Comparison of the Electronic Properties of Diarylamido-Based PNZ Pincer Ligands: Redox Activity at the Ligand and Donor Ability Toward the Metal

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Ⓢ *Supporting Information*

ABSTRACT: This paper presents the synthesis and characterization of a series of pincer ligands and their Ni, Pd, Pt, and Rh complexes. The ligands under examination are based on a diarylamine which is modified either by two phosphino (-PR$_2$) substituents in the *ortho*-positions (PNP ligands) or by a combination of a phosphino and an iminyl (−CH=NX) substituent (PNN ligands). The ligands can be broken down into three groups: (a) C$_{2v}$-symmetric PNP ligands with identical side −PR$_2$ donors, (b) C$_s$-symmetric PNP′ ligands with different −PR$_2$ side donors, and (c) PNN ligands containing a −P^{i}Pr$_2$ side donor. All of the ligands under study readily formed square-planar complexes of the types (PNZ)PdCl, (PNZ)Pd(OAc), and (PNZ)RhCO, where PNZ is the corresponding anionic tridentate pincer ligand. For select PNP ligands, (PNP)NiCl and (PNP)PtCl were also studied. The (PNZ)MCl complexes (M = Ni, Pd, Pt) underwent quasireversible oxidation in cyclic voltammetry experiments. Based on the close similarity of formal potentials for Ni, Pd, and Pt analogs, and based on the previous literature evidence, these oxidation events are ascribed primarily to the PNZ ligand, and the E$_{1/2}$ values can be used to compare the ease of oxidation of different ligands. A (PNP)PdCl complex containing methoxy substituents *para-* to the central nitrogen underwent two quasireversible oxidations. Two mono-oxidized complexes were isolated and structurally characterized in comparison to their neutral analog, revealing minimal changes in the bond distances and angles. Several other neutral complexes were also structurally characterized. The carbonyl stretching frequency in (PNZ)RhCO complexes was used to gauge the donating ability of the various pincer ligands toward the metal. Comparison of E$_{1/2}$ values for (PNZ)PdCl and ν$_{CO}$ values for (PNZ)RhCO revealed that the two are not consistently correlated across all the studied ligands and can be tuned to different degrees through judicious ligand alteration.
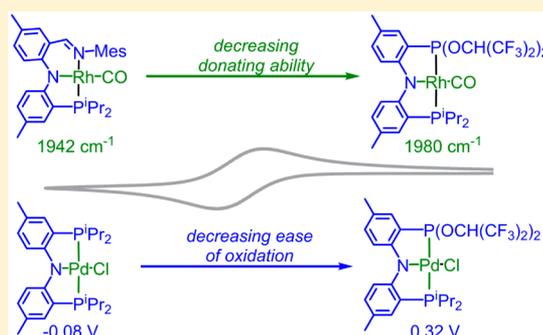
INTRODUCTION

The reactivity of a metal complex as a whole is derived from the interactions between the metal center and its surrounding ligands. In the traditional approach, the steric and electronic nature of the ancillary ligands is taken advantage of to modulate the reactivity at the metal center, but the ancillary ligands themselves remain "spectators"[1] and preserve their connectivity, composition, and charge. Recently, another approach to the utilization of supporting ligands has emerged in which they are designed to remain bound to the metal center but undergo chemical changes over the course of reactions. These ligands are often referred to as noninnocent and assist the metal center in carrying out desired transformations, most commonly by accepting or losing protons[2] or electrons. Redox-active noninnocent ligands have attracted significant attention.[3] These ligands provide a site other than the metal center for redox events to occur, serve as electron or hole reservoirs, and can be used to modify the electronic properties of the metal center. Common redox noninnocent ligand scaffolds include dithiolenes,[4] semiquinones,[5] diimines,[6−9] amido phenolates,[10−12] and terpyridines.[13] Redox noninnocent ligands are seen as a promising tool in enabling two-electron reactivity in the 3d metal series, a process necessary for organometallic catalysis.[14] Arguably the most prominent example of this approach is the use of Fe complexes of 2,6-bis(imino)pyridine ligands (**A**, Figure 1), which catalyze ethylene polymerization,[15,16] [2 + 2] cycloadditions;[17] enyne cyclizations;[18] hydrogenation of olefins, alkynes, and aryl azides;[19] and hydrosilylation.[20] Ligand **A** is an example of a noninnocent ligand capable of undergoing reduction vs its closed-shell (neutral) form. As a tridentate, meridionally chelating ligand, it can also be characterized as a pincer ligand.[21] Pincer ligands that are oxidizable have largely been based on the diarylamido
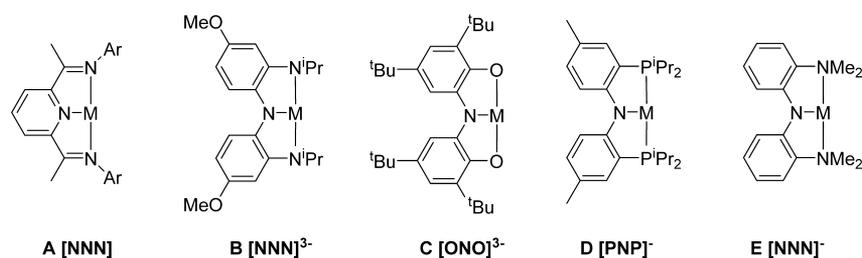
Figure 1. Redox active pincer ligands denoted by their three donor atoms and showing the charge of the closed-shell form.
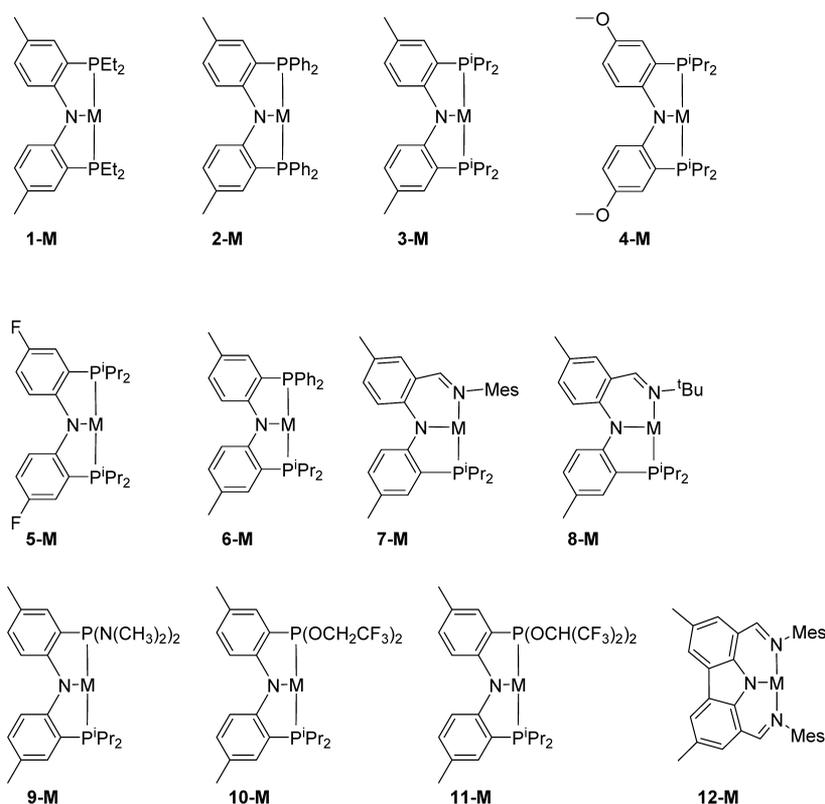

Figure 2. Generic representation of complexes of pincer ligands under study in this work.

backbone. Heyduk has reported the NNN[22,23] (**B**) and ONO[24] (**C**) redox noninnocent trianionic ligands (Figure 1), the former of which promotes catalytic nitrene transfer by complexes of a redox-inactive d[0] metal.[22] Our own group, in collaboration with Nocera et al.,[25] as well as Mindiola et al. investigated the redox noninnocence of the PNP (**D**) ligand,[26] while Vicic et al. reported on the noninnocence of [NNN]⁻ pincer ligands such as **E**.[27,28]

Owing to the convenient modularity of the diarylamido scaffold, a large number of derived pincer ligands have been reported, including various PNP,[29−31] SNS,[32] NNN,[33] and PNN ligands.[34] In this report, we aimed to analyze an array of diarylamido-based pincer complexes in order to systematically examine the effects of various substituents on the redox properties and on the overall donating ability of the pincer ligand toward the metal in group 10 and rhodium complexes. Analysis of three classes of ligands (Figure 2) is presented: C_{2v} symmetric PNP pincer ligands (contain two identical phosphine arms), C_s symmetric PNN ligands, and C_s symmetric PNP′ ligands (contain two different phosphine arms). The PNP′ ligands containing phosphines substituted with fluorinated alkoxy groups were inspired by the reports of

Milstein et al.,[35] Roddick et al.,[36] and van Koten et al.[37] describing aryl(bisphosphine) PCP pincer ligands with electron-withdrawing substituents on the phosphorus atoms.

■ RESULTS AND DISCUSSION

Synthesis of C_{2v} Symmetric PNP Ligands. PNP ligands can be prepared in their NH form (i.e., **1-H**, **2-H**,[38] **3-H**[29a]) or the NMe form (i.e., **4-Me**, **5-Me**[29c]). We have previously reported that N-methylated PNP ligands with two P[i]Pr₂ arms can give rise to group 9 and 10 PNP complexes via N−Me cleavage at the metal center.[29d] The synthesis of the new ligand **1-H** closely followed our previous syntheses of **2-H** and **3-H**. Trilithiation of a common precursor **A** with three equivalents of n-butyllithium followed by reaction with three equivalents ClPEt₂ yielded **1-H** as a yellow oil upon hydrolytic workup (Scheme 1). Analysis of the oil by ^{1}H NMR spectroscopy revealed that it was a mixture that contained an 87% composition of **1-H**; however, the crude ligand was adequate for the synthesis of **1-PdCl** (vide infra) without further purification.

The preparation of **4-Me** was carried out analogously to the synthesis of **5-Me**. Buchwald-Hartwig coupling of p-anisidine

Scheme 1. Synthetic Routes to C_{2v} Symmetric Ligands
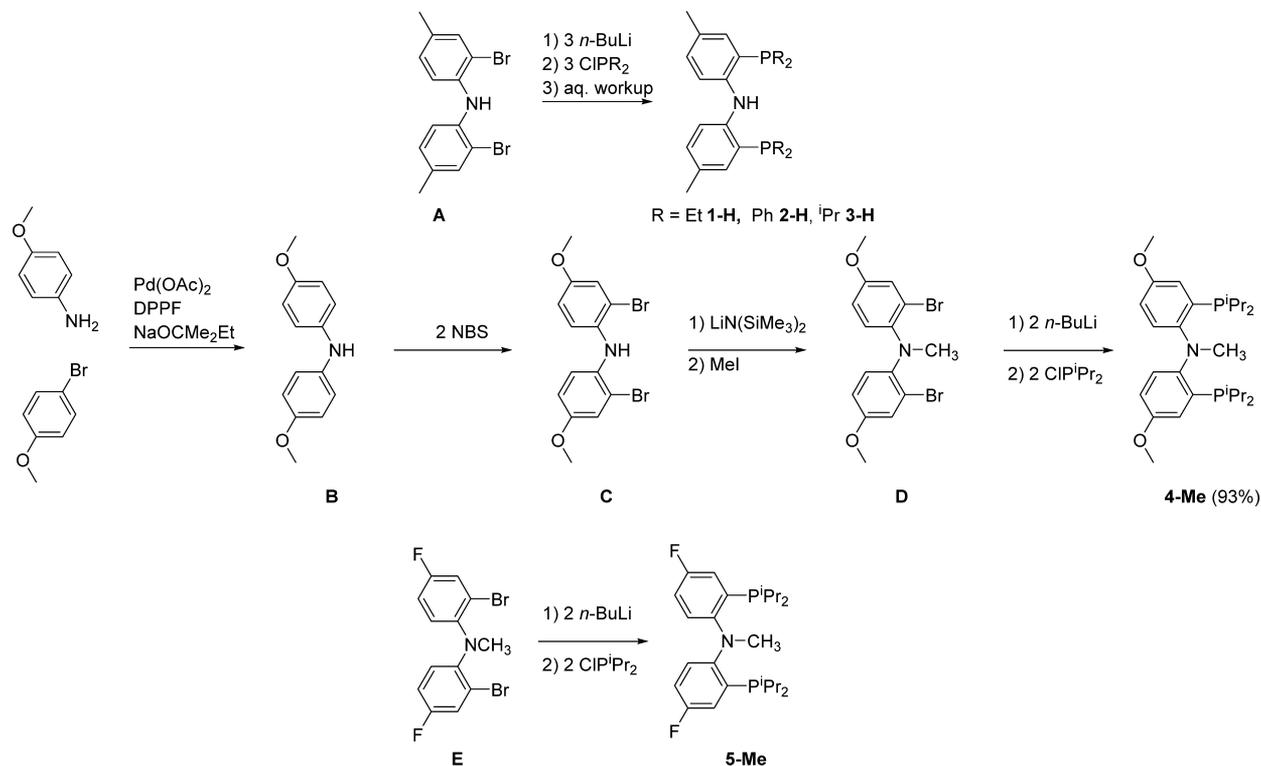
Scheme 2. Synthetic Routes to C_s Symmetric Pincer Ligands
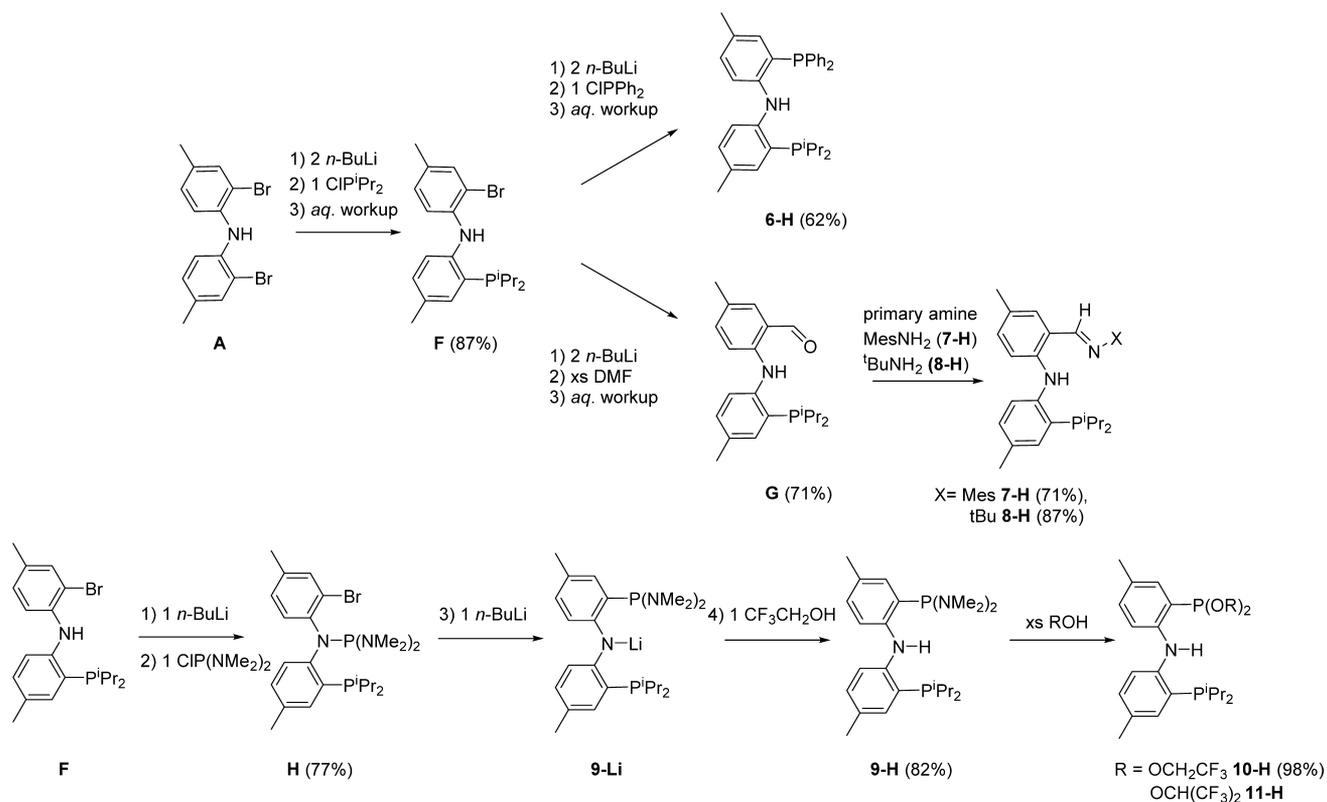
and *p*-bromoanisole produced bis(*p*-methoxyphenyl)amine (**B**). *Ortho*-bromination of **B** with two equivalents of *N*-bromosuccinimide followed by *N*-methylation gave the key precursor **D**. The addition of two equivalents of *n*-butyllithium

and subsequent quenching with ClP^{i}Pr$_2$ gave **4-Me** in a 93% yield.

