlenk tube fitted with a Teflon screw cap was charged with biphenyl amine **68** (2.420 g, 7.24 mmol, 1.0 equiv.) as a solution in a minimum in hexanes. Volatiles were removed under reduced pressure and the resulting residue was dried under vacuum for *ca.* 12 h. The Schlenk tube was sealed and brought into the glovebox. In the glovebox, the Schlenk tube was charged with *para*-tolyl-iodide (3.473 g, 0.016 mmol, 2.2 equiv.), NaO*t*Bu (2.087 g, 0.022 mmol, 3.0 equiv.), and toluene (20 mL). A toluene (5 mL) slurry of Pd_2dba_3 (dba: dibenzylideneacetone; 0.199 g, 0.217 mmol, 0.03 equiv.) and $P(^tBu)_3$ (0.141 g, 0.70 mmol, 0.10 equiv.) was added. The Schlenk flask was sealed, removed from the glovebox, and allowed to stir at room temperature. After *ca.* 16 h, an aliquot was removed from the reaction mixture under N_2 using Schlenk line technique and analyzed by GC-MS. Ditolyl amine product and *para*-tolyl-iodide was observed. The reaction mixture was poured into a round bottom flask and volatiles were removed under reduced pressure via rotary evaporation. The resulting dark oil was dissolved in a minimum of CH_2Cl_2 and filtered through silica. *para*-Tolyl-iodide was removed from the reaction crude by distillation using a Kugelrohr apparatus. The resulting dark oil was triturated with a minimum of MeOH to afford **69** as a light brown precipitate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (m, 1H,

Ar-*H*), 7.39 (m, 1H, Ar-*H*), 7.30 (m, 1H, Ar-*H*), 7.15 (m, 1H, Ar-*H*), 7.04 (d, 1H, Ar-*H*), 7.01 (m, 8H, tolyl Ar-*H*), 6.75 (d, 1H, Ar-*H*), 3.24 (s, 3H, -OCH_3), 2.29 (s, 6H, -N(Ph-*p*-CH_3)$_2$), 1.32 (s, 9H, -C(CH_3)$_3$). ^{1}H NMR (300 MHz, C_6D_6) δ 7.46 (d, 1H, Ar-*H*), 7.41 (m, 1H, Ar-*H*), 7.33 (m, 1H, Ar-*H*), 7.22 (m, 4H, tolyl Ar-*H*), 7.15 (d, 1H, Ar-*H*), 6.91 (m, 4H, tolyl Ar-*H*), 6.85 (m, 1H, Ar-*H*), 6.68 (m, 1H, Ar-*H*), 3.17 (s, 3H, -OCH_3), 2.06 (s, 6H, -N(Ph-*p*-CH_3)$_2$), 1.41 (s, 9H, -C(CH_3)$_3$).

Synthesis of 1-(2'-diisopropylphosphinophenyl)-4-ditolylamino-5-tert-butyl-6-methoxybenzene (70).



