EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201300263

# Rational Design of Rhodium Complexes Featuring κ$^4$-*N*,*N*,*N*,*N*- and κ$^5$-*N*,*N*,*N*,*P*,*P*-Bis(imino)pyridine Ligands

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**Keywords:** Rhodium / Coordination modes / Electronic structure / Ligand design / Non-innocent ligands

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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 by 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 alkylphosphane 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][$(COD)RhCl_2$], as validated by multinuclear NMR spectroscopy and single-crystal X-ray diffraction.

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## 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] and electronic[3] modularity, and ability to coordinate to a wide range of transition and alkali metal ions.[4] Furthermore, the capacity of these chelates to accept one or more electrons from a metal center has been well documented[5] and metrics to differentiate varying degrees of PDI reduction have been established.[6] This redox non-innocence has proven invaluable[7,8] for the advancement of base–metal hydrogenation,[9] hydrosilylation,[2a,10] and cyclization[11] catalysts whose activities rival traditionally employed precious metal complexes.[12] 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[9d] 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.[13] Although reduction of the respective ($^{Ar}$PDI)$FeBr_2$ starting complexes using sodium naphthalenide 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.[14] Although alkyl imine PDI substituents have allowed the preparation of asymmetric Co$^{I}$ hydrogenation catalysts,[9b] their use has not yet enabled the isolation of an ($^{R}$PDI)Fe (R = alkyl) hydrogenation catalyst.

Our 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)[15] and circumvent the need for steric bulk in catalyst design. While there have been several inspiring examples,[16–18] 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[19] and propensity to form diamagnetic complexes, rhodium was chosen as the metal for our initial investigation into the coordination chemistry of

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300263.

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.[9e,20–29] Although steric protection has allowed for the isolation of an unusual 14-electron ($\kappa^3$-*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,[28] the reactivity observed for ($^{Ar}$PDI)RhCl complexes has remained relatively undistinguished from that reported for ($^{R}$PDI)RhCl complexes bearing non-coordinating alkyl-substituted arms.[30–32] In one particularly relevant example, a monochloride complex bearing alkylamido imine substituents, ($^{MeCONHEt}$PDI)RhCl, was found to oxidatively add alkyl halides.[33] 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 (Figure 1, right).[33]

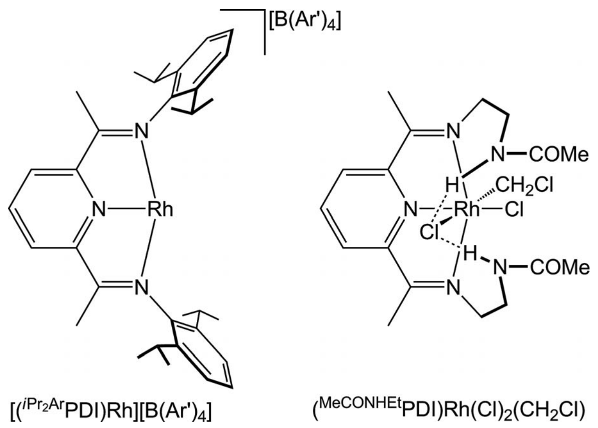


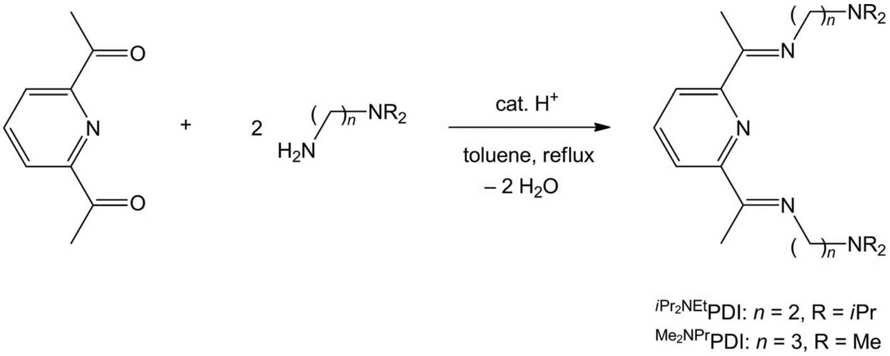
Figure 1. A persistent, three-coordinate cationic Rh complex supported by a sterically demanding PDI ligand (left).[28] At right, an octahedral (PDI)Rh complex featuring hydrogen bonding interactions between an apical chloride ligand and two amide arms.[33]

Considering the complexes shown in Figure 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, we detail our approach to this challenge with the expectation 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.

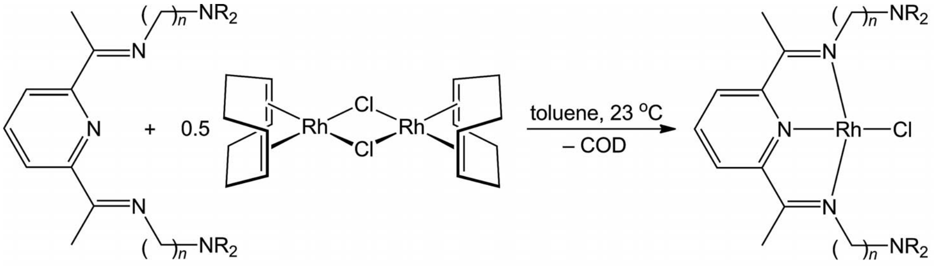
## Results and Discussion

Hoping to establish the ideal chain length for $\kappa^4$- or $\kappa^5$-PDI coordination to a rhodium center, this study commenced with the synthesis of $^{R}$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 $\kappa^5$-*N*,*N*,*N*,*N*,*N*- rather than $\kappa^4$-*N*,*N*,*N*,*N*-PDI chelation, the amine substituents were varied to include either methyl or isopropyl groups. As displayed in Equation (1), the condensation of 2,6-diacetylpyridine with 2 equiv. of either *N*,*N*-diisopropyl-1,2-ethanediamine or *N*,*N*-dimethyl-1,3-propanediamine afforded 2,6-(((CH$_3$)$_2$CH)$_2$NCH$_2$CH$_2$N=C(CH$_3$))$_2$C$_5$H$_3$N [$^{iPr_2NEt}$PDI] and 2,6-((CH$_3$)$_2$NCH$_2$CH$_2$CH$_2$N=C(CH$_3$))$_2$C$_5$H$_3$N [$^{Me_2NPr}$PDI], respectively.

Since several four-coordinate (PDI)RhCl complexes have been prepared following PDI ligand addition to a commercially available [(olefin)$_2$RhCl]$_2$ starting material,[20,21,23,24,26,29,31,33] 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,[12] it was hypothesized that a sufficiently donating imine substituent functionality may allow $\kappa^5$-PDI coordination. Additionally, since the redox-active core of PDI ligands is capable of accepting two electrons from a metal center,[6] the possibility of accessing a formally 20-electron ($\kappa^5$-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 four-coordinate (PDI)RhCl complex formation.[20,21,23,24,26,29,31,33] After stirring for 24 hours, evacuation of the solvent followed by washing of the solid with pentane allowed isolation of ($^{iPr_2NEt}$PDI)RhCl (**1**-Cl) and ($^{Me_2NPr}$PDI)RhCl (**2**-Cl), respectively [Equation (2)]. No evidence for ligand asymmetry resulting from



(1)



$^{iPr_2NEt}$PDI: $n = 2$, R = *i*Pr
$^{Me_2NPr}$PDI: $n = 3$, R = Me

**1-Cl**: $n = 2$, R = *i*Pr
**2-Cl**: $n = 3$, R = Me

(2)

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 **1**-Cl (see Figure S1 of the Supporting Information), two pronounced charge-transfer bands were observed at 302 nm ($\varepsilon$ = 7200 $\text{M}^{-1}$ cm$^{-1}$) and 452 nm ($\varepsilon$ = 4800 $\text{M}^{-1}$ 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 evaluation of the monochloride complexes by single-crystal X-ray diffraction was carried out. Single crystals of **1**-Cl 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 **1**-Cl (Figure 2) confirmed that the diisopropylaminoethyl arms of the PDI chelate were not coordinated to the rhodium center. The metrical parameters determined for **1**-Cl (Table 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)°. As reported for other structurally characterized pseudo square planar (PDI)RhCl complexes,[20,21,26,31] evidence for imine bond elongation is observed 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[6] 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. It is important to note that the Rh(1)–N(1), Rh(1)–N(2), and Rh(1)–N(3) distances of 2.030(3) Å, 1.884(3) Å, and 2.030(3) Å, respectively, 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][32] and are remarkably undistinguished from the same distances reported for related trivalent (PDI)Rh(Cl)$_2$(CH$_2$Cl) complexes.[31]

Table 1. Selected bond lengths [Å] and angles [°] for **1**-Cl and **2**-Cl.