Synthesis of C_s Symmetric PNP and PNN Ligands. Our syntheses of the C_s-symmetric PNP and PNN ligands (Scheme 2) rely on the conveniently accessible common precursor **F**. Its

preparation by selective lithiation/phosphination of **A** was previously reported by our group in 2011 when we used it for the synthesis of binucleating PNN ligands via **G**.[34] The new monomeric PNN ligands **7-H** and **8-H** were synthesized analogously, via Schiff-base condensation between **G** and a primary amine (2,4,6-trimethylaniline or *tert*-butylamine) in the presence of an acid catalyst (Scheme 1). **7-H** and **8-H** were isolated as yellow solids in 71% and 87% yields, respectively.

6-H was produced by dilithiation of **F** with two equivalents of *n*-butyllithium, followed by the addition of one equivalent of ClPPh$_2$. Aqueous workup and recrystallization in a pentane/toluene mixture yielded **6-H** as a colorless solid with a moderate yield of 62%. Our synthesis of **6-H** closely follows the synthesis of a related C$_s$-symmetric PNP′ ligand differing from **6-H** only in the absence of the Me groups *para* to the nitrogen on the diarylamine backbone by Liang et al.[39] **6-H** itself was previously reported by Goldberg et al., but via a different synthetic approach.[40]

The synthesis of **10-H** and **11-H** was envisaged to proceed via alcoholysis of **9-H** (Scheme 2). **9-H** could not be synthesized from **F** in the exact manner used for **6-H**, where dilithiation of **F** was followed by selective C-phosphination. Instead, the synthesis of **9-H** was carried out in a stepwise manner. Deprotonation of **F** with one equivalent of *n*-butyllithium, followed by N-phosphination with one equivalent of ClP(NMe$_2$)$_2$, produced **H**. The net migration of the P(NMe$_2$)$_2$ group to the *ortho*-carbon of the aryl ring to give **9-Li** was then observed upon the addition of a second equivalent of *n*-butyllithium. Controlled protolysis of **9-Li** with trifluoroethanol occurs readily and can be monitored via the disappearance of the yellow color of the reaction mixture. It is imperative that only one equivalent of trifluoroethanol be added to the reaction, because **9-H** is susceptible to reaction with excess trifluoroethanol. **9-H** was isolated as a white powder in a 78% yield. **10-H** and **11-H** were then formed by treatment of **9-H** with an excess of trifluoroethanol or hexafluoroisopropanol, respectively. **10-H** was obtained in greater than 98% yields as a colorless oil (>95% purity) upon removal of the volatiles *in vacuo*. Isolation of **11-H** by simple exposure to a vacuum was not possible as the formation of side products was evident by NMR spectroscopy. This was circumvented by producing the ligand in situ in the presence of excess hexafluoroisopropanol and then reacting it directly with a metal precursor (*vide infra*).

NMR Characterization of the Pincer Ligands. All of the ligands synthesized above were characterized in solution by multinuclear NMR spectroscopy. Table 1 reports the corresponding chemical shifts of their ^{31}P NMR and ^{1}H NMR (N—H or N—Me) resonances, as well as the symmetry observed by NMR spectroscopy at ambient temperature. Ligands with two different PR$_2$ groups displayed no discernible spin—spin coupling between the two inequivalent ^{31}P nuclei. The N—H hydrogens of PNP and PNN ligands resonate at chemical shifts similar to those previously reported for similar pincer ligands.[29c,34] Other spectroscopic details for the individual ligands can be found in the Supporting Information of this report.

Synthesis of Group 10 Pincer Complexes. The PNP and PNN ligands discussed in this publication are ideally suited to support a variety of square-planar pincer complexes of the general formula (PNZ)MX (M = Ni, Pd, Pt; Z = P, N; X = OAc, Cl). Two forms of the ligand precursor (N—H or N—Me) were used to introduce the amidoPNX ligand into the

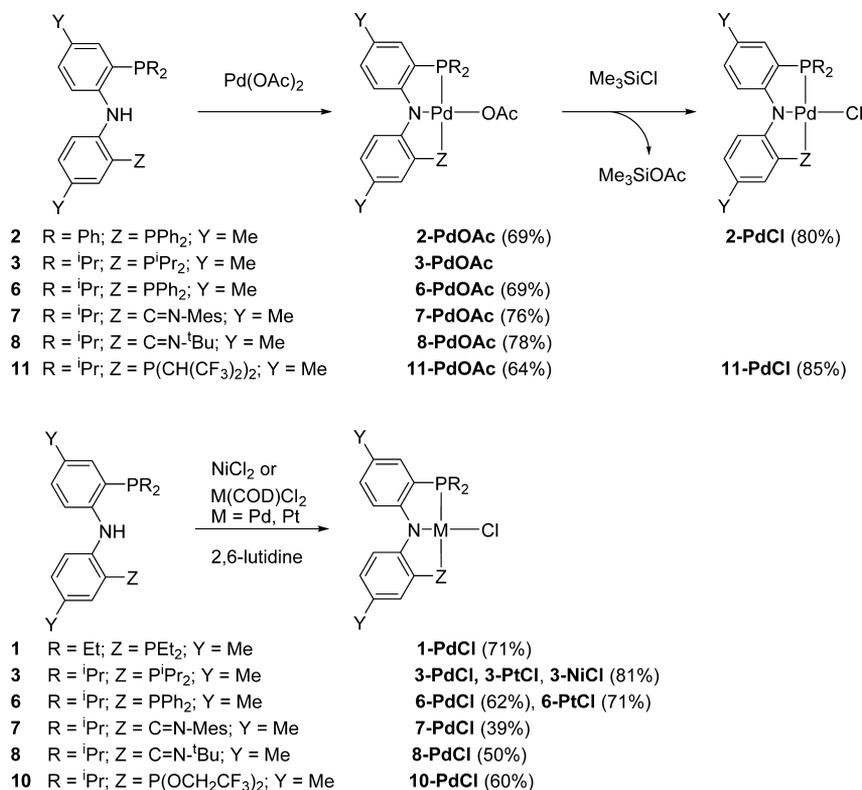**Table 1. Select NMR Data for PNP and PNN Pincer Ligands in C$_6$D$_6$ Solution**

pincer	δ, ^{31}P NMR	δ, ^{1}H NMR, N*H*	symmetry in solution
F	−13.9 P^{i}Pr$_2$	7.69 (d, 10 Hz)	C$_s$
6-H	−16.1 PPh$_2$	Overlapping with Ar signals	C$_s$
	−14.2 P^{i}Pr$_2$		
G	−8.0 P^{i}Pr$_2$	10.69 (s)	C$_s$
7-H	−5.8 P^{i}Pr$_2$	11.33 (s)	C$_s$
8-H	−7.3 P^{i}Pr$_2$	11.80 (s)	C$_s$
9-H	98.2 P(NMe$_2$)$_2$	8.55 (d, 8 Hz)	C$_s$
	−13.1 P^{i}Pr$_2$		
10-H	166.3 P(OCH$_2$CF$_3$)$_2$	7.43 (d, 5 Hz)	C$_s$
	−15.0 P^{i}Pr$_2$		
11-H^a	215.2 P(OCH(CF$_3$)$_2$)$_2$	NA	C$_s$
	35.9 (P^{i}Pr$_2$)		
1-H	−36.5 PEt$_2$	7.87 (t, 8 Hz)	C$_{2v}$
2-H	−18.9 PPh$_2$	7.08 (t, 6 Hz)	C$_{2v}$
3-H	−12.9 P^{i}Pr$_2$	8.23 (t, 8 Hz)	C$_{2v}$
4-Me	−6.3 P^{i}Pr$_2$	3.48 (s)	C$_{2v}$
5-Me	−6.2 P^{i}Pr$_2$	3.27 (s)	C$_{2v}$

^{a}**11-H** was not isolated; the spectra were collected in the reaction mixture in hexafluoroisopropanol.
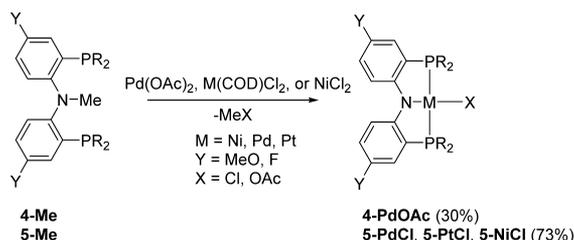
coordination sphere of a group 10 metal. In the case of the (PNZ)H form of the ligand, the direct reaction of the neutral pincer with a group 10 metal chloride (Pd(COD)Cl$_2$, NiCl$_2$ or Pt(COD)Cl$_2$) or acetate (Pd(OAc)$_2$) precursor generated (PNZ)MX. When a group 10 metal chloride was the reagent, the addition of a base such as 2,6-lutidine was necessary to remove the net HCl byproduct observed during the formation of (PNZ)MCl. In the case of Pd(OAc)$_2$, the addition of a base was not necessary, and the reaction produced (PNZ)PdOAc in conjunction with an equivalent of acetic acid as a byproduct. Compounds **1-PdCl**, **3-PdCl**,[29d] **6-PdCl**,[40] **7-PdCl**, **8-PdCl**, and **10-PdCl** were prepared by stirring one equivalent of the corresponding free ligand, with one equivalent of both 2,6-lutidine and Pd(COD)Cl$_2$ in diethyl ether. The colorless solution immediately became red, demonstrating conversion to the desired complexes with concomitant formation of a lutidinium chloride salt and free 1,5-cyclooctadiene. **6-PtCl** and **3-PtCl**[29d] were prepared in an analogous manner by treatment of one equivalent of the corresponding free ligand with one equivalent of both Pt(COD)Cl$_2$ and 2,6-lutidine. Compound **3-NiCl** was synthesized by heating a benzene solution of **3-H** with one equivalent of anhydrous NiCl$_2$ and one equivalent of 2,6-lutidine for 18 h.[29d] Compounds **2-PdOAc**,[29c] **6-PdOAc**, **7-PdOAc**, **8-PdOAc**, **10-PdOAc**, and **11-PdOAc** were all synthesized by stirring the corresponding free ligand and Pd(OAc)$_2$ in diethyl ether for 1 h. Each complex was then isolated upon workup as a red solid. These reactions are demonstrated graphically in Scheme 3.

In the case of (PNP)Me precursors **4-Me** and **5-Me**, the free ligand was reacted with a group 10 metal chloride precursor (Pd(COD)Cl$_2$, NiCl$_2$, or Pt(COD)Cl$_2$) to produce (PNP)MCl and an equivalent of MeCl by N—C cleavage (Scheme 4).[29c] **4-PdCl** was prepared from the reaction of **4-Me** and Pd(COD)Cl$_2$ in toluene. The reaction mixture was heated in an 80 °C oil bath for 3 days. Upon workup, **4-PdCl** was isolated as a green powder in a 41% yield. **4-PdOAc** was synthesized from the reaction of **4-Me** and Pd(OAc)$_2$. **5-PdCl**, **5-PtCl**, and **5-NiCl**
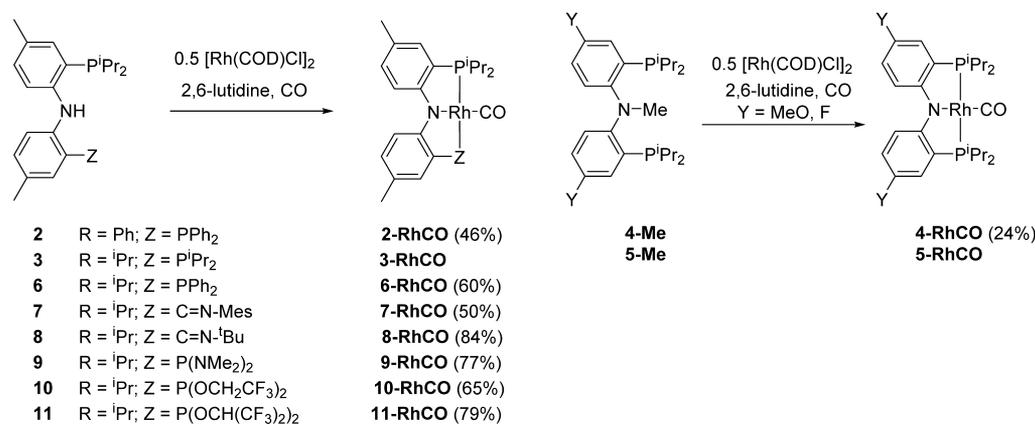
Scheme 3. N−H Cleavage

2	R = Ph; Z = PPh₂; Y = Me	**2-PdOAc** (69%)	**2-PdCl** (80%)
3	R = ⁱPr; Z = PⁱPr₂; Y = Me	**3-PdOAc**	
6	R = ⁱPr; Z = PPh₂; Y = Me	**6-PdOAc** (69%)	
7	R = ⁱPr; Z = C=N-Mes; Y = Me	**7-PdOAc** (76%)	
8	R = ⁱPr; Z = C=N-ᵗBu; Y = Me	**8-PdOAc** (78%)	
11	R = ⁱPr; Z = P(CH(CF₃)₂)₂; Y = Me	**11-PdOAc** (64%)	**11-PdCl** (85%)

1	R = Et; Z = PEt₂; Y = Me	**1-PdCl** (71%)
3	R = ⁱPr; Z = PⁱPr₂; Y = Me	**3-PdCl, 3-PtCl, 3-NiCl** (81%)
6	R = ⁱPr; Z = PPh₂; Y = Me	**6-PdCl** (62%), **6-PtCl** (71%)
7	R = ⁱPr; Z = C=N-Mes; Y = Me	**7-PdCl** (39%)
8	R = ⁱPr; Z = C=N-ᵗBu; Y = Me	**8-PdCl** (50%)
10	R = ⁱPr; Z = P(OCH₂CF₃)₂; Y = Me	**10-PdCl** (60%)

Scheme 4. N−Me Cleavage

4-Me	**4-PdOAc** (30%)
5-Me	**5-PdCl, 5-PtCl, 5-NiCl** (73%)

were prepared by heating a benzene solution of **5-Me** with Pd(COD)Cl₂, Pt(COD)Cl₂, or NiCl₂ for 18 h.[29d] The acetate ligand in (PNZ)PdOAc can be conveniently exchanged for chloride by reaction with Me₃SiCl, resulting in the formation of (PNZ)PdCl and expulsion of one equivalent of Me₃SiOAc.

