Synthesis and Reactivity of Group 9 Complexes Featuring Redox Non-Innocent Ligands

by

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ABSTRACT

Aminoalkyl- and phosphinoalkyl-substituted 2,6-bis(imino)pyridine (or pyridine diimine, PDI) ligands were synthesized with the interest of creating new, redox non-innocent κ^4- and κ^5- (^{L}PDI)M-X complexes. Ligands were first metallated onto rhodium, chosen for its propensity to form diamagnetic complexes. The addition of (^{N}PDI) ligands to $[(COD)RhCl]_2$ (COD = 1,5-cyclooctadiene) resulted in the formation of rhodium monochloride complexes with the general formula (^{N}PDI)RhCl (^{N}PDI = ^{iPr_2NEt}PDI or ^{Me_2NPr}PDI). The investigation of (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl by single crystal X-ray diffraction verified the absence of amine arm coordination and a pseudo square planar geometry about rhodium. Seeking to increase the ligand coordination number, the metallation of ^{P}PDI chelates featuring alkylphosphine imine substituents (^{P}PDI = ^{Ph_2PEt}PDI or ^{Ph_2PPr}PDI) was sought and resulted in the formation of cationic complexes featuring κ^5-*N*,*N*,*N*,*P*,*P*-PDI coordination. Adjusting the metallation stoichiometry allowed the preparation of $[(^{Ph_2PPr}PDI)Rh][(COD)RhCl_2]$, which was characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. An analogous ligand featuring phosphinoalkyl substituents on a redox non-innocent DI scaffold, ^{Ph_2PPr}DI, was then applied to $CoCl_2$ and 2 equiv. $NaEt_3BH$ was added, resulting in the formation of (^{Ph_2PPr}DI)CoH, as characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction. Bond distances within the DI core suggest a mono-reduced ligand coupled to a Co(II) metal center. The (^{Ph_2PPr}DI)CoH complex was then used to catalytically hydroborate alkynes under mild conditions to selectively yield *E*-vinylboronates. The catalytic conditions were optimized and applied to a range of sterically and functionally varied acetylenes.

For:

Abba and Ema

Naama Ben-Daat

David Levin

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Words cannot express how much the love, support, and encouragement of my family has helped me. Todah.

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1.1 Abstract

The addition of aminoalkyl-substituted 2,6-bis(imino)pyridine (or pyridine diimine, PDI) ligands to $[(COD)RhCl]_2$ (COD = 1,5-cyclooctadiene) resulted in the formation of rhodium monochloride complexes with the general formula (^{N}PDI)RhCl (^{N}PDI = ^{iPr_2NEt}PDI or ^{Me_2NPr}PDI). The investigation of (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl by single crystal X-ray diffraction verified the absence of amine arm coordination and a pseudo square planar geometry about rhodium. Replacement of the chloride ligand with an outer-sphere anion was achieved by adding $AgBF_4$ directly to (^{iPr_2NEt}PDI)RhCl to form [(^{iPr_2NEt}PDI)Rh][BF_4]. Alternatively, this complex was prepared upon chelate addition following the salt metathesis reaction between $AgBF_4$ and $[(COD)RhCl]_2$. Using the latter method, both [(^{N}PDI)Rh][BF_4] complexes were isolated and found to exhibit κ^4-*N*,*N*,*N*,*N*-PDI coordination regardless of arm length or steric bulk. In contrast, the metallation of ^{P}PDI chelates featuring alkylphosphine imine substituents (^{P}PDI = ^{Ph_2PEt}PDI or ^{Ph_2PPr}PDI) resulted in the formation of cationic complexes featuring κ^5-*N*,*N*,*N*,*P*,*P*-PDI coordination in all instances, [(^{P}PDI)Rh][X] (X = Cl, BF_4). Adjusting the metallation stoichiometry allowed the preparation of [(^{Ph_2PPr}PDI)Rh][$(COD)RhCl_2$], which was characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction.

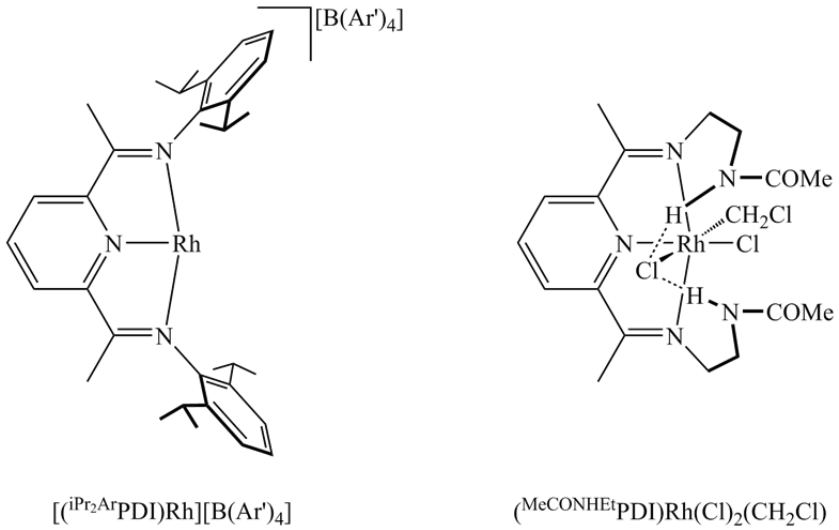
1.2 Introduction

In recent years, 2,6-bis(imino)pyridine (or pyridine diimine, PDI) ligands have become an increasingly utilized ligand class due to their ease of synthesis, [1] steric [2, 3] and electronic modularity, [4, 5, 6] and ability to coordinate to a wide range of transition and alkali metal ions. [7, 8] Furthermore, the capacity of these chelates to accept one or more electrons from a metal center has been well documented [9, 10] and metrics to differentiate varying degrees of PDI reduction have been established. [11] This redox non-innocence has proven invaluable [12, 13, 14] for the advancement of base-metal hydrogenation, [15, 16, 17, 18, 19] hydrosilylation, [2, 20, 21, 22] and cyclization [23, 24, 25, 26, 27] catalysts whose activity rival traditionally employed precious metal complexes. [28] Although impressive, these achievements have overwhelmingly relied on the use of sterically demanding aryl imine substituents (^{Ar}PDI). For example, the initial preparation of an (^{Ar}PDI)Fe hydrogenation catalyst depended on the incorporation of two 2,6-diisopropylphenyl imine substituents [18] whereas preliminary efforts to prepare analogues with less bulky imine substituents resulted in the formation of bis(ligand) complexes rather than catalytically relevant dinitrogen complexes. [29] Although reduction of the respective (^{Ar}PDI)$FeBr_2$ starting complexes using sodium napthalenide instead of sodium amalgam has since afforded highly active hydrogenation catalysts with smaller aryl groups, the success of this approach has remained limited to 2,6-diethylphenyl or 2,6-dimethylphenyl imine substituents. [30] Although alkyl imine PDI substituents have allowed the preparation of asymmetric Co(I) hydrogenation catalysts, [16] their use has not yet enabled the isolation of an (^{R}PDI)Fe (R = alkyl) hydrogenation catalyst.

This laboratory is developing redox non-innocent PDI ligands that are capable of coordinating to a metal center beyond their historically investigated κ^3-*N,N,N*-PDI core, as these chelates would be less susceptible to dissociation (chelate effect) [31] and circumvent the need for steric bulk in catalyst design. While there have been several inspiring examples, [32, 33, 34, 35, 36, 37, 38] relatively little effort has gone into the study of coordination complexes that feature a tetradentate or pentadentate PDI ligand. Although this methodology has the potential to slow catalytic processes by tying up metal coordination sites, it is hypothesized that increasing PDI denticity will enable the preparation of complexes and precatalysts that would otherwise be non-isolable.

Due to its moderate covalent radius (1.42 Å) in relation to other transition metals [39] and propensity to form diamagnetic complexes, rhodium was chosen for the initial investigation into the coordination chemistry of high-denticity PDI chelates. Like the aforementioned base-metal examples, recent (PDI)Rh chemistry has been dominated by the use of bulky aryl imine substituents. [19, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49] Although steric protection has allowed for the isolation of an unusual 14-electron (κ^3-*N,N,N*-PDI)Rh cation (Figure 1, left) following the addition of $NaB(Ar')_4$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] to the respective monochloride complex, [48] the reactivity observed for (^{Ar}PDI)RhCl complexes has remained relatively undistinguished from earlier reports on (^{R}PDI)RhCl complexes bearing non-coordinating alkyl-substituted arms. [50, 51, 52] In one particularly relevant example, a monochloride complex bearing alkylamido imine substituents, (^{MeCONHEt}PDI)RhCl, was found to oxidatively add alkylhalides. [53] Although evidence for amide coordination to the Rh center was not reported for the starting complex, hydrogen bonding between both amide hydrogen atoms

and one chloride ligand in (^{MeCONHEt}PDI)RhCl$_2$(CH$_2$Cl) was observed by single crystal X-ray diffraction shown in Figure 1, right. [53]



[(^{iPr_2Ar}PDI)Rh][B(Ar')$_4$] (^{MeCONHEt}PDI)Rh(Cl)$_2$(CH$_2$Cl)

FIGURE 1.1. Sample of published rhodium complexes featuring PDI ligands. At left, a persistent, three-coordinate cationic Rh complex supported by a sterically demanding PDI ligand. [48] At right, an octahedral (PDI)Rh complex featuring hydrogen bonding interactions between an apical chloride ligand and two amide arms. [53]

Considering the complexes shown in Figure 1.1, it was hypothesized that PDI imine substituents could be fitted with σ-donor atoms and tailored such that they might coordinate to rhodium beyond the ligand's terdentate redox-active core, potentially forcing reduction of the chelate. In this contribution, the approach to this challenge is detailed with the intent that lessons learned regarding PDI imine substituent chain length and the steric considerations of the σ-donor atom might be applied to the coordination chemistry of these chelates throughout the transition metal series.

1.3 Results and Discussion

Hoping to establish the ideal chain length for κ^4- or κ^5-PDI coordination to a rhodium center, this study commenced with the synthesis of ^{L}PDI ligands featuring imine substituents that have an ethyl or propyl bridge to a remote tertiary amine donor. Additionally, to probe the role of sterics in achieving κ^5-*N,N,N,N,N*- rather than κ^4-*N,N,N,N*-PDI chelation, the amine substituents were varied to include either methyl or isopropyl groups. As displayed in Figure 1.2, the condensation of 2,6-diacetylpyridine with 2 equiv. of either *N,N*-diisopropyl-1,2-ethanediamine or *N,N*-dimethyl-1,3-propanediamine allowed the preparation of 2,6-$(((CH_3)_2CH)_2NCH_2CH_2N{=}C(CH_3))_2C_5H_3N$ [^{iPr_2NEt}PDI] and 2,6-$((CH_3)_2N(CH_2)_3N{=}C(CH_3))_2C_5H_3N$ [^{Me_2NPr}PDI], respectively.

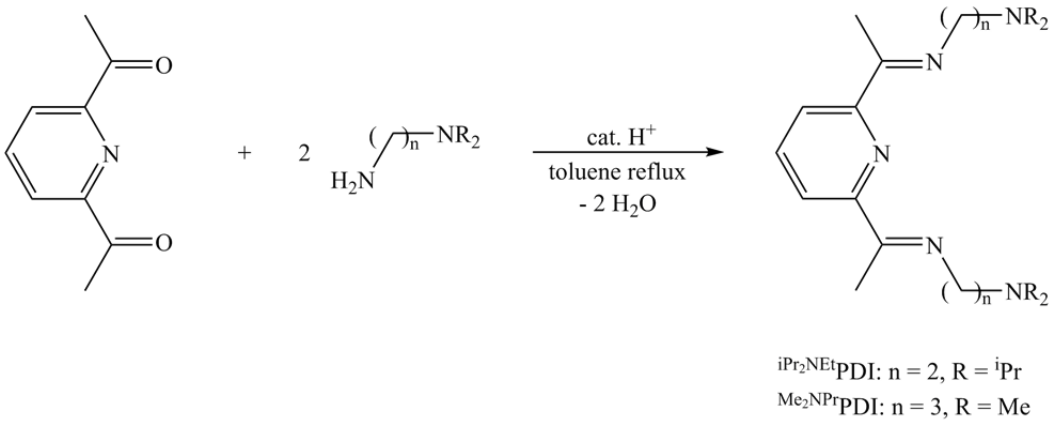


FIGURE 1.2. Preparation of PDI ligands with imine donor substituents.

Since several four-coordinate (PDI)RhCl complexes have been prepared following PDI ligand addition to a commercially available $[(olefin)_2RhCl]_2$ starting material, [40, 41, 43, 44, 46, 49, 51, 53] this approach to metallation was chosen as an entry point for investigating the coordination preferences of the newly prepared chelates.

Although square planar d^8 complexes of this type are energetically opposed to maintaining coordination to a fifth ligand, [28] it was hypothesized that a sufficiently donating imine substituent functionality may allow κ^5-PDI coordination. Additionally, since the redox-active core of PDI ligands is capable of accepting two electrons from a metal center, [11] the possibility of accessing a formally 20-electron (κ^5-PDI)RhCl complex featuring a chelate dianion was considered. Adding either ^{iPr_2NEt}PDI or ^{Me_2NPr}PDI to 0.5 equiv. of $[(COD)RhCl]_2$ in toluene solution at ambient temperature afforded a dark green solution, indicative of 4-coordinate (PDI)RhCl complex formation. [40, 41, 43, 44, 46, 49, 51, 53] After stirring for 24 h, evacuation of the solvent followed by washing of the solid with pentane allowed the isolation of (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl, respectively (Fig 1.3).

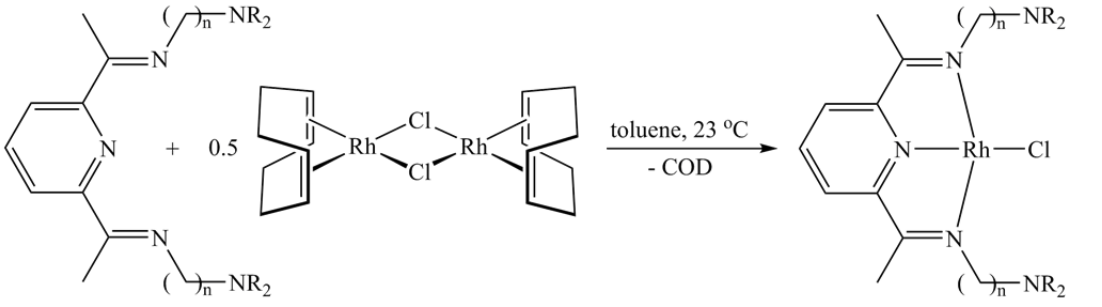


FIGURE 1.3. Preparation of (κ^3-PDI)RhCl complexes.

No evidence for ligand asymmetry resulting from the coordination of one chelate arm was observed by ^{1}H and ^{13}C NMR spectroscopy, further supporting the square planar formulation of these complexes. In the electronic spectrum of (^{iPr_2NEt}PDI)RhCl two

pronounced charge transfer bands were observed at 302 nm (ε = 7200 $M^{-1}cm^{-1}$) and 452 nm (ε = 4800 $M^{-1}cm^{-1}$) that are likely due to backbonding into the PDI chelate.

To verify that the PDI ligand amine arms were indeed non-coordinating, further investigation of the monochloride complexes by single crystal X-ray diffraction was carried out. Single crystals of (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl suitable for X-ray diffraction were grown from a concentrated solution of the complex in toluene/pentane at -35 °C. As expected, solving the solid state structure of (^{iPr_2NEt}PDI)RhCl (Figure 1.4, top) confirmed that the diisopropylaminoethyl arms of the PDI chelate were not coordinated to the rhodium center. However, the lack of coordination by the imine substituents of (^{Me_2NPr}PDI)RhCl (Figure 1.4, bottom) suggests that neither the isopropyl substituents nor the ethylene bridge in (^{iPr_2NEt}PDI)RhCl were responsible for the lack of pendent tertiary amine coordination. The metrical parameters determined for (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl (Table 1.1) indicate that the geometry about the metal is distorted from idealized square planar with an N(1)-Rh(1)-N(3) angle of 159.19(11)° and 159.19(13)º, respectively. As reported for other structurally characterized pseudo square planar (PDI)RhCl complexes, [40, 41, 46, 51] evidence for imine bond elongation is observed in (^{iPr_2NEt}PDI)RhCl with N(1)-C(2) and N(3)-C(8) distances of 1.316(4) Å and 1.303(4) Å, respectively. Shortening of the C_{imine}-$C_{pyridine}$ bonds relative to the distances expected for a neutral chelate [11] is also apparent with C(2)-C(3) and C(7)-C(8) distances of 1.452(5) Å and 1.467(4) Å, respectively. The metrical parameters found for (^{Me_2NPr}PDI)RhCl, including the Rh-N, N_{imine}-C_{imine}, and C_{imine}-$C_{pyridine}$ distances, are analogous to those determined for (^{iPr_2NEt}PDI)RhCl.

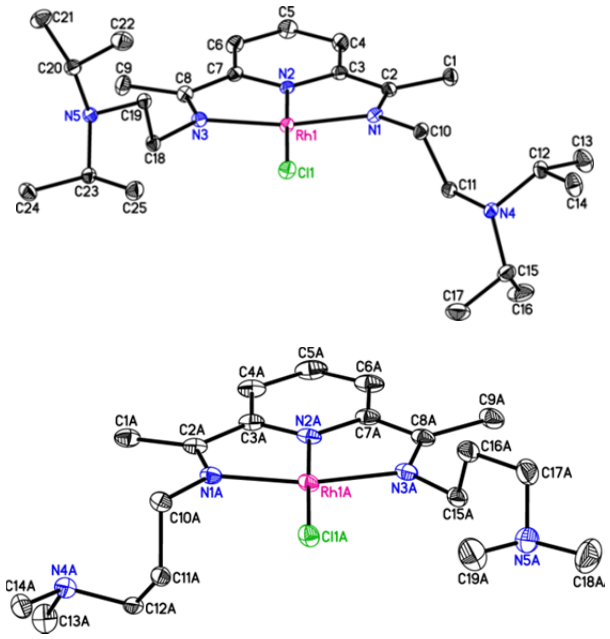


FIGURE 1.4. The solid-state structure of (^{iPr_2NEt}PDI)RhCl (top) and (^{Me_2NPr}PDI)RhCl (bottom) with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

TABLE 1.1. Selected bond lengths (Å) and angles (º) for (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl.

	(^{iPr_2NEt}PDI)RhCl	(^{Me_2NPr}PDI)RhCl
Rh(1)-N(1)	2.030(3)	2.030(3)
Rh(1)-N(2)	1.884(3)	1.889(3)
Rh(1)-N(3)	2.030(3)	2.032(3)
Rh(1)-Cl(1)	2.3476(9)	2.3621(9)
N(1)-C(2)	1.316(4)	1.316(5)
N(3)-C(8)	1.303(4)	1.303(5)
C(2)-C(3)	1.452(5)	1.462(5)
C(7)-C(8)	1.467(4)	1.475(5)
N(1)-Rh(1)-N(2)	79.76(11)	79.27(13)
N(1)-Rh(1)-N(3)	159.19(11)	159.13(12)
N(2)-Rh(1)-N(3)	79.44(11)	79.86(13)
N(2)-Rh(1)-Cl(1)	178.68(8)	176.92(9)

It is important to note that the Rh(1)-N(1), Rh(1)-N(2), and Rh(1)-N(3) distances are shorter than expected for a Rh^I complex (in associated Rh^I (imino)pyridine complexes, Rh-N_{imine} = 2.248(4)-2.283(3) Å; Rh-$N_{pyridine}$ = 2.255(5)-2.267(3) Å) [52] and

are remarkably undistinguished from the same distances reported for related trivalent (PDI)Rh(Cl)$_2$(CH$_2$Cl) complexes. [51]

Although the PDI chelate N_{imine}-C_{imine} and C_{imine}-$C_{pyridine}$ distances determined for both (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl suggest an electronic structure consistent with a PDI radical monoanion [11] that is antiferromagnetically coupled to a Rh(II) metal center, this seemingly bizarre possibility was first discarded for related (^{Ar}PDI)RhX (X = H, Me, Cl) complexes on the basis that they possess relatively normal ^{1}H NMR spectra (minimal shift versus free ligand reference values) when compared to their cobalt congeners. [45] In a more recent report by Burger and co-workers, [40] a comprehensive and thorough investigation into the electronic structure of complexes of the general type (PDI)MX (M = Rh, Ir; X = NCO, N_3, Cl, Me, OMe, OH, NH_2) revealed significant metal-to-ligand backbonding into the symmetric rather than the asymmetric PDI π* orbital, [11] as judged by DFT. For (PDI)IrCl, Mulliken population analysis revealed that the electron density of the HOMO is nearly evenly distributed between the PDI ligand (45%) and the metal center (37%, d_{xz}), with the balance of charge localized on the chloride ligand. [40] Extrapolating this knowledge to the solid state structures of (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl, it is believed that the electronic structure of these complexes is consistent with having significant π-backbonding from a Rh^{I} center into a neutral PDI ligand rather than a Rh^{III} center supported by a PDI dianion. This assessment is supported by the fact that second row transition metals have lower pairing energies and d-orbitals that more efficiently overlap with ligand-based π-orbitals than their first row congeners (due to radial expansion), [54, 55] decreasing the likelihood of populating a

destabilized orbital comprising the antibonding combination of π*-PDI and Rh 4d orbitals.