| | **1**-Cl | **2**-Cl |
|---|---|---|
| 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) |

The solid-state structure of **2**-Cl (Figure 3) was also determined by single-crystal X-ray diffraction. Similar to the molecular structure of **1**-Cl, a pseudo square-planar geometry about the metal center was observed with the chelate dimethylaminopropyl imine substituents clearly lying outside the bonding range of rhodium. Importantly, this suggested that neither the isopropyl substituents nor the ethylene bridge in **1**-Cl were responsible for the lack of pendant tertiary amine coordination. As shown in Table 1, the met-

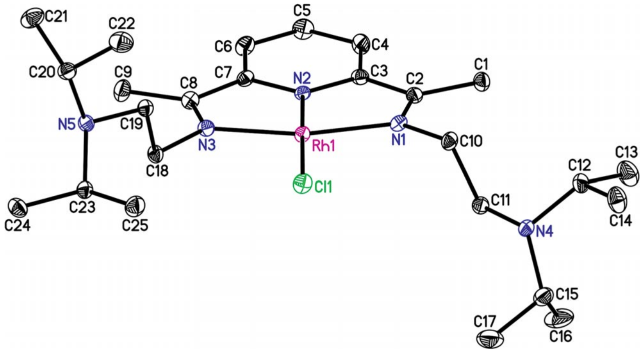


Figure 2. The solid-state structure of **1**-Cl with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

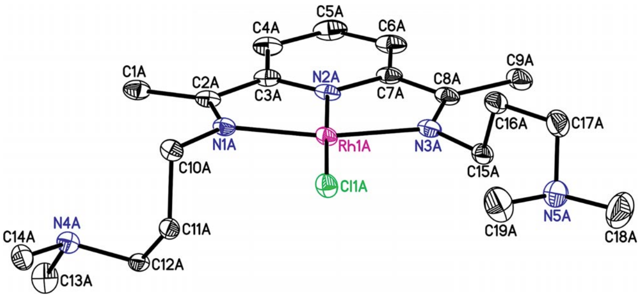


Figure 3. The solid-state structure of **2**-Cl with 30% probability ellipsoids. One of two complexes in the asymmetric unit shown with hydrogen atoms omitted for clarity.

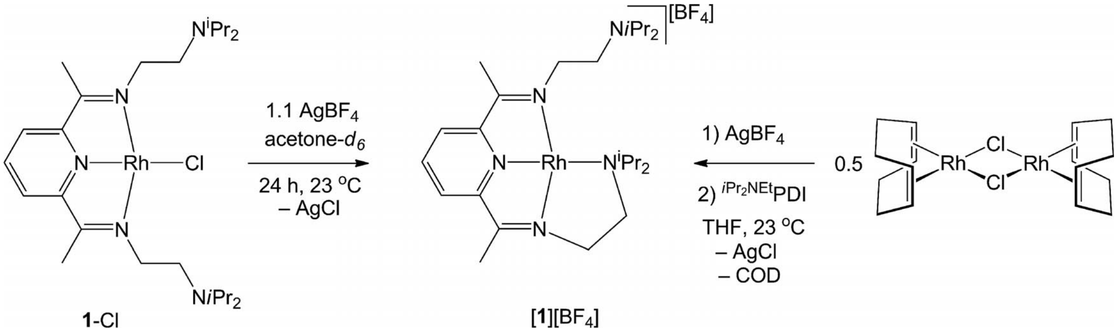
rical parameters found for **2**-Cl, including the Rh–N, $N_{imine}$–$C_{imine}$, and $C_{imine}$–$C_{pyridine}$ distances, are analogous to those determined for **2**-Cl.

Although the PDI chelate $N_{imine}$–$C_{imine}$ and $C_{imine}$–$C_{pyridine}$ distances determined for both **1**-Cl and **2**-Cl suggest an electronic structure consistent with a PDI radical monoanion[6] 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 $^1H$ NMR spectra (minimal shift vs. free ligand reference values) relative to their cobalt congeners.[25] In a more recent report by Burger and co-workers,[20] a comprehensive 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,[6] 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.[20] Extrapolating this knowledge to the solid-state structures of **1**-Cl and **2**-Cl, we believe 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),[34] 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 $d_{z^2}$ 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, left) is known to bind σ-donors including acetophenone and *p*-tolualdehyde.[28] Four-coordinate complexes of the type [($^{Ar}$PDI)Rh(THF)][X] (where the outer-sphere anion X = OTf or Al($OC_4F_9$)$_4$) have also been well-investigated.[20] Adding a slight excess of $AgBF_4$ to a solution of **1**-Cl in [D$_6$]acetone allowed the observation of a low-symmetry complex featuring broadened $^1H$ NMR resonances at ambient temperature [Equation (3), left arrow]. Cooling this solution to –20 °C (see Figure S2 of the Supporting Information) allowed observation of the slow exchange limit and verification of PDI ligand arm inequivalence by $^1H$ and $^{13}C$ NMR spectroscopy. These observations suggested that the resulting product, [($^{iPr_2NEt}$PDI)Rh][$BF_4$] ([**1**][$BF_4$]), contains a tetradentate PDI chelate whereby diisopropylaminoethyl ligand arm exchange occurs in solution at ambient temperature. The preparation of [**1**][$BF_4$] was also achieved upon adding $AgBF_4$ directly to 0.5 equiv. of [(COD)RhCl]$_2$,[35] followed by the addition of $^{iPr_2NEt}$PDI in THF solution [Equation (3), right arrow].

To determine if the sterically demanding isopropyl substituents in [**1**][$BF_4$] 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][$BF_4$] ([**2**][$BF_4$]) [Equation (4)]. Surprisingly, the ambient temperature $^1H$ NMR spectrum of [**2**][$BF_4$] 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 a [D$_6$]acetone solution of [**2**][$BF_4$] to –62 °C resulted in broadening of the imine substituent resonances (Figure S3 of the Supporting Information), and although the slow exchange limit was not reached, it is clear that this complex undergoes chelate arm exchange at a faster rate than [**1**][$BF_4$] in solution at ambient temperature. Although 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, [**2**][$BF_4$] 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 [**2**][$BF_4$] uncovered a κ$^4$-PDI chelate, with an overall coordination geometry that is best described as pseudo square planar (Fig-



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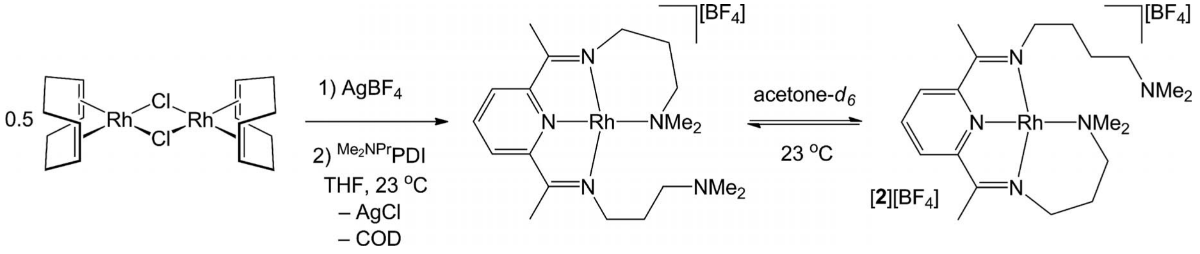


(4)

ure 4). The metrical parameters found for this complex (Table 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 **1**-Cl and **2**-Cl, 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 [**2**][$BF_4$].