This synthetic route was used to prepare compounds **2-PdCl**, **8-PdCl**, and **11-PdCl**.

Synthesis of (pincer)RhCO Complexes. (pincer)RhCO complexes were all synthesized through the reaction of a pincer ligand with 0.5 equiv of [Rh(COD)Cl]₂ in the presence of one equivalent of 2,6-lutidine under 1 atm of carbon monoxide (Scheme 5). The (pincer)Rh-CO complexes **1-RhCO**, **2-RhCO**, **3-RhCO**,[41] **4-RhCO**, **5-RhCO**,[41] **6-RhCO**, **7-RhCO**, **8-RhCO**, **9-RhCO**, **10-RhCO**, and **11-RhCO** were all synthesized by the given route. These complexes were all isolated as brown, yellow, or orange powders and have been fully characterized by infrared and multinuclear NMR spectroscopy.

Characterization of Rh and Pd Complexes. Spectroscopic and experimental data associated with the pincer complexes prepared in this work can be found in Table 2 and the Supporting Information of this work. It can be

Scheme 5. Synthetic Route to (pincer)RhCO Complexes

2	R = Ph; Z = PPh₂	**2-RhCO** (46%)	
3	R = ⁱPr; Z = PⁱPr₂	**3-RhCO**	
6	R = ⁱPr; Z = PPh₂	**6-RhCO** (60%)	
7	R = ⁱPr; Z = C=N-Mes	**7-RhCO** (50%)	
8	R = ⁱPr; Z = C=N-ᵗBu	**8-RhCO** (84%)	
9	R = ⁱPr; Z = P(NMe₂)₂	**9-RhCO** (77%)	
10	R = ⁱPr; Z = P(OCH₂CF₃)₂	**10-RhCO** (65%)	
11	R = ⁱPr; Z = P(OCH(CF₃)₂)₂	**11-RhCO** (79%)	

4-Me	**4-RhCO** (24%)
5-Me	**5-RhCO**

Table 2. NMR Features of (pincer)RhCO and (pincer)PdX Complexes

complex	^{31}P NMR (C$_6$D$_6$) δ ppm	J_{Rh-P} (Hz)	J_{P-P} (Hz)	color	symmetry
2-RhCO	41.3 (d)	135		orange	C$_{2v}$
3-RhCO	61.5 (d)	131		yellow	C$_{2v}$
4-RhCO	62.0 (d)	130		brown	C$_{2v}$
5-RhCO	61.5 (d)	131		yellow	C$_{2v}$
6-RhCO	64.7 (dd, P^{i}Pr$_2$)	133	270	yellow	C$_s$
	39.2 (dd, PPh$_2$)	134			
7-RhCO	76.3 (d)	130		red	C$_1$
8-RhCO	78.7 (d)	154		red	C$_1$
9-RhCO	130.9 (dd, P(NMe$_2$)$_2$)	163	315	yellow	C$_s$
	58.7 (dd, P^{i}Pr$_2$)	123			
10-RhCO	190.7 (dd, P (OCH$_2$CF$_3$)$_2$)	190	346	red	C$_s$
	60.1 (dd, P^{i}Pr$_2$)	125			
11-RhCO	207.5 (dd, P(OCH(CF$_3$)$_2$))	195	340	red	C$_s$
	59.3 (dd, P^{i}Pr$_2$)	127			
2-PdCl	30.2 (s)			green	C$_{2v}$
4-PdCl	47.9 (s)			green	C$_{2v}$
6-PdCl	54.0 (d, P^{i}Pr$_2$)		438	red	C$_s$
	25.9 (d, PPh$_2$)				
7-PdCl	70.3 (s)			red	C$_1$
8-PdCl	70.4 (s)			red	C$_1$
10-PdCl	159.2 (d, P(OCH$_2$CF$_3$)$_2$)		545	purple	C$_s$
	53.5 (d, P^{i}Pr$_2$)				
11-PdCl	172.3 (d, P(OCH(CF$_3$)$_2$)$_2$)		525	purple	C$_s$
	57.9 (d, P^{i}Pr$_2$)				
2-PdOAc	28.9 (s)			red	C$_{2v}$
4-PdOAc	48.1 (s)			red	C$_{2v}$
6-PdOAc	25.8 (d, P^{i}Pr$_2$)		412	red	C$_s$
	55.8 (d, PPh$_2$)				
7-PdOAc	65.6 (s)			red	C$_1$
8-PdOAc	66.3 (s)			red	C$_1$
11-PdOAc	176.2 (d, P(OCH(CF$_3$)$_2$)$_2$)		517	purple	C$_s$
	58.6 (d, P^{i}Pr$_2$)				

generally noted that metalation was accompanied by a downfield shift of the ^{31}P{^{1}H} NMR signal. In the case of the C$_s$ symmetric (PNP′)M complexes, large $^2J_{PP}$ values were observed, characteristic for spin–spin coupling between two inequivalent *trans*-phosphines. These $^2J_{PP}$ values were generally greater for PdCl complexes (>400 Hz) than for RhCO complexes (<350 Hz) and were largest for complexes of ligands **10** and **11**. The fluoroalkoxy-substituted phosphorus atoms also displayed the largest $^1J_{Rh-P}$ values.

The NMR spectra of **1-PdCl**, **1-PdOAc**, **2-PdCl**, **2-RhCO**, **3-PdCl**, **3-PdOAc**, **3-RhCO**, **4-PdCl**, **4-PdOAc**, **4-PdOAc**, and **4-RhCO** were consistent with C$_{2v}$ symmetry on the NMR time scale. **6-PdCl**, **6-RhCO**, **6-PdOAc**, **9-RhCO**, **10-PdCl**, **10-PdOAc**, **10-RhCO**, **11-PdCl**, **11-PdOAc**, and **11-RhCO** exist as C$_s$ symmetric complexes in solution. On the other hand, **7-PdCl**, **7-PdOAc**, **7-RhCO**, **8-PdCl**, **8-PdOAc**, and **8-RhCO** are consistent with C$_1$ symmetry on the NMR time scale. The

lower symmetry of the PNN pincer complexes suggests that the "flipping" of the two aromatic rings of the diarylamido backbone past each other is significantly slower in the PNN pincer complexes than in the PNP systems. The symmetry of these complexes is reflective of the symmetry observed for the binucleating PNN ligand complexes previously reported.[34]

Structural Analysis of Neutral Pincer Complexes in the Solid State. The solid-state structures of **8-PdOAc**, **8-PdCl**, **7-PdCl**, **11-RhCO**, and **6-RhCO**, as obtained by single-crystal X-ray diffractometry, are depicted in Figure 3, and select metric parameters are tabulated in Table 3. In each case, the environment about the metal center was found to be approximately square planar. One notable feature is that the pincer bite angles of complexes of ligands **7** and **8** are relaxed relative to those observed for the more traditional PNP ligands and closely resemble the bite angles observed in the binucleating PNN type pincer ligand complexes.[34] This expansion is related to incorporation of a six-membered ring containing the metal center. The angle is, however, not as expanded as that observed for the carbazole-based NNN complex, **12-PdCl**, whose pincer bite angle was observed to be ca. 176.8°.[33a] The bond distances of the donor atoms to Pd resemble those of previously reported similar compounds.[29c,33a,44]

The structure of **11-RhCO** contains an apparent close contact between the hydrogen of the hexafluoroisopropoxy group and Rh (d_{Rh-H} = 2.8143(5) Å). Such contacts between C−H hydrogens and square-planar d^8 metal centers along the axis perpendicular to the main coordination plane have been analyzed previously and can be viewed as a form of hydrogen bonding.[45] This is especially compelling here, given that the carbon of the C−H bond in question possesses three electron-withdrawing substituents.

Solid-State Structures of 5-NiCl, [5-NiCl][CHB$_{11}$Cl$_{11}$], 4-PdCl, and [4-PdCl][CHB$_{11}$Cl$_{11}$]. Chemical oxidation of **5-NiCl** with [Ag][CHB$_{11}$Cl$_{11}$] resulted in isolation of [**5-NiCl**][CHB$_{11}$Cl$_{11}$] as brown crystals. The chemical oxidation of **4-PdCl** with [*tris*(4-bromophenyl)aminium][CHB$_{11}$Cl$_{11}$] resulted in a rapid color change from purple to brown. The neutral amine was extracted from the reaction mixture with pentane. Slow diffusion of pentane into a dichloromethane solution of crude [**4-PdCl**][CHB$_{11}$Cl$_{11}$] resulted in precipitation of orange crystals of [**4-PdCl**][CHB$_{11}$Cl$_{11}$] with a 95% yield. Single crystals of **5-NiCl**, [**5-NiCl**][CHB$_{11}$Cl$_{11}$], **4-PdCl**, and [**4-PdCl**][CHB$_{11}$Cl$_{11}$] were subjected to an X-ray diffraction study (Figure 4) which allowed for the determination of the solid-state structures. In all four structures, the geometry about the metal center is approximately square planar. The carborane anion in [**5-NiCl**][CHB$_{11}$Cl$_{11}$] and [**4-PdCl**][CHB$_{11}$Cl$_{11}$] is well separated from the cation and can be considered noncoordinating. Close inspection of the metric parameters of **5-NiCl** and [**5-NiCl**][CHB$_{11}$Cl$_{11}$] (Table 4) revealed little difference between the corresponding bond angles and distances, apart from modest shortening of the Ni−N and Ni−Cl bonds upon oxidation. Similarly, only minor changes in the metric parameters were revealed upon close inspection of the molecular structures of **4-PdCl** and [**4-PdCl**][CHB$_{11}$Cl$_{11}$] (Table 5). Szilagyi, Meyer, and Mindiola undertook a thorough study of the analogous **3-NiCl** and [**3-NiCl**][OTf] employing NMR, EPR, UV−vis, and multiedge XAS spectroscopy in addition to structural and theoretical studies.[26] They also found a similar close correspondence between the structures of the neutral and cationic complexes
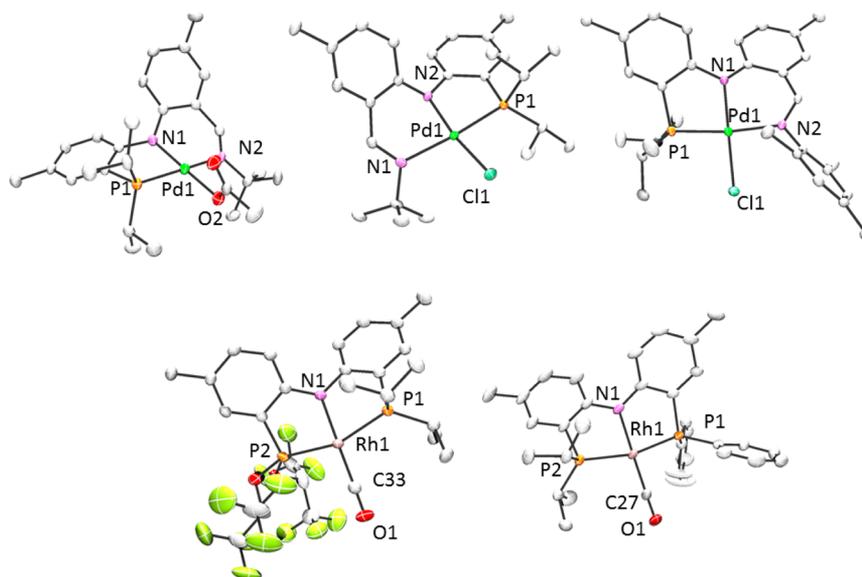
Figure 3. POV-Ray renditions[42] of the ORTEP drawings[43] (50% probability ellipsoids) of 8-PdOAc, 8-PdCl, 7-PdCl, 11-RhCO, and 6-RhCO showing selected labeling. Hydrogen atoms are omitted for clarity. Top left: 8-PdOAc. Top center: 8-PdCl; dichloromethane of cocrystallization not shown. Top right: 7-PdCl. Bottom left: 11-RhCO. Bottom right: 6-RhCO.

Table 3. Comparison of the Metric Parameters Associated with Group 10 Pincer Complexes

complex	d(M–X) (Å)	d(M–amido) (Å)	d(M–P$_1$) (Å)	d(M–P$_2$/N (imine)) (Å)	pincer bite angle[a] (deg)
8-PdOAc	2.0554(3)	2.002(3)	2.2348(13)	2.138(3)	168.21(7)
3-PdCl[b]	2.3157(7)	2.0258(19)	2.2914(4)	2.2914(4)	163.54(3)
6-PdCl	2.314(4)	2.028(1)	2.300(4)	2.278(4)	163.72(1)
8-PdCl	2.3433(7)	2.018(2)	2.2180(6)	2.1543(17)	170.99 (3)
7-PdCl	2.3224(9)	2.0201(18)	2.2311(10)	2.1022(18)	171.24(5)
4-PdCl	2.3320(9)	2.039(2)	2.2894(15)	2.2840(15)	169.28(3)
12-PdCl[c]	2.3081(15)	1.989(5)	2.060(5)/2.065(5)		176.77(17)
complex	d(M–CO) /d(C–O) (Å)	d(M–amido) (Å)	d(M–P$_1$) (Å)	d(M–P$_2$) (Å)	bite angle (deg)
11-RhCO	1.829(4)/1.148(5)	2.070(3)	2.3122(10)	2.2184(10)	160.00(3)
6-RhCO	1.8180(16)/1.149(2)	2.0643(12)	2.2861(4)	2.2777(4)	162.045(14)

[a]The term pincer bite angle refers to the angle formed by the two trans donor atoms of the pincer ligand and the metal center (e.g., P–M–P). [b]Taken from ref 29a. [c]Taken from ref 33a.

and concluded that oxidation takes place at the ligand, with no change in the oxidation state of Ni.

Analysis of the Electronic Properties. Our investigation of the electronic properties of the pincer ligands discussed within this report was a two part endeavor where we (a) obtained cyclic voltammograms for (pincer)MCl compounds of group 10 metals and (b) measured the IR stretching frequencies of (pincer)RhCO compounds. Our underlying assumptions are that the redox potentials obtained from CV studies report on the ease of oxidation of the pincer ligand (reflects the "electron-richness" of the π-system of the ligand) and that the ν(CO) IR stretching frequencies give insight into the "electron-richness" of the metal center. The "electron-richness" of the metal center is a direct reflection of the donating ability of the pincer ligand toward the metal center.