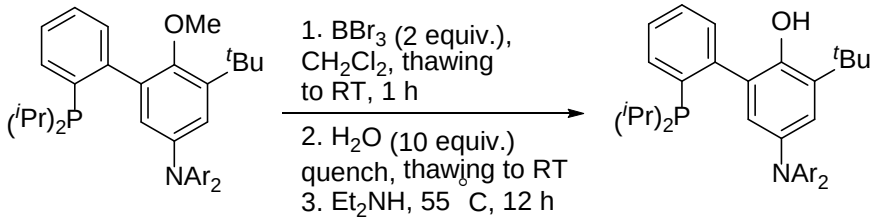
-Ar = -*p*-Tolyl
69

-Ar = -*p*-Tolyl
70

In a glovebox, a 100 mL Schlenk tube was charged with a colorless solution of biphenyl bromide **69** (0.163 g, 0.32 mmol, 1.0 equiv.) in Et_2O (20 mL). The Schlenk tube was removed from the glovebox and cooled to -78 °C in a dry ice/acetone bath. Under N_2, ^{t}BuLi (1.7 M in pentane, 0.66 mmol, 0.40 mL, 2.1 equiv.) was added via syringe to the solution. The resulting yellow-orange mixture was stirred for *ca.* 3 h at -78 °C. After *ca.* 3 h, chlorodiisopropylphosphine (0.053 g, 0.06 mL, 0.35 mmol, 1.1 equiv.) was added to the cold solution slowly via syringe. After addition, the reaction mixture was stirred 1 h at -78 °C. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 12 h. The volatile materials were removed under reduced pressure. In the glovebox, the pale yellow residue was extracted with three portions of pentane (20 mL each) and the combined organic layer

was filtered through Celite. The volatiles were removed from the filtrate under reduced pressure and a red oil was observed. Crude **70** was treated with BBr_3 without further purification in a subsequent deprotection step. ^1H NMR (300 MHz, C_6D_6) δ 7.45 (d, 1H, Ar-*H*), 7.36 (m, 1H, Ar-*H*), 7.30 (m, 1H, Ar-*H*), 7.22 (d, 4H, tolyl Ar-*H*), 7.08 – 7.02 (m, 3H, Ar-*H*), 6.88 (d, 4H, tolyl Ar-*H*), 3.03 (s, 3H, -OC*H*$_3$), 2.03 (s, 6H, -N(Ph-*p*-CH_3)$_2$), 1.78 – 1.56 (m, 2H, -C*H*(CH_3)$_2$), 1.15 – 0.78 (m, 9H, -CH(C*H*$_3$)$_2$, obscured by residual (^{i}Pr)$_2$PCl), 0.71 (m, 3H, -CH(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ -0.09.

Synthesis of 2-(2'-diisopropylphosphinophenyl)-4-ditolylamino-6-tert-butyl-phenol (71).



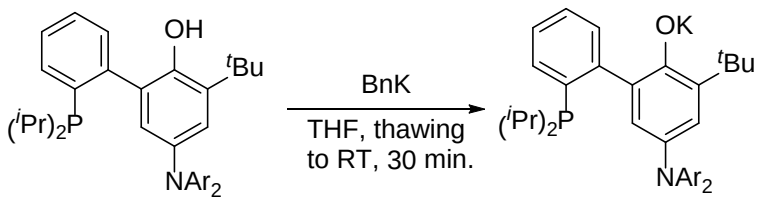
-Ar = -*p*-Tolyl **70**

-Ar = -*p*-Tolyl **71**

In the glovebox, a 20 mL scintillation vial was charged with anisole **70** (0.150 g, 0.27 mmol, 1.0 equiv.), CH_2Cl_2 (4 mL), a stir bar. An orange solution was observed. The solution was frozen in a liquid N_2-chilled cold well. BBr_3 (0.136 g, 0.05 mL, 2.0 BBr_3) was added via syringe to the thawing solution of **70**. The solution was allowed to thaw to room temperature. A dark red solution was observed. The reaction mixture was transferred to a 100 mL Schlenk tube fitted with a Teflon screw cap. The Schlenk tube was sealed and brought into a glovebox containing protic solvents under an N_2 atmosphere. H_2O (0.049 g, 0.05 mL, 2.72 mmol, 10.0 equiv.) was added to the reaction mixture. An exotherm was observed. An additional portion of H_2O (0.049 g,