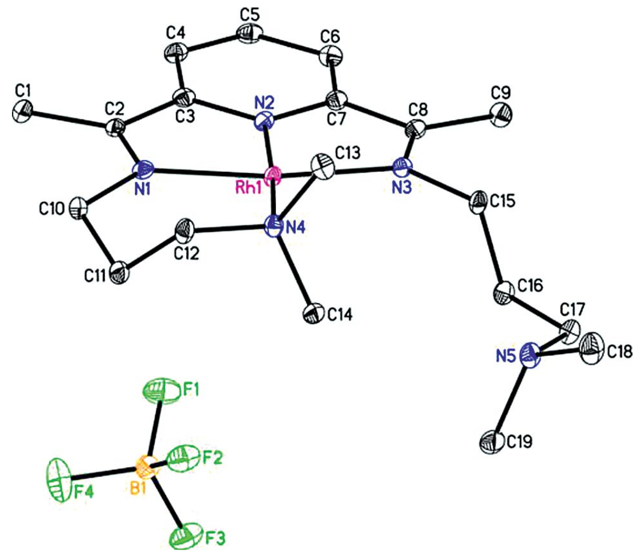


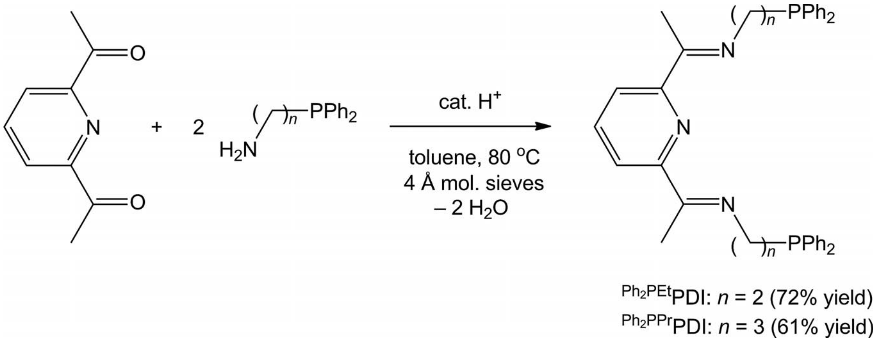
Figure 4. The solid-state structure of [**2**][$BF_4$] with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for [**2**][$BF_4$].

| | | | |
|---|---|---|---|
| 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) | | |

At this stage, it was theorized that replacing the pendant amine donors with stronger σ-donating functionalities might allow for pentadentate PDI ligand coordination to a central rhodium chloride moiety, affording pseudo octahedral ($\kappa^5$-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- ([**1**][$BF_4$]) and propyl-bridged ([**2**][$BF_4$]) amine arms are capable of coordinating to rhodium, bis(imino)pyridine ligands featuring alkylphosphane imine substituents were designed. In contrast to the alkylamine-substituted PDI ligands, the condensation of 2,6-diacetylpyridine with 2 equiv. of either 2-(diphenylphosphanyl)-1-ethylamine or 3-(diphenylphosphanyl)-1-propylamine to synthesize $((C_6H_5)_2PCH_2CH_2N{=}C(CH_3))_2C_5H_3N$ [$^{Ph_2PEt}$PDI] and 2,6-$((C_6H_5)_2PCH_2CH_2CH_2N{=}C(CH_3))_2C_5H_3N$ [$^{Ph_2PPr}$PDI], respectively, was conducted in a thick-walled glass bomb in the presence of 4 Å molecular sieves [Equation (5)]. 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. Although $^{Ph_2PPr}$PDI coordination to copper has been explored,[36] the successful isolation of $^{Ph_2PEt}$PDI and $^{Ph_2PPr}$PDI had not been previously achieved.

With the desired phosphanylalkyl-substituted PDI chelates in hand, their metallation with rhodium was investigated. Notably, the addition of $^{Ph_2PEt}$PDI to 0.5 equiv. of $[(COD)RhCl]_2$ in toluene [Equation (6)] resulted in an immediate color change from the initial orange 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 phosphanylethyl arm was coordinated to the rhodium center. 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 [D$_6$]DMSO features only a doublet at $\delta$ = 43.64 ppm with $J_{RhP}$ coupling of 135.4 Hz, consistent with $\kappa^5$-*N*,*N*,*N*,*P*,*P*-PDI coordination. Although the composition of this complex was well understood, its relative lack of



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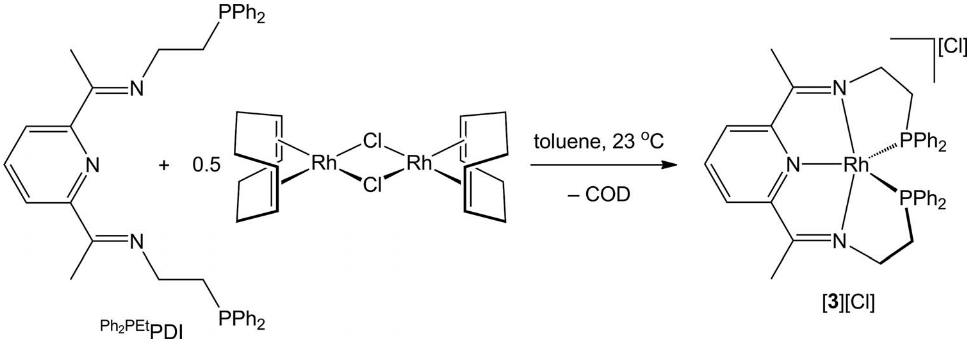

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solubility in a range of solvents initially suggested that the chloride ligand was no longer an inner-sphere ligand, leading to the assignment of this complex as [($^{Ph_2PEt}$PDI)Rh][Cl] ([**3**][Cl]).

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] ([**4**][Cl]) (Figure 5, top), on the basis of multinuclear NMR spectroscopy. The UV/Vis spectrum of [**4**][Cl] in DMSO solution was notably different than the one collected for **1**-Cl, with charge-transfer bands observed at 317 nm ($\varepsilon$ = 12400 $\text{M}^{-1}\,\text{cm}^{-1}$), 362 nm ($\varepsilon$ = 8000 $\text{M}^{-1}\,\text{cm}^{-1}$), 530 nm ($\varepsilon$ = 8800 $\text{M}^{-1}\,\text{cm}^{-1}$), and 671 nm ($\varepsilon$ = 2900 $\text{M}^{-1}\,\text{cm}^{-1}$) (Figure S1 of the Supporting Information), providing additional evidence of phosphane ligand arm coordination. Because neither [**3**][Cl] nor [**4**][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 [**4**][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). This reaction (Figure 5, bottom) also resulted in the formation of a purple precipitate, and complete consumption of the $[(COD)RhCl]_2$ starting material was 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,[37] the resulting purple precipitate was presumed to be [($^{Ph_2PPr}$PDI)Rh]$[(COD)RhCl_2]$ ([**4**]$[(COD)RhCl_2]$). This formulation was further supported by elemental analysis and multinuclear NMR spectroscopy.

Fortunately, [**4**]$[(COD)RhCl_2]$ exhibited slightly better solubility than [**4**][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 [**4**]$[(COD)RhCl_2]$ (Figure 6) confirmed that this complex features $\kappa^5$-*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 [**4**]$[(COD)RhCl_2]$ are displayed in Table 3. 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 **1**-Cl, **2**-Cl, and [**2**]$[BF_4]$, 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 lengths of 1.427(5) Å and 1.435(5) Å, respectively, consistent with an increase in electron density upon coordination of two strongly donating phosphane 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 ob-

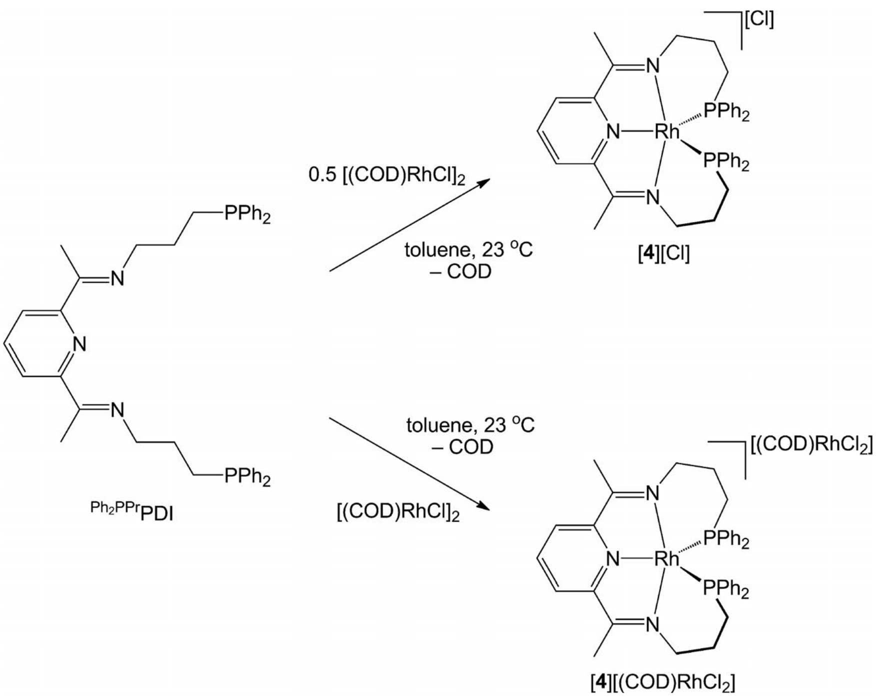
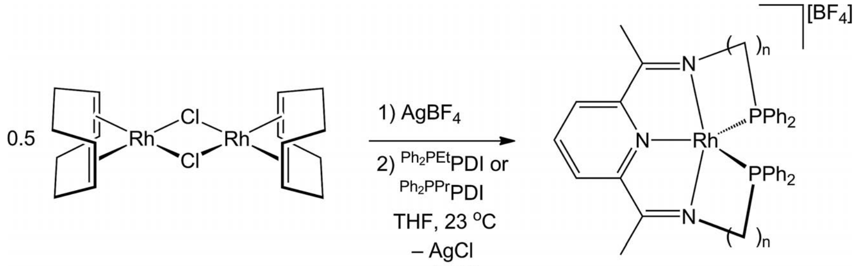