The redox properties of **1-PdCl**, **2-PdCl**, **3-PdCl**, **3-PtCl**, **3-NiCl**, **4-PdCl**, **5-PdCl**, **5-PtCl**, **5-NiCl**, **6-PdCl**, **6-PtCl**, **7-PdCl**, **8-PdCl**, **10-PdCl**, **11-PdCl**, and **12-PdCl** were investigated by cyclic voltammetry using 0.3 M [Bu$_4$N][PF$_6$] as the electrolyte in dichloromethane. Ferrocene was used as an internal standard, and the potentials reported in Table 6 are referenced vs the ferrocene/ferrocenium redox couple.[46] It is noteworthy that the redox potentials of the (pincer)PdCl

complexes can be varied within a range of about 0.6 V within the framework of diarylamido-based PNZ ligands; this range expands to almost 1 V (−0.27 to 0.69 V) if the carbazole-based ligand (**12**) is included. The cyclic voltammograms of **1-PdCl**, **2-PdCl**, **3-PdCl** **3-PtCl**, **3-NiCl**, **5-PdCl**, **5-PtCl**, **5-NiCl**, **6-PdCl**, **6-PtCl**, **7-PdCl**, **8-PdCl**, **10-PdCl**, **11-PdCl**, and **12-PdCl** exhibit quasi-reversible one-electron redox events. The notable exception to this observation is the cyclic voltammogram obtained for **4-PdCl**, which is characterized as having two quasi-reversible one-electron redox events. Further studies on the noninnocent character of this ligand are in progress.

The data reported in Table 5 are consistent with the notion of ligand-based redox events in (pincer)MCl complexes. This is supported by three major observations. (1) The redox potential appears to be affected to a great degree by substituents conjugated with the diarylamido π-system but are remote from the metal center (*vide infra*). (2) Only small changes in the $E_{1/2}$ values are observed upon varying the identity of the metal (e.g., **3-PdCl**, **3-PtCl**, and **3-NiCl**).[47] (3) Exchange of the diarylamido backbone for a carbazole unit has the largest effect on the redox potential. The ionization potential of carbazole is considerably higher than that of diphenylamine, so the greater difficulty in oxidizing **12-PdCl** is to be expected.[48] This is
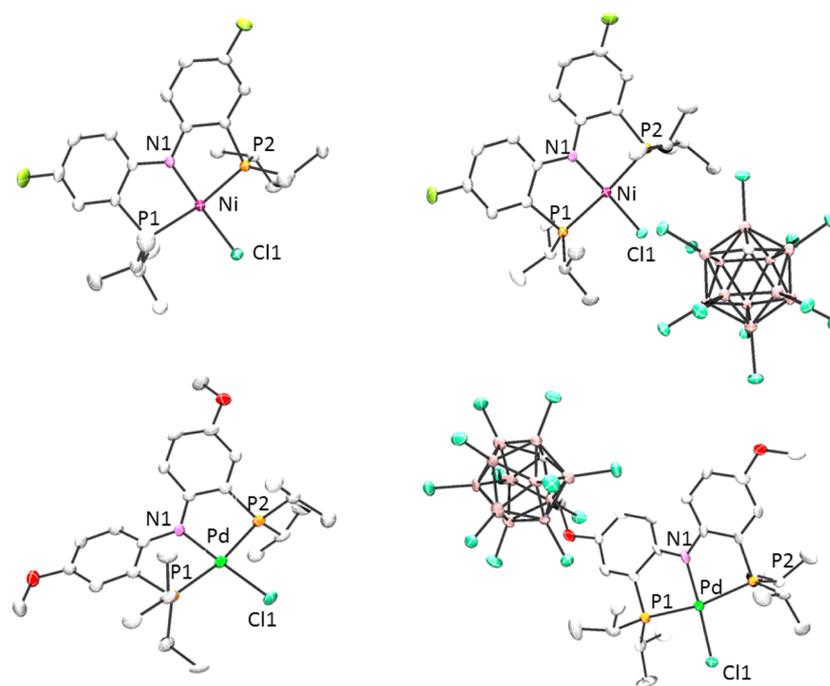
Figure 4. POV-Ray renditions of ORTEP[43] drawings (50% probability ellipsoids) of **5-NiCl** (top left), [**5-NiCl**][**CHB₁₁Cl₁₁**] (top right), **4-PdCl** (bottom left), and [**4-PdCl**][**CHB₁₁Cl₁₁**] (bottom right). Selected bond distances (Å) and angles (deg) are reported in Tables 4 and 5. Hydrogen atoms in all structures and cocrystallized toluene in the structure of 4-PdCl are omitted for clarity. For the structure of [**4-PdCl**][**CHB₁₁Cl₁₁**], only one of the two crystallographically independent cation/anion pairs is shown.

Table 4. Metric Parameters Associated with 5-NiCl and [5-NiCl][CHB₁₁Cl₁₁]

metric (Å or deg)	5-NiCl	[5-NiCl][CHB₁₁Cl₁₁]
Ni−Cl (Å)	2.1841(7)	2.1520(7)
Ni−N (Å)	1.8947(19)	1.859(2)
Ni−P(1) (Å)	2.1746(7)	2.1910(7)
Ni−P(2) (Å)	2.1998(7)	2.2158(7)
Cl−Ni−N (deg)	175.45(7)	170.08(6)
Cl−Ni−P(1) (deg)	92.62(3)	91.66(3)
N−Ni−P(1) (deg)	85.33(6)	87.13(6)
P(1)−Ni-P(2) (deg)	170.18(2)	168.48(3)

Table 5. Selected Bond Distances (Å) and Angles (deg) from the Solid-State X-ray Studies of 4-PdCl and [4-PdCl][CHB₁₁Cl₁₁][a]

metric (Å or deg)	4-PdCl	[4-PdCl][CHB₁₁Cl₁₁]
Pd1−N(1) (Å)	2.039(2)	2.013(6)
Pd1−P(1) (Å)	2.2923(9)	2.300(2)
Pd1−P(2) (Å)	2.2998(9)	2.2845(19)
O−C$_{Ar}$	1.393(3)	1.354(8)
O−C$_{Ar}$	1.384(3)	1.356(9)
Pd1−Cl(1) (Å)	2.3320(9)	2.299(2)
N1−Pd−P(1) (deg)	84.78(7)	83.11(17)
N1−Pd−P(2) (deg)	84.71(7)	84.59(17)
P1−Pd1−P(2) (deg)	169.28(3)	166.39(8)
N1−Pd1−Cl(2) (deg)	178.09(7)	172.01(18)
P1−Pd1−Cl(1) (deg)	94.00(4)	97.99(7)
P2−Pd1−Cl(1) (deg)	96.45(4)	95.00(7)

[a]For [**4-PdCl**][**CHB₁₁Cl₁₁**], metric parameters for only one of the two crystallographically independent cations are given.

clearly not just a consequence of the nitrogenous side donors in **12**: the redox potentials for **7-PdCl** and **8-PdCl** are not so

Table 6. $E_{1/2}$ (V) for (pincer)MCl Complexes

ligand	Pd−Cl E/V vs Fc/Fc⁺	Pt−Cl E/V vs Fc/Fc⁺	Ni−Cl E/V vs Fc/Fc⁺
4	−0.27 (**4-PdCl**)		
	0.94		
3	−0.08 (**3-PdCl**)	−0.11 (**3-PtCl**)	−0.19 (**3-NiCl**)
1	−0.05 (**1-PdCl**)		
6	−0.02 (**6-PdCl**)	−0.05 (**6-PtCl**)	
7	0.04 (**7-PdCl**)		
2	0.04 (**2-PdCl**)		
8	0.06 (**8-PdCl**)		
5	0.11 (**5-PdCl**)	0.06 (**5-PdCl**)	−0.01 (**5-PdCl**)
10	0.15 (**10-PdCl**)		
11	0.32 (**11-PdCl**)		
12	0.69 (**12-PdCl**)		

dramatically different from the PNP analogs. In addition, the reported $E_{1/2}$ value for the (NNN*)NiCl complex by Vicic et al. (−0.12 V vs Fc/Fc⁺, NNN* = (2-Me₂NC₆H₄)₂N) is quite close to that of **3-NiCl**, reflecting the similarity of the diarylamido backbones.[27]

A comparison of the ν(CO) frequencies of **2-RhCO**, **3-RhCO**,[41] **4-RhCO**, **5-RhCO**, **6-RhCO**, **7-RhCO**, **8-RhCO**, **9-RhCO**, **10-RhCO**, **11-RhCO**, **13-RhCO**,[49] **14-RhCO**,[50] **15-RhCO**,[51] **16-RhCO**,[52] **17-RhCO**,[53] **18-RhCO**,[30a] and **19-RhCO**[35] allowed for an assessment of the donor strength of the corresponding pincer ligands toward Rh via the extent of backbonding to CO (see Table 7).[54] It is important to note that the magnitude of ν(CO) may be influenced by factors other than the "electron-richness" of the metal center; such influences have been discussed in the literature.[55,54d] However, we expect that within the confines of our study, various other influences on the differences in ν(CO) are minimal because of the similarity among the analyzed complexes. A survey of the

Table 7

ligand	Pd−Cl E/V vs Fc/Fc⁺	ν(CO) (cm⁻¹)
4	−0.27 (**4-PdCl**)	1933 (**4-RhCO**)
	0.94	
3	−0.08 (**3-PdCl**)	1938 (**3-RhCO**)
1	−0.05 (**1-PdCl**)	
6	−0.02 (**6-PdCl**)	1941 (**10-RhCO**)
7	0.04 (**7-PdCl**)	1942 (**6-RhCO**)
2	0.04 (**2-PdCl**)	1952 (**2-RhCO**)
8	0.06 (**8-PdCl**)	1930 (**8-RhCO**)
5	0.11 (**5-PdCl**)	1944 (**5-RhCO**)
10	0.15 (**10-PdCl**)	1960 (**17-RhCO**)
11	0.32 (**11-PdCl**)	1980 (**11-RhCO**)

$\nu(CO)$ values for a series of (pincer)RhCO complexes is summarized in Figure 5. The IR spectra of **2-RhCO**, **4-RhCO**, **5-RhCO**, **6-RhCO**, **7-RhCO**, **8-RhCO**, **9-RhCO**, **10-RhCO**, and **11-RhCO** were collected in this work under the same conditions and on the same instrument. The $\nu(CO)$ values for **3-RhCO**,[41] **13-RhCO**,[49] **14-RhCO**,[50] **15-RhCO**,[51] **16-RhCO**,[52] **17-RhCO**,[53] **18-RhCO**,[30a] and **19-RhCO**[35] come from literature sources and have been obtained on different instruments and in different media, which may cause deviations on the order of a few wavenumbers.[56] The $\nu(CO)$ frequencies of these (pincer)RhCO compounds range from 1900 to 1980 cm⁻¹, a span of 80 cm⁻¹. The lowest stretching frequency, and thus the most donating pincer ligand in this series, is observed for **14-RhCO** where the pincer combines trialkylphosphine side arms with the central alkyl donor. The new complex with a bis(hexafluoroisopropoxy)phosphino arm (**11-RhCO**) is the least donating pincer in this series, with the highest $\nu(CO)$ value. Fluoroalkoxy substituents on phosphorus have been

recognized as resulting in some of the most strongly π-accepting PX_3 ligands.[57] Rh complexes of fluoroalkoxy-substituted phosphines have recently been used in the direct coupling of arenes with aryl iodides[58] and in designs relevant to water and HX photosplitting catalysis.[59]

It is instructive to examine the relationship between $\nu(CO)$ values for (pincer)RhCO complexes and $E_{1/2}$ values for (pincer)PdCl complexes as a function of the nature of the pincer ligand. The numerical values are collected in Table 6, and Figure 6 shows these values plotted in a graphical form. There does not appear to be a smooth relationship between $\nu(CO)$ and $E_{1/2}$ that encompasses the whole set of ligands. For example, it is quite obvious that the ligand responsible for the lowest $\nu(CO)$ (**8-RhCO**) does not give rise to the easiest oxidation. On the other hand, there are trends that can be identified within smaller subsets of ligands wherein only substituents at specific sites are varied. The red trendline (ligands shown explicitly in Figure 7) in Figure 6 connects ligands 3, 6, 2, 10, and 11. These are all PNP ligands with a constant diarylamido backbone (Me groups *para* to N) with varying substituents on the phosphorus atoms (R in Scheme 3). This subset shows a smooth, approximately linear relationship, with the increase in $\nu(CO)$ corresponding to an increase in $E_{1/2}$. The blue trendline (ligands shown explicitly in Figure 7) connects ligands 4, 3, and 5. This subset of PNP ligands shares the same two P^{i}Pr$_2$ side donors with varying substituents *para* to N in the diarylamine (Y in Scheme 4). Here, an increase in $\nu(CO)$ also corresponds to an increase in $E_{1/2}$, but it is clear that the slope of this trendline is very different: the rather large changes in $E_{1/2}$ correspond to relatively small changes in $\nu(CO)$. The (PNP)M complexes can be viewed as a system composed of four fused rings: the two aromatic rings of the