0.05 mL, 2.72 mmol, 10.0 equiv.) was added. No exotherm was observed. Volatiles were removed under reduced pressure. Volatiles were removed under reduced pressure to afford an orange solvent. Et_2NH (4 mL) was added to the Schlenk tube. The Schlenk tube was sealed, removed from the glovebox, and placed in an oil bath pre-heated to *55* °C for 16 h. The reaction was removed from the oil bath and allowed to cool to room temperature. Volatiles were removed under reduced pressure on the Schlenk line. A yellow oil and white solid were observed. The Schlenk tube was returned to a glovebox containing protic solvents under an N_2 atmosphere. The yellow residue was extracted with 3 portions of pentane (2 mL each). The combined pentane solution was filtered through alumina. Volatiles were removed under reduced pressure to afford phenol **71** (0.099 g, 0.18 mmol, 67.7%). Material of this purity was placed under vacuum with heating on the Schlenk, brought into a drybox under inert atmosphere, and deprotonated without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 1H, Ar-*H*), 7.71 – 7.50 (m, 3H, Ar-*H*), 7.35 (m, 1H, Ar-*H*), 7.25 – 7.10 (m, 2H, Ar-*H*), 6.96 (m, 1H, Ar-*H*), 5.37 (s, 1H, -O*H*), 2.54 (s, 8H, -N(Ph-*p*-C*H*$_3$)$_2$), 2.43 (m, 1H, -C*H*(CH_3)$_2$), 2.16 (m, 1H, -C*H*(CH_3)$_2$), 1.64 (s, 9H, -C(C*H*$_3$)$_3$), 1.42 – 1.20 (m, 6H, -CH(C*H*$_3$)$_2$), 1.18 – 0.99 (m, 6H, -CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 0.81. ^{1}H NMR (300 MHz, C_6D_6) δ 7.52 (d, 1H, Ar-*H*), 7.29 (d, 4H, tolyl Ar-*H*), 7.10 – 6.98 (m, 3H, Ar-*H*), 6.95 (d, 4H, tolyl Ar-*H*), 5.22 (s, 1H, -O*H*), 2.10 (s, 8H, -N(Ph-*p*-C*H*$_3$)$_2$), 1.90 (m, 1H, -C*H*(CH_3)$_2$), 1.75 (m, 1H, -C*H*(CH_3)$_2$), 1.53 (s, 9H, -C(C*H*$_3$)$_3$, 1.03 – 0.84 (m, 9H, -CH(C*H*$_3$)$_2$), 0.72 (m, 2H, -CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ 0.26.

Synthesis of [potassium][2-(2'-diisopropylphosphinophenyl)-4-ditolylamino-6-tert-butyl-phenoxide] (72).



71 **72**

-Ar = -*p*-Tolyl

In the glovebox, a 20 mL scintillation vial was charged with phenol **71** (0.215 g, 0.40 mmol, 1.0 equiv.), THF (2 mL), and a stir bar. A light red solution was observed. A separate 20 mL vial was charged with BnK (0.063 g, 0.48 mmol, 1.2 equiv.) and THF (2 mL). Both solution were frozen in a liquid N_2-chilled cold well. The just-thawed solution of BnK was added dropwise to a thawing solution of phenol **71**. A dark red color was observed upon completion of addition. Volatiles were removed under reduced pressure. Hexanes (2 mL) was added and the resulting dark red residue was titurated. Volatiles were removed under reduced pressure. The resulting residue was extracted with C_6H_6 (3 times, 2 mL). The combined C_6H_6 solution was filtered through Celite and volatiles were removed to afford a red powder which was used for metallation with metal halides without further purification. ^{1}H NMR (300 MHz, C_6D_6) δ 7.46 – 7.36 (m, 4H, Ar-*H*), 7.06 – 6.85 (m, 8H, tolyl Ar-*H*), 1.94 (m, br, 2H, -C*H*$(CH_3)_2$), 1.39 (s, 9H, -C(C*H*$_3)_3$), 1.23 (s, 6H, -N(Ph-*p*-C*H*$_3)_2$), 0.99 – 0.81 (m, 12H, -CH(C*H*$_3)_2$). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6) δ -4.29.