Figure 5. The preparation of cationic rhodium complexes featuring a five-coordinate $^{Ph_2PPr}$PDI chelate.

servation is not overly surprising since the symmetric π* orbital on PDI is heavily localized at the $C_{imine}$–$C_{pyridine}$ bonds.[6] Even though these metrical parameters are more consistent with a PDI dianion than those determined for the other structures discussed in this manuscript, it remains unlikely that [**4**][(COD)RhCl$_2$] possesses a true Rh$^{III}$ center.[20,34] The metrical parameters of the (COD)RhCl$_2$ anion (Table 3) are unremarkable in the sense that the overall geometry about rhodium is nearly 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 fashion similar to that used for [**1**][BF$_4$] and [**2**][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 [Equation (7)] allowed the preparation of purple [($^{Ph_2PEt}$PDI)Rh][BF$_4$] ([**3**][BF$_4$]) or [($^{Ph_2PPr}$PDI)Rh][BF$_4$] ([**4**][BF$_4$]), respectively. Although they feature bands with slightly different $\lambda_{max}$ values and extinction coefficients, the UV/Vis spectra of [**4**][Cl] and [**4**][BF$_4$] were found to be relatively indistinguishable (Table S1 of the Supporting Information). The $^1$H, $^{13}$C, and $^{31}$P NMR spectra of [**3**][BF$_4$] and [**4**][BF$_4$] were directly comparable to those obtained for [**3**][Cl] and [**4**][Cl], respectively, and the $^1H\{^{31}P\}$ NMR spectra of both tetrafluoroborate complexes revealed resolved PDI *p*-pyridine (t, 1 H) and backbone methyl (s, 6 H) resonances, confirming the observation of phosphorus-derived *J* coupling (for representative spectra, see Figure S4 of the Supporting Information). 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.

Since ethyl- and propyl-bridged PDI donor arms were found to coordinate to rhodium, and to 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 evi-



[**3**][BF$_4$]: *n* = 2
[**4**][BF$_4$]: *n* = 3

(7)

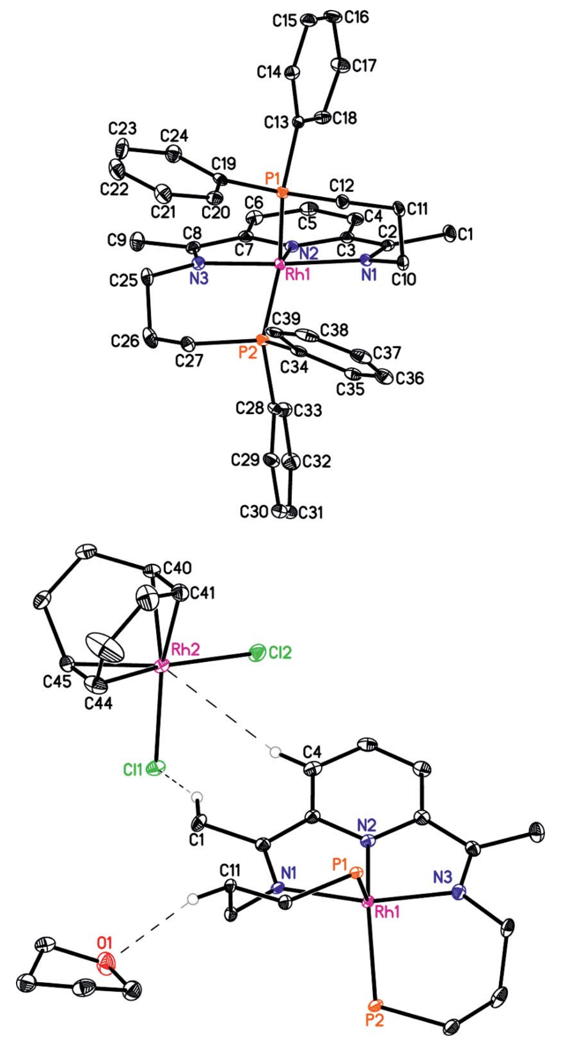


Figure 6. The solid-state structure of [**4**][(COD)RhCl$_2$] with 30% probability ellipsoids. At top, the [(κ$^5$-*N*,*N*,*N*,*P*,*P*-$^{\mathrm{Ph_2PPr}}$PDI)Rh] cation shown without hydrogen atoms, co-crystallized tetrahydrofuran molecule, and (COD)RhCl$_2$ anion for clarity. At bottom, the spatial 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 3. Selected bond lengths [Å] and angles [°] for [**4**][(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) | | |

dence 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 phosphane-substituted PDI ligands such as $^{\mathrm{Ph_2PEt}}$PDI and $^{\mathrm{Ph_2PPr}}$PDI might be capable of stabilizing reactive precatalysts or intermediates, it is possible that the inclusion of strong field phosphane donors may completely prevent a targeted transformation from taking place. Fortunately, if pendant chelate arms are desired to improve the characteristics of a given PDI-supported catalyst, the imine substituents described in this manuscript can be modified to contain stronger or weaker donor atoms, longer or shorter bridges to those atoms, in addition to more or less bulky donor substituents with a range of electronic properties.

## 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 $^{\mathrm{P}}$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$_2$]$^-$ counterion. 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.

## Experimental Section

**General:** All synthetic reactions were performed in an MBraun glove box under an atmosphere of purified nitrogen. Aldrich or Acros anhydrous solvents were purged with nitrogen and stored in the glovebox over activated 4 Å molecular sieves and sodium before use. [D$_6$]Benzene, [D$_6$]acetone, and [D$_6$]dimethyl sulfoxide were purchased from Cambridge Isotope Laboratories and dried with 4 Å molecular sieves prior to use. [(COD)RhCl]$_2$ was purchased from Acros and used as received, while AgBF$_4$, 2-(diphenylphosphanyl)-1-ethylamine and 3-(diphenylphosphanyl)-1-propylamine were used as received from Strem. 2,6-Diacetylpyridine, *p*-toluenesulfonic acid, *N*,*N*-diisopropyl-1,2-ethanediamine, and *N*,*N*-dimethyl-1,3-propanediamine were purchased from TCI America and used as received. 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 with either a Varian 400-MR or Bruker Advance III 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 spectroscopic data (ppm) is reported relative to $H_3PO_4$. Elemental analyses were performed at either Robertson Microlit Laboratories Inc. (Ledgewood, NJ) or with a Perkin–Elmer 2400 Series elemental analyzer at the Goldwater Environmental Laboratory (Arizona State University). All UV/Vis spectra were collected with a Perkin–Elmer Lambda 18 Spectrometer using a two-beam liquid cell. The spectrometer utilized both deuterium and halogen lamps with a change-over occurring 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-$K_\alpha$ radiation. Either a full sphere (**1**-Cl, **2**-Cl, and [**2**][$BF_4$]) or hemisphere ([**4**][(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 **2**-Cl 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 [**4**][(COD)$RhCl_2$] was found to have disorder at two COD methylene positions that could not be further refined. The crystallographic parameters for **1**-Cl, **2**-Cl, [**2**][$BF_4$], and [**4**][(COD)$RhCl_2$] are provided in Table S2 of the Supporting Information.

**$2,6\text{-}(((CH_3)_2CH)_2NCH_2CH_2N{=}C(CH_3))_2C_5H_3N$ ($^{iPr_2NEt}$PDI):** A 250 mL round-bottomed flask was charged with 2,6-diacetylpyridine (1.001 g, 6.134 mmol), *N*,*N*-diisopropyl-1,2-ethanediamine (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 deep yellow in color and a small amount of water was observed in the trap. Upon cooling to ambient temperature, pentane (approx. 50 mL) was then 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 (74%) of a yellowish-orange oil identified as $^{iPr_2NEt}$PDI. $C_{25}H_{45}N_5$ (415.66): calcd. C 72.24, H 10.91, N 16.85; found C 72.24, H 10.98, N 16.58. $^{1}$H NMR ([$D_6$]benzene): $\delta$ = 8.41 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.30 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 3.63 (t, $J$ = 7.1 Hz, 4 H, $NCH_2$), 2.99 (m, 8 H, $NCH_2$ and $NCH(CH_3)_2$), 2.37 (s, 6 H, $N{=}CCH_3$), 1.03 (d, $J$ = 6.7 Hz, 24 H, $NCH(CH_3)_2$) ppm. $^{13}$C{$^{1}$H} NMR ([$D_6$]benzene): $\delta$ = 165.42 ($N{=}C$), 156.25 (*o-pyr*), 135.88 (*p-pyr*), 120.85 (*m-pyr*), 55.18 ($NCH_2$), 48.84 ($NCH_2$), 46.15 ($NCH(CH_3)_2$), 20.82 ($NCH(CH_3)_2$), 13.16 ($N{=}CCH_3$) ppm.