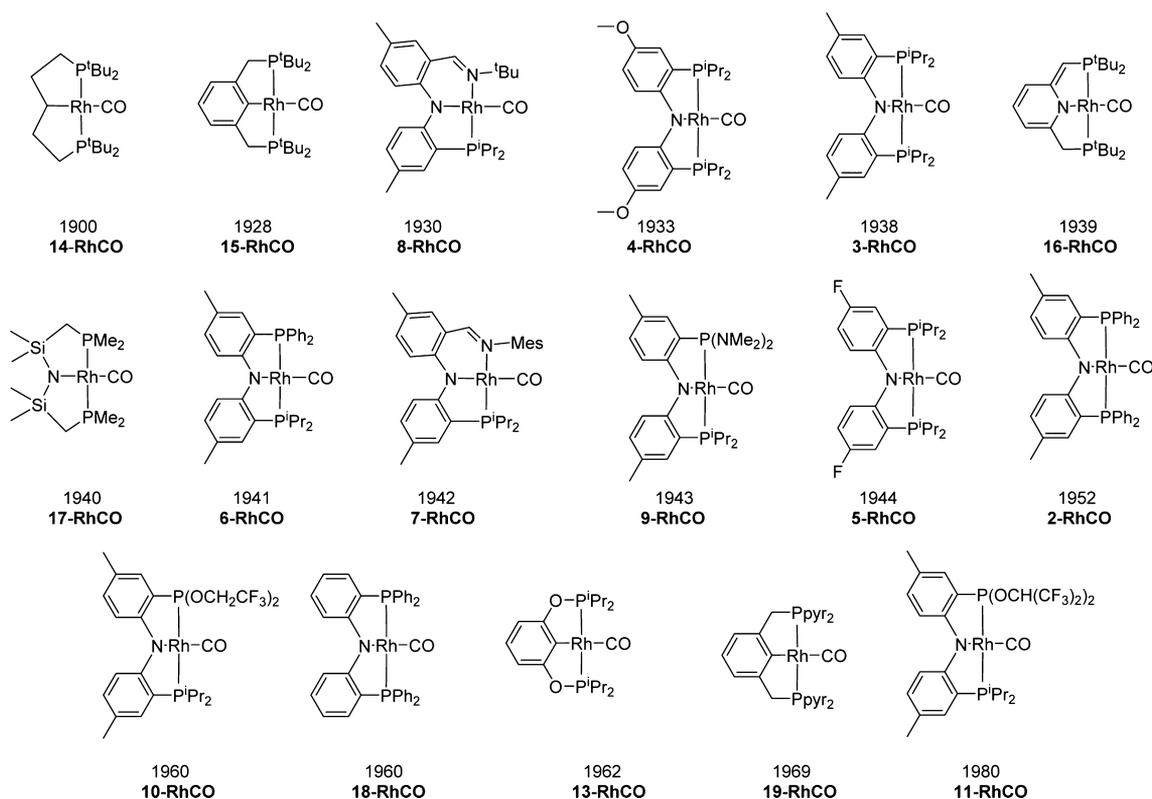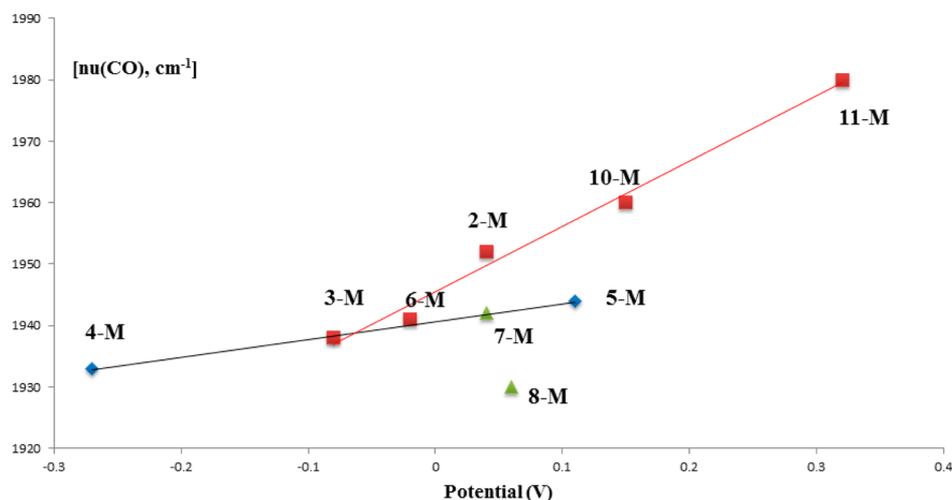**Figure 5.** $\nu(CO)$ values (cm⁻¹) for a series of (pincer)RhCO complexes.

Figure 6. A plot of $\nu(CO)$ values (cm^{-1}) in (pincer)RhCO vs $E_{1/2}$ values (V) for (pincer)PdCl complexes.

4-RhCO (1933 cm^{-1}) **3-RhCO** (1938 cm^{-1}) **5-RhCO** (1944 cm^{-1})
4-PdCl (-0.27 V)   **3-PdCl** (-0.08 V)   **5-PdCl** (0.11 V)

3-RhCO (1938 cm^{-1}) **6-RhCO** (1941 cm^{-1}) **2-RhCO** (1952 cm^{-1}) **10-RhCO** (1960 cm^{-1}) **11-RhCO** (1980 cm^{-1})
3-PdCl (-0.08 V)   **6-PdCl** (-0.02 V)   **2-PdCl** (0.04 V)   **10-PdCl** (0.15 V)   **11-PdCl** (0.32 V)
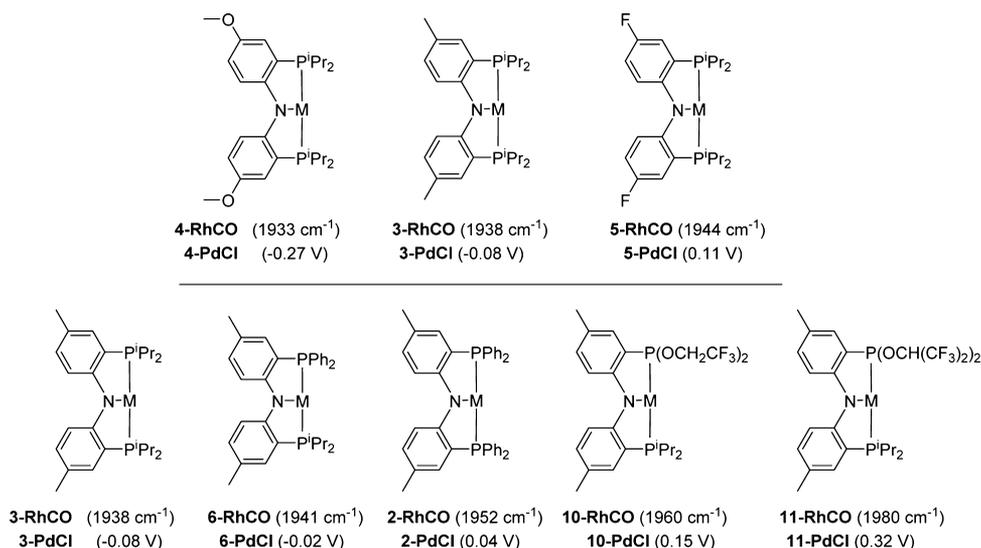
Figure 7. Top: the ligand series comprising the blue trendline in Figure 6. Bottom: the ligand series comprising the red trendline in Figure 6.

diarylamino backbone and the two five-membered metallacycles about the metal center. This four-ring system is constant for (PNP)M complexes with the same M, and the blue and the red trendlines in Figure 6 explore the influence of the substituents on this system. The red trendline explores substituents on P, close to the metal, and so for changes across the set there is a more pronounced effect on $\nu(CO)$ than in the blue trendline, where the substituents changing are conjugated with the diarylamido π-system and are relatively remote from the metal. It understandable that the two PNN ligands (**7** and **8**) do not fall onto either the blue or the red trendline, as the change to PNN involves a change to the four-ring core. While an imine as an N-donor toward Rh is apparently more donating than a phosphine, the iminyl (−HC=NX) as a substituent on the diarylamine backbone is probably somewhat π-electron-withdrawing.[60]

■ CONCLUSION

In summary, a series of new pincer ligands based on the diarylamido backbone have been prepared which incorporate a variety of substituents that change the stereo and electronic properties of the ligand. In the context of this work, we were

especially interested in exploring the relationship between the redox activity of the metal-bound pincer ligand and the electronic effect of the pincer on the metal center. The electronic properties of a series of pincer ligands were analyzed on the basis of redox potentials observed for group 10 metal complexes (PNZ)MCl (P = phosphine, Z = phosphine or imine) and $\nu(CO)$ values in the corresponding (PNZ)RhCO complexes. Overall, this analysis is consistent with the oxidation of (PNZ)MCl being ligand-based as it is more affected by substituents on the diarylamine backbone, whereas the $\nu(CO)$ in (PNZ)RhCO and thus the donor ability of the pincer ligand toward the metal is more strongly affected by the nature of the donors directly attached to the metal. As a final note, the metal and the oxidizable pincer ligand are directly connected, and their electronic properties cannot be modified completely independently. However, judicious choice of the donor atoms and the nature of their substituents as well as modifications to the diarylamido framework allows for some control of the degree to which the redox activity of the ligand and the electronic effect of the ligand on a metal center are influenced.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise specified, all manipulations were performed under an atmosphere of argon using a standard Schlenk line or a glovebox. Toluene, diethyl ether, hexanes, tetrahydrofuran, dichloromethane, trimethylsilyl chloride, C_6D_6, 2,6-lutidine, and toluene-d_8 were all dried over CaH_2; distilled or vacuum transferred; and then stored over molecular sieves in an argon filled glovebox. Pd(COD)Cl_2,[61] **A**,[62] **3-H**,[29a] **5-Me**,[29c] **3-PdCl**,[29d] **3-PdOAc**, **3-PtCl**, **3-NiCl**,[29d] **5-PdCl**,[29c] **5-PdOAc**,[29c] **5-PtCl**,[29d] **5-NiCl**,[29d] **2-PdCl**,[29c] **5-Me**,[29c] **F**,[34] and **G**[34] were prepared according to the published procedures. 2,6-Lutidine and DMF were dried over CaH_2 and distilled prior to use. All other chemicals used were received from commercial venders. NMR spectra were recorded on an Inova 300 (^{1}H, ^{13}C, ^{31}P), Inova 500 (^{1}H, ^{13}C, ^{31}P, ^{19}F), or a Varian 500 (^{1}H, ^{13}C, ^{31}P, ^{19}F) spectrometer. ^{31}P and ^{19}F NMR spectra were referenced externally using H_3PO_4 (85%, 0 ppm) and CF_3COOH (−78.5 ppm), respectively. Electrochemical studies were carried out using a CH Instruments Model 700 D Series Electrochemical Analyzer and Workstation in conjunction with a three electrode cell. The working electrode was a CHI 104 glassy carbon disk with a 3.0 mm diameter, and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was a $Ag/AgNO_3$ electrode. This was separated from solution by a fine porosity frit. CVs were conducted in dichloromethane with 0.3 M [Bu$_4$N][PF$_6$] as the supporting electrolyte at scan rate of 100 mV/s. The concentrations of the analyte solutions were approximately 1.00×10^{-3} M. CVs were referenced to the Fe(Cp)$_2$/ Fe(Cp)$_2^+$ redox couple. Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K$_\alpha$ = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling, were carried out using the Bruker APEXII software. Elemental analyses were performed by CALI Laboratories, Parsippany, New Jersey. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR Spectrometer with a diamond ATR. The samples were analyzed in the solid state.

A. A 3000 mL three-necked flask was charged with ditolylamine (142 g, 0.400 mol), a stir bar, and CH_2Cl_2 (1.50 L). N-bromosuccinimide (142 g, 0.800 mol) was subsequently added to the reaction mixture in 10 portions over the course of 2.5 h. The reaction was vigorously stirred at ambient temperature for 48 h. To ensure quantitative conversion to the desired product, a 1 mL aliquot was removed and dried *in vacuo* in a J. Young tube. A ^{1}H NMR experiment was conducted in $CDCl_3$ concluding that 99% conversion to the desired product had occurred. The volatiles were then removed *in vacuo*, and the resulting black solid was dissolved in pentane (1.20 L), stirred vigorously over silica gel for 30 min, and then filtered through a pad of Celite. Removal of the volatiles *in vacuo* and recrystallization in cold pentane at −35 °C resulted in pure product as a white solid. An additional fraction was obtained by again washing the black residue with pentane (4 × 200 mL). The pentane solution was then concentrated under a vacuum, and the resulting solution was recrystallized at −35 °C to obtain a second crop of **A** (181.6 g, 0.510 mmol, 71%). ^{1}H NMR (CDCl$_3$): δ 7.38 (s, 2H, Ar *H*), 7.09 (d, 2H, J_{HH} = 8 Hz, Ar *H*), 6.98 (d, 2H, J_{HH} = 8 Hz, Ar *H*), 6.16 (s, 1H, N*H*), 2.26 (s, 6H, Ar C*H$_3$*).

B. In the glovebox, a Schlenk flask was charged with p-anisidine (20.0 g, 162 mmol), Pd(OAc)$_2$ (200 mg, 0.892 mmol), DPPF (640 mg, 1.16 mmol), and toluene (250 mL). Degassed 4-bromoanisole (20.4 mL, 162 mmol) and sodium *tert*-pentoxide (20.6 g, 187 mmol) were quickly added to the reaction mixture under an atmosphere of argon. The reaction was refluxed for 36 h and then cooled to ambient temperature. A 1 mL aliquot was removed from the reaction mixture and dried in a J. Young tube. ^{1}H NMR analysis revealed conversion to the coupled product. The reaction was quenched with 3.3 mL of degassed H_2O and stirred for an additional 40 min prior to removing the volatiles *in vacuo*. The resulting solid was then dissolved in dichloromethane, stirred over silica gel, and then filtered through a pad of Celite. The solution was then concentrated and stored at −35 °C for 12 h. The resulting precipitate was then collected and dried in

vacuo to yield **B** as a colorless solid (25.3 g, 110 mmol, 69%). ^{1}H NMR (C_6D_6): δ 6.81 (d, *J* = 7 Hz, 4H, Ar *H*), 6.76 (d, *J* = 7 Hz, 4H, Ar *H*), 4.77 (s, 1H, N*H*), 3.35 (s, 6H, C*H$_3$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 154.8 (s, 3° Ar *C*), 138.4 (s, 3° Ar *C*), 119.9 (s, Ar *C*H), 115.0 (s, Ar *C*H), 55.2 (s, O*C*H$_3$).

C. A Schlenk flask was charged with **B** (5.05 g, 22.1 mmol), a stir bar, and dichloromethane (250 mL). N-bromosuccinimide (7.85 g, 44.1 mmol) was then added to the reaction vessel in small portions over the course of 10 min. The reaction mixture was stirred for 24 h under a steady flow of argon, and then a small aliquot was removed and dried *in vacuo*. ^{1}H NMR analysis revealed 99% conversion to **C**. The volatiles were removed, and the resulting solid was dissolved in tetrahydrofuran, filtered through a pad of Celite, and dried. The solution was then concentrated, layered with pentane, and stored at −35 °C to yield purple crystals. Removal of the volatiles a second time resulted in isolation of **C** (7.73 g, 20.1 mmol, 91%) as a purple solid. ^{1}H NMR (C_6D_6): δ 7.09 (d, 2H, J_{HH} = 3 Hz, Ar *H*), 6.82 (d, 2H, J_{HH} = 9 Hz, Ar *H*), 6.56 (dd, 2H, J_{HH} = 3 Hz, J_{HH} = 9 Hz, Ar *H*), 6.00 (s, 1H, N*H*), 3.13 (s, 6H, C*H$_3$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.4 (Ar *C*N), 135.4 (Ar *C*P), 120.4 (Ar *C*), 118.3 (Ar *C*), 115.7 (Ar *C*CH$_3$), 115.0 (Ar *C*), 55.3 (*C*H$_3$).

D. A Schlenk flask was charged with hexamethyldisilazane (1.0 mL, 5.0 mmol), n-butyllithium (2.0 mL of a 2.5 M solution in hexanes, 5.0 mmol), and tetrahydrofuran (5 mL). The reaction mixture was stirred for 20 min, and then **C** (1.7 g, 4.5 mmol) was added. After 5 min of continued stirring, CH_3I (0.42 mL, 6.7 mmol) was added to the solution. The reaction mixture was stirred overnight, and then the volatiles were removed *in vacuo*. The resulting colorless solid was taken up in diethyl ether and filtered through a bed of silica gel. The addition of pentane to the ethereal solution resulted in copious precipitation. The precipitation was collected to yield **D** as a colorless powder (0.78 g, 2.0 mmol, 44%). ^{1}H NMR (C_6D_6): δ 7.16 (d, J_{HH} = 3 Hz, 2H, Ar *H*), 6.70 (d, J_{HH} = 9 Hz, 2H, Ar *H*), 6.62 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar *H*), 3.13 (s, 6H, OC*H$_3$*), 2.93 (s, 3H, NC*H$_3$*). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.6 (s), 142.9 (s), 124.6 (s), 121.5 (s), 119.5 (s), 114.5 (s).