REFERENCES

(1) (a) Gray, H. B.; Williams, R.; Bernal, I.; Billig, E. *J. Am. Chem. Soc.* **1962**, *84*, 3596-3597; (b) Billig, E.; Williams, R.; Bernal, I.; Waters, J. H.; Gray, H. B. *Inorg. Chem.* **1964**, *3*, 663-666.
(2) Yu, R. P.; Darmon, J. M.; Milsmann, C.; Margulieux, G. W.; Stieber, S. C. E.; DeBeer, S.; Chirik, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 13168-13184.
(3) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* **2006**, *128*, 8410-8411.
(4) Lu, C. C.; Bill, E.; Weyhermüller, T.; Bothe, E.; Wieghardt, K. *J. Am. Chem. Soc.* **2008**, *130*, 3181-3197.
(5) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794-795.
(6) (a) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143-7144; (b) J. P. Britovsek, G.; C. Gibson, V.; J. McTavish, S.; A. Solan, G.; J. P. White, A.; J. Williams, D.; J. P. Britovsek, G.; S. Kimberley, B.; J. Maddox, P. *Chem. Commun.* **1998**, 849-850.
(7) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8772-8774.
(8) Stubbe, J.; van der Donk, W. A. *Chem. Rev.* **1998**, *98*, 705-762.
(9) (a) Lin, S.; Herbert, D. E.; Velian, A.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2013**, *135*, 15830-15840; (b) Chao, S. T.; Lara, N. C.; Lin, S.; Day, M. W.; Agapie, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 7529-7532; (c) Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296-6297; (d) Lin, S.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2011**, *133*, 3828-3831; (e) Suseno, S.; Horak, K. T.; Day, M. W.; Agapie, T. *Organometallics* **2013**; (f) Buss, J. A.; Edouard, G. A.; Cheng, C.; Shi, J.; Agapie, T. *J. Am. Chem. Soc.* **2014**, *136*, 11272-11275.
(10) (a) Kelley, P.; Lin, S.; Edouard, G.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 5480-5483; (b) Edouard, G. A.; Kelley, P.; Herbert, D. E.; Agapie, T. *Organometallics* **2015**, *34*, 5254-5277.
(11) (a) McGuinness, D. S. *Chem. Rev.* **2011**, *111*, 2321-2341; (b) Agapie, T. *Coord. Chem. Rev.* **2011**, *255*, 861-880.
(12) Lu, F.; Zarkesh, R. A.; Heyduk, A. F. *Eur. J. Inorg. Chem.* **2012**, *2012*, 467-470.
(13) Mirbach, M. F.; Saus, A.; Krings, A. M.; Mirbach, M. J. *J Organomet Chem* **1981**, *205*, 229-237.
(14) Antonini, S.; Calderazzo, F.; Englert, U.; Grigiotti, E.; Pampaloni, G.; Zanello, P. *J. Organomet. Chem.* **2004**, *689*, 2158-2168.
(15) O'Donnell, T. A.; Phillips, K. A. *Inorg Chem* **1973**, *12*, 1437-1438.
(16) Hynes, R. C.; Preston, K. F.; Springs, J. J.; Tse, J. S.; Williams, A. J. *Journal of the Chemical Society, Faraday Transactions* **1991**, *87*, 3121.
(17) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272-2273.
(18) Cámpora, J.; Reyes, M. L.; Hackl, T.; Monge, A.; Ruiz, C. *Organometallics* **2000**, *19*, 2950-2952.
(19) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712-4718.
(20) Keim, W. *Angew. Chem. Int. Ed.* **2013**, *52*, 12492-12496.
(21) Abbott-Laboratories *U. S. Patent #39135* **2009**, 100.
(22) Xiao, Z.-P.; Wang, Y.-C.; Du, G.-Y.; Wu, J.; Luo, T.; Yi, S.-F. *Synth. Commun.* **2010**, *40*, 661-665.
(23) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

(24) Klet, R. C.; VanderVelde, D. G.; Labinger, J. A.; Bercaw, J. E. *Chem. Commun.* **2012**, *48*, 6657-6659.
(25) Maaranen, J.; Hoikka, J.; Rauotio, S. *U. S. Patent* **2007**, *37939 A1*.
(26) Kaschube, W.; Pörschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525-532.
(27) Greiser, T.; Kopf, J.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1980**, *191*, 1-6.
(28) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.
(29) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877-910.
(30) Albrecht, M.; Schneider, M. *Synthesis* **2000**, *2000*, 1557-1560.
(31) Hodges, J. A.; Raines, R. T. *Org. Lett.* **2006**, *8*, 4695-4697.