Since repulsion of the amine donors by the filled d_{z2} orbital of rhodium could prevent coordination of a fifth or sixth ligand, the preparation of formal Rh^{I} complexes featuring an outer-sphere anion was targeted. It was also anticipated that this approach would enable amine-functionalized PDI ligand arm coordination because [(^{iPr_2Ar}PDI)Rh][B(Ar')$_4$] (Figure 1.1, left) is known to bind σ-donors including acetophenone and *p*-tolualdehyde. [48] Four-coordinate complexes of the type [(^{Ar}PDI)Rh(THF)][X] (where the outer-sphere anion X = OTf or Al(OC$_4$F$_9$)$_4$) have also been well-investigated. [40] Adding a slight excess of $AgBF_4$ to a solution of (^{iPr_2NEt}PDI)RhCl in acetone-d_6 allowed the observation of a low-symmetry complex featuring broadened ^{1}H NMR resonances at ambient temperature (Figure 1.5, top, left arrow). Cooling this solution to -20 °C allowed observation of the slow exchange limit and verification of PDI ligand arm inequivalence by ^{1}H and ^{13}C NMR spectroscopy. These observations suggested that the resulting product, [(^{iPr_2NEt}PDI)Rh][BF_4], contains a tetradentate PDI chelate whereby diisopropylaminoethyl ligand arm exchange occurs in solution at ambient temperature. The preparation of [(^{iPr_2NEt}PDI)Rh][BF_4] was also achieved upon adding $AgBF_4$ directly to 0.5 equiv. of [(COD)RhCl]$_2$, [56] followed by the addition of ^{iPr_2NEt}PDI in THF solution (Figure 1.5, top, right arrow).

To determine if the sterically demanding isopropyl substituents in [(^{iPr_2NEt}PDI)Rh][BF_4] play a role in discouraging pentadentate ^{N}PDI coordination, studies involving the related dimethylamino-substituted PDI ligand became warranted.

Expectedly, the addition of ^{Me_2NPr}PDI following the reaction between $AgBF_4$ and 0.5 equiv. of $[(COD)RhCl]_2$ resulted in the preparation of $[(^{Me_2NPr}PDI)Rh][BF_4]$ (Figure 1.5, bottom).

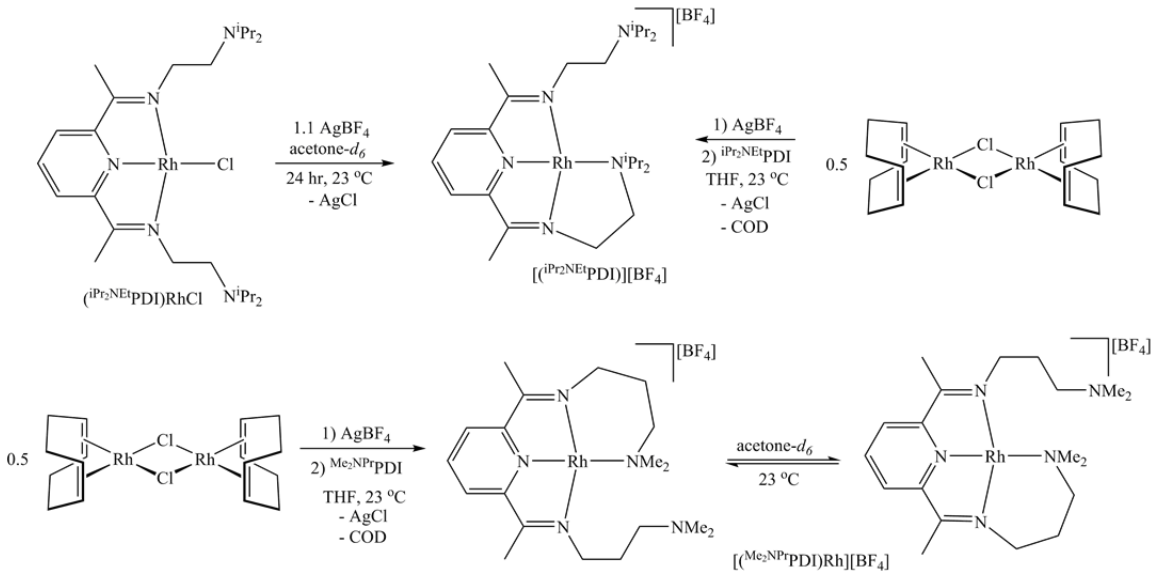


FIGURE 1.5. Preparation of $[(^{iPr_2NEt}PDI)Rh][BF_4]$ (top) and $[(^{Me_2NPr}PDI)Rh][BF_4]$ (bottom).

Surprisingly, the ambient temperature ^{1}H NMR spectrum of $[(^{Me_2NPr}PDI)Rh][BF_4]$ suggested that this complex was C_{2v}-symmetric, as only three methylene arm resonances were detected. Upon closer inspection, it was realized that if persistent κ^5-*N,N,N,N,N*-PDI coordination had been achieved, twice as many chelate arm resonances would be observed. Cooling an acetone-d_6 solution of $[(^{Me_2NPr}PDI)Rh][BF_4]$ to -62 °C resulted in broadening of the imine substituent resonances, and although the slow exchange limit was not reached, it is clear that this complex undergoes chelate arm exchange at a faster rate than $[(^{iPr_2NEt}PDI)Rh][BF_4]$ in solution at ambient temperature. While these spectroscopic observations do not differentiate the roles of imine substituent arm length

and steric bulk in substitution, it appears that functionalized PDI arms featuring either an ethyl- or propyl-bridge are capable of coordinating to a central rhodium atom.

To substantiate these claims, [(^{Me_2NPr}PDI)Rh][BF_4] was recrystallized from an acetone/pentane mixture at -35 °C and single crystals suitable for X-ray diffraction were obtained. As anticipated, the molecular structure determination of [(^{Me_2NPr}PDI)Rh][BF_4] uncovered a κ^4-PDI chelate, with an overall coordination geometry that is best described as pseudo square planar (Figure 1.6).

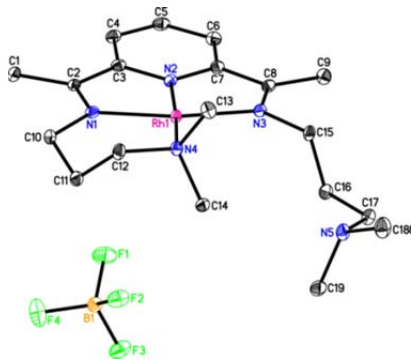


FIGURE 1.6. The solid-state structure of [(^{Me_2NPr}PDI)Rh][BF_4] with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

TABLE 1.2. Selected bond lengths (Å) and angles (º) for [(^{Me_2NPr}PDI)Rh][BF_4].

Rh(1)-N(1)	2.016(2)	N(1)-Rh(1)-N(2)	79.52(9)
Rh(1)-N(2)	1.902(2)	N(1)-Rh(1)-N(3)	157.74(9)
Rh(1)-N(3)	2.084 (2)	N(1)-Rh(1)-N(4)	96.96(9)
Rh(1)-N(4)	2.143(2)	N(2)-Rh(1)-N(3)	78.49(9)
N(1)-C(2)	1.309(3)	N(2)-Rh(1)-N(4)	173.11(9)
N(3)-C(8)	1.305(3)		
C(2)-C(3)	1.460(4)		
C(7)-C(8)	1.475(4)		

The metrical parameters found for this complex (Table 1.2) expose a deviation from linearity between the central rhodium atom and chelate imine nitrogen atoms with an N(1)-Rh(1)-N(3) angle of 157.74(9)°. Although less pronounced, a deviation from

linearity along the pyridine-Rh-amine axis can also be seen with an N(2)-Rh(1)-N(4) angle of 173.11(9)°. Notably, the tertiary amine nitrogen atom is located further from the Rh center than the PDI chelate donors due to its lack of π-acidity. As with (^{iPr_2NEt}PDI)RhCl and (^{Me_2NPr}PDI)RhCl, slightly elongated N_{imine}-C_{imine} distances of 1.309(3) Å and 1.305(3) Å with shortened C_{imine}-$C_{pyridine}$ distances of 1.460(4) Å and 1.475(4) Å are observed in the solid state structure of [(^{Me_2NPr}PDI)Rh][BF_4].

At this stage, it was theorized that replacing the pendent amine donors with stronger σ-donating functionalities might allow for pentadentate PDI ligand coordination to a central rhodium chloride moiety, affording pseudo octahedral (κ^5-PDI)RhCl complexes. Isolating formal 20-electron complexes of this type was of particular interest from the outset of the study, as they would likely feature a Rh^{III} center supported by a true PDI dianion. Keeping in mind that ethyl- ([(^{iPr_2NEt}PDI)Rh][BF_4]) and propyl-bridged ([(^{Me_2NPr}PDI)Rh][BF_4]) amine arms are capable of coordinating to rhodium, bis(imino)pyridine ligands featuring alkylphosphine imine substituents were designed. In contrast to the alkylamine-substituted PDI ligands, the condensation of 2,6-diacetylpyridine with 2 equiv. of either 2-(diphenylphosphino)-1-ethylamine or 3-(diphenylphosphino)-1-propylamine to synthesize $((C_6H_5)_2PCH_2CH_2N{=}C(CH_3))_2C_5H_3N$ [^{Ph_2PEt}PDI] and 2,6-$((C_6H_5)_2PCH_2CH_2\ CH_2N{=}C(CH_3))_2C_5H_3N$ [^{Ph_2PPr}PDI], respectively, was conducted in a thick-walled glass bomb in the presence of 4 Å molecular sieves (Figure 1.7). Following filtration and solvent removal, recrystallization of either ligand from a concentrated ether solution at -35 °C afforded analytically pure yellow crystals as judged by elemental analysis and multinuclear NMR spectroscopy. While ^{Ph_2PPr}PDI

coordination to copper has been explored, [57] the successful isolation of ^{Ph_2PEt}PDI and ^{Ph_2PPr}PDI had not been previously achieved.

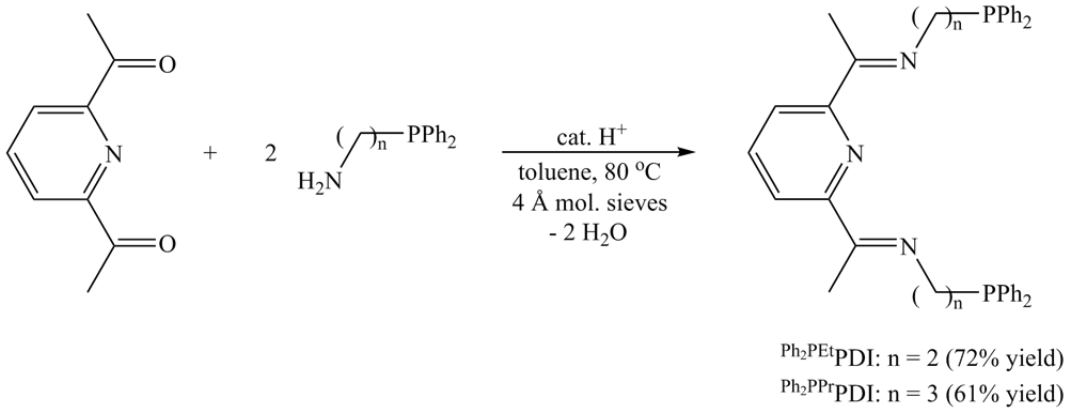


FIGURE 1.7. Preparation of PDI ligands with phosphine donor substituents.

With the desired phosphinoalkyl-substituted PDI chelates in hand, their metalation with rhodium was investigated. Notably, the addition of ^{Ph_2PEt}PDI to 0.5 equiv. of $[(COD)RhCl]_2$ in toluene (Figure 1.8) resulted in an immediate color change from the initial yellow solution to dark purple. As the reaction progressed at ambient temperature, purple precipitate began to form which was collected after stirring for two days. After washing the solid with several pentane fractions to remove any residual COD ligand, analysis of the precipitate by ^{1}H NMR spectroscopy revealed four chelate arm resonances, suggesting that at least one phosphinoethyl arm was coordinated to the rhodium center.

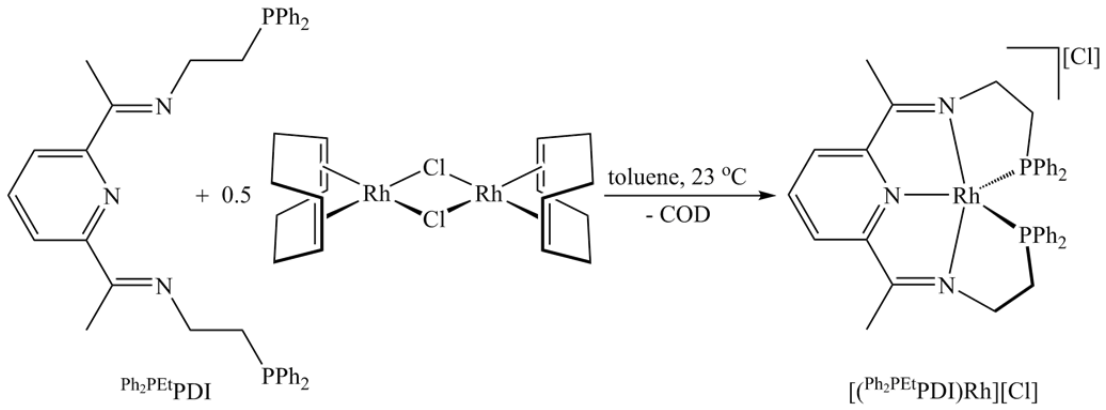


FIGURE 1.8. Preparation of [(^{Ph_2PEt}PDI)Rh][Cl].

Surprisingly, the ^{1}H NMR spectrum of this complex uncovered ^{31}P-coupling to the PDI backbone methyl (t, 6 H) and *p*-pyridine (m, 1 H) resonances in addition to the ethyl-bridged chelate arms, a feature not observed for the free chelates. Close investigation of this complex by ^{13}C NMR spectroscopy revealed only two methylene resonances, confirming that both PDI arms were bound to rhodium. As anticipated, the ^{31}P NMR spectrum of this complex in DMSO-d_6 features only a doublet at 43.64 ppm with J_{RhP} coupling of 135.4 Hz, consistent with κ^5-*N,N,N,P,P*-PDI coordination. Although the composition of this complex was well understood, its relative lack of solubility in a range of solvents initially suggested that the chloride ligand was no longer an inner-sphere ligand, leading to the assignment of this complex as [(^{Ph_2PEt}PDI)Rh][Cl].

Similar to the metallation of ^{Ph_2PEt}PDI, the addition of ^{Ph_2PPr}PDI to 0.5 equiv. of [(COD)RhCl]$_2$ afforded a purple solid identified as [(^{Ph_2PPr}PDI)Rh][Cl] (Figure 1.9, top), as judged by multinuclear NMR spectroscopy. The UV-visible spectrum of [(^{Ph_2PPr}PDI)Rh][Cl] in DMSO solution was notably different than the one collected for (^{Ph_2PEt}PDI)RhCl, with charge transfer bands observed at 317 nm (ε = 12400 $M^{-1}cm^{-1}$), 362

nm ($\varepsilon = 8000\ M^{-1}cm^{-1}$), 530 nm ($\varepsilon = 8800\ M^{-1}cm^{-1}$), and 671 nm ($\varepsilon = 2900\ M^{-1}cm^{-1}$), providing additional evidence of phosphine ligand arm coordination.

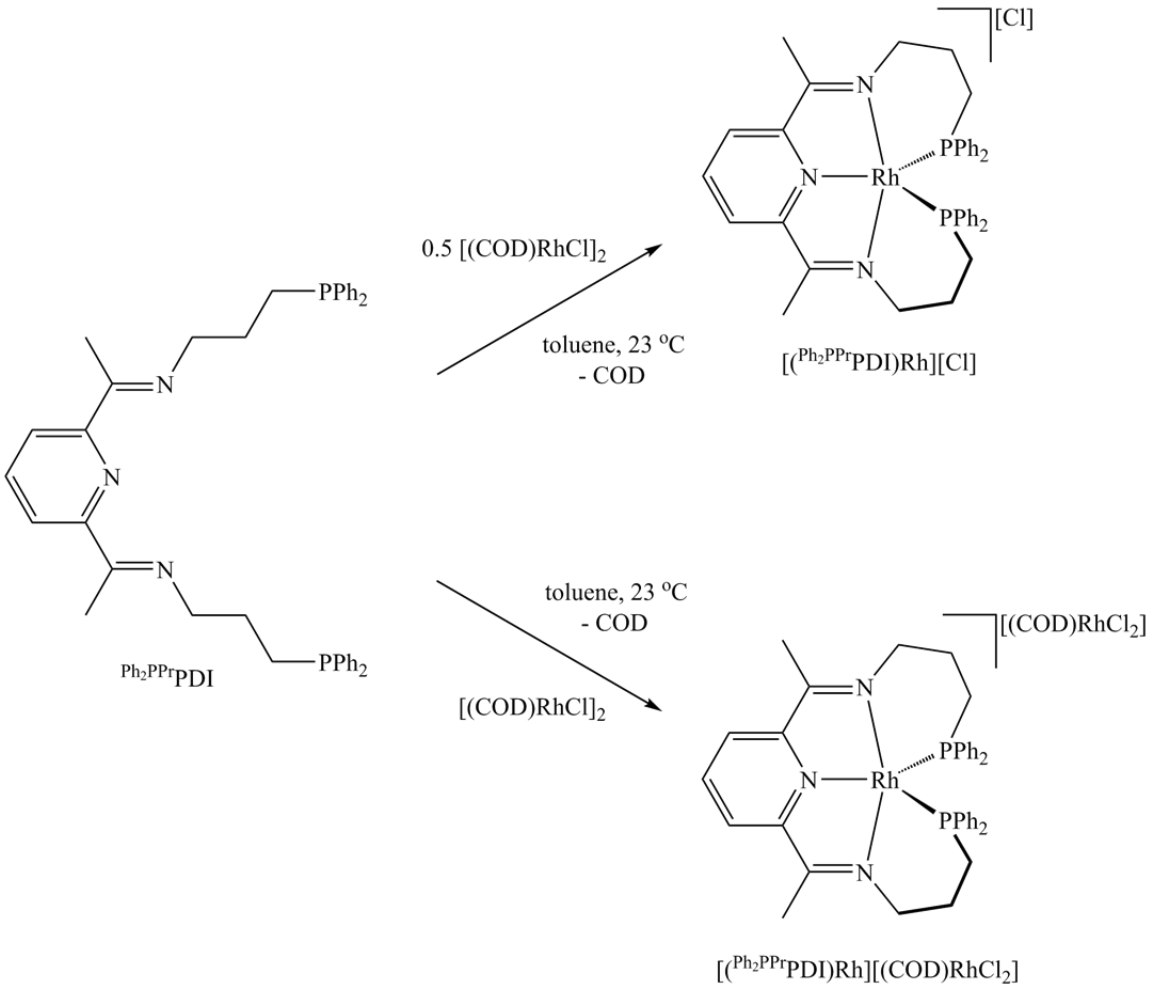


FIGURE 1.9. Preparation of [(^{Ph_2PPr}PDI)Rh][Cl] and [(^{Ph_2PPr}PDI)Rh][(COD)$RhCl_2$].