F. **A** (13 g, 36 mmol) was dissolved in anhydrous diethyl ether (100 mL) and cooled with a dry ice/acetone bath. The amine solution was then treated with n-butyllithium (29 mL, 2.5 M in hexanes) in a dropwise fashion via an addition funnel. The reaction was then stirred for 30 min before being warmed to room temperature to yield a yellow solution. The reaction was again cooled with a dry ice/acetone bath, and ClP^{i}Pr$_2$ (12 mL, 73 mmol) was added in a dropwise fashion via syringe, resulting in an immediate color change from yellow to orange. The reaction was stirred for 12 h before being hydrolyzed with an ethanol/H_2O solution (2.5 mL, 1:1). Stirring was commenced for an additional 1 h before removing the volatiles *in vacuo*. The resulting colorless solid was then extracted in a pentane/diethyl ether solution (10:1) and stirred vigorously over silica gel for 30 min before being filtered through a pad of Celite. The volatiles were removed, and the resulting white solid was washed with 3 × 5 mL portions of pentane to yield pure product as a white solid (12 g, 87%). ^{1}H NMR (C_6D_6): δ 7.69 (d, 1H, *J* = 10 Hz, N*H*), 7.23 (m, 3H, Ar *H*), 7.17 (m (overlapping with solvent), 1H, Ar *H*). 6.90 (d, 1H, *J* = 8 Hz, Ar *H*), 6.71 (d, 1H, *J* = 9 Hz, Ar *H*), 2.18 (s, 3H, Ar C*H$_3$*), 1.96 (m, 2H, C*H*(CH$_3$)$_2$), 1.93 (s, 3H, Ar C*H$_3$*), 1.06 (dd, 6H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(C*H$_3$*)$_2$), 0.92 (dd, 6H, J_{PH} = 11 Hz, J_{HH} = 7 Hz, CH(C*H$_3$*)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 146.1 (d, J_{CP} = 19 Hz, *C*N), 139.7 (Ar *C*), 133.9 (Ar *C*), 133.9 (d, J_{CP} = 2 Hz, Ar *C*H), 131.0 (Ar *C*), 130.7 (Ar *C*), 130.0 (Ar *C*). 128.9 (Ar *C*), 128.3 (Ar *C*), 118.5 (d, J_{CP} = 3 Hz, Ar *C*H), 116.5 (Ar *C*), 114.1 (Ar *C*), 23.2 (d, J_{CP} = 11 Hz, *C*H(CH$_3$)$_2$), 20.9 (Ar *C*H$_3$), 20.4 (Ar *C*H$_3$), 20.2 (d, J_{CP} = 10 Hz, CH(*C*H$_3$)$_2$), 18.9 (d, J_{CP} = 8 Hz, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −13.9.

Note: Often times, a small amount of **3-H** is formed. This can be readily removed by washing the solid with a small amount of pentane. ^{1}H NMR (C_6D_6): δ 8.28 (t, 1H, J_{PH} = 8 Hz, N *H*), 7.38 (d, 2H, *J* = 6 Hz, Ar *H*), 7.19 (s, 2H, Ar *H*), 6.91 (d, 2H, *J* = 8 Hz, Ar *H*), 2.18 (s, 6H, Ar C*H$_3$*), 2.01 (m, 4H, C*H*(CH$_3$)$_2$), 1.12 (dd, 12H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(C*H$_3$*)$_2$), 0.97 (dd, J_{PH} = 12 Hz, J_{HH} = 7 Hz, 12H, CH(C*H$_3$*)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ −12.9.

G. A Schlenk flask was charged with **F** (1.2 g, 3.1 mmol), a stir bar, and diethyl ether (25 mL). *n*-Butyllithium (2.5 mL, 6.1 mmol, 2.5 M in hexanes) was then added dropwise via addition funnel. The mixture was stirred for 1 h, and then DMF (0.50 mL, 6.2 mmol) was added to the reaction vessel. The mixture was stirred for 20 h and then quenched with a degassed solution of ethanol/water (3:1, 1.0 mL). The volatiles were removed *in vacuo*, and the resulting yellow solid was dissolved in diethyl ether and stirred vigorously over silica gel before being passed through a pad of Celite. The ethereal solution was then concentrated *in vacuo* and stored at −35 °C. The resulting yellow precipitate was dried to yield **G** as a yellow solid (0.74 g, 2.2 mmol, 71%). If **F** is still present in the solid, it can be removed via column chromatography (with silica gel) using first pentane to remove **F** and then ethyl acetate to wash **G** completely off the column. ^{1}H NMR (C$_6$D$_6$): δ 10.69 (s, 1H, N*H*), 9.71 (s, 1H, (O)C*H*), 7.30 (dd, 1H, J_{PH} = 4 Hz, J_{HH} = 8 Hz, Ar *H*), 7.25 (s, 1H, Ar *H*), 7.05 (d, 1H, J_{HH} = 8 Hz, Ar *H*), 6.90 (d, 1H, J_{HH} = 8 Hz, Ar *H*), 6.84–6.80 (m, 2H, Ar *H*), 2.16 (s, 3H, C*H$_3$*), 1.98 (m, 2H, C*H*(CH$_3$)$_2$), 1.97 (s, 3H, C*H$_3$*), 1.07 (dd, 6H, J_{HH} = 7 Hz, J_{PH} = 15 Hz, CH(C*H$_3$*)$_2$), 0.92 (dd, 6H, J_{HH} = 7 Hz, J_{PH} = 12 Hz, CH(C*H$_3$*)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 10.69 (s, 1H, N*H*), 9.71 (s, 1H, imine C*H*), 7.30 (d, 1H, J_{HH} = 8 Hz, Ar *H*), 7.25 (s, 1H, Ar *H*), 7.05 (d, 1H, J_{HH} = 8 Hz, Ar *H*), 6.90 (d, 1H, J_{HH} = 8 Hz, Ar *H*), 6.84 (s, 1H, Ar *H*), 2.16 (s, 3H, C*H$_3$*), 1.98 (m, 2H, C*H*(CH$_3$)$_2$), 1.97 (s, 3H, C*H$_3$*), 1.07 (d, 6H, J_{HH} = 7 Hz, CH(C*H$_3$*)$_2$), 0.92 (d, 6H, J_{HH} = 7 Hz, CH(C*H$_3$*)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 193.5 ((O)*C*H), 146.3 (*C*C(O)H), 143.7 (d, J_{CP} = 23 Hz, Ar *C*N), 136.5 (Ar *C*H), 136.2 (Ar *C*H), 134.5 (Ar *C*H), 133.1 (Ar *C*), 130.4 (Ar *C*H), 129.8 (d, J_{CP} = 23 Hz, Ar *C*), 125.8 (Ar *C*), 124.1 (Ar *C*H), 120.5 (Ar *C*), 113.4 (Ar *C*H), 23.5 (d, J_{CP} = 14 Hz, CH(*C*H$_3$)$_2$), 21.1 (Ar *C*H$_3$), 20.3 (d, J_{CP} = 20 Hz, CH(*C*H$_3$)$_2$), 20.0 (Ar *C*H$_3$), 19.2 (d, J_{CP} = 10 Hz, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −8.0 (s).

[Tris(4-bromophenyl)aminium][CHB$_{11}$Cl$_{11}$]. A Schlenk flask was charged with Na[CHB$_{11}$Cl$_{11}$] (628 mg, 1.15 mmol), *tris*(4-bromophenyl)amine (555 mg, 1.15 mmol), PhI(OAc)$_2$ (185 mg, 0.575 mmol), and dichloromethane (10 mL). Trimethylsilyl chloride (209 μL, 1.15 mmol) was then added to the colorless solution, resulting in a color change to royal blue. Stirring was continued for 30 min, and then the volatiles were removed extensively under a vacuum. The resulting blue powder was dissolved in dichloromethane and filtered through a pad of Celite. The dichloromethane solution was then layered with pentane, and slow diffusion at −35 °C resulted in isolation of [*tris*(4-bromophenyl)aminium][CHB$_{11}$Cl$_{11}$] (457 mg, 40%) as a paramagnetic blue powder. Elemental analysis, calculated: C, 22.73; H, 1.31. Found C, 22.87; H, 1.17.

1-H. In a 25 mL Schlenk flask under Ar, **A** (0.42 g, 1.2 mmol) was dissolved in diethyl ether. The solution was placed in a freezer for 1 h at −35 °C. *n*-Butyllithium (1.6 mL of 2.5 M solution in hexanes, 3.9 mmol) was then added, and the solution was stirred overnight. The solution was cooled to −35 °C in a freezer for 1 h; then ClPEt$_2$ (0.53 mL, 4.4 mmol) was added. The mixture immediately became bright yellow-orange. After 3 h, the reaction was quenched with 30 μL of degassed H$_2$O/MeOH solution. The solution was stirred for 20 min, and then the volatiles were removed. The product was extracted with pentane and toluene, then filtered over Celite and silica gel, yielding a pale yellow solution. The volatiles were reduced, leaving a yellow oil. The oil was found to be a mixture containing approximately 87% desired ligand by ^{31}P NMR. This mixture was used without further purification for the synthesis of **1-PdCl**. ^{1}H NMR (C$_6$D$_6$): δ 7.87 (t, J_{PH} = 8 Hz, 1H, N*H*), 7.28 (dd, J = 4 Hz, J = 8 Hz, 2H, Ar *H*), 7.19 (br s, 2H, Ar *H*), 6.93 (dd, J = 2 Hz, J = 8 Hz, 2H, Ar *H*), 2.21 (s, 6H, Ar C*H$_3$*), 1.60 (m, 8H, C*H$_2$*CH$_3$), 1.02 (m, 12H, CH$_2$C*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 146.3 (m), 131.4, 130.5, 129.9, 126.8 (m), 117.4, 20.9, 19.7 (d, J_{PC} = 8 Hz), 10.3 (m). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −36.5.

1-PdCl. In a 25 mL Schlenk flask, under Ar, Pd(COD)Cl$_2$ (86 mg, 0.33 mmol) was added to a toluene solution of **1-H** (0.12 g, 0.33 mmol). The solution became a dark red and was stirred overnight at RT. After 12 h, solution was filtered through Celite and silica gel. The volatiles were removed, and a red oily solid was dissolved in toluene. The product was recrystallized from a toluene solution layered with pentane to yield red crystals of **1-PdCl** (0.11 g, 0.22 mmol, 73%

isolated yield). ^{1}H NMR (C$_6$D$_6$): δ 7.72 (dvt, J_{HH} = 8 Hz, J_{PH} = 3 Hz, 2H, Ar *H*), 6.77 (d, J_{HH} = 8.5 Hz, 2H, Ar *H*), 6.73 (vt, J_{PH} = 6 Hz, 2H, Ar *H*), 2.10 (s, 6H, Ar C*H$_3$*), 1.86 (m, 4H, C*H$_2$*CH$_3$), 1.49 (m, 4H, C*H$_2$*CH$_3$), 1.25 (m, 12H, CH$_2$C*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 161.6 (vt, J_{PC} = 11.5 Hz), 132.7, 131.5, 126.3 (vt, J_{PC} = 4 Hz), 120.9 (vt, J_{PC} = 20 Hz), 116.2 (vt, J_{PC} = 7 Hz), 20.2, 19.1 (vt, J_{PC} = 14 Hz), 8.9. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 33.5. Elemental analysis, calculated for C$_{22}$H$_{32}$ClNP$_2$Pd: C, 51.38; H, 6.27%. Found: C, 51.68; H, 6.52%.

2-PdOAc. A Schlenk flask was charged with **2-H** (1.00 g, 1.76 mmol), Pd(OAc)$_2$ (396 mg, 1.76 mmol) and toluene (5 mL). The reaction mixture was stirred for 18 h, and then the resulting solid was taken up in additional toluene and recrystallized at −35 °C to yield **2-PdOAc** as a red solid (0.906 g, 1.24 mmol 69%). ^{1}H NMR (C$_6$D$_6$): δ 8.01 (m, 8H, Ar *H*), 7.65 (d, 2H, J = 11 Hz, Ar *H*), 7.05−6.97 (m, 14H, 8 Hz), 6.67 (d, 2H, J_{HH} = 8 Hz, Ar *H*), 1.93 (s, 3H, C*H$_3$*), 1.89 (s, 6H, C*H$_3$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 29.6. ^{1}H NMR (CDCl$_3$): δ 7.82−7.78 (m, 8H, Ar *H*), 7.47−7.42 (m, 14H, Ar *H*), 6.86 (d, 2H, J = 8 Hz, Ar *H*), 6.83 (m, 2H, Ar *H*), 2.13 (s, 6H, Ar C*H$_3$*), 1.68 (s, 3H, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 176.0 (O*A*c), 160.2 (d, J_{CP} = 27 Hz, Ar *C*N), 133.9 (Ar *C*H), 133.8 (Ar *C*H), 132.7 (Ar *C*H), 131.1 (Ar *C*), 130.9 (Ar *C*H), 130.7 (Ar *C*H), 129.2 (Ar *C*), 128.8 (Ar *C*H), 127.0 (Ar *C*), 121.8 (Ar *C*), 116.8 (Ar *C*H), 23.6 (O*A*c), 20.3 (Ar *C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 28.9.

2-PdCl. A Schlenk flask was charged with **2-PdOAc** (117 mg, 0.160 mmol), a stir bar, diethyl ether (5 mL), and Me$_3$SiCl (100 μL, 0.801 mmol) and stirred for 12 h at room temperature. The volatiles were then removed *in vacuo* while being warmed in a 100 °C oil bath, resulting in a green powder. The solid was then recrystallized in pentane to yield **2-PdCl** as a green powder (83.0 mg, 0.127 mmol, 80%).