**$2,6\text{-}((CH_3)_2NCH_2CH_2CH_2N{=}C(CH_3))_2C_5H_3N$ ($^{Me_2NPr}$PDI):** A 250-mL round-bottomed flask was charged with 2,6-diacetylpyridine (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 (44%) of a brown oil identified as $^{Me_2NPr}$PDI. $C_{19}H_{33}N_5$ (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 ([$D_6$]benzene): $\delta$ = 8.37 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.27 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 3.50 (t, $J$ = 7 Hz, 4 H, $NCH_2$), 2.41 (t, $J$ = 7 Hz, 4 H, $NCH_2$), 2.32 (s, 6 H, $N{=}CCH_3$), 2.16 (s, 12 H, $N(CH_3)_2$), 2.00 (pseudo quint, $J$ = 7 Hz, 6 H, $CH_2CH_2$) ppm. $^{13}$C{$^{1}$H} NMR ([$D_6$]benzene): $\delta$ = 165.92 ($N{=}C$), 156.59 (*o-pyr*), 136.32 (*p-pyr*), 121.32 (*m-pyr*), 58.06 ($NCH_2$), 50.55 ($NCH_2$), 45.74 ($CH_2CH_2$), 29.69 ($N(CH_3)_2$), 13.41 ($N{=}CCH_3$) ppm.

**($^{iPr_2NEt}$PDI)RhCl (1-Cl):** 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 (approx. 10 mL). The solution immediately adopted a green color and became dark-green after approximately 15 min. The solution was set to stir for 36 h at which time the toluene was removed under vacuum. The resulting product was washed with pentane (approx. 10 mL) several times to remove any excess free ligand and dried in vacuo to yield 0.197 g (98%) of a dark-green microcrystalline solid identified as **1**-Cl. Further purification of the complex was achieved following recrystallization from a toluene/pentane solution. $C_{25}H_{45}ClN_5Rh$ (554.02): calcd. C 54.20, H 8.19, N 12.64; found C 54.42, H 8.33, N 12.25. $^{1}$H NMR ([$D_6$]benzene): $\delta$ = 7.75 (t, $J$ = 8 Hz, 1 H, *p-pyr*), 6.69 (d, $J$ = 8 Hz, 2 H, *m-pyr*), 4.38 (t, $J$ = 6 Hz, 4 H, $NCH_2$), 3.38 (t, $J$ = 6 Hz, 4 H, $NCH_2$), 2.96 (sept, $J$ = 6.7 Hz, 4 H, $NCH(CH_3)_2$), 1.45 (s, 6 H, $N{=}CCH_3$), 0.94 (d, $J$ = 6.7 Hz, 24 H, $NCH(CH_3)_2$) ppm. $^{13}$C{$^{1}$H} NMR ([$D_6$]benzene): $\delta$ = 165.15 ($N{=}C$), 157.02 (*o-pyr*), 123.38 (*m-pyr*), 122.38 (*p-pyr*), 57.93 ($NCH_2$), 49.28 ($NCH(CH_3)_2$), 46.68 ($NCH_2$), 21.60 ($NCH(CH_3)_2$), 15.68 ($N{=}CCH_3$) ppm. UV/Vis (toluene): $\lambda_{max}$ (nm) = 302 ($\varepsilon$ = 7200 $\text{M}^{-1}\,\text{cm}^{-1}$), 452 ($\varepsilon$ = 4800 $\text{M}^{-1}\,\text{cm}^{-1}$), 581 ($\varepsilon$ = 1400 $\text{M}^{-1}\,\text{cm}^{-1}$), 647 ($\varepsilon$ = 1000 $\text{M}^{-1}\,\text{cm}^{-1}$), 764 ($\varepsilon$ = 580 $\text{M}^{-1}\,\text{cm}^{-1}$).

**($^{Me_2NPr}$PDI)RhCl (2-Cl):** Under $N_2$ atmosphere, a 20 mL scintillation vial was charged with $[(COD)RhCl]_2$ (0.052 g, 0.105 mmol), $^{Me_2NPr}$PDI (0.075 g, 0.225 mmol), and toluene (approx. 10 mL). The solution began turning green instantly, and was dark-green in color after approximately 30 min. 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 (84%) of a dark-green microcrystalline solid identified as **2**-Cl was obtained. Elemental analysis of **2**-Cl was unsatisfactory and the $^{13}$C spectrum of this complex is provided as Figure S5 of the Supporting Information as a measure of purity. $^{1}$H NMR ([$D_6$]benzene): $\delta$ = 7.80 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 6.63 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 4.46 (t, $J$ = 7 Hz, 4 H, $NCH_2$), 2.42 (pseudo quint, $J$ = 6.5 Hz, 4 H, $CH_2CH_2$), 2.31 (t, $J$ = 6.5 Hz, 4 H, $NCH_2$), 2.08 (s, 12 H, $NCH_3$), 1.30 (s, 6 H, $N{=}CCH_3$) ppm. $^{13}$C{$^{1}$H} NMR ([$D_6$]benzene): $\delta$ = 164.82 ($N{=}C$), 156.83 (*o-pyr*), 122.45 (*m-pyr*), 121.26 (*p-pyr*), 56.66 ($NCH_2$), 53.89 ($NCH_2$), 45.10 ($NCH_3$), 28.34 ($NCH_2CH_2$), 13.89 ($N{=}CCH_3$) ppm.

**[($^{iPr_2NEt}$PDI)Rh][$BF_4$] ([1][$BF_4$]):** 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 $^{^{i}Pr_2NEt}$PDI (0.099 g, 0.238 mmol) was then added without delay. 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 (90%) of a dark brown microcrystalline solid identified as [**1**][$BF_4$] upon drying. Alternatively, this complex was prepared following the stoichiometric addition of $AgBF_4$ to **1**-Cl. $C_{25}H_{45}BF_4N_5Rh$ (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 ([$D_6$]acetone, 25 °C): $\delta$ = 8.32 (t, $J$ = 8 Hz, 1 H, *p-pyr*), 7.99 (broad m, 1 H, *m-pyr*), 7.57 (broad m, 1 H, *m-pyr*), 4.38 (broad m, 2 H, $NCH_2$), 4.10 (broad m, 2 H, $NCH_2$), 3.69 (broad m, 2 H, $NCH_2$), 3.58 (broad m, 2 H, $NCH(CH_3)_2$), 3.15 (broad m, 2 H, $NCH(CH_3)_2$), 3.01 (broad m, 2 H, $NCH_2$), 2.63 (broad s, 3 H, $N{=}CCH_3$), 1.77 (broad s, 3 H, $N{=}CCH_3$), 1.40 (broad m, $J$ = 6.7 Hz, 12 H, $NCH(CH_3)_2$), 1.02 (broad m, $J$ = 6.7 Hz, 12 H, $NCH(CH_3)_2$) ppm. $^1$H NMR ([$D_6$]acetone, –20 °C): $\delta$ = 8.35 (t, $J$ = 7.9 Hz, 1 H, *p-pyr*), 8.04 (d, $J$ = 7.9 Hz, 1 H, *m-pyr*), 7.61 (d, $J$ = 7.9 Hz, 1 H, *m-pyr*), 4.40 (broad t, $J$ = 5.9 Hz, 2 H, $NCH_2$), 4.09 (broad t, $J$ = 5.9 Hz, 2 H, $NCH_2$), 3.71 (t, 6.6 Hz, 2 H, $NCH_2$), 3.57 (sept, $J$ = 6.5 Hz, 2 H, $NCH(CH_3)_2$), 3.15 (sept, $J$ = 6.5 Hz, 2 H, $NCH(CH_3)_2$), 2.98 (t, $J$ = 5.8 Hz, 2 H, $NCH_2$), 2.66 (s, 3 H, $N{=}CCH_3$), 1.79 (s, 3 H, $N{=}CCH_3$), 1.42 (d, $J$ = 6.5 Hz, 6 H, $NCH(CH_3)_2$), 1.39 (d, $J$ = 6.5 Hz, 6 H, $NCH(CH_3)_2$), 1.00 (d, $J$ = 6.5 Hz, 12 H, $NCH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR ([$D_6$]acetone, –20 °C): $\delta$ = 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 ($NCH_2$), 55.97 ($NCH_2$), 52.99 ($NCH_2$), 47.72 ($NCH_2$), 44.72 ($NCH_2$), 23.62 ($NCH(CH_3)_2$), 20.31 ($NCH(CH_3)_2$), 18.80 ($NCH(CH_3)_2$), 15.95 ($N{=}CCH_3$), 14.87 ($N{=}CCH_3$) ppm.