As neither [(^{Ph_2PEt}PDI)Rh][Cl] nor [(^{Ph_2PPr}PDI)Rh][Cl] were readily soluble in common crystallization solvents such as toluene, tetrahydrofuran, or acetone, related compounds featuring better solubility were desired so that the presence of an outer-sphere anion could be confirmed by single crystal X-ray diffraction. Since it was observed that [(^{Ph_2PPr}PDI)Rh][Cl] appeared soluble in toluene at early reaction times and later

precipitated from solution, the metallation reaction was adjusted such that a stoichiometric amount of ^{Ph_2PPr}PDI was added to $[(COD)RhCl]_2$ (i.e., one molecule of ligand per two rhodium equivalents). While this reaction (Figure 1.9, bottom) also resulted in the formation of a purple precipitate, complete consumption of the $[(COD)RhCl]_2$ starting material had been achieved. Realizing that the stoichiometric addition of a chelating ligand to $[(COD)RhCl]_2$ is well-known to result in the formation of ionic complexes featuring a $[(COD)RhCl_2]$ anion [58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68], the resulting purple precipitate was presumed to be $[(^{Ph_2PPr}PDI)Rh][(COD)RhCl_2]$. This formulation was further supported by elemental analysis and multinuclear NMR spectroscopy.

Fortunately, $[(^{Ph_2PPr}PDI)Rh][(COD)RhCl_2]$ exhibited slightly better solubility than $[(^{Ph_2PPr}PDI)Rh][Cl]$ and single crystals suitable for X-ray diffraction were obtained from the slow evaporation of a THF solution at ambient temperature. Solving the molecular structure of $[(^{Ph_2PPr}PDI)Rh][(COD)RhCl_2]$ (Figure 1.10) confirmed that this complex features κ^5-*N,N,N,P,P*-PDI ligand coordination in addition to an outer-sphere $(COD)RhCl_2$ anion. The overall coordination geometry about the PDI-supported rhodium center is best described as pseudo trigonal bipyramidal, and the relevant metrical parameters for $[(^{Ph_2PPr}PDI)Rh][(COD)RhCl_2]$ are displayed in Table 1.3.

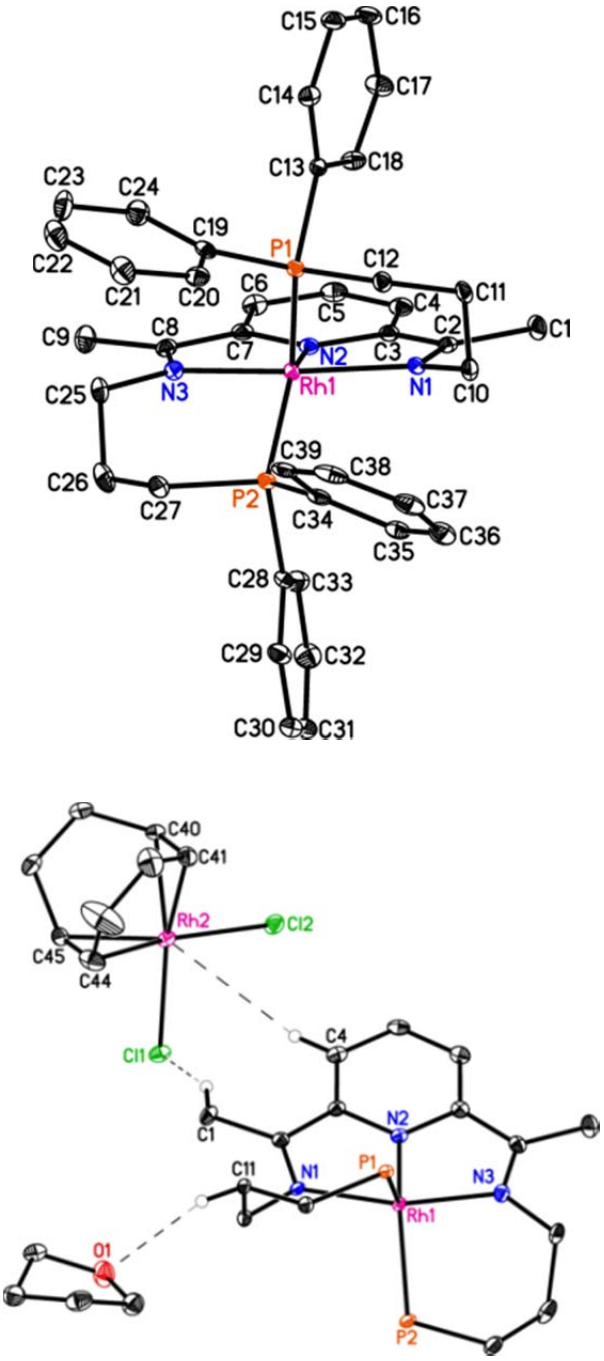


FIGURE 1.10. The solid state structure of [(^{Ph_2PPr}PDI)Rh][(COD)RhCl$_2$] with 30% probability ellipsoids. At top, the [(κ^5-*N*,*N*,*N*,*P*,*P*-^{Ph_2PPr}PDI)Rh] cation shown without hydrogen atoms, co-crystallized tetrahydrofuran molecule, and (COD)RhCl$_2$ anion for clarity. At bottom, the spatial relationship of all three structure components shown with close contacts between PDI chelate hydrogen atoms, the cation, and co-crystallized THF molecule. The latter illustration was prepared using symmetry operators (1-x, 1-y, 1-z) for the cation and THF molecule, and (2-x, 1-y, 1-z) for (COD)RhCl$_2$.

TABLE 1.3. Selected bond lengths (Å) and angles (º) for [(^{Ph_2PPr}PDI)Rh][(COD)RhCl$_2$]

Rh(1)-N(1)	2.029(3)	N(1)-Rh(1)-N(2)	78.95(12)
Rh(1)-N(2)	1.926(3)	N(1)-Rh(1)-N(3)	157.10(12)
Rh(1)-N(3)	2.046(3)	N(1)-Rh(1)-P(1)	88.01(8)
Rh(1)-P(1)	2.2926(9)	N(1)-Rh(1)-P(2)	103.62(9)
Rh(1)-P(2)	2.3101(10)	N(2)-Rh(1)-P(1)	119.79(8)
N(1)-C(2)	1.335(5)	N(2)-Rh(1)-P(2)	141.15(8)
N(3)-C(8)	1.322(5)	P(1)-Rh(1)-P(2)	99.06(3)
C(2)-C(3)	1.427(5)		
C(7)-C(8)	1.435(5)		
Rh(2)-Cl(1)	2.3847(9)	Cl(1)-Rh(2)-Cl(2)	90.56(3)
Rh(2)-Cl(2)	2.3773(10)	C(40)-Rh(2)-C(45)	82.43(16)
Rh(2)-C(40)	2.104(4)	C(41)-Rh(2)-C(44)	81.91(16)
Rh(2)-C(41)	2.100(4)		
Rh(2)-C(44)	2.099(4)		
Rh(2)-C(45)	2.102(4)		
C(40)-C(41)	1.417(6)		
C(44)-C(45)	1.402(6)		

Although the anticipated deviation from linearity between the rhodium center and imine nitrogen donors is observed with an N(1)-Rh(1)-N(3) angle of 157.10(12)°, there are also deviations from trigonal bipyramidal geometry in the equatorial plane with P(1)-Rh(1)-P(2) and N(2)-Rh(1)-P(2) angles of 99.06(3)° and 141.15(8)°, respectively. Relative to the solid state structures of (^{Ph_2PEt}PDI)RhCl, (^{Me_2NPr}PDI)RhCl, and [(^{Me_2NPr}PDI)Rh][BF_4], evidence for increased backbonding into the redox-active core of the PDI is observed with C(2)-C(3) and C(7)-C(8) bond distances of 1.427(5) Å and 1.435(5) Å, respectively, consistent with an increase in electron density upon coordination of two strongly-donating phosphine arms. This feature is less pronounced when considering the N(1)-C(2) and N(3)-C(8) distances of 1.335(5) Å and 1.322(5) Å. However, this observation is not overly surprising since the symmetric π^* orbital on PDI is heavily localized at the C_{imine}-$C_{pyridine}$ bonds. [11] Even though these metrical

parameters are more consistent with a PDI dianion than those determined for the other structures discussed, it remains unlikely that [(^{Ph_2PPr}PDI)Rh][(COD)RhCl$_2$] possesses a true Rh(III) center. [40, 54, 55] The metrical parameters of the (COD)RhCl$_2$ anion (Table 1.3) are unremarkable in the sense that the overall geometry about rhodium is near square planar and backbonding into the COD ligand is responsible for lengthening of the C(40)-C(41) and C(44)-C(45) bonds to 1.417(6) Å and 1.402(6) Å, respectively.

Finally, κ^5-*N,N,N,P,P*-PDI complexes featuring a tetrafluoroborate counterion were prepared in a similar fashion to [(^{Ph_2PEt}PDI)Rh][BF$_4$] and [(^{Me_2NPr}PDI)Rh][BF$_4$]. After filtering the reaction between AgBF$_4$ and 0.5 equiv. of [(COD)RhCl]$_2$, the addition of either ^{Ph_2PEt}PDI or ^{Ph_2PPr}PDI (Figure 1.11) allowed the preparation of purple [(^{Ph_2PEt}PDI)Rh][BF$_4$] or [(^{Ph_2PPr}PDI)Rh][BF$_4$], respectively. Although they feature bands with slightly different λ_{max} values and extinction coefficients, the UV-vis spectra of [(^{Ph_2PPr}PDI)Rh][Cl] and [(^{Ph_2PPr}PDI)Rh][BF$_4$] were found to be relatively indistinguishable. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of [(^{Ph_2PEt}PDI)Rh][BF$_4$] and [(^{Ph_2PPr}PDI)Rh][BF$_4$] were directly comparable to those obtained for [(^{Ph_2PEt}PDI)Rh][Cl] and [(^{Ph_2PPr}PDI)Rh][Cl], respectively, and the ^{1}H{^{31}P} NMR spectrum of both tetrafluoroborate complexes revealed resolved PDI *p*-pyridine (t, 1 H) and backbone methyl (s, 6 H) resonances, confirming the observation of phosphine-derived *J* coupling. Importantly, the synthesis of these complexes directly from [(COD)RhCl]$_2$ further emphasizes the propensity of both ^{Ph_2PEt}PDI and ^{Ph_2PPr}PDI to form pentadentate coordination complexes.

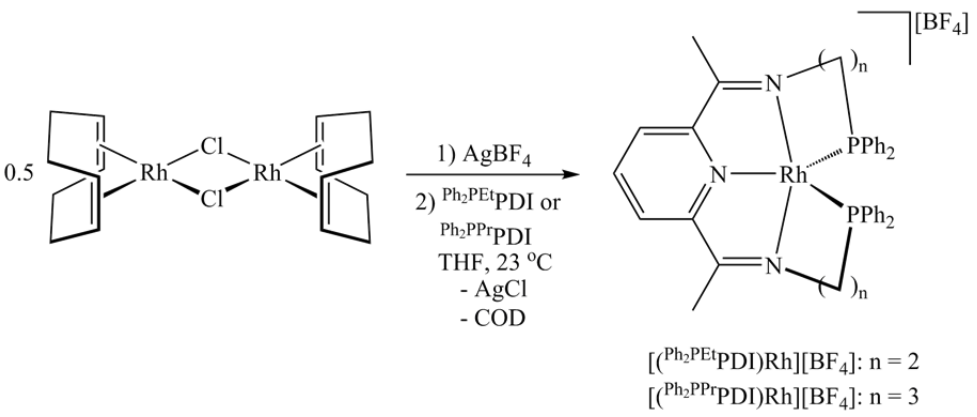


FIGURE 1.11. Preparation of [(^{Ph_2PEt}PDI)Rh][BF_4] and [(^{Ph_2PPr}PDI)Rh][BF_4].

Since ethyl- and propyl-bridged PDI donor arms were found to coordinate to rhodium, and allow for the isolation of complexes featuring either κ^4-*N,N,N,N*- or κ^5-*N,N,N,P,P*-PDI chelation, it is worth discussing the impact this investigation may have when considering ligands of this nature for homogeneous catalytic applications. Since evidence for chelate arm exchange was observed for each amine-bound κ^4-*N,N,N,N*-PDI complex, it is implied that weakly coordinating donor substituents of this type might readily dissociate to allow for a catalytic transformation while offering the potential to stabilize coordinatively unsaturated, high-energy intermediates. On the other hand, although phosphine-substituted PDI ligands such as ^{Ph_2PEt}PDI and ^{Ph_2PPr}PDI might be capable of stabilizing reactive precatalysts or intermediates, it is possible that the inclusion of strong field phosphine donors may completely prevent a targeted transformation from taking place. Fortunately, if pendent chelate arms are desired to improve the characteristics of a given PDI-supported catalyst, the described imine substituents can be modified to contain stronger or weaker donor atoms, longer or shorter bridges to those atoms, and more or less bulky donor substituents with a range of electronic properties.

1.4 Conclusions

The first rhodium complexes featuring either a tetradentate or pentadentate redox-active bis(imino)pyridine ligand have been prepared and characterized using single crystal X-ray diffraction and a range of supporting techniques. Although not observed for neutral monochloride complexes, the coordination of tertiary amine functionalities allowed κ^4-*N,N,N,N*-PDI chelation when rhodium complexes featuring an outer-sphere tetrafluoroborate anion were prepared. In contrast, the metallation of ^{P}PDI ligands onto $[(COD)RhCl]_2$ forced the chloride ligand to leave the rhodium coordination sphere, forming complexes featuring a pentadentate PDI ligand and either a $[Cl]^-$ or $[(COD)RhCl_2]^-$ counter ion. Knowing that the range of second generation PDI ligands described in this study are capable of κ^4- and κ^5-coordination to a metal center, it is believed that this approach to expanding redox-active ligand complexity may prove worthwhile for the optimization of current transition metal catalysts and inspire the development of new ones.

1.5 Experimental

General Considerations: All synthetic reactions were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Aldrich or Acros anhydrous solvents were purged with nitrogen and stored in the glovebox over activated 4Å molecular sieves and sodium before use. Benzene-d_6, acetone-d_6, and dimethylsulfoxide-d_6 were purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves prior to use. $[(COD)RhCl]_2$ was purchased from Acros and used as received, while $AgBF_4$, 2-(diphenylphosphino)-1-ethylamine, 3-(diphenylphosphino)-1-propylamine and were

used as received from Strem. 2,6-Diacetylpyridine, *p*-toluenesulfonic acid, *N*,*N*-diisopropylethylenediamine, *N*,*N*-dimethyl-1,3-propanediamine, *N*,*N*-dimethyl-1,2-ethanediamine, *N*,*N*,2,2-tetramethyl-1,3-propanediamine were purchased from TCI America. All of the gases used in this study were obtained from Praxair.

Solution ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a Varian 400 MHz or Bruker 400 MHz NMR spectrometer. All ^{1}H and ^{13}C NMR chemical shifts (ppm) are reported relative to $SiMe_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR data (ppm) is reported relative to H_3PO_4. Elemental analyses were performed at either Robertson Microlit Laboratories Inc. (Ledgewood, NJ) or on a PerkinElmer 2400 Series elemental analyzer at the Goldwater Environmental Laboratory (Arizona State University). All UV-Vis spectra were collected on a PerkinElmer Lambda 18 Spectrometer with a two-beam liquid cell. The spectrometer utilized both deuterium and halogen lamps with a change-over frequency at 300 nm.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and transferred to a glass fiber or mitogen mount with either Apiezon N grease or paraffin oil. They were then mounted on the goniometer head of a Bruker APEX (Arizona State University) or APEX II diffractometer (University of Arizona) equipped with Mo K_α radiation. Either a full sphere ((^{Ph_2PEt}PDI)RhCl, (^{Me_2NPr}PDI)RhCl and [(^{Me_2NPr}PDI)Rh][BF_4]) or hemisphere ([(^{Ph_2PPr}PDI)Rh][(COD)$RhCl_2$]) routine was used for data collection and determination of the lattice constants. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved by direct methods (SHELXS),

completed by subsequent Fourier synthesis, and refined by full-matrix, least-squares procedures on $|F|^2$ (SHELXL). The solid-state structure of (^{Me_2NPr}PDI)RhCl was found to contain two complexes in the asymmetric unit that have stacked PDI chelates approximately 3.6 Å apart; however, they are significantly offset and rotated from one another. The molecular structure of [(^{Ph_2PPr}PDI)Rh][(COD)-RhCl2] was found to have disorder at two COD methylene positions that could not be further refined.

Preparation of 2,6-(((CH$_3$)$_2$CH)$_2$NCH$_2$CH$_2$N=C(CH$_3$))$_2$C$_5$H$_3$N (^{iPr_2NEt}PDI): A 250 mL round-bottomed flask was charged with 2,6-diacetylpyridine (1.001 g, 6.14 mmol), *N,N*-diisopropylethylenediamine (1.764 g, 12.23 mmol), *p*-toluenesulfonic acid (0.010 g, 0.058 mmol) and toluene (approx. 100 mL). The initial pale yellow solution was fitted with a Dean-Stark trap and reflux condenser and was set to reflux for 18 h. Over this time, the solution became deeper yellow in color and a small amount of water was observed in the trap. Upon cooling to ambient temperature, pentane (approx. 50 mL) was added and the resulting solution was placed at 12 ˚C for 24 h. The solution was filtered through Celite to remove the residual *p*-toluenesulfonic acid and the solvent was removed *in vacuo* to yield 1.884 g (4.533 mmol, 74%) of a yellowish-orange oil identified as ^{iPr_2NEt}PDI. Analysis for $C_{25}H_{45}N_5$ (415.66): Calc. C, 72.24; H, 10.91; N, 16.85. Found: C, 72.24; H, 10.98; N, 16.58. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.41 (d, 7.8 Hz, 2H, *m-pyr*), 7.30 (t, 7.8 Hz, 1H, *p-pyr*), 3.63 (t, 7.1 Hz, 4H, NCH_2), 2.99 (m, 8H, NCH_2 and NCH(CH$_3$)$_2$), 2.37 (s, 6H, N=CCH_3), 1.03 (d, 6.7 Hz, 24H, NCH(CH_3)$_2$). ^{13}C{^{1}H}NMR (C_6D_6, 125 MHz): δ 165.42 (N=*C*), 156.25 (*o-pyr*), 135.88 (*p-pyr*), 120.85 (*m-pyr*), 55.18 (N*C*H$_2$), 48.84 (N*C*H$_2$), 46.15 (N*C*H(CH$_3$)$_2$), 20.82 (NCH(*C*H$_3$)$_2$), 13.16 (N=C*C*H$_3$).

Preparation of 2,6-$((CH_3)_2NCH_2CH_2CH_2N=C(CH_3))_2C_5H_3N$ (^{Me_2NPr}PDI): A 250-mL round-bottomed flask was charged with 2,6-diacetylepyridine (0.500 g, 3.07 mmol), *N*,*N*-dimethyl-1,3-propanediamine (0.642 g, 6.28 mmol), *p*-toluenesulfonic acid (0.006 g, 0.034 mmol) and toluene (approx.. 100 mL). The solution was initially pale yellow in color and the reaction was set to reflux for 34 h with a Dean-Stark trap. Over this time, the color deepened to a yellowish-orange. The reaction was cooled to room temperature, at which time pentane (50 mL) was added and the flask was placed at 12 ˚C for 25 h. The solution was then filtered through Celite and the solvent was removed *in vacuo* to yield 0.452 g (1.364 mmol, 44%) of a brown oil identified as ^{Me_2NPr}PDI. Analysis for $C_{19}H_{33}N_5$ (331.50): Calcd C, 68.84; H, 10.03; N, 21.13. Found: C, 68.89; H, 9.85; N, 21.10. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.37 (d, 7.8 Hz, 2H, *m-pyr*), 7.27 (t, 7.8 Hz, 1H, *p-pyr*), 3.50 (t, 7 Hz, 4H, NCH_2), 2.41 (t, 7 Hz, 4H, NCH_2), 2.32 (s, 4H, N=CCH_3), 2.16 (s, 12H, N(CH_3)$_2$), 2.00 (pseudo quint., 7 Hz, 6H, CH_2CH_2). ^{13}C{^{1}H}NMR (C_6D_6, 125 MHz): δ 165.92 (N=*C*), 156.59 (*o-pyr*), 136.32 (*p-pyr*), 121.32 (*m-pyr*), 58.06 (N*C*H$_2$), 50.55 (N*C*H$_2$), 45.74 (CH_2CH_2), 29.69 (N(*C*H$_3$)$_2$), 13.41 (N=C*C*H$_3$).