2-RhCO. A Schlenk flask was charged with **2-H** (302 mg, 0.534 mmol), [Rh(COD)Cl]$_2$ (132 mg, 0.267 mmol), 2,6-lutidine (61.0 μL, 0.534 mmol), diethyl ether (10 mL) and a stir bar. Exposure to CO (1 atm) resulted in formation of an orange solution. The reaction mixture was stirred for 12 h, and then the volatiles were removed *in vacuo*. The resulting solid was taken up in dichloromethane and passed through a pad of Celite. The solution was then concentrated and layered with diethyl ether. Recrystallization at −35 °C resulted in the isolation of **2-RhCO** as an orange solid (165 mg, 0.246 mmol, 46%). ^{1}H NMR (CDCl$_3$): δ 8.12 (m, 10H, Ar *H*), 7.44 (s, 2H, Ar *H*), 7.34 (t, J_{PH} = 3 Hz, 2H, Ar *H*), 7.26 (m, 10H, Ar *H*), 7.06 (d, J_{HH} = 9 Hz, 2H, Ar *H*), 2.24 (s, 6H, C*H$_3$*). ^{1}H{^{31}P} NMR (CDCl$_3$): δ 8.12 (m, 10H, Ar *H*), 7.44 (s, 2H, Ar *H*), 7.34 (s, 2H, Ar *H*), 7.26 (m, 10H, Ar *H*), 7.06 (d, J_{HH} = 9 Hz, 2H, Ar *H*), 2.24 (s, 6H, C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 196.3 (d, J = 13 Hz, *C*O), 161.2 (t, J_{CP} = 14 Hz, Ar *C*), 135.2 (Ar *C*), 135.0 (Ar *C*), 134.8 (Ar *C*), 134.7 (Ar *C*), 134.6 (Ar *C*), 134.6 (Ar *C*), 133.3 (Ar *C*), 131.2 (Ar *C*), 129.7 (t, J_{CP} = 5 Hz, Ar *C*), 128.9 (Ar *C*), 126.9 (Ar *C*), 123.7 (t, J_{CP} = 23 Hz, Ar *C*), 116.7 (d, J_{CP} = 21 Hz, Ar *C*), 21.4 (*C*H$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 41.1 (d, J_{RhP} = 136 Hz). ^{1}H NMR (C$_6$D$_6$): δ 7.82 (m, 9H, Ar *H*), 7.04 (m, 3H, Ar *H*), 6.97 (m, 12H, Ar *H*), 6.77 (d, J_{HH} = 9 Hz, 2H, Ar *H*), 1.95 (s, 6H, C*H$_3$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 41.3 (d, J_{RhP} = 135 Hz). IR ν(CO) = 1952 cm^{-1}.

3-NiCl. A C$_6$D$_6$ solution of **3-NiOAc** (55 mg, 0.10 mmol) was charged with Me$_3$SiCl (4.0 μL, 0.30 mmol). The reaction's progress was monitored by ^{31}P NMR spectroscopy. After 18 h, only one signal was observed at 34.2 ppm. The volatiles were then removed *in vacuo* to yield a green powder (43 mg, 0.082 mmol, 81%).

4-Me. A Schlenk flask was charged with **D** (0.68 g, 1.7 mmol), a stir bar, diethyl ether (10 mL), and *n*-butyllithium (1.4 mL, 3.4 mmol). After 1 h, ClP^{i}Pr$_2$ (0.54 mL, 3.4 mmol) was added to the ethereal solution via syringe. The reaction was stirred for 2 h and then filtered through a pad of silica gel. Removal of the volatiles under a vacuum and recrystallization in pentane gave **4-Me** as a colorless powder (0.75 g, 1.6 mmol, 93%). ^{1}H NMR (C$_6$D$_6$): δ 7.17 (dd, J_{HH} = 3 Hz, J_{PH} = 2 Hz, 2H, Ar *H*), 6.90 (dd, J_{HH} = 9 Hz, J_{PH} = 3 Hz, 2H, Ar *H*), 6.68 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar *H*), 3.48 (s, 3H, NC*H$_3$*), 3.38 (s, 6H, OC*H$_3$*), 2.13−1.97 (m, 4H, C*H*(CH$_3$)$_2$), 1.18 (dd, J_{PH} = 13 Hz, J_{HH} = 8 Hz, 12H, CH(C*H$_3$*)$_2$), 1.01 (dd, J_{PH} = 12 Hz, J_{HH} = 7 Hz, 12H,

CH(CH$_3$)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.17 (dd, J_{HH} = 3 Hz, 2H, Ar H), 6.90 (dd, J_{HH} = 9 Hz, 2H, Ar H), 6.68 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar H), 3.48 (s, 3H, NCH_3), 3.38 (s, 6H, OCH_3), 2.13−1.97 (m, 4H, CH(CH$_3$)$_2$), 1.18 (dd, J_{HH} = 8 Hz, 12H, CH(CH_3)$_2$), 1.01 (dd, J_{HH} = 7 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 155.7 (s, 3° C, Ar CN), 152.4 (d, J_{CP} = 5 Hz, 3° C, Ar C), 134.3 (d, J_{CP} = 10 Hz, 3° C, Ar C), 124.8 (s, Ar C), 120.0 (s, Ar C), 114.2 (s, Ar C), 55.0 (s, OCH_3), 25.0 (d, J_{CP} = 1 Hz, CH(CH$_3$)$_2$), 21.1 (s, CH$_3$), 20.3 (s, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −6.2 (s).

4-PdCl. A Teflon stoppered Schlenk flask was charged with toluene (10 mL), a stir bar, **4-Me** (541 mg, 1.14 mmol), and Pd(COD)Cl$_2$ (324 mg, 1.14 mmol). The reaction vessel was then placed in an 80 °C oil bath for 3 days. After warming the reaction vessel to room temperature, the toluene solution was passed through a pad of silica gel and washed with diethyl ether. Removal of the volatiles and recrystallization at −35 °C in toluene gave **4-PdCl** as a green powder (281 mg, 467 mmol, 41%). ^{1}H NMR (C$_6$D$_6$): δ 7.61 (d, 2H, J_{HH} = 9 Hz, Ar H), 6.71 (s, 2H, Ar H), 6.62 (d, 2H, J_{HH} = 9 Hz, Ar H), 3.38 (s, 6H, MeO), 2.27−2.24 (m, 4H, CH(CH$_3$)$_2$), 1.42 (dvt, 12H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.11 (dvt, 12H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.61 (d, 2H, J_{HH} = 9 Hz, Ar H), 6.71 (s, 2H, Ar H), 6.62 (d, 2H, J_{HH} = 9 Hz, Ar H), 3.38 (s, 6H, CH_3O), 2.27−2.24 (m, 4H, CH(CH$_3$)$_2$), 1.42 (d, 12H, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.11 (d, 12H, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 159.0 (Ar CN), 151.4 (Ar C), 119.2 (Ar C), 117.7 (Ar CH, appears to be two overlapping peaks), 116.0 (Ar CH), 55.7 (OCH_3), 25.1 (t, J_{CP} = 12 Hz, CH(CH$_3$)$_2$), 18.69 (CH_3), 18.0 (CH_3). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 47.9. Elemental analysis, calculated: C, 51.84; H, 6.69. Found: C, 51.76; H, 6.74.

[4-PdCl][CHB$_{11}$Cl$_{11}$]. A Schlenk flask was charged with **4-PdCl** (85 mg, 0.14 mmol), [*tris*(4-bromophenyl)aminium][CHB$_{11}$Cl$_{11}$] (0.14 g, 0.14 mmol), a stir bar, and dichloromethane (5 mL). An immediate color change to brown is observed, and a brown precipitate forms. After 30 min, the volatiles were removed under a vacuum, and the resulting brown precipitate was washed with diethyl ether. The solid was then dissolved in a minimal amount of dichloromethane and stored at −35 °C for 36 h. The resulting brown crystals were then collected by decanting off the solvent. ^{1}H NMR analysis revealed that the amine has been completely removed, and no signals corresponding to a diamagnetic complex were observed. Elemental analysis, calculated: C, 28.82; H3.76. Found: C, 28.76; H 3.62.

4-PdOAc. A J. Young tube was charged with **4-Me** (40 mg, 0.11 mmol), Pd(OAc)$_2$ (25 mg, 0.11 mmol), and C$_6$D$_6$ (1 mL). The reaction mixture immediately turned a deep red color. The volatiles were removed *in vacuo*, and the resulting red solid was taken up in diethyl ether and filtered through a pad of silica gel. The volatiles were again removed while heating at 100 °C to yield **4-PdOAc** as a red powder (20 mg, 32 μmol, 30%). ^{1}H NMR (C$_6$D$_6$): δ 7.57 (d, 2H, J = 9 Hz, Ar H), 6.68 (s, 2H, Ar H), 6.61 (d, J = 3 Hz, Ar H), 3.39 (s, 6H, Ar CH_3), 2.26−2.24 (m, 4H, CH(CH$_3$)$_2$), 2.23 (s, 3H, OAc), 1.36 (dvt, 12H, J_{PH} = 17 Hz, J_{HH} = 8 Hz, CH(CH_3)$_2$), 1.09 (dvt, 12H, J_{PH} = 15 Hz, J_{HH} = 8 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 175.8 (C≡O), 159.0 (t, J_{CP} = 11 Hz, CN), 151.2 (t, J_{CP} = 4 Hz), 119.6 (t, J_{CP} = 19 Hz), 117.8, 117.6, 116.3 (t, J_{CP} = 8 Hz), 55.7 (MeO), 24.7 (t, J_{CP} = 11 Hz, CH(CH$_3$)$_2$), 23.3 (OAc), 18.4 (CH(CH_3)$_2$), 17.7 (CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 48.1.

4-Rh(CH$_3$)(Cl). A J. Young tube was charged with **4-Me** (0.18 g, 0.38 mmol), [Rh(COD)Cl]$_2$ (93 mg, 0.19 mmol), and C$_6$D$_6$ (1.5 mL). After the reaction mixture at 90 °C for 18 h, a color change from red to green was observed. The solution was passed through a pad of silica gel, using diethyl ether to ensure quantitative transfer. The volatiles were removed *in vacuo*, and the resulting solid was washed three times with toluene. The volatiles were again removed, and the oil was taken up in a 1:1 mixture of pentane to diethyl ether and recrystallized at 35 °C to yield **4-Rh(CH$_3$)(Cl)** as a green powder (66 mg, 0.11 μmol, 29%). ^{1}H NMR (C$_6$D$_6$): δ 7.76 (dt, J_{HH} = 9 Hz, J_{PH} = 2 Hz, 2H, Ar H), 6.82 (dvt, J_{PH} = 8 Hz, J_{HH} = 4 Hz, 2H, Ar H), 6.64 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar H), 3.43 (s, 6H, OCH_3), 2.61 (m, J = 7 Hz, 2H, CH(CH$_3$)$_2$), 2.38−2.34 (m, 2H, CH(CH$_3$)$_2$), 2.33 (m, 3H, Rh CH_3), 1.49 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H, CHCH_3)$_2$),

1.15 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 12H, CHCH_3)$_2$), 0.98 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H, CHCH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.76 (d, J_{HH} = 9 Hz 2H, Ar H), 6.82 (d, J_{HH} = 4 Hz, 2H, Ar H), 6.64 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar H), 3.43 (s, 6H, OCH_3), 2.61 (m, J = 7 Hz, 2H, CH(CH$_3$)$_2$), 2.38−2.34 (m, 2H, CH(CH$_3$)$_2$), 2.33 (d, J_{RhH} = 3 Hz, 3H, Rh CH_3), 1.49 (d, J_{HH} = 7 Hz, 6H, CHCH_3)$_2$), 1.15 (d, J_{HH} = 7 Hz, 12H, CHCH_3)$_2$), 0.98 (d, J_{HH} = 7 Hz, 6H, CHCH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 158.1 (s, 3° Ar C), 151.2 (s, 3° Ar C), 121.0 (s, 3° Ar C), 118.0 (s, Ar CH), 117.8 (s, Ar CH), 117.1 (s, Ar CH), 55.7 (s, OCH_3), 27.0 (d, J_{CP} = 11 Hz, CH(CH$_3$)$_2$), 24.2 (d, J_{CP} = 12 Hz, CH(CH_3)$_2$), 19.4 (d, J_{CP} = 33 Hz, CH(CH_3)$_2$), 18.1 (d, J_{CP} = 17 Hz, CH(CH_3)$_2$), 2.0 (d, J_{RhC} = 33 Hz, Rh CH_3). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 36.5 (d, J_{RhP} = 109 Hz).

4-RhCO. A J. Young tube was charged with **4-Rh(CH$_3$)Cl** (44 mg, 72 μmol), CO (1 atm), and C$_6$D$_6$ (1 mL). The J. Young tube was placed in a 70 °C oil bath for 18 h. Crystals were then obtained by layering the benzene solution with diethyl ether. The brown crystals were collected by decanting the solvent layer and drying the resulting orange blocks under a vacuum. **4-RhCO** was isolated as an orange powder (10 mg, 17 μmol, 24%). ^{1}H NMR (C$_6$D$_6$): δ 7.64 (d, J_{HH} = 9 Hz, 2H, Ar H), 6.80 (q, J_{PH} = 4 Hz, 2H, Ar H), 6.64 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar H), 3.44 (s, 6H, OCH_3), 2.14−2.06 (m, 4H, CH(CH$_3$)$_2$), 1.24 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 12H, CH(CH)$_3$)$_2$), 1.03 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 12H, CH(CH)$_3$)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.64 (d, J_{HH} = 9 Hz, 2H, Ar H), 6.80 (s, 2H, Ar H), 6.64 (dd, J_{HH} = 9 Hz, J_{HH} = 3 Hz, 2H, Ar H), 3.44 (s, 6H, OCH_3), 2.10 (hept, J_{HH} = 7 Hz, 4H, CH(CH$_3$)$_2$), 1.24 (d, J_{HH} = 7 Hz, 12H, CH(CH)$_3$)$_2$), 1.03 (d, J_{HH} = 7 Hz, 12H, CH(CH)$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 198.2 (d, J_{RhC} = 65 Hz, CO), 159.1 (d, J_{CP} = 15 Hz, 3° Ar C), 150.9 (s, 3° Ar C), 122.2 (t, J_{CP} = 17 Hz, 3° Ar C), 118.1 (s, Ar CH), 116.9 (s, Ar CH), 115.1 (s, Ar CH), 55.8 (s, OCH_3), 25.8 (s, CH(CH_3)$_2$), 19.5 (s, CH_3), 18.5 (s, CH_3). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 62.0 (d, J_{RhP} = 135 Hz). IR ν(CO): 1933 cm^{-1}.

5-NiCl. A Schlenk flask was charged with **5-Me** (3.00 g, 6.65 mmol), NiCl$_2$·(H$_2$O)$_6$ (1.90 g, 7.98 mmol), toluene (25 mL), and a stir bar. The reaction mixture was then refluxed under a flow of argon for 6 h. The solution was then passed through a pad of Celite. The volatiles were then removed *in vacuo*, and the resulting green solid was washed with pentane to yield **5-NiCl** (2.58 g, 73%). ^{1}H NMR (C$_6$D$_6$): δ7.13 (ddt, J_{HH} = 9 Hz, J_{HH} = 4 Hz, J_{PH} = 2 Hz, 2H, Ar H), 6.75 (dq, J_{HH}= 7 Hz, J_{HH} = 4 Hz, 2H, Ar H), 6.57 (td, J_{RhC} = 8 Hz, J_{HH} = 3 Hz, 2H, Ar H), 2.03 (m, 4H, CH(CH$_3$)$_2$), 1.41 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 12H, CH(CH_3)$_2$), 1.10 (dvt, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 12H, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ7.13 (dd, J = 9 Hz, J = 4 Hz, 2H), 6.75 (dd, J = 7 Hz, J = 4 Hz, 2H), 6.57 (td, J = 8 Hz, J = 3 Hz, 1H), 2.03 (hept, J = 7 Hz, 4H), 1.41 (d, J = 7 Hz, 12H), 1.10 (d, J = 7 Hz, 12H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ160.5 (t, J_{CP} = 13 Hz, Ar C), 155.4 (s, Ar C), 153.5 (s, Ar C), 121.8 (t, J_{CP} = 18 Hz, Ar C), 117.9 (dd, J_{CF} = 101 Hz, J_{CP} = 22 Hz, Ar C), 116.4 (d, J_{CP} = 9 Hz, Ar C), 24.0 (t, J_{CP} = 12 Hz, P(CH(CH$_3$)$_2$)$_2$), 18.4 (s, P(CH(CH$_3$)$_2$)$_2$), 17.5 (s, P(CH(CH$_3$)$_2$)$_2$). ^{19}F NMR (C$_6$D$_6$): δ −128.6 (q, J_{RhC} = 8 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ32.7 (s). Elemental analysis, calculated: C, 60.11; H, 6.39. Found: C, 60.06; H, 6.42.