**[($^{Me_2NPr}$PDI)Rh][$BF_4$] ([2][$BF_4$]):** Under $N_2$ atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.100 g, 0.203 mmol), $AgBF_4$ (0.087 g, 0.446 mmol) and 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 pentane (5 mL), then dried to yield 0.174 g (82%) of a dark brown microcrystalline solid identified as [**2**][$BF_4$]. Elemental analysis of [**2**][$BF_4$] was unsatisfactory and the $^{13}$C spectrum of this complex is provided as Figure S6 of the Supporting Information as a measure of purity. $^1$H NMR ([$D_6$]acetone, 25 °C): $\delta$ = 8.35 (t, $J$ = 8 Hz, 1 H, *p-pyr*), 7.86 (d, $J$ = 8 Hz, 2 H, *m-pyr*), 4.05 (t, $J$ = 7 Hz, 4 H, $NCH_2$), 2.78 (t, $J$ = 5.7 Hz, 4 H, $NCH_2$), 2.60 (s, 12 H, $N(CH_3)_2$), 2.34 (s, 6 H, $N{=}CCH_3$), 2.21 (pseudo quint, $J$ = 6.3 Hz, 4 H, $CH_2CH_2$) ppm. $^{13}C\{^1H\}$ NMR ([$D_6$]acetone): $\delta$ 169.63 ($N{=}C$), 130.29 (*m-pyr*), 123.56 (*p-pyr*), 60.78 ($NCH_2$), 54.19 ($NCH_2$), 47.42 ($NCH_3$), 23.13 ($NCH_2CH_2$), 15.02 ($N{=}CCH_3$) ppm, one resonance not located.

**2,6-(($C_6H_5$)$_2PCH_2CH_2N{=}C(CH_3)$)$_2C_5H_3N$ ($^{Ph_2PEt}$PDI):** A 250-mL thick-walled glass bomb was charged with 2,6-diacetylpyridine (0.407 g, 2.49 mmol), 2-(diphenylphosphanyl)-1-ethylamine (1.120 g, 4.89 mmol), *p*-toluenesulfonic acid (0.010 g, 0.060 mmol), toluene (10 mL), and 4 Å 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 24 h, a light yellow crystalline solid had precipitated. Decanting the mother liquor and subsequent drying allowed the isolation of 1.098 g (72%) of a crystalline yellow solid identified as $^{Ph_2PEt}$PDI. $C_{37}H_{37}N_3P_2$ (585.67): calcd. C 75.88, H 6.37, N 7.18; found C 75.80, H 6.11, N 7.22. $^1$H NMR ($CDCl_3$): $\delta$ = 7.93 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.62 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 7.49 (t, $J$ = 6 Hz, 8 H, *o-phenyl*), 7.33 (m, 12 H, *m-phenyl*, *p-phenyl*), 3.68 (pseudo quart, $J$ = 7.4 Hz, 4 H, $CH_2$), 2.56 (t, $J$ = 8 Hz, 4 H, $CH_2$), 2.29 (s, 6 H, $N{=}CCH_3$) ppm. $^1$H NMR ([$D_6$]benzene): $\delta$ = 8.27 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.52 (t, $J$ = 7.6 Hz, 8 H, *o-phenyl*), 7.25 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 7.08 (m, 12 H, *m-phenyl*, *p-phenyl*), 3.65 (pseudo quart, $J$ = 7.2 Hz, 4 H, $CH_2$), 2.58 (t, $J$ = 7.6 Hz, 4 H, $CH_2$), 2.12 (s, 6 H, $N{=}CCH_3$) ppm. $^{13}$C NMR ([$D_6$]benzene): $\delta$ = 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, $CH_2$), 30.35 (d, $J_{CP}$ = 12.7 Hz, $CH_2$), 22.31 ($N{=}C$), 12.93 ($CH_2CH_2$) ppm. $^{31}$P NMR ($CDCl_3$): $\delta$ = –16.50 ($PPh_2$) ppm. $^{31}$P NMR ([$D_6$]benzene): $\delta$ = –16.52 ($PPh_2$) ppm.

**2,6-(($C_6H_5$)$_2PCH_2CH_2CH_2N{=}C(CH_3)$)$_2C_5H_3N$ ($^{Ph_2PPr}$PDI):** A 250-mL thick-walled glass bomb was charged with 2,6-diacetylpyridine (0.400 g, 2.451 mmol), 3-(diphenylphosphanyl)-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 (61%) of crystalline yellow $^{Ph_2PPr}$PDI was obtained. $C_{39}H_{41}N_3P_2$ (613.72): calcd. C 75.88, H 6.73, N 6.85; found C 75.85, H 6.92, N 6.74. $^1$H NMR ($CDCl_3$): $\delta$ = 8.08 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.71 (t, $J$ = 7.8 Hz, 1 H, *p-pyr*), 7.46 (m, 8 H, *o-phenyl*), 7.32 (m, 12 H, *m-phenyl*, *p-phenyl*), 3.61 (pseudo quart, $J$ = 7 Hz, 4 H, $CH_2$), 2.37 (s, 6 H, $N{=}CCH_3$), 2.23 (m, 4 H, $CH_2$), 1.93 (pseudo quint, $J$ = 7 Hz, 4 H, $CH_2CH_2$) ppm. $^1$H NMR ([$D_6$]benzene): $\delta$ = 8.32 (d, $J$ = 8 Hz, 2 H, *m-pyr*), 7.53 (t, $J$ = 6.8 Hz, 8 H, *o-phenyl*), 7.24 (t, $J$ = 8 Hz, 1 H, *p-pyr*), 7.09 (m, 12 H, *m-phenyl*, *p-phenyl*), 3.38 (pseudo quart, $J$ = 6.7 Hz, 4 H, $CH_2$), 2.26 (m, 10 H, $CH_2$, $N{=}CCH_3$), 2.04 (pseudo quint, $J$ = 6.8 Hz, 4 H, $CH_2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 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, $CH_2$), 27.51 (d, $J_{CP}$ = 15.7 Hz, $CH_2CH_2CH_2$) 26.17 (d, $J_{CP}$ = 11.2 Hz, $CH_2$), 14.01 ($N{=}CCH_3$) ppm. $^{31}$P NMR ($CDCl_3$): $\delta$ = –18.50 ($PPh_2$) ppm. $^{31}$P NMR ([$D_6$]benzene): $\delta$ = –18.70 ($PPh_2$) ppm.

**[($^{Ph_2PEt}$PDI)Rh][Cl] ([3][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 (84%) of a purple microcrystalline solid identified as [**3**][Cl]. $C_{37}H_{37}ClN_3P_2Rh$ (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 ([$D_6$]DMSO): $\delta$ = 8.34 (d, $J$ = 7.6 Hz, 2 H, *m-pyr*), 7.69 (broad m, 1 H, *p-pyr*), 7.45 (t, $J$ = 6.8 Hz, 2 H, *phenyl*), 7.30 (t, $J$ = 6.8 Hz, 4 H, *phenyl*), 7.18 (t, $J$ = 7.2 Hz, 2 H, *phenyl*), 7.06 (pseudo quart, 8 H, *phenyl*), 6.51 (m, 4 H, *phenyl*), 4.49 (broad m, 2 H, $CH_2$), 3.89 (broad m, $J$ = 7.6 Hz, 2 H, $CH_2$), 2.82 (broad m, 2 H, $CH_2$), 2.65 (t, $J_{PH}$ = 6.8 Hz, 6 H, $N{=}CCH_3$), 1.76 (broad m, 2 H, $CH_2$) ppm.

$^{13}$C NMR ([D$_6$]DMSO): $\delta$ 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 (*C*H$_2$), 25.54 (*C*H$_2$), 15.82 (N=C*C*H$_3$) ppm, one resonance not located. $^{31}$P NMR ([D$_6$]DMSO): $\delta$ 43.64 (d, $J_{RhP}$ = 135.4 Hz, *P*Ph$_2$).