Preparation of (^{iPr_2NEt}PDI)RhCl: Under N_2 atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.050 g, 0.101 mmol), ^{iPr_2NEt}PDI (0.101 g, 0.243 mmol), and toluene (10 mL). The solution immediately adopted a green color and became dark-green after approximately 15 minutes. The solution was set to stir for 36 h at which time the toluene was removed under vacuum. The resulting product was washed with a small amount of pentane to remove any excess free ligand and dried *in vacuo* to yield 0.197 g (0.356 mmol, 98%) of a dark-green microcrystalline solid identified as (^{iPr_2NEt}PDI)RhCl. Further purification of the complex was achieved following recrystallization from a

toluene/pentane solution. Analysis for $C_{25}H_{45}N_5ClRh$ (554.02): Calcd C, 54.20; H, 8.19; N, 12.64. Found: C, 55.00; H, 9.02; N, 12.22. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.75 (t, 8 Hz, 1H, *p-pyr*), 6.69 (d, 8 Hz, 2H, *m-pyr*), 4.38 (t, 6 Hz, 4H, NCH_2), 3.38 (t, 6 Hz, 4H, NCH_2), 2.96 (sept, 6.7 Hz, 4H, NCH(CH_3)$_2$), 1.45 (s, 6H, N=CCH_3), 0.94 (d, 6.7 Hz, 24H, NCH(CH_3)$_2$). ^{13}C{^{1}H}NMR (C_6D_6, 125 MHz): δ 165.15 (N=*C*), 157.02 (*o-pyr*), 123.38 (*m-pyr*), 122.38 (*p-pyr*), 57.93 (N*C*H$_2$), 49.28 (N*C*H(CH_3)$_2$), 46.68 (N*C*H$_2$), 21.6 (NCH(*C*H$_3$)$_2$), 15.68 (N=C*C*H$_3$). UV-vis (toluene): λ_{max} (nm) = 302 (ε = 7200 M^{-1} cm^{-1}), 452 (ε = 4800 M^{-1} cm^{-1}), 581 (ε = 1400 M^{-1} cm^{-1}), 647 (ε = 1000 M^{-1} cm^{-1}), 764 (ε = 580 M^{-1} cm^{-1}).

Preparation of (^{Me_2NPr}PDI)RhCl: Under N_2 atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.052 g, 0.105 mmol), ^{Me_2NPr}PDI (0.0746 g, 0.2250 mmol), and toluene (approx. 10 mL). The solution began turning green instantly, and was dark green in color after approximately 30 minutes. After stirring for 72 h, the solvent was removed *in vacuo* and the resulting solid was washed with a small amount of pentane to remove free ligand. After drying, 0.082 g (0.175 mmol, 84%) of a dark-green microcrystalline solid identified as (^{Me_2NPr}PDI)RhCl was obtained. Analysis for $C_{19}H_{33}N_5RhCl$ (469.86): Calcd C, 48.57; H, 7.08; N, 14.91. Found: C, 48.26; H, 7.17; N, 11.98. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.8 (t, 7.8 Hz, 1H, *p-pyr*), 6.63 (d, 7.8 Hz, 2H, *m-pyr*), 4.46 (t, 7 Hz, 4H, NCH_2), 2.42 (pseudo quint. 6.5 Hz, 4H, CH_2CH_2), 2.31 (t, 6.5 Hz, 4H, NCH_2), 2.08 (s, 12H, NCH_3), 1.30 (s, 6H, N=CCH_3). ^{13}C{^{1}H}NMR (C_6D_6, 125 MHz): δ 164.82 (N=*C*), 156.83 (*o-pyr*), 122.45 (*m-pyr*), 121.26 (*p-pyr*), 56.66 (N*C*H$_2$), 53.89 (N*C*H$_2$), 45.10 (N*C*H$_3$), 28.34 (NCH$_2$*C*H$_2$), 13.89 (N=C*C*H$_3$).

Preparation of [(^{iPr_2NEt}PDI)Rh][BF_4]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.050 g, 0.102 mmol), and $AgBF_4$ (0.045 g, 0.230 mmol) suspended in THF (5 mL). The suspension was stirred in the dark for 1 h, resulting in the precipitation of a light beige solid (AgCl), which was removed by filtration leaving a pale yellow solution. A THF solution (3 mL) of ^{iPr_2NEt}PDI (0.099 g, 0.238 mmol) was then added. The solution instantly darkened in color. The reaction was allowed to stir for 48 h, at which point the solvent was removed *in vacuo*. The product was washed with pentane (5 mL), yielding 0.111 g (0.183 mmol, 90%) of a dark brown microcrystalline solid identified as [(^{iPr_2NEt}PDI)Rh][BF_4] upon drying. Analysis for $C_{25}H_{45}N_5BF_4Rh$ (605.37): Calcd C, 49.60; H, 7.49; N, 11.57. Found: C, 49.82; H, 7.18; N, 10.88. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 8.32 (t, 8 Hz, 1H, *p-pyr*), 7.99 (br. s, 2H, *m-pyr*), 7.57 (br. s, 2 H, *m-pyr*), 4.38 (br. s, 4H, NCH_2), 4.10 (br. s, 4H, NCH_2), 3.69 (br. s, 2H, NCH_2), 3.58 (br. s, 2H, NCH(CH_3)$_2$), 3.15 (br. s, 2H, NCH(CH_3)$_2$), 3.01 (br. s, 4H, NCH_2), 2.63 (br. s, 3H, N=CCH_3), 1.77 (br. s, 3H, N=CCH_3), 1.40 (br. s, 6.7 Hz, 24H, NCH(CH_3)$_2$), 1.02 (br. s, 6.7 Hz, 24H, NCH(CH_3)$_2$). ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, -20 ˚C): δ 8.35 (t, 12 Hz, 1H, *p-pyr*), 8.04 (d, 7.9 Hz, 1H, *m-pyr*), 7.61 (d, 7.9 Hz, 1H, *m-pyr*), 4.40 (br. t, 5.9Hz, 2H, NCH_2), 4.09 (t, 5.9 Hz, 2H, NCH_2), 3.71 (t, 6.6 Hz, 2H, NCH_2), 3.57 (sept, 6.5 Hz, 2H, NCH(CH_3)$_2$), 3.15 (sept, 6.5 Hz, 2H, NCH(CH_3)$_2$), 2.98 (t, 5.8 Hz, 2H, NCH_2), 2.66 (s, 3H, N=CCH_3), 1.79 (s, 3H, N=CCH_3), 1.42 (d, 6.5 Hz, 6H, NCH(CH_3)$_2$), 1.39 (d, 6.5 Hz, 6H, NCH(CH_3)$_2$), 1.00 (d, 6.5 Hz, 12H, NCH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$, 125 MHz, -20 ˚C): δ 173.52 (N=*C*), 161.82 (N=*C*), 157.53 (*o-pyr*), 156.68 (*o-pyr*), 130.46 (*p-pyr*), 124.56 (m-*pyr*), 122.47 (m-*pyr*), 57.33 (N*C*H_2),

55.97 (N*C*H_2), 52.99 (N*C*H_2), 47.72 (N*C*H_2), 44.72 (N*C*H_2), 3.62 (N*C*H(CH_3)$_2$), 20.31 (NCH(*C*H_3)$_2$), 18.80 (NCH(*C*H_3)$_2$), 15.95 (N=C*C*H_3), 14.87 (N=C*C*H_3).

Preparation of [(^{Me_2NPr}PDI)Rh][BF_4]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.100 g, 0.203 mmol), and $AgBF_4$ (0.087 g, 0.446 mmol) suspended in THF (5 mL). The suspension was stirred in the dark for 1 h, resulting in the precipitation of a light beige solid (AgCl) which was removed by filtration. To the resulting pale yellow solution, a THF solution (3 mL) containing ^{Me_2NPr}PDI (0.135 g, 0.407 mmol) was added. The solution instantly darkened in color. The reaction was stirred for 24 h, at which point the solvent was removed *in vacuo*. The product was washed with 5 mL pentane, then dried to yield 0.174 g (0.334 mmol, 82%) of a dark brown microcrystalline solid identified as [(^{Me_2NPr}PDI)Rh][BF_4]. Analysis for $C_{19}H_{33}N_5BF_4Rh$ (521.21): Calcd C, 43.78; H, 6.38; N, 13.44. Found: C, 43.43; H, 6.63; N, 11.96. ^{1}H NMR ((CD_3)$_2$CO, 400 MHz): δ 8.07 (t, 8 Hz, 1H, *p-pyr*), 7.59 (d, 8Hz, 2H, *m-pyr*), 3.77 (t, 7 Hz, 4H, NC*H*$_2$), 2.54 (t, 5.7 Hz, 4H, NC*H*$_2$), 2.34 (s, 12H, N(C*H*$_3$)$_2$), 2.08 (s, 6H, N=CC*H*$_3$), 1.94 (quint, 6.3 Hz, 4 H, CH_2C*H*$_2$). ^{13}C{^{1}H} NMR (((CD_3)$_2$CO, 125 MHz): δ 169.63 (N=*C*), 130.29 (*m-pyr*), 123.56 (*p-pyr*), 60.78 (N*C*H_2), 54.19 (N*C*H_2), 47.42 (N*C*H_3), 23.13 (NCH$_2$*C*H_2), 15.02 (N=C*C*H_3), one resonance not located.

Preparation of 2,6-((C_6H_5)$_2$PCH_2CH_2N=C(CH_3))$_2$$C_5H_3N$ (^{Ph_2PEt}PDI): Under inert atmosphere, a 250-mL thick-walled glass bomb was charged with 2,6-diacetylpyridine (0.407 g, 2.494 mmol), 2-(diphenylphosphino)-1-ethylamine (1.120 g, 4.887 mmol), *p*-toluenesulfonic acid (0.010 g, 0.060 mmol), toluene (10 mL), and 4Å molecular sieves (approx. 10 cm^3). The initial pale yellow solution was set to stir at 80 ˚C for 24 h. After cooling to ambient temperature, the bomb was transferred to a glovebox where the

resulting solution was filtered through Celite with excess ethyl ether. The solvent was then removed *in vacuo* to yield a yellow oil. The oil was dissolved in ethyl ether (approx. 2 mL) and the resulting solution was placed in the glovebox freezer at -35 ˚C. After a 24 h, a light yellow crystalline solid had precipitated. Decanting the mother liquor and subsequent drying allowed the isolation of 1.098 g (1.875 mmol, 72 %) of a crystalline yellow solid identified as ^{Ph_2PEt}PDI. Analysis for $C_{39}H_{41}N_3P_2$ (585.67): Calcd C, 75.88; H, 6.73; N, 6.85. Found C, 75.85; H, 6.92; N, 6.74. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, 7.8 Hz, 2H, *m-pyr*), 7.62 (t, 7.8 Hz, 1H, *p-pyr*), 7.49 (t, 6 Hz, 8H, *o-phenyl*), 7.33 (m, 12H, *m-phenyl*, *p-phenyl*), 3.68 (pseudo quart, 7.4 Hz, 4H, PCH_2), 2.56 (t, 8 Hz, 4H, NCH_2), 2.29 (s, 6H, N=CCH_3). ^{1}H NMR ((C_6D_6, 400 MHz): δ 8.27 (d, 7.8 Hz, 2H, *m-pyr*), 7.52 (t, 7.6 Hz, 8H, *o-phenyl*), 7.25 (t, 7.8 Hz, 1H, *p-pyr*), 7.08 (m, 12H, *m-phenyl*, *p-phenyl*), 3.65 (pseudo quart, 7.2 Hz, 4H, PCH_2), 2.58 (t, 7.6 Hz, 4H, NCH_2), 2.12 (s, 6 H, N=CCH_3).). ^{13}C{^{1}H} NMR ((((C_6D_6, 125 MHz): δ 165.72 (N=*C*), 155.87 (*o-pyr*), 139.49 (d, J_{CP} = 14.2 Hz, *phenyl*), 135.85 (*p-pyr*), 132.85 (d, J_{CP} = 19.5 Hz, *phenyl*), 128.32 (d, J_{CP} = 6.7 Hz, *phenyl*), 128.23 (*phenyl*), 121.19 (*m-pyr*), 49.48 (d, J_{CP} = 20.2 Hz, P*C*H_2), 30.35 (d, J_{CP} = 12.7 Hz, N*C*H_2), 22.31 (N=C), 12.93 (CH_2*C*H_2). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -16.50 (*P*Ph_2). ^{31}P{^{1}H} NMR ((C_6D_6, 162 MHz): δ -16.52 (*P*Ph_2).

Preparation of 2,6-((C_6H_5)$_2$P $CH_2CH_2CH_2N$=C(CH_3))$_2C_5H_3N$ (^{Ph_2PPr}PDI): Under inert atmosphere, a 250-mL schlenk tube was charged with 2,6-diacetylpyridine (0.400 g, 2.451 mmol), 3-(diphenylphosphino)-1-propylamine (1.195 g, 4.912 mmol), *p*-toluenesulfonic acid (0.010 g, 0.060 mmol), toluene (10 mL) , and 4 Å molecular sieves (approx. 10 cm^3). The initial solution was pale yellow in color and was set to stir at 80 ˚C

for 24 h. After cooling to ambient temperature, the bomb was transferred to a glovebox where the resulting solution was filtered through Celite with excess ethyl ether. The solvent was removed *in vacuo,* resulting in the isolation of a yellow oil. The oil was dissolved in ethyl ether (2 mL) and placed in a -35 ˚C freezer. Light yellow crystals were collected after decanting the mother liquor. After drying, 0.918 g (1.496 mmol, 61%) of crystalline yellow ^{Ph_2PPr}PDI was obtained. Analysis for $C_{37}H_{37}N_3P_2$ (613.72): Calcd C, 75.88; H, 6.37; N, 7.18. Found C, 75.80; H, 6.11; N, 7.22. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, 7.8 Hz, 2H, *m-pyr*), 7.71 (t, 7.8 Hz, 1H, *p-pyr*), 7.46 (m, 8H, *o-phenyl*), 7.32 (m, 12H, *m-phenyl*, *p-phenyl*), 3.61 (pseudo quart, 7 Hz, 4H, PCH_2), 2.37 (s, 6H, N=CCH_3), 2.23 (m, 4H, NCH_2), 1.93 (pseudo quint., 7 Hz, 4H, CH_2CH_2). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.32 (d, 8 Hz, 2H, *m-pyr*), 7.53 (t, 6.8 Hz, 8H, *o-phenyl*), 7.24 (t, 8 Hz, 1H, *p-pyr*), 7.09 (m, 12H, *m-phenyl*, *p-phenyl*), 3.38 (pseudo quart, 6.7 Hz, 4H, PCH_2), 2.26 (m, 10H, NCH_2, N=CCH_3), 2.04 (pseudo quint., 6.8 Hz, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.08 (N=*C*), 156.23 (*o-pyr*), 139.04 (d, J_{CP} = 12.7 Hz, *phenyl*), 136.64 (*p-pyr*), 132.92 (d, J_{CP} = 18.7 Hz, *phenyl*), 128.69 (*phenyl*), 128.55 (*phenyl*), 121.14 (*m-pyr*), 53.35 (d, J_{CP} = 13.5 Hz, *C*H_2), 27.51 (d, J_{CP} = 15.7 Hz, $CH_2CH_2CH_2$) 26.17 (d, J_{CP} = 11.2 Hz, *C*H_2), 14.01 (N=C*C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ -18.50 (*P*Ph_2). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ -18.70 (*P*Ph_2).

Preparation of [(^{Ph_2PEt}PDI)Rh][Cl]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.051 g, 0.103 mmol), ^{Ph_2PEt}PDI (0.134 g, 0.229 mmol), and toluene (approx. 10 mL). The solution turned purple almost instantly and continued to darken in color. The reaction was allowed to stir for 48 h, at which time the toluene was removed under vacuum. The resulting solid was washed with a small amount of

pentane to remove any residual free ligand to yield 0.126 g (0.174 mmol, 84%) of a purple microcrystalline solid identified as [(^{Ph_2PEt}PDI)Rh][Cl]. Analysis for $C_{37}H_{37}N_3P_2RhCl$ (724.03): Calcd C, 61.38; H, 5.15; N, 5.80. Found: C, 61.55; H, 5.52; N, 5.86. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.34 (d, 7.6 Hz, 2H, *m-pyr*), 7.69 (br. s, 1H, *p-pyr*), 7.45 (t, 6.8 Hz, 2H, *phenyl*), 7.30 (t, 6.7 Hz, 4H, *phenyl*), 7.18 (t, 7.2 Hz, 2H, *phenyl*), 7.06 (pseudo quart, 8H, *phenyl*), 6.51 (m, 4H, *phenyl*), 4.49 (br. s, 2H, NCH_2), 3.89 (br. t, 7.6 Hz, 2H, PCH_2), 2.82 (br. s, 2H, NCH_2), 2.65 (t, 6.8 Hz, 6H, N=CCH_3), 1.76 (br. s, 2H, PCH_2). ^{13}C{^{1}H} NMR ($(CD_3)_2SO$, 125 MHz): δ 160.24 (N=*C*), 147.12 (*o-pyr*), 135.42 (*i-phenyl*), 132.10 (*phenyl*), 131.08 (*phenyl*), 130.52 (*phenyl*), 130.20 (*phenyl*), 129.22 (*phenyl*), 128.74 (*phenyl*), 125.03 (*m-pyr*), 51.88 (N*C*H$_2$), 25.54 (P*C*H$_2$), 15.82 (N=C*C*H$_3$), one resonance not located. ^{31}P{^{1}H} NMR ($(CD_3)_2SO$, 162 MHz): δ 43.64 (d, J_{PRh} = 135.42 Hz, *P*Ph$_2$).

Preparation of [(^{Ph_2PPr}PDI)Rh][Cl]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.201 g, 0.408 mmol), ^{Ph_2PPr}PDI (0.498 g, 0.812 mmol), and toluene (approx. 10 mL). The resulting solution turned purple almost instantly and continued to darken while stirring at ambient temperature for 48 h. The toluene was removed *in vacuo* and the product was washed with a small amount of pentane to remove any residual free ligand. After drying, 0.475 g (0.632 mmol, 78%) of a purple microcrystalline solid identified [(^{Ph_2PPr}PDI)Rh][Cl] was collected. Analysis for $C_{39}H_{41}N_3P_2RhCl$ (752.08): Calcd C, 62.28; H, 5.50; N, 5.59. Found C, 62.87; H, 5.69; N, 5.57. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.57 (d, 8.0 Hz, 2H, *m-pyr*), 7.83 (m, 1H, *p-pyr*), 7.60 (m, 6H, *phenyl*), 7.15 (m, 6H, *phenyl*), 6.97 (t, 7.6 Hz, 4H, *phenyl*), 6.27 (br.t, 8.4 Hz, 4H, *phenyl*), 4.47 (br. d, 2H, NCH_2), 3.41 (t, 12 Hz, 2H, PCH_2), 2.69 (t, 11.3 Hz, 6H,

N=CCH_3), 2.29 (br. s, 6.3 Hz, 2H, NCH_2), 1.97 (br. s, 2H, CH_2CH_2), 1.71 (t, 12 Hz, 2H, PCH_2), 1.17 (br. t, 2H, CH_2CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125 MHz): δ 160.73 (N=*C*), 145.80 (*o-pyr*), 135.63 (t, J_{CP} = 17.95 *i-phenyl*), 132.73 (*phenyl*), 131.25 (*phenyl*), 130.50 (*phenyl*), 130.23 (*phenyl*), 129.38 (*phenyl*), 128.71 (*phenyl*), 128.60 (*phenyl*), 125.52 (*m-pyr*), 120.05 (*p-pyr*), 55.51 (N*C*H_2), 27.47 (CH_2CH_2), 23.54 (P*C*H_2), 15.44 (N=C*C*H_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$, 162 MHz): δ 32.88 (d, J_{PRh} = 138.47 Hz, *P*Ph_2).

Preparation of [(^{Ph_2PPr}PDI)Rh][(COD)RhCl$_2$]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.060 g, 0.122 mmol), ^{Ph_2PPr}PDI (0.075 g, 0.122 mmol), and acetone (approx. 10 mL) . The resulting solution turned purple upon addition of reagents and was stirred at ambient temperature for 24 h. The acetone was removed in vacuo and the product was washed with 10 mL pentane to remove free COD. After drying, 0.067 g (0.067 mmol, 55%) of a dark purple microcrystalline solid identified [(^{Ph_2PPr}PDI)Rh] [(COD)RhCl$_2$] was collected. Analysis for $C_{47}H_{53}N_3P_2Rh_2Cl_2$ (998.62): Calcd C, 56.53; H, 5.35; N, 4.21. Found C, 56.59; H, 5.63; N, 4.21. ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.57 (d, 7.6 Hz, 2H, *m-pyr*), 7.82 (t, 4.3 Hz, 1H, *p-pyr*), 7.60 (m, 7.0 Hz, 6H, *phenyl*), 7.15 (m, 6H, *phenyl*), 6.97 (t, 7.8 Hz, 4H, *phenyl*), 6.27 (br. t, 4H, *phenyl*), 4.46 (br d, 2H, NCH_2), 4.33 (s, 4H, COD), 3.41 (t, 11.2 Hz, 2H, PCH_2), 2.69 (t, 5.9 Hz, 6H, N=CCH_3), 2.37 (br. s, 6H, COD), 2.29 (br. s, 2H, NCH_2), 2.08 (br. s, 2H, CH_2CH_2), 1.70 (m, 2H, PCH_2), 1.16 (br. s, 2H, CH_2CH_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125 MHz): δ 160.71 (N=*C*), 145.77 (*o-pyr*), 135.71 (*i-phenyl*), 132.73 (*phenyl*), 131.25 (*phenyl*), 130.51 (*phenyl*), 130.23 (*phenyl*), 129.39 (*phenyl*), 128.66 (*phenyl*), 125.53 (*m-pyr*), 120.05 (*p-pyr*), 84.99 (COD), 55.50 (N*C*H_2), 30.75 (COD), 27.46 (CH_2CH_2), 23.54

(PCH_2), 15.45 (N=C*C*H_3), one resonance not located. $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$, 162 MHz): δ 31.63 (d, J_{PRh} = 138.48 Hz, *P*Ph_2).

Preparation of [(^{Ph_2PEt}PDI)Rh][BF_4]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.023 g, 0.046 mmol) and $AgBF_4$ (0.020 g, 0.105 mmol) suspended in 4 mL of THF. The suspension was stirred in the dark for 1 h, resulting in the precipitation of a light beige solid (AgCl) which was removed by filtration. To the resulting pale yellow solution, a THF solution (3 mL) containing ^{Ph_2PEt}PDI (0.054 g, 0.092 mmol) was added. The solution instantly darkened in color. The reaction was stirred for 24 h, at which point the solvent was removed *in vacuo*. The product was washed with pentane (5 mL) then dried to yield 0.048 g (0.062 mmol, 68%) of a blue/purple microcrystalline solid identified as [(^{Ph_2PEt}PDI)Rh][BF_4]. Analysis for $C_{37}H_{37}N_3P_2BF_4Rh$ (775.37): Calcd C, 57.31; H, 4.81; N, 5.42. Found: C, 57.54; H, 5.20; N, 5.27. (OR: Found: C, 56.59; H, 5.44; N, 5.049.) ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.54 (d, 7.8 Hz, 2H, *m-pyr*), 7.90 (br. s, 1H, *p-pyr*), 7.66 (t, 6.3 Hz, 2H, *phenyl*), 7.51 (t, 7.0 Hz, 4H, *phenyl*), 7.39 (t, 7.2 Hz, 2H, *phenyl*), 7.26 (pseudo quart, 8H, *phenyl*), 6.72 (pseudo quart, 3.7Hz, 4H, *phenyl*), 4.70 (br. s, 2H, NCH_2), 4.10 (br. t, 6.7 Hz, 2H, PCH_2), 3.43 (br. s, 2H, NCH_2), 3.01 (pseudo d, 7.0 Hz, 2H, PCH_2), 2.85 (t, 6.8 Hz, 6H, N=CCH_3). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 125 MHz): δ 160.24 (N=*C*), 147.13 (*o-pyr*), 135.42 (t, J_{CP} = 17.2, *i-phenyl*), 132.11 (*phenyl*), 131.09 (*phenyl*), 130.52 (*phenyl*), 130.22 (*phenyl*), 129.27 (*phenyl*), 128.76 (*phenyl*), 125.08 (*m-pyr*), 125.15 (*p-pyr*), 51.87 (N*C*H_2), 35.51 (t, J_{CP} = 16.4, P*C*H_2), 15.82 (N=C*C*H_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$, 162 MHz): δ 42.42 (d, J_{PRh} = 135.42 Hz, *P*Ph_2).

Preparation of [(^{Ph_2PPr}PDI)Rh][BF_4]: Under N_2 atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.040g, 0.081mmol), and $AgBF_4$ (0.035 g, 0.178 mmol) suspended in THF (5 mL). The suspension was stirred in the dark for 1 h, resulting in the precipitation of a light beige solid (AgCl) which was removed by filtration. To the resulting pale yellow solution, a THF solution (3 mL) containing ^{Ph_2PPr}PDI (0.100 g, 0.162 mmol) was added. The solution instantly darkened in color. The reaction was stirred for 24 h, at which point the solvent was removed *in vacuo*. The product was washed with 5 mL pentane then dried to yield 0.103 g (0.128 mmol, 79%) of a purple microcrystalline solid identified as [(^{Ph_2PPr}PDI)Rh]BF_4]. Analysis for $C_{39}H_{41}N_3P_2BF_4Rh$ (803.43): Calcd C, 58.30; H, 5.14; N, 5.23. Found: C, 58.04; H, 5.25; N, 5.07. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.57 (d, 7.6 Hz, 2H, *m-pyr*), 7.83 (br. s, 1H, *p-pyr*), 7.60 (pseudo quart, 7.0 Hz, 6H, *phenyl*), 7.15 (br. s, 6H, *phenyl*), 6.97 (t, 7.2 Hz, 4H, *phenyl*), 6.28 (br. t, 4H, *phenyl*), 4.47 (pseudo d, 10 Hz, 2H, NCH_2), 3.42 (t, 10.8 Hz, 2H, PCH_2), 2.69 (t, 5.5 Hz, 6H, N=CCH_3), 2.29 (br. s, 2H, NCH_2), 1.99 (br. s, 2H, CH_2CH_2), 1.71 (m, 2H, PCH_2), 1.17 (br. s, 2H, CH_2CH_2). ^{13}C{^{1}H} NMR ($(CD_3)_2SO$, 125 MHz): δ 160.73 (N=*C*), 145.79 (*o-pyr*), 135.71 (t, J_{CP} = 18.0 Hz, *i-phenyl*), 132.73 (t, J_{CP} = 6.0 Hz, *phenyl*), 131.25 (*phenyl*), 130.51 (*phenyl*), 130.23 (*phenyl*), 129.39 (*phenyl*), 128.66 (t, J_{CP} = 4.5, *phenyl*), 125.53 (*m-pyr*), 120.05 (*p-pyr*), 55.51 (NCH_2), 27.48 (CH_2CH_2), 23.55 (t, J_{CP} = 11.2, PCH_2), 15.43 (N=CCH_3). ^{31}P{^{1}H} NMR ($(CD_3)_2SO$, 162 MHz): δ 31.64 (d, J_{PRh} = 138.09 Hz, *P*Ph_2).

1.6 References

[1] Bianchini, C., Giambastiani, G., Rios, I. G., Mantovani, G., Meli, A., Segarra, A. M., *Coord. Chem. Rev*. 2006, *250*, 1391-1418, and references therein.

[2] Tondreau, A. M., Atienza, C. C. H., Darmon, J. M., Milsmann, C., Hoyt, H. M., Weller, K. J., Nye, S. A., Lewis, K. M., Boyer, J., Delis, J. G. P., Lobkovsky, E., Chirik, P. J., *Organometallics* 2012, *31*, 4886-4893.

[3] Cámpora, J., Cartes, M. Á., Rodríguez-Delgado, A., Naz, A. M., Palma, P., Pérez, C. M., *Inorg. Chem*. 2009, *48*, 3679-3691.

[4] Darmon, J. M., Turner, Z. R., Lobkovsky, E., Chirik, P. J., *Organometallics* 2012, *31*, 2275-2285.

[5] Smit, T. M., Tomov, A. K., Britovsek, G. J. P., Gibson, V. C., White, A. J. P., Williams, D. J., *Catal. Sci. Technol*. 2012, *2*, 643-655.

[6] Araujo, C. M., Doherty, M. D., Konezny, S. J., Luca, O. R., Usyatinsky, A., Grade, H., Lobkovsky, E., Soloveichik, G. L., Crabtree, R. H., Batista, V. S., *Dalton Trans*. 2012, *41*, 3562-3573.

[7] Gibson, V. C., Redshaw, C., Solan, G. A., *Chem. Rev*. 2007, *107*, 1745-1776.

[8] Blackmore, I. J., Gibson, V. C., Hitchcock, P. B., Rees, C. W., Williams, D. J., White, A. J. P., *J. Am. Chem. Soc*. 2005, *127*, 6012-6020.

[9] Caulton, K. G., *Eur. J. Inorg. Chem*. 2012, *3*, 435-443, and references therein.

[10] de Bruin, B., Bill, E., Bothe, E., Weyhermüller, T., Wieghardt, K., *Inorg. Chem*. 2000, *39*, 2936-2947.

[11] Knijnenburg, Q., Gambarotta, S., Budzelaar, P. H. M., *Dalton Trans*. 2006, *46*, 5442-5448.

[12] Lyaskovskyy, V., de Bruin, B., *ACS Catal*. 2012, *2*, 270-279.

[13] Praneeth, V. K. K., Ringenberg, M. R., Ward, T. R., *Angew. Chem. Int. Ed*. 2012, *51*, 2-9.

[14] Chirik, P. J., Wieghardt, K., *Science* 2010, *327*, 794-795.

[15] Yu, R. P., Darmon, J. M., Hoyt, H. M., Margulieux, G. W., Turner, Z. R., Chirik, P. J., *ACS Catal*. 2012, *2*, 1760-1768.

[16] Monfette, S., Turner, Z. R., Semproni, S. P., Chirik, P. J., *J. Am. Chem. Soc*. 2012, *134*, 4561-4564.

[17] Trovitch, R. J., Lobkovsky, E., Bill, E., Chirik, P. J., *Organometallics* 2008, *27*, 1470-1478.

[18] Bart, S. C., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2004, *126*, 13794-13807.

[19] Knijnenburg, Q., Horton, A. D., van der Heijden, H., Kooistra, T. M., Hetterscheid, D. G. H., Smits, J. M. M., de Bruin, B., Budzelaar, P. H. M., Gal, A. W., *J. Mol. Catal. A*: *Chem*. 2005, *232*, 151-159.

[20] Atienza, C. C. H., Tondreau, A. M., Weller, K. J., Lewis, K. M., Cruse, R. W., Nye, S. A., Boyer, J. L., Delis, J. G. P., Chirik, P. J., *ACS Catal*. 2012, *2*, 2169-2172.

[21] Tondreau, A. M., Atienza, C. C. H., Weller, K. J., Nye, S. A., Lewis, K. M., Delis, J. G. P., Chirik, P. J., *Science*, 2012, *335*, 567-570.

[22] Tondreau, A. M., Lobkovsky, E., Chirik, P. J., *Org. Lett*. 2008, *10*, 2789-2792.

[23] Karpiniec, S. S., McGuinness, D. S., Britovsek, G. J. P., Patel, J., *Organometallics* 2012, *31*, 3439-3442.

[24] Russell, S. K., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2011, *133*, 8858-8861.

[25] Sylvester, K. T., Chirik, P. J., *J. Am. Chem. Soc*. 2009, *131*, 8772-8774.

[26] Takeuchi, D., Matsuura, R., Park, S., Osakada, K., *J. Am. Chem. Soc*. 2007, *129*, 7002-7003.

[27] Bouwkamp, M. W., Bowman, A. C., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2006, *128*, 13340-13341.

[28] Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., *Principals and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987.

[29] Wile, B. M., Trovitch, R. J., Bart, S. C., Tondreau, A. M., Lobkovsky, E. , Milsmann, C., Bill, E., Wieghardt, K., Chirik, P. J., *Inorg. Chem*. 2009, *48*, 4190-4200.

[30] Russell, S. K., Darmon, J. M., Lobkovsky, E., Chirik, P. J., *Inorg. Chem*. 2012, *49*, 2782-2792.

[31] Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: Hoboken, NJ, 2005.

[32] Khanmohammadi, H., Amani, S., Lang, H., Rueeffer, T., *Inorg. Chim. Acta* 2007, *360*, 579-587.

[33] Adams, H., Bailey, N. A., Debaecker, N., Fenton, D. E., Kanda, W., Latour, J.-M., Okawa, H., Sakiyama, H., *Angew. Chem. Int. Ed.* 1995, *34*, 2535-2537.

[34] Adams, H., Bailey, N. A., Dwyer, M. J. S., Fenton, D. E., Hellier, P. C., Hempstead, P. D., Latour, J.-M., *J. Chem. Soc., Dalton Trans*. 1993, *8*, 1207-1216.

[35] Wagnon, B. K., Jackels, S. C., *Inorg. Chem*. 1989, *28*, 1923-1927.

[36] Keypour, H., Rezaeivala, M., Valencia, L., Perez-Lourido, P., *Polyhedron* 2008, *27*, 3172-3176.

[37] Adams, H., Bailey, N. A., Carlisle, W. D., Fenton, D. E., Rossi, G., *J. Chem. Soc., Dalton Trans*. 1990, *4*, 1271-1283.

[38] Cabral, J. de O., Cabral, M. F., Drew, M. G. B., Nelson, S. M., Rodgers, A., *Inorg. Chim. Acta* 1977, *25*, L77-L79.

[39] Cordero, B., Gómez, V., Platero-Prats, A. E., Revés, M., Echeverría, J., Cremades, E., Barragán, F., Alvarez, S., *Dalton Trans*. 2008, *21*, 2832-2838.

[40] Sieh, D., Schlimm, M., Andernach, L., Angersbach, F., Nückel, S., Schöffel, J., Šušnjar, N., Burger, P., *Eur. J. Inorg. Chem*. 2012, *3*, 444-462.

[41] Sieh, D., Schöffel, J., Burger, P., *Dalton Trans*. 2011, *40*, 9512.

[42] Schöffel, J., Šušnjar, N., Nückel, S., Sieh, D., Burger, P., *Eur. J. Inorg. Chem*. 2010, 4911-4915.

[43] Buil, M. L., Esteruelas, M. A., Niembro, S., Olivan, M., Orzechowski, L., Pelayo, C., Vallibera, A., *Organometallics* 2010, *29*, 4375-4383.

[44] Kooistra, T. M., Hetterscheid, D. G. H., Schwartz, E., Knijnenburg, Q., Budzelaar, P. H. M., Gal, A. W., *Inorg. Chim. Acta* 2004, *357*, 2945-2952.

[45] Knijnenburg, Q., Hetterscheid, D. G. H., Kooistra, T. M., Budzelaar, P. H. M., *Eur. J. Inorg. Chem*. 2004, *6*, 1204-1211.

[46] Nückel, S., Burger, P., *Organometallics*, 2001, *20*, 4345-4359.

[47] Dias, E. L., Brookhart, M., White, P. S., *J. Am. Chem. Soc*. 2001, *123*, 2442-2443.

[48] Dias, E. L., Brookhart, M., White, P. S., *Chem. Commun*. 2001, *5*, 423-424.

[49] Dias, E. L., Brookhart, M., White, P. S., *Organometallics* 2000, *19*, 4995-5004.

[50] Haarman, H. F., Bregman, F. R., van Leeuwen, P. W. N. M., Vrieze, K., *Organometallics* 1997, *16*, 979-985.

[51] Haarman, H. F., Ernsting, J-M., Kranenburg, M., Kooijman, H., Veldman, N., Spek, A. L., van Leeuwen, P. W. N. M., Vrieze, K., *Organometallics* 1997, *16*, 887-900.

[52] Haarman, H. F., Bregman, F. R., Ernsting, J.-M., Veldman, N., Spek, A. L., Vrieze, K., *Organometallics* 1997, *16*, 54-67.

[53] Burkill, H. A., Vilar, R., White, A. J. P., *Inorg. Chim. Acta* 2006, *359*, 3709-3722.

[54] Huheey, J. E., Inorganic Chemistry: Principles of Structure and Reactivity, 3rd ed., Harper & Row, New York, 1983, pp. 368-458.

[55] Burdett, J. K., *Chemical Bonds: A Dialog*; John Wiley & Sons: Chichester, England, 1997, pp. 33-39 and pp. 54-66.

[56] Feller, M., Diskin-Posner, Y., Shimon, L. J. W., Ben-Ari, E., Milstein, D., *Organometallics* 2012, *31*, 4083-4101.

[57] Lockemeyer, R., *Synthesis and Reactivity of Heterobinuclear Metal Complexes*. Ph.D. Dissertation, University of Delaware, 1987.

[58] Tejel, C., del Río, M. P., Asensio, L., van den Bruele, F. J., Ciriano, M. A., Tsichlis i Spithas, N., Hetterscheid, D. G. H., de Bruin, B., *Inorg. Chem*. 2011, *50*, 7524-7534.

[59] Bantu, B., Wurst, K., Buchmeiser, M. R., *J. Organomet. Chem*. 2007, *692*, 5272-5278.

[60] Martínez, A. P., Garcia, M. P., Lahoz, F. J., Oro, L. A., *Inorg. Chim. Acta* 2003, *347*, 86-98.

[61] Esquius, G., Pons, J., Yáñez, R., Ros, J., *J. Organomet. Chem*. 2001, *619*, 14-23.

[62] Bikrani, M., Garralda, M. A., Ibarlucea, L., Pinilla, E., *J. Organomet. Chem*. 1995, *489*, 93-99.

[63] Imhoff, P., Elsevier, C. J., *J. Organomet. Chem*. 1989, *361*, C61-C65.

[64] Estruelas, M. A., Oro, L. A., Apreda, M. C., Foces-Foces, C., Cano, F. H., Claramunt, R. M., Lopez, C., Elguero, J., Begtrup, M., *J. Organomet. Chem*. 1988, *344*, 93-108.

[65] Crociani, B., Di Bianca, F., Paci, M., Boschi, T., *Inorg. Chim. Acta*. 1988, *145*, 253-265.

[66] Fernandez, M. J., Del Val, J. J., Oro, L. A., Palacios, F., Barluenga, J., *Polyhedron* 1987, *6*, 1999-2002.

[67] Garralda, M. A., Ibarlucea, L., *J. Organomet. Chem*. 1986, *311*, 225-231.

[68] Vasapollo, G., Sacco, A., Nobile, C. F., Pellinghelli, M. A., Lanfranchi, M., *J. Organomet. Chem*. 1986, *312*, 249-262.

CHAPTER 2 – A κ^4-DIAZADIENE COBALT(I) HYDRIDE CATALYST FOR ALKYNE AND NITRILE HYDROBORATION

2.1 Abstract

Reductive elimination and oxidative addition reactions are key processes in the industrial preparation of chemicals. Initially noble metal catalysts, that are stable to redox changes, were developed to mediate these 2-electron reaction pathways. However, as precious metals are expensive and toxic; there is great interest in developing catalysts with inexpensive and less toxic base metals. While base metal complexes may not be tolerant of redox changes without decomposition, redox-active ligands are known to stabilize the metal center in its preferred oxidation state throughout a catalytic transformation. Herein a flexible, redox-active diimine ligand scaffold featuring diphenylphosphinopropyl imine substituents, ^{Ph_2PPr}DI, was applied to cobalt. A dichloride precatalyst was synthesized and reduced to the corresponding hydride complex which has been isolated and characterized. ^{1}H NMR spectroscopy shows a diamagnetic complex with a hydride peak at -19.80 ppm which is split into a doublet of doublets by two different phosphine environments. Single crystal X-ray diffraction reveals the expected distorted trigonal bipyramidal structure. Although the complex possesses a formal Co(I) oxidation state, bond distances within the DI core suggest a mono-reduced ligand coupled to a Co(II) metal center. The (^{Ph_2PPr}DI)CoH complex was then used to catalytically hydroborate alkynes under mild conditions to selectively yield *E*-vinylboronates. The catalytic conditions were optimized and applied to a range of sterically and functionally varied acetylenes.