**[($^{Ph_2PPr}$PDI)Rh][Cl] ([4][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 (78 %) of a purple microcrystalline solid identified [**4**][Cl] was collected. $C_{39}H_{41}ClN_3P_2Rh$ (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 ([D$_6$]DMSO): $\delta$ = 8.57 (d, $J$ = 8.0 Hz, 2 H, *m-pyr*), 7.83 (broad m, 1 H, *p-pyr*), 7.60 (m, 6 H, *phenyl*), 7.15 (m, 6 H, *phenyl*), 6.97 (t, $J$ = 7.6 Hz, 4 H, *phenyl*), 6.27 (broad t, $J$ = 8.4 Hz, 4 H, *phenyl*), 4.47 (broad m, 2 H, C*H*$_2$), 3.41 (broad t, $J$ = 11.5 Hz, 2 H, C*H*$_2$), 2.69 (t, $J_{PH}$ = 5.7 Hz, 6 H, N=CC*H*$_3$), 2.29 (broad m, 6.3 Hz, 2 H, C*H*$_2$), 1.97 (broad m, 2 H, CH$_2$C*H*$_2$), 1.71 (t, $J$ = 12 Hz, 2 H, C*H*$_2$), 1.17 (broad m, 2 H, CH$_2$C*H*$_2$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 160.73 (N=*C*), 145.80 (*o-pyr*), 135.63 (t, $J_{CP}$ = 18.0 Hz, *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 (*C*H$_2$), 27.47 (CH$_2$*C*H$_2$), 23.54 (*C*H$_2$), 15.44 (N=C*C*H$_3$) ppm. $^{31}$P NMR ([D$_6$]DMSO): $\delta$ = 32.88 (d, $J_{RhP}$ = 138.5 Hz, *P*Ph$_2$) ppm. UV/Vis (DMSO): $\lambda_{max}$ (nm) = 317 ($\varepsilon$ = 12400 M$^{-1}$cm$^{-1}$), 362 ($\varepsilon$ = 8000 M$^{-1}$cm$^{-1}$), 530 ($\varepsilon$ = 8800 M$^{-1}$cm$^{-1}$), 671 ($\varepsilon$ = 2900 M$^{-1}$cm$^{-1}$).

**[($^{Ph_2PPr}$PDI)Rh][(COD)RhCl$_2$] ([4][(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 reagent addition and was stirred at ambient temperature for 24 h. The acetone was removed in vacuo and the product was washed with pentane (10 mL) to remove free COD. After drying, 0.068 g (55 %) of a dark purple microcrystalline solid identified ([**4**][(COD) RhCl$_2$]) was collected. $C_{47}H_{53}Cl_2N_3P_2Rh_2$ (998.62): calcd. C 56.53, H 5.35, N 4.21; found C 56.59, H 5.63, N 4.26. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 8.57 (d, $J$ = 7.6 Hz, 2 H, *m-pyr*), 7.82 (broad m, 1 H, *p-pyr*), 7.60 (m, $J$ = 7.0 Hz, 6 H, *phenyl*), 7.15 (m, 6 H, *phenyl*), 6.97 (t, $J$ = 7.8 Hz, 4 H, *phenyl*), 6.27 (broad t, 4 H, *phenyl*), 4.46 (broad m, 2 H, C*H*$_2$), 4.33 (broad m, 4 H, *COD*), 3.41 (t, $J$ = 11.2 Hz, 2 H, C*H*$_2$), 2.69 (t, $J_{PH}$ = 6.0 Hz, 6 H, N=CC*H*$_3$), 2.37 (broad m, 6 H, *COD*), 2.29 (broad m, 2 H, C*H*$_2$), 2.08 (broad m, 2 H, CH$_2$C*H*$_2$), 1.70 (m, 2 H, C*H*$_2$), 1.16 (broad m, 2 H, CH$_2$C*H*$_2$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ 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 (*C*H$_2$), 30.75 (*COD*), 27.46 (CH$_2$*C*H$_2$), 23.54 (*C*H$_2$), 15.45 (N=C*C*H$_3$) ppm, one resonance not located. $^{31}$P NMR ([D$_6$]DMSO): $\delta$ 31.63 (d, $J_{RhP}$ = 138.5 Hz, *P*Ph$_2$).

**[($^{Ph_2PEt}$PDI)Rh][BF$_4$] ([3][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 THF (4 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 $^{Ph_2PEt}$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 (68 %) of a blue/purple microcrystalline solid identified as [**3**][BF$_4$]. $C_{37}H_{37}BF_4N_3P_2Rh$ (775.37): calcd. C 57.31, H 4.81, N 5.42; found C 57.54, H 5.20, N 5.27. $^1$H NMR ([D$_6$]DMSO): $\delta$ = 8.54 (d, $J$ = 7.8 Hz, 2 H, *m-pyr*), 7.90 (pseudo sept, $J$ = 4.0 Hz, 1 H, *p-pyr*), 7.66 (t, $J$ = 6.3 Hz, 2 H, *phenyl*), 7.51 (t, $J$ = 7.0 Hz, 4 H, *phenyl*), 7.39 (t, $J$ = 7.2 Hz, 2 H, *phenyl*), 7.26 (pseudo quart, 8 H, *phenyl*), 6.72 (pseudo quart, $J$ = 3.7 Hz, 4 H, *phenyl*), 4.70 (broad m, 2 H, C*H*$_2$), 4.10 (broad m, 2 H, C*H*$_2$), 3.43 (broad m, 2 H, C*H*$_2$), 3.01 (broad m, 2 H, C*H*$_2$), 2.85 (t, $J_{PH}$ = 7.2 Hz, 6 H, N=CC*H*$_3$) ppm. $^1$H{$^{31}$P} NMR ([D$_6$]DMSO): $\delta$ = 8.54 (d, $J$ = 8.0 Hz, 2 H, *m-pyr*), 7.90 (t, $J$ = 8.0 Hz, 1 H, *p-pyr*), 7.66 (t, $J$ = 7.5 Hz, 2 H, *phenyl*), 7.51 (t, $J$ = 7.5 Hz, 4 H, *phenyl*), 7.38 (t, $J$ = 7.5 Hz, 2 H, *phenyl*), 7.27 (m, 8 H, *phenyl*), 6.72 (d, $J$ = 7.5 Hz, 4 H, *phenyl*), 4.70 (broad m, 2 H, C*H*$_2$), 4.10 (broad m, 2 H, C*H*$_2$), 3.43 (broad m, 2 H, C*H*$_2$), 3.01 (broad m, 2 H, C*H*$_2$), 2.85 (s, 6 H, N=CC*H*$_3$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 160.24 (N=*C*), 147.13 (*o-pyr*), 135.42 (t, $J_{CP}$ = 17.2 Hz, *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 (*C*H$_2$), 35.51 (t, $J_{CP}$ = 16.4 Hz, *C*H$_2$), 15.82 (N=C*C*H$_3$) ppm. $^{31}$P NMR ([D$_6$]DMSO): $\delta$ = 42.42 (d, $J_{RhP}$ = 135.4 Hz, *P*Ph$_2$) ppm.

**[($^{Ph_2PPr}$PDI)Rh][BF$_4$] ([4][BF$_4$]):** Under N$_2$ atmosphere, a 20 mL scintillation vial was charged with [(COD)RhCl]$_2$ (0.040 g, 0.081 mmol), 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 (3 mL) solution 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 pentane (5 mL) then dried to yield 0.103 g (79 %) of a purple microcrystalline solid identified as [**4**][BF$_4$]. $C_{39}H_{41}BF_4N_3P_2Rh$ (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 ([D$_6$]DMSO): $\delta$ = 8.57 (d, $J$ = 7.6 Hz, 2 H, *m-pyr*), 7.83 (broad m, 1 H, *p-pyr*), 7.60 (pseudo quart, $J$ = 7.0 Hz, 6 H, *phenyl*), 7.15 (broad m, 6 H, *phenyl*), 6.97 (t, $J$ = 7.2 Hz, 4 H, *phenyl*), 6.28 (broad t, 4 H, *phenyl*), 4.47 (pseudo d, $J$ = 10 Hz, 2 H, C*H*$_2$), 3.42 (t, $J$ = 10.8 Hz, 2 H, C*H*$_2$), 2.69 (t, $J_{PH}$ = 5.5 Hz, 6 H, N=CC*H*$_3$), 2.29 (broad m, 2 H, C*H*$_2$), 1.99 (broad m, 2 H, CH$_2$C*H*$_2$), 1.71 (m, 2 H, C*H*$_2$), 1.17 (broad m, 2 H, CH$_2$C*H*$_2$) ppm. $^{13}$C NMR ([D$_6$]DMSO): $\delta$ = 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 Hz, *phenyl*), 125.53 (*m-pyr*), 120.05 (*p-pyr*), 55.51 (*C*H$_2$), 27.48 (CH$_2$*C*H$_2$), 23.55 (t, $J_{CP}$ = 11.2 Hz, *C*H$_2$), 15.43 (N=C*C*H$_3$) ppm. $^{31}$P NMR ([D$_6$]DMSO): $\delta$ = 31.64 (d, $J_{RhP}$ = 138.1 Hz, *P*Ph$_2$) ppm. UV/Vis (DMSO): $\lambda_{max}$ (nm) = 317 ($\varepsilon$ = 8900 M$^{-1}$cm$^{-1}$), 362 ($\varepsilon$ = 6600 M$^{-1}$cm$^{-1}$), 530 ($\varepsilon$ = 6600 M$^{-1}$cm$^{-1}$), 671 ($\varepsilon$ = 3400 M$^{-1}$cm$^{-1}$).