2.2 Introduction

Despite the cost and toxicity of precious metals [1] they have remained popular due to their stability during two-electron processes crucial to catalytic reaction pathways such as oxidative addition and reductive elimination. To find utility, base metal catalysts need to overcome one-electron redox changes that can limit catalytic efficiency or cause irreversible catalyst decomposition. However, utilization of redox non-innocent ligands such as pyridine diimine (PDI) and diimine (DI) can 'confer nobility' on 1st row transition metal centers. [2] Redox-active ligands on base metals stabilize radical-transferred precursors and intermediates that participate in novel synthetic pathways. Cobalt is inexpensive and non-toxic, compared to its second and third row congeners, and has been applied in several catalytic applications including hydrogenation, [3] olefin polymerization, [4] cycloaddition, [5] and the hydrosilylation of alkenes, [1] alkynes, [1] and ketones. [6]

Another synthetic transformation that researchers have been attempting is the hydroboration of unsaturated carbon-carbon and carbon-heteroatom multiple bonds. [7] Catalysts active for these reactions are shown in Figure 2.1. Gunanathan *et al.* [8] and Obligacion *et al*. [9] developed catalysts which yield *cis*-vinylborolanes utilizing (PNP)RuH_2(H_2) and (^{Ar}PDI)CoCH_3. While the Ru catalyst was found to operate at very low catalyst loading, the reaction required 24 h to reach completion. In contrast, Obligacion *et al*. achieved complete conversion for most substrates in 6 h at ambient temperature by using a 3 mol% catalyst loading. Pereira and Srebnik [10] and Plikhta *et al.* [11] developed catalytic systems for *trans*-vinylborolanes utilizing zirconium and

rhodium metal centers at 0.2 mol% and 2 mol% loadings, respectively. Requiring 24 h for reaction to reach complete conversion, Pereira and Srebnik demonstrated catalysis over a range of substrates, while Plikhta *et al*. only discussed reactivity with phenylacetylene.

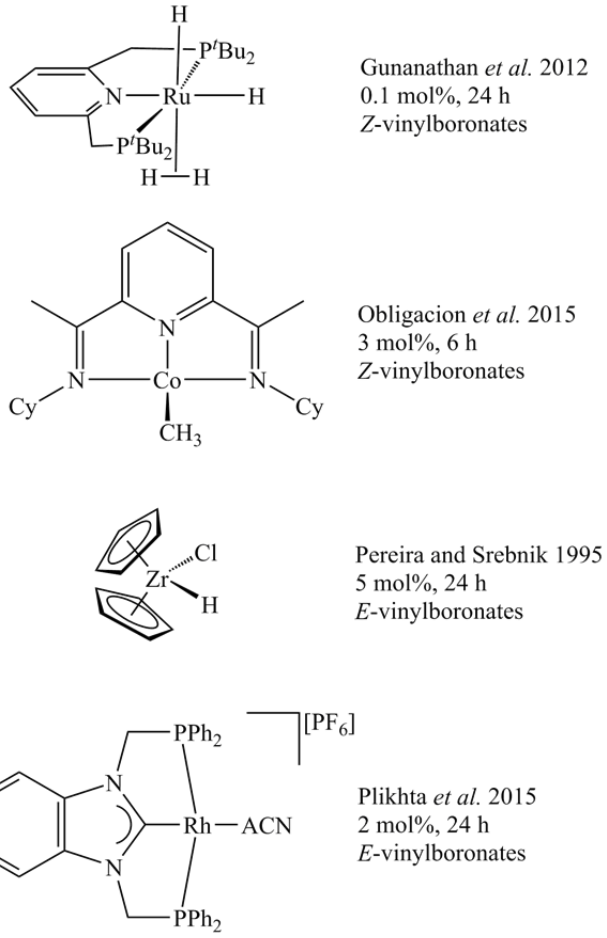


FIGURE 2.1. Represetation of alkyne hydroboration catalysts.

In this contribution insights obtained from κ^4- and κ^5-coordinate rhodium studies [12] lead to the development of an analogous cobalt complex: (^{Ph_2PPr}DI)CoH; which was synthesized and found to catalytically hydroborate a scope of alkyne substrates at 1 mol% catalyst loading, demonstrating selectivity for *trans*-vinylborolanes and some functional

group tolerance. This novel cobalt-hydride complex is also the first to selectively catalyze the addition of a single HBPin across the C≡N bond of benzonitrile to the imine-borane.

2.3 Results and Discussion

Synthesis and Characterization of Cobalt Complexes

The redox non-innocent diimine ligand, ^{Ph_2PPr}DI, was synthesized using Schiff base condensation as previously reported, [13] and added to acetonitrile solution of anhydrous cobalt dichloride under inert atmosphere. After 24 h of stirring at ambient temperature (^{Ph_2PPr}DI)$CoCl_2$ was collected by filtration. A ^{1}H NMR spectrum collected in ACN-d_3 supported a paramagnetic Co(II) metal center. This dichloride precursor was then suspended in diethyl ether and reacted with a slight excess of sodium triethylborohydride and allowed to stir at ambient temperature for two days, as indicated in Figure 2.2. Dark green microcrystalline (^{Ph_2PPr}DI)CoH was separated from unreacted starting material by filtration and dried *in vacuo*.

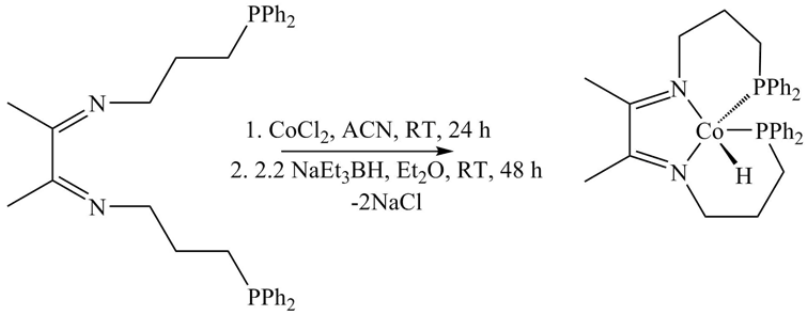


FIGURE 2.2. Preparation of (^{Ph_2PPr}DI)CoH.

The ^{1}H NMR spectroscopic investigation of (^{Ph_2PPr}DI)CoH suggested inequivalence in the donor arms and revealed a Co-H signal at -19.80 ppm. Single-crystal X-ray diffraction, shown in Figure 2.3 revealed the complex to have a distorted trigonal bipyramidal geometry, where one phosphine is in the equatorial plane with the diimine chelate core. Selected bond distances highlighted in Table 2.1 show shortened diimine C-C bond lengths and lengthened C-N imine bond lengths, suggesting a monoreduced DI radical anion. [14] A reduced diimine ligand supports the theory that this formally Co(I) complex possesses a low-spin Co(II) center that is antiferromagnetically coupled to the DI radical. The hydride ligand was located in the difference map with a Co(1)-H(1) bond length of 1.439 Å, which is comparable to reported cobalt-hydride lengths. [15]

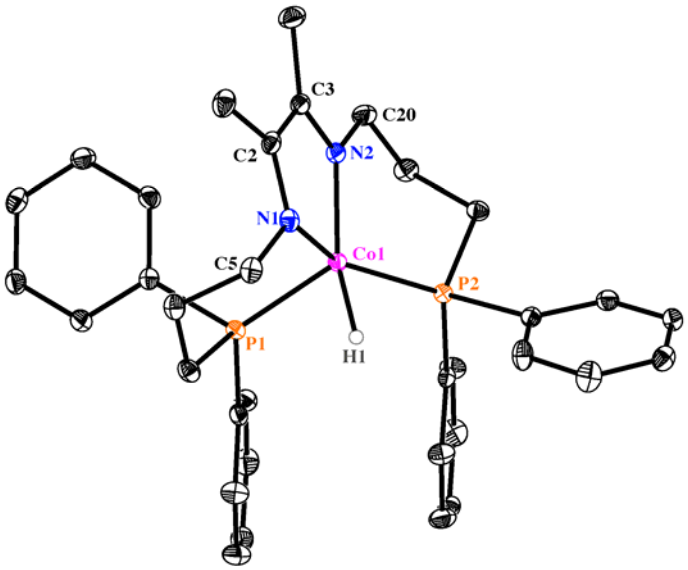


FIGURE 2.3. Solid state structure of (^{Ph_2PPr}DI)CoH with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

TABLE 2.1. Selected bond lengths (Å) and angles (º) for (^{Ph_2PPr}DI)CoH.

Co-N(1)	1.8869(14)	N(1)-Co-P(1)	93.82(5)
Co-N(2)	1.9164(15)	N(2)-Co-P(2)	96.85(5)
Co-P(1)	2.1464(5)	N(1)-Co-N(2)	81.83(6)
Co-P(2)	2.1367(5)	P(1)-Co-P(2)	114.437(19)
Co-H(1)	1.439(19)		
N(1)-C(2)	1.347(2)		
N(2)-C(3)	1.357(2)		
C(2)-C(3)	1.401(3)		

Optimization of Alkyne Hydroboration:

Preliminary screening for catalytic activity of (^{Ph_2PPr}DI)CoH found the complex to be effective at the hydroboration of alkynes, the general process for which is shown in Figure 2.4. As shown in entry 1 of Table 1.2, the reaction of 1-hexyne with pinacolborane using 5 mol% (^{Ph_2PPr}DI)CoH in C_6D_6 resulted in an average conversion of 81% at 2 h. ^{1}H NMR spectroscopy showed only one product: the *trans*-alkenyl-borolane product.

Entries 2 and 3 of Table 1.2 were then conducted to confirm that simple cobalt precursors do not efficiently mediate this reaction. To this end, two cobalt complexes were screened for catalytic activity under the same conditions: $CoCl_2$ and $(Ph_3P)_3CoCl$. At 24 h, $CoCl_2$ showed no catalytic activity and $(Ph_3P)_3CoCl$ achieved only 58% conversion. A benzene-d_6 solution of precatalyst (^{Ph_2PPr}DI)$CoCl_2$ with 1-hexyne and pinacolborane was prepared; no dissolution of (^{Ph_2PPr}DI)$CoCl_2$ was observed. Two equiv. of $NaEt_3BH$ were then added, after which the solution became a dark green color. ^{1}H NMR spectroscopy after 2 h showed complete conversion to *E*-hexenyl-borolane (Entry 4).

To resolve the conversion inconsistency in entry 1, the ratio of 1-hexyne to pinacolborane was optimized (entries 5 and 6 of Table 1.2). A ratio of 1:2 was tested, as was a slight excess of 1:1.25. NMR spectroscopy showed the reaction reaching completion in 2 h using a 1:1.25 ratio of 1-hexyne to borane. This ratio was used for all further reactions.

Having optimized the substrate ratio, the next step was to determine the limit of reactivity. The catalyst loading was lowered to 1.0 mol% (entry 7) and the reaction went to completion after 2 h, at ambient temperature. Two additional experiments were run at even lower catalyst loading of 0.1 mol%, under neat conditions (entries 8 and 9). One reaction was quenched at 2 h and found to have reached completion, the other was given 1 hour to react and was found to attain 90 % conversion. This results in a TOF of 900 h^{-1}, and was determined to be the limit of catalytic activity.

Since different reactivity is sometimes observed with catecholborane, [16, 17, 18] the final experiment (entry 10) was run using the optimized substrate ratio of 1:1.25 1-hexyne: catecholborane at 0.1 mol%, neat and at ambient temperature. After 2 h the reaction was quenched; NMR results showed 93% conversion, which is not significantly different result from pinacolborane reactivity.

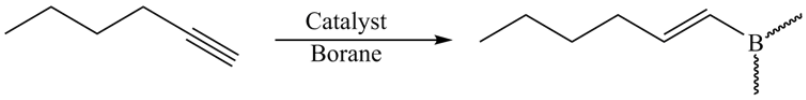


FIGURE 2.4. General scheme for alkyne hydroboration optimization reactions.

TABLE 2.2. Optimization of alkyne hydroboration conditions.

Catalyst	Mol% / Solvent	Borane / Time	1-Hexyne : Borane	% Conversion (24h)
(^{Ph_2PPr}DI)CoH	5.0 / C_6D_6	HBPin / 2h	1:1	81[a]
$CoCl_2$	5.0 / C_6D_6	HBPin / 2h	1:1	0 (0)
$(Ph_3P)_3CoCl$	5.0 / C_6D_6	HBPin / 2h	1:1	39 (58)
(^{Ph_2PPr}DI)$CoCl_2$ + 2$NaEt_3BH$	5.0 / C_6D_6	HBPin / 2h	1:1	>99
(^{Ph_2PPr}DI)CoH	5.0 / C_6D_6	HBPin / 2h	1:2	>99
(^{Ph_2PPr}DI)CoH	5.0 / C_6D_6	HBPin / 2h	1:1.25	>99
(^{Ph_2PPr}DI)CoH	1.0 / C_6D_6	HBPin / 2h	1:1.25	>99
(^{Ph_2PPr}DI)CoH	0.1 / neat	HBPin / 2h	1:1.25	>99
(^{Ph_2PPr}DI)CoH	0.1 / neat	HBPin / 1h	1:1.25	90
(^{Ph_2PPr}DI)CoH	0.1 / neat	HBCat / 2h	1:1.25	93

a. Average of 5 trials. Anisole used as internal standard.

Substrate Scope:

Following the optimization of alkyne hydroboration using (^{Ph_2PPr}DI)CoH, the scope of this reaction was screened at 1 mol%, Table 2.3. The general conditions are shown in Figure 2.5. Phenylacetylene (entry 1), along with several aryl-substituted alkynes featuring electron-withdrawing (entry 2) and electron-donating groups (entries 3 and 4) were found to have good reactivity and selectivity towards *E*-alkenyl borolanes. A preliminary screening of functional group tolerance is demonstrated in entries 5 and 6, where ether and amide groups did not interfere with conversion or selectivity. Aliphatic alkynes (entries 7 and 8) showed complete conversion at 6 h and 2 h respectively. It should be noted that (^{Ph_2PPr}DI)CoH is selective for *E*-alkenylborolanes even though the (PDI)CoMe catalyst previously reported by Obligacion and coworkers [9] was selective for *Z*-alkenylborolanes.

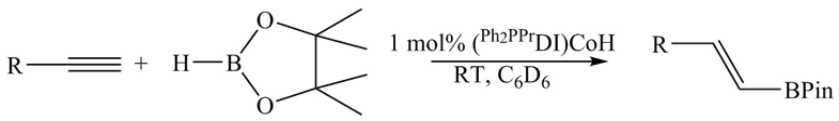
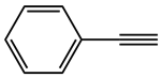
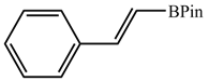
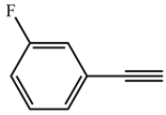
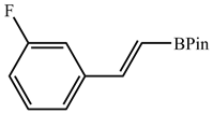
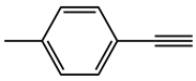
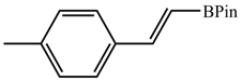
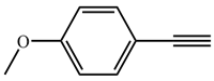
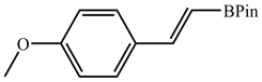
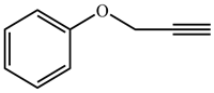
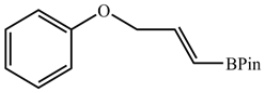
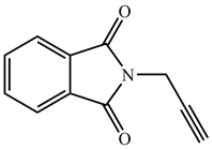
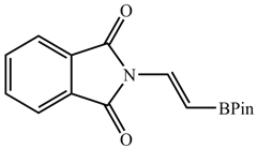
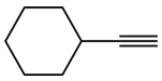
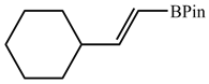
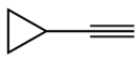
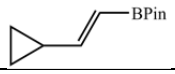


FIGURE 2.5. General scheme for substrate scope reactions.

TABLE 2.3. Substrate scope showing conversion percentages and selectivities.

Substrate	Time	Conversion	*E*-Selectivity	Product	Reference
	6 h 24 h	60 % 67 %	94 %		[10]
	6 h 24 h	63 % 72 %	97 %		[19]
	2 h 6 h	74 % >99 %	93 %		[20]
	2 h	>99 %	95 %		[19]
	6 h 24 h	80 % >99 %	>99 %		[20]
	6 h	>99 %	>99 %		[21]
	6 h	>99 %	>99 %		[22]
	2 h	>99 %	96 %		[8, 9]

a. *E/Z* selectivities determined by ^{1}H NMR spectroscopy.
1,4-Dioxane used as internal standard.

Optimized Reactions:

Four aliphatic substrates were chosen for optimized catalysis at 0.1 mol% under neat conditions and were allowed to react for 2 h; the general procedure is shown in Figure 2.6. The products were then isolated by column chromatography upon treating silica gel with triethylamine to prevent product isomerization. Table 2.4 shows the conversion percentages and isolated yield results. Each entry in table 2.4 has a TOF of 500 h^{-1}, based on percent conversion.

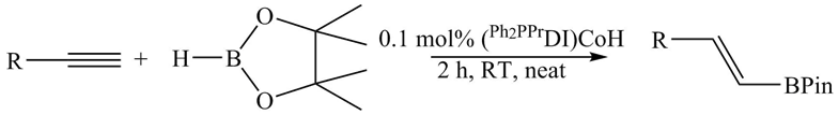
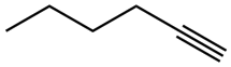
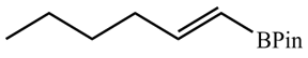
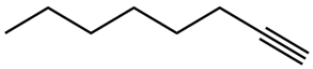
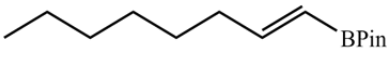
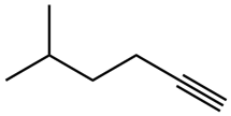
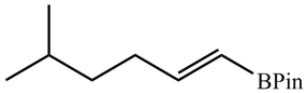
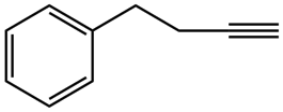
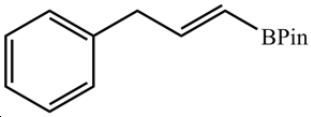


FIGURE 2.6. General scheme for optimized reactions at 0.1 mol% catalyst loading.

TABLE 2.4. Scaled-up hydroboration of aliphatic alkynes and isolated yields.

Substrate	Conversion (Isolated Yield)	Product
	>99 % (92.9%)	
	>99 % (42.0%)	
	>99 % (85.3%)	
	>99 % (84.4%)	

Nitrile Hydroboration:

Given the activity of (^{Ph_2PPr}DI)CoH for alkyne hydroboration, the reduction of nitriles in analogous fashion was sought. A review of the literature for nitrile hydroboration catalysts revealed three very different catalysts shown in Figure 2.7.

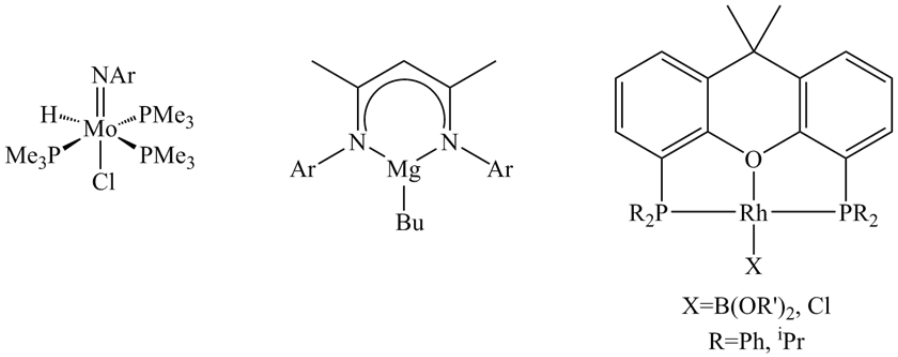


FIGURE 2.7. Selected nitrile hydroboration catalysts.

The molybdenum catalyst (Fig 2.7, left) was published by Khalimon *et al.* in 2012 [23] and is the earliest report of a catalyzed nitrile hydroboration. The magnesium catalyst (Fig 2.7, middle) was published by Weetman *et al.* in 2016 [24] whereby extensive kinetics studies were conducted and crystallographic characterization of the resulting amines was carried out. Both catalysts were reported go mediate the general reaction shown in Figure 2.8 where two equivalents of borane are added to the nitrile to yield the corresponding amine.

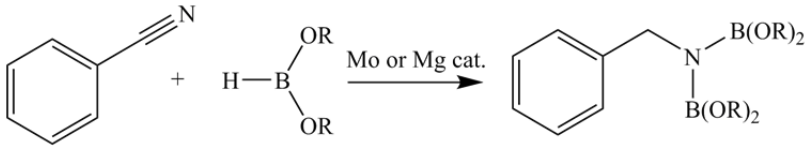


FIGURE 2.8. Reaction scheme for Khalimon *et al*, and Weetman *et al*. catalysts.

The POP-Rh catalyst is discussed here as it was the only system to mention an imine-boryl intermediate in a catalytic process. It was first proposed by Jiang et al. [25] as a mechanistic study of borylation of nitriles using diboron substrates. The theoretical report investigated utilizing a precious d^9 metal to break the phenyl-carbon bond in a benzonitrile molecule and add a borolane group in its place. Kinuta *et al.* [26] followed up on this idea in 2014 with another theoretical study. This study proposed several possible reaction mechanisms for the diboron addition to benzonitrile, one of which showed a boryl isocyanide being generated as a side product and coordinating with an additive (1,4-diazabicyclo[2.2.2]octane, DABCO) to prevent it from reacting with the desired product: the Ph-BR_2. Finally, in 2105 Esteruelas *et al*. [27] experimentally confirmed the mechanism as described above.

Literature review did not find any reports which sought to synthesize or isolate an imine-boryl compound; the only mentions being a dimerized aldimino-diorganoborane [28] and a study that sought to hydroborate allylimines and found competing dehyrogrenative borylation when using catecholborane, which was solved by using pinacolborane. [16] Adding 1 mol% CoH to a benzene-d_6 solution of benzonitrile and pinacolborane was found to result in formation of N-(phenylmethylene)-boranamine, as shown in Figure 2.9. Near complete conversion was attained by 24 h, as shown in Table 2.5. This is believed to be the first report of selective hydroboration of a nitrile to an imine product.

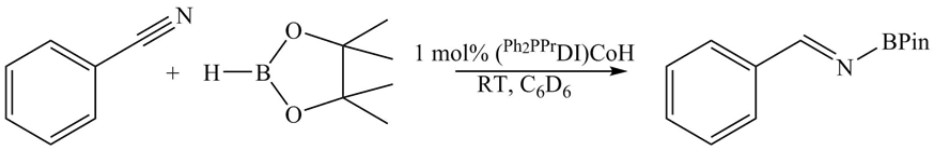
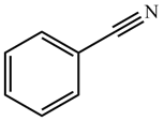
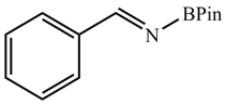


FIGURE 2.9. Proposed scheme for nitrile hydroboration.

TABLE 2.5. Catalytic nitrile hydroboration over time.

Substrate	Time	Conversion	Product
	6 h	86 %	
	24 h	97 %	

1,4-Dioxane used as internal standard.

2.4 Conclusions

A tetradentate diimine cobalt hydride complex was synthesized and characterized using multinuclear NMR spectroscopy and single crystal X-ray diffraction. Though formally Co(I), bond distances revealed a mono-reduced diimine radical that is antiferromagnetically coupled to a low-spin Co(II) metal center. The complex was applied to the hydroboration of alkynes and found to selectively produce *E*-vinylborolanes under mild conditions. Comparison of complex to cobalt reference compounds demonstrated better reactivity than inorganic Co(I) and Co(II) sources. Systematic varying of the reaction conditions resulted in an optimized reaction methodology, which was then applied to a scope of sterically and electronically varied substrates at 1 mol% (^{Ph_2PPr}DI)CoH loading. With most substrates reaching complete conversion within 24 h, several aliphatic substrates were screened for synthetic viability. This second set of catalytic experiments was run at 0.1 mol% for 2 h under mild conditions, products were isolated via column chromatography and recovered in high

yield. Results from nitrile hydroboration demonstrate a new route to selective imine-borane synthesis, previously unachieved. Prior to publication, a more definitive characterization of the (^{Ph_2PPr}DI)$CoCl_2$ precursor should be obtained, and a scope of nitrile substrates is desired.

2.5 Experimental

General Considerations: All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen. Toluene, tetrahydrofuran, diethyl ether, and pentane were purchased from Sigma-Aldrich, purified using a Pure Process Technology solvent system, and stored in the glovebox over activated 4Å molecular sieves and sodium before use. Benzene-d_6, chloroform-d, and acetone-d_6 were purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves. Celite was purchased from Acros Organics. Cobalt dichloride was purchased from Strem; benzonitrile was purchased from TCI, both were used as received. Chlorortis(triphenylphosphine)cobalt(I), 1-octyne, and phenyl propargyl ether were purchased from Fisher Scientific. 4-Ethynyltoluene was purchased from Santa Cruz Biotechnology. 5-Methyl-1-hexyne and cyclohexylacetylene were purchased from Alfa Aesar. 3-Fluorophenylacetylene and 4-phenyl-1-butyne were obtained from Oakwood Products Inc. Cyclopropylacetylene, N-propargyl phthalimide, and 4-ethynylanisole were purchased from Combi-Blocks. 1-Hexyne, 3-Hexyne, phenylacetylene, trimethylsilylacetylene, anisole, 1,4-dioxane, pinacolborane, catecholborane, and sodium triethylborohydride were purchased from Sigma Aldrich; acetonitrile was purchased from Sigma Aldrich and dried over 4Å molecular sieves prior to use. Acetylenes were purified

according to literature procedure before use. [9] ^{Ph_2PPr}DI was synthesized according to literature procedure. [13]

Solution ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a Varian 400 MHz or Varian 500 MHz NMR spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) are reported relative to $Si(Me)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR chemical shifts (ppm) are reported relative to phosphoric acid, ^{11}B NMR chemical shifts (ppm) are reported relative to pinacolborane.

Elemental analyses were performed at Robertson Microlit Laboratories Inc. (Ledgewood, NJ). Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and transferred to a glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer equipped with Mo Kα radiation. A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least-squares procedures on [F^2].

Preparation of $(H_5C_6)_2P(CH_2)_3N=C(CH_3)C(CH_3)=N(CH_2)_3P(C_6H_5)_2CoCl_2$ (^{Ph_2PPr}DI)$CoCl_2$: Under inert atmosphere, ACN solutions (approx. 8 mL) of $CoCl_2$ (0.060 g, 0.458 mmol) and ^{Ph_2PPr}DI (0.247 g, 0.461 mmol) were prepared in 20 mL scintillation vials and stirred for 45 min at ambient temperature. The ligand solution was then pipetted into cobalt dichloride solution; color darkened upon addition, and mixture

was allowed to stir for 24 h. Product was filtered through Celite, solvent was removed under reduced pressure, and washed with pentane (10 mL) to remove any unreacted ligand. A dark microcrystalline solid was isolated, yielding 0.213 g (0.151 mmol, 80%) of ^{Ph_2PPr}DICoCl$_2$. Analysis for $C_{34}H_{38}N_2P_2CoCl_2$ (666.44): Calcd. C, 61.27%; H, 5.75%; N, 4.20%. Found: C, 61.48%; H, 5.82%; N, 4.01%. ^{1}H NMR (C_6D_6, 400 MHz): δ 99.42 (peak width at half-height of 6729 Hz), 17.57 (3447 Hz), 8.77 (89 Hz), 4.77 (153 Hz), 3.88 (188 Hz), -1.69 (209 Hz), -44.68 (811 Hz).

Preparation of (^{Ph_2PPr}DI)CoH: Under inert atmosphere, a scintillation vial was charged with an ethyl ether solution (12 mL) of ^{Ph_2PPr}DICoCl$_2$ (0.138 g, 0.2069 mmol); no dissolution was observed. 2.2 equiv. $NaEt_3BH$ as 1 M solution in toluene was measured using a 1 mL syringe (0.45 mL, 0.45 mmol). The reaction rapidly turned dark green as a soluble product was formed. Reaction was allowed to stir at ambient temperature for 24 h, then filtered through Celite and dried under reduced pressure. A dark green microcrystalline solid was isolated yielding 0.082 g (0.137 mmol, 66.0%) of (^{Ph_2PPr}DI)CoH. $C_{34}H_{38}N_2P_2CoH$ (596.568): Calcd. C, 68.45%; H, 6.59%; N, 4.70%. Found: C, 68.86%; H, 7.51%; N, 4.86%. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.64 (t, 4H, phenyl), 7.12 (t, 4H, phenyl), 7.00 (m, 6H, phenyl), 6.96 (t, 4H, phenyl), 6.88 (m, 6H, phenyl), 6.83 (m, 6H, phenyl), 6.76 (t, 2H, phenyl), 6.72 (t, 3H, phenyl), 6.65 (t, 3H, phenyl), 4.81 (t, 12.1 Hz, 2H, CH_2), 4.51 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 3.09 (m, 2H, CH_2CH_2), 2.52 (m, 2H, CH_2CH_2), 1.51 (dd, 22.3 Hz, 7.8 Hz, CH_3), -19.80 (dd, 90.2 Hz, 39.3 Hz, 1H, Co*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 142.66 (phenyl), 140.09 (phenyl), 139.72 (phenyl), 139.52 (phenyl), 135.72 (d, J_{CP} = 13.0 Hz, phenyl), 133.42 (d, J_{CP} = 11.4 Hz, phenyl), 131.05 (dd, J_{CP} = 10.3, 3.2 Hz, phenyl), 128.83 (phenyl), 128.74

(phenyl), 128.65 (phenyl), 128.46 (phenyl), 128.27 (phenyl), 128.09 (phenyl), 128.05 (phenyl), 128.02 (phenyl), 127.99 (phenyl), 127.94 (phenyl), 127.87 (phenyl), 127.64 (CCH$_3$), 127.43 (CCH$_3$), 61.79 (CH$_2$), 55.19 (CH$_2$), 31.12 (d, J_{CP} = 25.2 Hz, CH$_2$), 30.54 (CH$_2$), 28.95 (d, J_{CP} = 15.7 Hz, CH$_2$), 26.86 (d, J_{CP} = 12.6 Hz, CH$_2$), 17.25 (d, J_{CP} = 4.0 Hz, CH$_3$), 15.19 (d, J_{CP} = 4.0 Hz, CH$_3$). ^{31}P{^{1}H}NMR (C_6D_6, 162 MHz): δ 75.34 (br), 50.75 (br).

General Procedures for the Hydroboration of Alkynes:

A. Optimization Reactions: In a nitrogen-filled glovebox, a scintillation vial was charged with 0.003 g of cobalt catalyst. In a second vial 1-hexyne, borane substrate, and anisole were added in indicated quantities via 50 µL syringe to 0.6 mL C_6D_6. Reaction was allowed to stir for 2 h at ambient temperature, after which it was transferred to a *J*-Young tube and NMR was taken.

B. Substrate Scope: In a nitrogen-filled glovebox, a scintillation vial was charged with 0.003 g (0.005 mmol) of (^{Ph_2PPr}DI)CoH. A separate vial was charged with 0.8 mL C_6D_6, HBPin (122 µL, 0.84 mmol), alkyne (approx. 74 µL, approx. 0.670 mmol), and 1,4-dioxane (14 µL, 0.17 mmol). 0.2 mL of substrate solution was set aside as reference for internal standard calculations; the remaining 0.6 mL of substrate solution was added to solid cobalt catalyst resulting in reaction conditions of 1:125:100:25 catalyst: HBPin:alkyne:1.4-dioxane. Reaction was allowed to stir for 2 h at ambient temperature, then transferred to a J. Young tube and NMR was taken.

C. Optimized Reactions and Isolated Yields In a nitrogen-filled glovebox, a scintillation vial was charged with 0.003 g (0.005 mmol) of (^{Ph_2PPr}DI)CoH. In a separate

vial alkyne (approx. 0.58 mL, approx. 5.03 mmol) and 1250 equiv. of HBPin (0.91 mL, 6.28 mmol) were mixed. Substrate mixture was added to catalyst and allowed to stir at ambient temperature. After 2 h reaction was quenched by exposure to air and product was isolated by column chromatography over silica gel deactivated with 2% NEt_3 in 100:1, then 20:1 hexane/ether as the eluent.

Optimization Reactions:

Control 1-Hexyne Hydroboration using $CoCl_2$ and $(Ph_3P)_3CoCl$ (5 mol%): Following General Procedure A, cobalt complexes $CoCl_2$ and $(Ph_3P)_3CoCl$ were screened for catalytic activity at 5 mol%. This was done to compare reactivity of catalyst to Co(II) and Co(I) reference complexes, and, as $CoCl_2$ is insoluble in benzene-d_6, this served as a preliminary check of homogeneity. No reactivity was observed for $CoCl_2$ after 24 h, and $(Ph_3P)_3CoCl$ only attained 58% conversion after 24 h.

In-Situ Reduction of (^{Ph_2PPr}DI)$CoCl_2$ with $NaEt_3BH$: Following General Procedure A, dichloride catalyst was reduced in situ by addition of 2.2 equiv. $NaEt_3BH$ and probed for catalytic activity at 5 mol %. The precursor is insoluble in benzene-d_6, however, reaction with $NaEt_3BH$ formed soluble hydride, which allowed 1-hexyne reduction to reach completion in 2 h.

Trial for Optimization of Substrate Ratio: Attempts to determine catalytic activity of CoH at 5 mol% were inconsistent, five trials resulted in an average conversion of 81.4% at 2 h. Therefore, following General Procedure A, the ratio of pinacolborane to 1-hexyne

was determined. Ratios of 1:1, 1:1.25, and 1:2 were explored. Reaction went to completion when using a slight excess of HBPin.

Trial for Optimization of Catalyst Loading: Having optimized the substrate ratio, catalyst loading was varied to determine catalyst effectiveness at 1 mol% and 0.1 mol%. In both experiments, catalysis proceeded to completion in 2 h at ambient temperature. To probe the limit of reactivity, the reaction time at 0.1 mol% was halved. Following General Procedure A, reaction was quenched at 1 h and conversion determined by ^{1}H NMR. Yielded TOF of 900 h^{-1}.

Trial for Optimization of Borane Substrate: Following General Procedure A, pinacolborane was compared to sterically bulkier catecholborane. HBCat only attained 93 % conversion at 2 h.

Determination of Substrate Scope Products

4,4,5,5-Tetramethyl-2-[(1*E*)-2-phenylethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was 60 % (67%) at 6 h (24 h) with 94% *E*-selectivity. Spectra consistent with previously reported data. [10]

4,4,5,5-Tetramethyl-2-[*(1E)*-2-(3-fluorophenyl)ethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was 63 % (72%) at 6 h (24 h) with 97% *E*-selectivity. Spectra consistent with previously reported data. [19]

4,4,5,5-Tetramethyl-2-[(1*E*)-2-(4-methylphenyl)ethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was 74 % (>99%) at 2 h (6 h) with 94% *E*-selectivity. Spectra consistent with previously reported data. [20]

4,4,5,5-Tetramethyl-2-[(1*E*)-2-(-4-methoxyphenyl)ethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was >99% at 2 h with 95% *E*-selectivity. Spectra consistent with previously reported data. [19]

4,4,5,5-Tetramethyl-2-[(1*E*)-3-phenoxy-1-propen-1-yl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was 80 % (>99%) at 6 h (24 h) with >99% *E*-selectivity. Spectra consistent with previously reported data. [20]

2-[(1*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]-1*H*-isoindole-1,3(2*H*)-dione: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was >99% at 6 h with >99% *E*-selectivity. Spectra consistent with previously reported data. [21]

4,4,5,5-Tetramethyl-2-[(1*E*)-2-cyclohexylethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR

spectroscopy, conversion determined by 1,4-dioxane internal reference was >99% at 6 h with >99% *E*-selectivity. Spectra consistent with previously reported data. [22]

4,4,5,5-Tetramethyl-2-[(1*E*)-2-cyclopropylethenyl]-1,3,2-dioxaborolane: Complex was synthesized catalytically following General Procedure B. Product identified by ^{1}H NMR spectroscopy, conversion determined by 1,4-dioxane internal reference was >99% at 2 h with >99% *E*-selectivity. Spectra consistent with previously reported data. [8, 9]

Characterization of Isolated Products

4,4,5,5-tetramethyl-2-(1*E*)-1-hexen-1-yl-1,3,2-dioxaborolane: Compound was synthesized from 1-hexyne using General Procedure C, and isolated as a clear liquid in 93% yield (0.985 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.62 (dt, J = 18.4 Hz, 6.7 Hz, 1H, C*H*), 5.42 (dd. J = 18.0 Hz, 1.5 Hz, 1H , C*H*), 2.17 (q, J = 7.0, 2H, CH_2), 1.36 (m, 4H, CH_2), 1.26 (s, 12H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 154.98 (CH), 83.16 (*C*H), 35.70 (*C*H_2), 31.11 (*C*CH_3), 30.56 (*C*H_2), 24.97 (*C*H_3), 22.45 (*C*H_2), 14.11 (*C*H_3). ^{11}B{^{1}H}NMR ($CDCl_3$, 128 MHz): δ 29.71.

4,4,5,5-tetramethyl-2-(1*E*)-1-octen-1-yl-1,3,2-dioxaborolane: Compound was synthesized from 1-octyne using General Procedure C, and isolated as a clear liquid in 42% yield (0.502 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.63 (dt, J = 17.9 Hz, 6.3 Hz, 1H, C*H*), 5.42 (dt, J = 17.9 Hz, 1.3 Hz, 1H, C*H*), 2.14 (q, J = 7.0 Hz, 2H, CH_2), 1.42 (quint, J = 7.3 Hz, 2H, CH_2), 1.28 (m, 18H, CH_2, CH_3), 0.88 (m, 3H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.06 (*C*H), 83.18 (*C*H), 36.05 (*C*H_2), 31.93 (*C*CH_3), 29.13 (*C*H_2), 28.41 (*C*H_2), 24.98 (*C*H_3), 22.80 (*C*H_2), 14.30 (*C*H_3). ^{11}B{^{1}H}NMR ($CDCl_3$, 128 MHz): δ 28.74.

4,4,5,5-tetramethyl-2-(1*E*)-5-methyl-1-hexen-1-yl-1,3,2-dioxaborolane: Compound was synthesized from 5-methyl-1-hexyne using General Procedure C, and isolated as a clear liquid in 85% yield (1.028 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.63 (dt, J = 18.0 Hz, 6.5 Hz, 1H, C*H*), 5.42 (dt, J = 18.0 Hz, 1.5 Hz, 1H, C*H*), 2.15 (q, J = 7.8 Hz, 2H, CH_2), 1.56 (quint, J = 6.4 Hz, 1H, C*H*), 1.30 (m, 4H, CH_2), 1.26 (s, 12H CH_3), 0.87 (d, J = 6.9 Hz, 6H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.17 (*C*H), 83.19 (*C*H), 37.57 (*C*H_2), 33.87 (*C*H_2), 31.81 (*C*CH_3), 27.67 (*C*H_3), 24.99 (*C*H_3), 22.67 (*C*H_2), 14.33 (*C*H_3). ^{11}B{^{1}H}NMR ($CDCl_3$, 128 MHz): δ 29.33.

4,4,5,5-tetramethyl-2-[(1*E*)-4-phenyl-1-buten-1-yl]-1,3,2-dioxaborolane: Compound was synthesized from 4-phenyl-1-butyne using General Procedure C, and isolated as a clear liquid in 84% yield (1.239 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (m, 2H, *phenyl*), 7.19 (m, 4H, *phenyl*), 6.71 (dt, J = 18.0 Hz, 6.2 Hz, 1H, C*H*), 5.51 (dt, J = 18.1 Hz, 1.5 Hz, 1H, C*H*), 2.75 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 1.27 (s, 12H, CH_3). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 153.62 (*C*H), 141.99 (*phenyl*), 128.54 (*phenyl*), 126.06 (*phenyl*), 83.26 (*C*H), 37.69 (*C*H_2), 34.80 (*C*CH_3), 24.99 (*C*H_3). ^{11}B{^{1}H}NMR ($CDCl_3$, 128 MHz): δ 28.51.

Nitrile Hydroboration: In a nitrogen-filled glovebox, a scintillation vial was charged with 0.003 g (0.005 mmol) of (^{Ph2PPr}DI)CoH. A separate vial was charged with 0.8 mL C_6D_6, HBPin (122 µL, 0.84 mmol), benzonitrile (69 µL, 0.690 mmol), and 1,4-dioxane (14 µL, 0.17 mmol). 0.2 mL of substrate solution was set aside as reference for internal standard calculations; the remaining 0.6 mL of substrate solution was added to solid cobalt catalyst resulting in reaction conditions of 1:125:100:25 catalyst:

HBPin:benzonitrile:1.4-dioxane. Reaction was allowed to stir for 2 h at ambient temperature, then transferred to a J. Young tube and NMR was taken, percent conversion determined by integration using internal standard found 86% at 6 h and 97% at 24 h of 4,4,5,5-tetramethyl-1,3,2-dioxo-N-(phenylmethylene)-boranamine.