**Supporting Information** (see footnote on the first page of this article): UV/Vis data collected for **1**-Cl, [**4**][Cl], and [**4**][BF$_4$], variable temperature $^1$H NMR spectroscopic data for [**1**][BF$_4$], and a comparison of $^1$H and $^1$H{$^{31}$P} NMR spectra for [**3**][Cl] are also provided.

CCDC-926033 (for **1**-Cl), -926030 (for **2**-Cl), -926031 (for [**2**][BF$_4$]), and -926032 (for [**4**][(COD)RhCl$_2$]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgments

This work was supported as part of the Center for Bio-Inspired Solar Fuel Production, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0001016. Brian Cherry (Arizona State University) is acknowledged for his help with the collection of multinuclear and variable-temperature NMR spectroscopic data. Sue Roberts (University of Arizona) is thanked for her assistance in collecting single-crystal X-ray diffraction data.

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

[2] a) A. M. Tondreau, C. C. H. Atienza, J. M. Darmon, C. Milsmann, H. M. Hoyt, K. J. Weller, S. A. Nye, K. M. Lewis, J. Boyer, J. G. P. Delis, E. Lobkovsky, P. J. Chirik, *Organometallics* **2012**, *31*, 4886–4893; b) J. Cámpora, M. Á. Cartes, A. Rodríguez-Delgado, A. M. Naz, P. Palma, C. M. Pérez, *Inorg. Chem.* **2009**, *48*, 3679–3691.

[3] a) J. M. Darmon, Z. R. Turner, E. Lobkovsky, P. J. Chirik, *Organometallics* **2012**, *31*, 2275–2285; b) T. M. Smit, A. K. Tomov, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, *Catal. Sci. Technol.* **2012**, *2*, 643–655; c) C. M. Araujo, M. D. Doherty, S. J. Konezny, O. R. Luca, A. Usyatinsky, H. Grade, E. Lobkovsky, G. L. Soloveichik, R. H. Crabtree, V. S. Batista, *Dalton Trans.* **2012**, *41*, 3562–3573.

[4] a) V. C. Gibson, C. Redshaw, G. A. Solan, *Chem. Rev.* **2007**, *107*, 1745–1776; b) I. J. Blackmore, V. C. Gibson, P. B. Hitchcock, C. W. Rees, D. J. Williams, A. J. P. White, *J. Am. Chem. Soc.* **2005**, *127*, 6012–6020.

[5] a) K. G. Caulton, *Eur. J. Inorg. Chem.* **2012**, 435–443, and references cited therein b) B. de Bruin, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 2936–2947.

[6] Q. Knijnenburg, S. Gambarotta, P. H. M. Budzelaar, *Dalton Trans.* **2006**, 5442–5448.

[7] a) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270–279; b) V. K. K. Praneeth, M. R. Ringenberg, T. R. Ward, *Angew. Chem.* **2012**, *124*, 10374–10380; *Angew. Chem. Int. Ed.* **2012**, *51*, 10228–10234.

[8] P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794–795.

[9] a) R. P. Yu, J. M. Darmon, H. M. Hoyt, G. W. Margulieux, Z. R. Turner, P. J. Chirik, *ACS Catal.* **2012**, *2*, 1760–1764; b) S. Monfette, Z. R. Turner, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 4561–4564; c) R. J. Trovitch, E. Lobkovsky, E. Bill, P. J. Chirik, *Organometallics* **2008**, *27*, 1470–1478; d) S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794–13807; e) Q. Knijnenburg, A. D. Horton, H. van der Heijden, T. M. Kooistra, D. G. H. Hetterscheid, J. M. M. Smits, B. de Bruin, P. H. M. Budzelaar, A. W. Gal, *J. Mol. Catal. A* **2005**, *232*, 151–159.

[10] a) C. C. H. Atienza, A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P. J. Chirik, *ACS Catal.* **2012**, *2*, 2169–2172; b) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567–570; c) A. M. Tondreau, E. Lobkovsky, P. J. Chirik, *Org. Lett.* **2008**, *10*, 2789–2792.

[11] a) S. S. Karpiniec, D. S. McGuinness, G. J. P. Britovsek, J. Patel, *Organometallics* **2012**, *31*, 3439–3442; b) S. K. Russell, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2011**, *133*, 8858–8861; c) K. T. Sylvester, P. J. Chirik, *J. Am. Chem. Soc.* **2009**, *131*, 8772–8774; d) D. Takeuchi, R. Matsuura, S. Park, K. Osakada, *J. Am. Chem. Soc.* **2007**, *129*, 7002–7003; e) M. W. Bouwkamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 13340–13341.

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

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

[14] S. K. Russell, J. M. Darmon, E. Lobkovsky, P. J. Chirik, *Inorg. Chem.* **2010**, *49*, 2782–2792.

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

[16] For $^{R_2NEt}$PDI, see: a) H. Khanmohammadi, S. Amani, H. Lang, T. Rueeffer, *Inorg. Chim. Acta* **2007**, *360*, 579–587; b) H. Adams, N. A. Bailey, N. Debaecker, D. E. Fenton, W. Kanda, J.-M. Latour, H. Okawa, H. Sakiyama, *Angew. Chem.* **1995**, *107*, 2749–2751; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2535–2537; c) H. Adams, N. A. Bailey, M. J. S. Dwyer, D. E. Fenton, P. C. Hellier, P. D. Hempstead, J. M. Latour, *J. Chem. Soc., Dalton Trans.* **1993**, *8*, 1207–1216; d) B. K. Wagnon, S. C. Jackels, *Inorg. Chem.* **1989**, *28*, 1923–1927.

[17] For $^{R_2NPr}$PDI, see: a) H. Keypour, M. Rezaeivala, L. Valencia, P. Perez-Lourido, *Polyhedron* **2008**, *27*, 3172–3176; b) H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton, G. Rossi, *J. Chem. Soc., Dalton Trans.* **1990**, 1271–1283.

[18] For $^{R_2PPr}$PDI, see: J. de O. Cabral, M. F. Cabral, M. G. B. Drew, S. M. Nelson, A. Rodgers, *Inorg. Chim. Acta* **1977**, *25*, L77–L79.

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

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

[21] D. Sieh, J. Schöffel, P. Burger, *Dalton Trans.* **2011**, *40*, 9512–9524.

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

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

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

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

[26] S. Nückel, P. Burger, *Organometallics* **2001**, *20*, 4345–4359.

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

[28] E. L. Dias, M. Brookhart, P. S. White, *Chem. Commun.* **2001**, 423–424.

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

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

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

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

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

[34] a) J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed., Harper & Row, New York, **1983**, p. 368–458; b) J. K. Burdett, *Chemical Bonds: A Dialog*, John Wiley & Sons, Chichester, UK, **1997**, p. 33–39 and p. 54–66.

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

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

[37] a) C. Tejel, M. P. del Río, L. Asensio, F. J. van den Bruele, M. A. Ciriano, N. Tsichlis i Spithas, D. G. H. Hetterscheid, B. de Bruin, *Inorg. Chem.* **2011**, *50*, 7524–7534; b) B. Bantu, K. Wurst, M. R. Buchmeiser, *J. Organomet. Chem.* **2007**, *692*, 5272–5278; c) A. P. Martínez, M. P. Garcia, F. J. Lahoz, L. A. Oro, *Inorg. Chim. Acta* **2003**, *347*, 86–98; d) G. Esquius, J. Pons, R. Yáñez, J. Ros, *J. Organomet. Chem.* **2001**, *619*, 14–23; e) M. Bikrani, M. A. Garralda, L. Ibarlucea, E. Pinilla, *J. Organomet. Chem.* **1995**, *489*, 93–99; f) P. Imhoff, C. J. Elsevier, *J. Organomet. Chem.* **1989**, *361*, C61–C65; g) M. A. Esteruelas, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, R. M. Claramunt, C. Lopez, J. Elguero, M. Begtrup, *J. Organomet. Chem.* **1988**, *344*, 93–108; h) B. Crociani, F. Di Bianca, M. Paci, T. Boschi, *Inorg. Chim. Acta* **1988**, *145*, 253–265; i) M. J. Fernandez, J. J. Del Val, L. A. Oro, F. Palacios, J. Barluenga, *Polyhedron* **1987**, *6*, 1999–2002; j) M. A. Garralda, L. Ibarlucea, *J. Organomet. Chem.* **1986**, *311*, 225–231; k) G. Vasapollo, A. Sacco, C. F. Nobile, M. A. Pellinghelli, M. Lanfranchi, *J. Organomet. Chem.* **1986**, *312*, 249–262.

Received: February 24, 2013