2.6 References

[1] Sun, J., Deng, L., *ACS Catal.* 2016, *6*, 290-300.

[2] Chirik, P., Wieghardt, K., *Science* 2010, *327*, 794-795.

[3] Zhang, G., Yin, Z., Tan, J., *RSC Adv.* 2016, *6*, 22419-22423.

[4] Small, B., *Acc. Chem. Res.* 2015, *48*, 2599-2611.

[5] Schmidt, V. A., Hoyt, J. M., Margulieux, G. W., Chirik, P. J., *J. Am. Chem. Soc.* 2015, *137*, 7903-7914.

[6] Sauer, D. C., Wadepohl, H., Gade, L. H., *Inorg. Chem.* 2012, *51*, 12948-12958.

[7] Chong, C. C., Kinjo, R. *ACS Catal.* 2015, *5*, 3238-3259, and references therein.

[8] Gunanathan, C. Hölcher, M., Pan, F., Leitner, W., *J. Am. Chem. Soc.* 2012, *134*, 14349-14352.

[9] Obligacion, J. V., Neely, J. M., Yazdani, A. N., Pappas, I., Chirik, P. J., *J. Am. Chem. Soc.* 2015, *137*, 5855-5858.

[10] Plikhta, A., Pöthig, A., Herdtweck, E., Rieger, B., *Inorg. Chem.* 2015, *54*, 9517-9528.

[11] Pereira, S., Srebnik, M., *Organometallics* 1995, *14*, 3127-3128.

[12] Ben-Daat, H., Hall, G. B., Groy, T. L., Trovitch R. J., *Eur. J. Inorg. Chem*. 2013, *25*, 4430-4442.

[13] Porter, T. M., Hall, G. B., Groy, T. L., Trovitch, R. J., *Dalton Trans* 2013, *42*, 14689-14692.

[14] Muresan, N., Chlopek, K., Weyhermüller, T., Neese, F., Wieghardt, K., *Inorg. Chem.* 2007, *46*, 5327-5337.

[15] Ciancanelli, R., Noll, B. C., DuBois, D. L., DuBois, M. R., *J. Am. Chem. Soc.* 2002, *124*, 2984-2992.

[16] Vogels, C. M., O'Connor, P. E., Phillips, T. E., Watson, K. J., Shaver, M. P., Hayes, P. G., Westcott, S. A., *Can. J. Chem.* 2001, *79*, 1898-1905.

[17] Drinkel, E. E., Wu, L. W., Linden, A., Dorta, R., *Organometallics* 2015, *33*, 627-636.

[18] Tseng, K.-N. T., Kampf, J. W., Szymczak, N. K., *ACS Catal.* 2015, *5*, 411-415.

[19] Zhao, J., Niu, Z., Fu, H., Li, Y., *Chem. Commun.*2014, *50*, 2058-2060.

[20] Yao, Z. J., Hong, S., Zhang, W., Liu, M., Deng, W., *Tetrahedron Lett.* 2016, *57*, 910-913.

[21] Takaya, J., Kirai, N., Iwasawa, N., *J. Am. Chem. Soc.* 2011, *133*, 12980-12983.

[22] Morimoto, M., Miura, T., Murakami, M., *Angew. Chem. Int. Ed.* 2015, *54*, 12659-12663.

[23] Khalimon, A. Y., Farha, P., Kuzmina, L. G., Nikonov, G. L., *Chem. Commun*. 2012, *48*, 455-457.

[24] Weetman, C., Anker, M. D., Arrowsmith, M., Hill, M. S., Kocio-Köhn, G., Liptrot, D. J., Mahon, M. F., *Chem. Sci.* 2016, *7*, 628-641.

[25] Jiang, Y., Yu, H., Fu, Y., *Organometallics* 2013, *32*, 926-936.

[26] Kinuta, H., Takahashi, H., Tobisu, M., Mori, S., Chatani, N., *Bull. Chem. Soc. Jpn.* 2014, *87*, 655-669.

[27] Esteruelas, M. A., Oliván, M., Vélez, A., *J. Am. Chem. Soc.* 2015, *137*, 12321-12329.

[28] Yalpani, M., Köster, R., Boese, R., *Chem. Ber.* 1993, *126*, 285-288.

REFERENCES

CHAPTER 1

[1] Bianchini, C., Giambastiani, G., Rios, I. G., Mantovani, G., Meli, A., Segarra, A. M., *Coord*. *Chem*. *Rev*. 2006, *250*, 1391-1418, and references therein.

[2] Tondreau, A. M., Atienza, C. C. H., Darmon, J. M., Milsmann, C., Hoyt, H. M., Weller, K. J., Nye, S. A., Lewis, K. M., Boyer, J., Delis, J. G. P., Lobkovsky, E., Chirik, P. J., *Organometallics* 2012, *31*, 4886-4893.

[3] Cámpora, J., Cartes, M. Á., Rodríguez-Delgado, A., Naz, A. M., Palma, P., Pérez, C. M., *Inorg*. *Chem*. 2009, *48*, 3679-3691.

[4] Darmon, J. M., Turner, Z. R., Lobkovsky, E., Chirik, P. J., *Organometallics* 2012, *31*, 2275-2285.

[5] Smit, T. M., Tomov, A. K., Britovsek, G. J. P., Gibson, V. C., White, A. J. P., Williams, D. J., *Catal*. *Sci*. *Technol*. 2012, *2*, 643-655.

[6] Araujo, C. M., Doherty, M. D., Konezny, S. J., Luca, O. R., Usyatinsky, A., Grade, H., Lobkovsky, E., Soloveichik, G. L., Crabtree, R. H., Batista, V. S., *Dalton Trans*. 2012, *41*, 3562-3573.

[7] Gibson, V. C., Redshaw, C., Solan, G. A., *Chem*. *Rev*. 2007, *107*, 1745-1776.

[8] Blackmore, I. J., Gibson, V. C., Hitchcock, P. B., Rees, C. W., Williams, D. J., White, A. J. P., *J*. *Am*. *Chem*. *Soc*. 2005, *127*, 6012-6020.

[9] Caulton, K. G., *Eur*. *J*. *Inorg*. *Chem*. 2012, *3*, 435-443, and references therein.

[10] de Bruin, B., Bill, E., Bothe, E., Weyhermüller, T., Wieghardt, K., *Inorg*. *Chem*. 2000, *39*, 2936-2947.

[11] Knijnenburg, Q., Gambarotta, S., Budzelaar, P. H. M., *Dalton Trans*. 2006, 46, 5442-5448.

[12] Lyaskovskyy, V., de Bruin, B., *ACS Catal*. 2012, *2*, 270-279.

[13] Praneeth, V. K. K., Ringenberg, M. R., Ward, T. R., *Angew*. *Chem*. *Int*. *Ed*. 2012, *51*, 2-9.

[14] Chirik, P. J., Wieghardt, K., *Science* 2010, *327*, 794-795.

[15] Yu, R. P., Darmon, J. M., Hoyt, H. M., Margulieux, G. W., Turner, Z. R., Chirik, P. J., *ACS Catal*. 2012, *2*, 1760-1768.

[16] Monfette, S., Turner, Z. R., Semproni, S. P., Chirik, P. J., *J*. *Am*. *Chem*. *Soc*. 2012, *134*, 4561-4564.

[17] Trovitch, R. J., Lobkovsky, E., Bill, E., Chirik, P. J., *Organometallics* 2008, *27*, 1470-1478.

[18] Bart, S. C., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2004, *126*, 13794-13807.

[19] Knijnenburg, Q., Horton, A. D., van der Heijden, H., Kooistra, T. M., Hetterscheid, D. G. H., Smits, J. M. M., de Bruin, B., Budzelaar, P. H. M., Gal, A. W., *J. Mol. Catal. A*: *Chem*. 2005, *232*, 151-159.

[20] Atienza, C. C. H., Tondreau, A. M., Weller, K. J., Lewis, K. M., Cruse, R. W., Nye, S. A., Boyer, J. L., Delis, J. G. P., Chirik, P. J., *ACS Catal*. 2012, *2*, 2169-2172.

[21] Tondreau, A. M., Atienza, C. C. H., Weller, K. J., Nye, S. A., Lewis, K. M., Delis, J. G. P., Chirik, P. J., *Science*, 2012, *335*, 567-570.

[22] Tondreau, A. M., Lobkovsky, E., Chirik, P. J., *Org. Lett*. 2008, *10*, 2789-2792.

[23] Karpiniec, S. S., McGuinness, D. S., Britovsek, G. J. P., Patel, J., *Organometallics* 2012, *31*, 3439-3442.

[24] Russell, S. K., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2011, *133*, 8858-8861.

[25] Sylvester, K. T., Chirik, P. J., *J. Am. Chem. Soc*. 2009, *131*, 8772-8774.

[26] Takeuchi, D., Matsuura, R., Park, S., Osakada, K., *J. Am. Chem. Soc*. 2007, *129*, 7002-7003.

[27] Bouwkamp, M. W., Bowman, A. C., Lobkovsky, E., Chirik, P. J., *J. Am. Chem. Soc*. 2006, *128*, 13340-13341.

[28] Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G., *Principals and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987.

[29] Wile, B. M., Trovitch, R. J., Bart, S. C., Tondreau, A. M., Lobkovsky, E. , Milsmann, C., Bill, E., Wieghardt, K., Chirik, P. J., *Inorg. Chem*. 2009, *48*, 4190-4200.

[30] Russell, S. K., Darmon, J. M., Lobkovsky, E., Chirik, P. J., *Inorg. Chem*. 2012, *49*, 2782-2792.

[31] Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: Hoboken, NJ, 2005.

[32] Khanmohammadi, H., Amani, S., Lang, H., Rueeffer, T., *Inorg. Chim. Acta* 2007, *360*, 579-587.

[33] Adams, H., Bailey, N. A., Debaecker, N., Fenton, D. E., Kanda, W., Latour, J.-M., Okawa, H., Sakiyama, H., *Angew. Chem. Int. Ed.* 1995, *34*, 2535-2537.

[34] Adams, H., Bailey, N. A., Dwyer, M. J. S., Fenton, D. E., Hellier, P. C., Hempstead, P. D., Latour, J.-M., *J. Chem. Soc., Dalton Trans*. 1993, *8*, 1207-1216.

[35] Wagnon, B. K., Jackels, S. C., *Inorg. Chem*. 1989, *28*, 1923-1927.

[36] Keypour, H., Rezaeivala, M., Valencia, L., Perez-Lourido, P., *Polyhedron* 2008, *27*, 3172-3176.

[37] Adams, H., Bailey, N. A., Carlisle, W. D., Fenton, D. E., Rossi, G., *J. Chem. Soc., Dalton Trans*. 1990, *4*, 1271-1283.

[38] Cabral, J. de O., Cabral, M. F., Drew, M. G. B., Nelson, S. M., Rodgers, A., *Inorg. Chim. Acta* 1977, *25*, L77-L79.

[39] Cordero, B., Gómez, V., Platero-Prats, A. E., Revés, M., Echeverría, J., Cremades, E., Barragán, F., Alvarez, S., *Dalton Trans*. 2008, *21*, 2832-2838.

[40] Sieh, D., Schlimm, M., Andernach, L., Angersbach, F., Nückel, S., Schöffel, J., Šušnjar, N., Burger, P., *Eur. J. Inorg. Chem*. 2012, *3*, 444-462.

[41] Sieh, D., Schöffel, J., Burger, P., *Dalton Trans*. 2011, *40*, 9512.

[42] Schöffel, J., Šušnjar, N., Nückel, S., Sieh, D., Burger, P., *Eur. J. Inorg. Chem*. 2010, 4911-4915.

[43] Buil, M. L., Esteruelas, M. A., Niembro, S., Olivan, M., Orzechowski, L., Pelayo, C., Vallibera, A., *Organometallics* 2010, *29*, 4375-4383.

[44] Kooistra, T. M., Hetterscheid, D. G. H., Schwartz, E., Knijnenburg, Q., Budzelaar, P. H. M., Gal, A. W., *Inorg. Chim. Acta* 2004, *357*, 2945-2952.

[45] Knijnenburg, Q., Hetterscheid, D. G. H., Kooistra, T. M., Budzelaar, P. H. M., *Eur. J. Inorg. Chem*. 2004, *6*, 1204-1211.

[46] Nückel, S., Burger, P., *Organometallics*, 2001, *20*, 4345-4359.

[47] Dias, E. L., Brookhart, M., White, P. S., *J. Am. Chem. Soc*. 2001, *123*, 2442-2443.

[48] Dias, E. L., Brookhart, M., White, P. S., *Chem. Commun*. 2001, *5*, 423-424.

[49] Dias, E. L., Brookhart, M., White, P. S., *Organometallics* 2000, *19*, 4995-5004.

[50] Haarman, H. F., Bregman, F. R., van Leeuwen, P. W. N. M., Vrieze, K., *Organometallics* 1997, *16*, 979-985.

[51] Haarman, H. F., Ernsting, J.-M., Kranenburg, M., Kooijman, H., Veldman, N., Spek, A. L., van Leeuwen, P. W. N. M., Vrieze, K., *Organometallics* 1997, *16*, 887-900.

[52] Haarman, H. F., Bregman, F. R., Ernsting, J.-M., Veldman, N., Spek, A. L., Vrieze, K., *Organometallics* 1997, *16*, 54-67.

[53] Burkill, H. A., Vilar, R., White, A. J. P., *Inorg. Chim. Acta* 2006, *359*, 3709-3722.

[54] Huheey, J. E., Inorganic Chemistry: Principles of Structure and Reactivity, 3rd ed., Harper & Row, New York, 1983, pp. 368-458.

[55] Burdett, J. K., *Chemical Bonds: A Dialog*; John Wiley & Sons: Chichester, England, 1997, pp. 33-39 and pp. 54-66.

[56] Feller, M., Diskin-Posner, Y., Shimon, L. J. W., Ben-Ari, E., Milstein, D., *Organometallics* 2012, *31*, 4083-4101.

[57] Lockemeyer, R., *Synthesis and Reactivity of Heterobinuclear Metal Complexes*. Ph.D. Dissertation, University of Delaware, 1987.

[58] Tejel, C., del Río, M. P., Asensio, L., van den Bruele, F. J., Ciriano, M. A., Tsichlis i Spithas, N., Hetterscheid, D. G. H., de Bruin, B., *Inorg. Chem*. 2011, *50*, 7524-7534.

[59] Bantu, B., Wurst, K., Buchmeiser, M. R., *J. Organomet. Chem*. 2007, *692*, 5272-5278.

[60] Martínez, A. P., Garcia, M. P., Lahoz, F. J., Oro, L. A., *Inorg. Chim. Acta* 2003, *347*, 86-98.

[61] Esquius, G., Pons, J., Yáñez, R., Ros, J., *J. Organomet. Chem*. 2001, *619*, 14-23.

[62] Bikrani, M., Garralda, M. A., Ibarlucea, L., Pinilla, E., *J. Organomet. Chem*. 1995, *489*, 93-99.

[63] Imhoff, P., Elsevier, C. J., *J. Organomet. Chem*. 1989, *361*, C61-C65.

[64] Estruelas, M. A., Oro, L. A., Apreda, M. C., Foces-Foces, C., Cano, F. H., Claramunt, R. M., Lopez, C., Elguero, J., Begtrup, M., *J. Organomet. Chem*. 1988, *344*, 93-108.

[65] Crociani, B., Di Bianca, F., Paci, M., Boschi, T., *Inorg. Chim. Acta*. 1988, *145*, 253-265.

[66] Fernandez, M. J., Del Val, J. J., Oro, L. A., Palacios, F., Barluenga, J., *Polyhedron* 1987, *6*, 1999-2002.

[67] Garralda, M. A., Ibarlucea, L., *J. Organomet. Chem*. 1986, *311*, 225-231.

[68] Vasapollo, G., Sacco, A., Nobile, C. F., Pellinghelli, M. A., Lanfranchi, M., *J. Organomet. Chem*. 1986, *312*, 249-262.

CHAPTER 2

[1] Sun, J., Deng, L., *ACS Catal.* 2016, *6*, 290-300.

[2] Chirik, P., Wieghardt, K., *Science* 2010, *327*, 794-795.

[3] Zhang, G., Yin, Z., Tan, J., *RSC Adv.* 2016, *6*, 22419-22423.

[4] Small, B., *Acc. Chem. Res.* 2015, *48*, 2599-2611.

[5] Schmidt, V. A., Hoyt, J. M., Margulieux, G. W., Chirik, P. J., *J. Am. Chem. Soc.* 2015, *137*, 7903-7914.

[6] Sauer, D. C., Wadepohl, H., Gade, L. H., *Inorg. Chem.* 2012, *51*, 12948-12958.

[7] Chong, C. C., Kinjo, R. *ACS Catal.* 2015, *5*, 3238-3259, and references therein.

[8] Gunanathan, C. Hölcher, M., Pan, F., Leitner, W., *J. Am. Chem. Soc.* 2012, *134*, 14349-14352.

[9] Obligacion, J. V., Neely, J. M., Yazdani, A. N., Pappas, I., Chirik, P. J., *J. Am. Chem. Soc.* 2015, *137*, 5855-5858.

[10] Plikhta, A., Pöthig, A., Herdtweck, E., Rieger, B., *Inorg. Chem.* 2015, *54*, 9517-9528.

[11] Pereira, S., Srebnik, M., *Organometallics* 1995, *14*, 3127-3128.

[12] Porter, T. M., Hall, G. B., Groy, T. L., Trovitch, R. J., *Dalton Trans* 2013, *42*, 14689-14692.

[13] Muresan, N., Chlopek, K., Weyhermüller, T., Neese, F., Wieghardt, K., *Inorg. Chem.* 2007, *46*, 5327-5337.

[14] Ciancanelli, R., Noll, B. C., DuBois, D. L., DuBois, M. R., *J. Am. Chem. Soc.* 2002, *124*, 2984-2992.

[15] Vogels, C. M., O'Connor, P. E., Phillips, T. E., Watson, K. J., Shaver, M. P., Hayes, P. G., Westcott, S. A., *Can. J. Chem.* 2001, *79*, 1898-1905.

[16] Drinkel, E. E., Wu, L. W., Linden, A., Dorta, R., *Organometallics* 2015, *33*, 627-636.

[17] Tseng, K.-N. T., Kampf, J. W., Szymczak, N. K., *ACS Catal.* 2015, *5*, 411-415.

[18] Zhao, J., Niu, Z., Fu, H., Li, Y., *Chem. Commun.*2014, *50*, 2058-2060.

[19] Yao, Z. J., Hong, S., Zhang, W., Liu, M., Deng, W., *Tetrahedron Lett.* 2016, *57*, 910-913.

[20] Takaya, J., Kirai, N., Iwasawa, N., *J. Am. Chem. Soc.* 2011, *133*, 12980-12983.

[21] Morimoto, M., Miura, T., Murakami, M., *Angew. Chem. Int. Ed.* 2015, *54*, 12659-12663.

[22] Khalimon, A. Y., Farha, P., Kuzmina, L. G., Nikonov, G. L., *Chem. Commun*. 2012, *48*, 455-457.

[23] Weetman, C., Anker, M. D., Arrowsmith, M., Hill, M. S., Kocio-Köhn, G., Liptrot, D. J., Mahon, M. F., *Chem. Sci.* 2016, *7*, 628-641.

[24] Jiang, Y., Yu, H., Fu, Y., *Organometallics* 2013, *32*, 926-936.

[25] Kinuta, H., Takahashi, H., Tobisu, M., Mori, S., Chatani, N., *Bull. Chem. Soc. Jpn.* 2014, *87*, 655-669.

[26] Esteruelas, M. A., Oliván, M., Vélez, A., *J. Am. Chem. Soc.* 2015, *137*, 12321-12329.

[27] Yalpani, M., Köster, R., Boese, R., *Chem. Ber.* 1993, *126*, 285-288.

APPENDIX A

PUBLISHED PORTIONS

Chapter 1 was published previously in the journal referenced below.

Ben-Daat, H., Hall, G. B., Groy, T. L., Trovitch R. J., *Eur. J. Inorg. Chem*. 2013, *25*, 4430-4442.