6-H. A Schlenk flask was charged with **F** (0.98 g, 2.5 mmol) and a stir bar. The solid was then dissolved in diethyl ether (30 mL), and the resulting solution was cooled to −35 °C in the glovebox freezer. *n*-Butyllithium (2.0 mL, 0.80 mmol, 2.5 M in hexanes) was then added slowly to the reaction flask via syringe, resulting in a bright yellow solution. The reaction mixture was then stirred for 2 h at ambient temperature. ClPPh$_2$ (0.50 mL, 2.5 mmol) was added slowly via syringe, resulting in a red solution. The reaction mixture was stirred overnight and then quenched with degassed H$_2$O (0.20 mL). Stirring was commenced for an additional hour, resulting in a colorless solution. The volatiles were then removed *in vacuo*, and the flask was brought into the glovebox where it was dissolved in diethyl ether and stirred vigorously over silica gel. The resultant mixture was then filtered through a pad of Celite, and the diethyl ether was removed *in vacuo*. The resulting colorless solid was then dissolved in a 1:1 mixture of pentane and toluene and recrystallized at −35 °C to yield **6-H** as a colorless solid (0.78 g, 1.6 mmol, 62%). ^{1}H NMR (C$_6$D$_6$): δ 7.65 (dd,

1H, J_{PH} = 11 Hz, J_{HH} = 3 Hz), 7.49−7.46 (m, 4H), 7.39 (dd, 1H, J = 5 Hz, J = 9 Hz), 7.23 (dd, 1H, J = 5 Hz, J = 9 Hz), 7.11 (s, 1H), 7.08−6.99 (m, 6H), 6.95 (d, 1H, J = 4 Hz), 6.88 (dd, 2H, J_{HH} = 8 Hz, J_{PH} = 20 Hz), 2.15 (s, 3H, Ar CH_3), 1.95 (s, 3H, Ar CH_3), 1.87 (m, 2H, CH(CH$_3$)$_2$), 1.01 (dd, 6H, J_{HH} = 7 Hz, J_{PH} = 15 Hz, CH(CH_3)$_2$), 0.87 (dd, 6H, J_{HH} = 7 Hz, J_{PH} =12 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.2 (d, J_{CP} = 19 Hz, quaternary CN), 144.4 (d, J_{CP} = 20 Hz, quaternary CN), 136.4 (d, J_{CP} = 10 Hz, Ar C), 134.3 (Ar C), 134.2 (Ar C), 134.1 (Ar C), 133.6 (Ar C), 131.2 (Ar C), 130.4 (Ar C), 130.2 (Ar C), 128.8 (Ar C), 128.7 (Ar C), 128.6 (Ar C), 128.5 (Ar C), 128.4 (Ar C), 121.8 (d, J_{CP} = 16 Hz, Ar C), 119.2 (Ar C), 116.5 (Ar C), 23.1 (d, $J_{C−P}$ = 11 Hz, CH(CH$_3$)$_2$), 20.9 (Ar-CH_3), 20.8, (Ar-CH_3), 20.1 (d, J_{CP} = 19 Hz, CH(CH_3)$_2$), 19.0 (d, J_{CP} = 9 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −16.1 (s), −14.2 (br s).

6-PdCl. A Schlenk flask was charged with a stir bar, **6-H** (0.27 g, 0.54 mmol), and Pd(COD)Cl$_2$ (0.15 g, 0.54 mmol). The solids were dissolved in toluene (10 mL), resulting in a dark red solution. 2,6-Lutidine (63 μL, 0.54 mmol) was added to the mixture via syringe. The resulting solution was stirred for 12 h and then filtered through a pad of silica gel. The volatiles were removed *in vacuo*, and the resulting red oil was dissolved in a 1:1 mixture of pentane to toluene and then stored at −35 °C. The resulting precipitate was dried *in vacuo* and recrystallized in benzene to yield **6-PdCl** as a red powder (0.23 g, 62%). ^{1}H NMR (C$_6$D$_6$): δ 8.00−7.95 (m, 4H, Ar H), 7.77 (dd, 1H, J = 8 Hz, J = 5 Hz, Ar H), 7.67 (dd, 1H, J = 9 Hz, J = 4 Hz, Ar H) 7.03−6.98 (m, 7H, Ar H), 6.80 (d, 1H, J = 9 Hz, Ar H), 6.76−6.73 (m, 2H, Ar H), 2.31−2.23 (m, 2H, CH(CH$_3$)$_2$), 2.10 (s, 3H, Ar CH_3), 1.90 (s, 3H, Ar CH_3), 1.42 (dd, 6H, J_{PH} = 17 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.06 (dd, 6H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 54.0 (d, J_{PP} = 438 Hz), 25.9 (d, J_{PP} = 438 Hz). ^{1}H NMR (CDCl$_3$): δ 7.77−7.73 (m, 4H, Ar H), 7.49 (dd, 1H, J = 9 Hz, J = 5 Hz, Ar H), 7.45−7.40 (m, 7H, Ar H), 6.92 (d, 1H, J = 9 Hz, Ar H), 6.88 (t, 2H, J = 7 Hz, Ar H), 6.82 (d, 1H, J = 10 Hz, Ar H), 2.60 (m, 2H, CH(CH$_3$)$_2$), 2.22 (s, 3H, Ar CH_3), 2.14 (s, 3H, Ar CH_3), 1.48 (dd, 6H, J_{PH} = 17 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.31 (dd, 6H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 161.2 (d, J_{CP} = 21 Hz, Ar CN), 160.8 (d, J_{CP} = 26 Hz, Ar CN), 137.8 (Ar C), 133.7 (d, J_{CP} = 2 Hz, Ar CH), 133.6 (d, J_{CP} = 2 Hz, Ar CH), 132.8 (d, J_{CP} = 2 Hz, Ar CH), 132.4 (Ar C), 132.3 (d, J_{CP} = 2 Hz, Ar CH), 130.8 (d, J_{CP} = 4 Hz, Ar CH), 130.7, (d, J_{CP} = 2 Hz, Ar CH), 130.5 (d, J_{CP} = 3 Hz, Ar CH), 129.2 (Ar C), 128.8 (d, J_{CP} = 11 Hz, Ar CH), 128.3 (Ar C), 126.7 (d, J_{CP} = 7 Hz, Ar CH), 126.5 (d, J_{CP} = 7 Hz, Ar CH), 125.4 (s, Ar C), 120.9, (d, J_{CP} = 3 Hz, Ar C), 120.5 (d, J_{CP} = 3 Hz, Ar C), 118.7 (d, J_{CP} = 3 Hz, Ar C), 118.4 (d, J_{CP} = 3 Hz Ar C), 116.4 (d, J_{CP} = 13 Hz, Ar CH), 116.1 (d, J_{CP} = 14 Hz, Ar CH), 25.1 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_3$), 24.9 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_3$), 20.4 (Ar CH_3), 20.3 (Ar CH_3), 18.7 (d, J_{CP} = 5 Hz, CH(CH$_3$)$_3$), 18.1 (d, J_{CP} = 2 Hz, CH(CH$_3$)$_3$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 55.6 (d, J_{PP} = 433 Hz), 27.2 (d, J_{PP} = 433 Hz). Elemental analysis, calculated: C, 60.20; H, 5.68; N, 2.19. Found: C, 60.13; H, 5.63; N, 2.04.

6-PdOAc. A Schlenk flask was charged with a stir bar, **6-H** (0.31 g, 0.62 mmol), and Pd(OAc)$_2$ (0.14 g, 0.62 mmol). The solids were dissolved in toluene (10 mL), resulting in a dark red solution. The resulting solution was stirred for 4 h and then filtered through a pad of silica gel. The volatiles were removed *in vacuo*, and the resulting red solid was washed with 3 × 5 mL portions of toluene to yield **6-Pd(OAc)** as a red powder (0.37 mg, 69%). ^{1}H NMR (CDCl$_3$): δ 7.79−7.74 (m, 4H, Ar H), 7.46−7.40 (m, 7H, Ar H), 7.37 (dd, 1H, J = 9 Hz, J = 4 Hz, Ar H), 6.89−6.80 (m, 4H, Ar H), 2.60 (m, 2H, CH(CH$_3$)$_2$), 2.22 (s, 3H, Ar CH_3), 2.12 (s, 3H, Ar CH_3), 1.78 (s, 3H, CH_3), 1.41 (dd, 6H, J_{PH} = 18 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.23 (dd, 6H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 176.5(C=O), 161.1 (d, J_{CP} = 21 Hz, Ar CN), 160.8 (d, J_{CP} = 26 Hz, Ar CN), 134.2 (Ar CH), 133.6 (d, J_{CP} = 2 Hz, Ar CH), 133.5 (d, J_{CP} = 2 Hz, Ar CH), 132.7 (d, J_{CP} = 3 Hz, Ar CH), 132.4 (Ar CH), 132.1 (d, J_{CP} = 2 Hz, Ar CH), 131.1 (d, J_{CP} = 3 Hz, Ar CH), 130.7 (d, J_{CP} = 3 Hz, Ar CH), 129.2 (Ar CH), 128.8 (d, J_{CP} = 10 Hz, Ar CH), 128.3 (Ar CH), 126.7 (Ar CH), 126.4 (Ar CH), 126.3 (Ar CH), 126.3 (Ar CH), 125.4 (Ar CH), 121.2 (d, J_{CP} = 3 Hz, Ar C), 120.8 (d, J_{CP} = 3 Hz, Ar C), 118.8 (d, J_{CP} = 3 Hz, Ar C), 118.5 (d, J_{CP} = 3 Hz, Ar C), 116.9 (d,

J_{CP} = 13 Hz, Ar C), 116.0 (d, J_{CP} = 13 Hz, Ar C), 24.5 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_3$), 24.4 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_3$), 23.0 (CH$_3$), 20.4 (Ar CH$_3$), 20.3 (Ar CH$_3$), 18.4 (d, J_{CP} = 6 Hz, CH(CH$_3$)$_3$), 17.7 (d, J_{CP} = 3 Hz, CH(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 55.8 (d, J_{PP} = 412 Hz), 25.8 (d, J_{PP} = 412 Hz).

6-RhCO. A J. Young tube was charged with **6-H** (24 mg, 47 μmol), [Rh(COD)Cl]$_2$ (24 mg, 48 μmol), 2,6-lutidine (5.5 μL, 48 μmol), and C$_6$D$_6$ (1 mL). The mixture was then degassed, and then CO (1 atm) was added, resulting in a red color change. The volatiles were then removed, and the resulting solid was filtered through a pad of silica gel with fluorobenzene. Removal of the fluorobenzene *in vacuo* resulted in pure **6-RhCO**, which was isolated as a yellow solid after washing with 3 mL portions of toluene (25 mg, 40 μmol, 60%). ^{1}H NMR (C$_6$D$_6$): δ 7.92−7.85 (m, 4H, Ar H), 7.80 (dd, 1H, J_{PH} = 9 Hz, J_{HH} = 5 Hz, Ar H), 7.74 (dd, 1H, J_{PH} = 8 Hz, J_{HH} = 4 Hz, Ar H), 7.07 (d, 1H, J_{PH} = 10 Hz, Ar H), 7.00−6.97 (m, 6H, Ar H), 6.89 (d, 1H, J_{PH} = 8 Hz, Ar H), 6.82−6.78 (m, 3H, Ar H), 2.20−2.13 (m, 2H, CH(CH$_3$)$_2$), 2.17 (s, 3H, Ar CH_3), 1.95 (s, 3H, Ar CH_3), 1.27 (dd, 6H, J_{PH} = 17 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.98 (dd, 6H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 197.2 (CO), 162.6 (t, J_{CP} = 22 Hz, CN), 135.3 (Ar C), 135.0 (Ar C), 134.9 (Ar C), 134.1 (d, J_{CP} = 13 Hz, Ar C), 133.2 (Ar C), 132.6 (d, J_{CP} = 13 Hz, Ar C), 130.4 (Ar C), 129.2 (d, J_{CP} = 11 Hz, Ar C), 126.2 (d, J_{CP} = 7 Hz, Ar C), 125.8 (d, J_{CP} = 7 Hz, Ar C), 123.6 (d, J_{CP} = 44 Hz, Ar C), 121.8 (d, J_{CP} = 37 Hz, Ar C), 116.8 (d, J_{CP} = 12 Hz, Ar C), 115.9 (d, J_{CP} = 13 Hz, Ar C), 25.9 (d, J_{CP} = 23 Hz, CH(CH$_3$)$_2$), 20.9 (Ar CH$_3$), 20.6 (Ar CH$_3$), 20.0 (d, J_{CP} = 6 Hz, CH(CH$_3$)$_2$), 18.9 (CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 64.7 (dd, J_{PP} = 270 Hz, J_{RhP} = 133 Hz), 39.2 (dd, J_{PP} = 270 Hz, J_{RhP} = 134 Hz). IR: 1941 cm$^{−1}$.

6-PtCl. A vial was charged with **6-H** (52 mg, 0.10 mmol), Pt(COD)Cl$_2$ (39 mg, 0.10 mmol), and toluene (3 mL). 2,6-Lutidine (12 μL, 0.10 mmol) was added to the solution via microsyringe. The reaction was allowed to react for 30 min, and then the volatiles were removed *in vacuo*. The resulting yellow solid was filtered through a pad of silica gel with toluene and a small amount of diethyl ether. NMR analysis after removal of the volatiles revealed a slight impurity. The solid was again filtered through silica gel using CH$_2$Cl$_2$, and the volatiles were again removed under a vacuum to yield pure product as a yellow solid (56 mg, 77 μmol, 71%). Crystals were obtained by dissolving the solid in dichloromethane and storing the solution at −35 °C. ^{1}H NMR (CDCl$_3$): δ 7.79−7.75 (m, 4H, Ar H), 7.56 (dd, 1H, J = 6 Hz, J = 9 Hz, Ar H), 7.49 (dd, J = 5 Hz, J = 9 Hz, 1H, Ar H), 7.45−7.41 (m, 6H, Ar H), 6.98 (d, 1H, J = 9 Hz, Ar H), 6.90−6.86 (m, 3H, Ar H), 2.80−2.77 (m, 2H, CH(CH$_3$)$_2$), 2.25 (s, 3H, Ar CH_3), 2.17 (s, 3H, Ar CH_3), 1.46 (dd, 6H, J_{HH} 7 Hz, J_{PH} 17 Hz, CH(CH_3)$_2$), 1.29 (dd, 6H, J_{HH} 7 Hz, J_{PH} 16 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 134.7, 133.8, 133.7, 132.6, 132.4, 132.1, 131.2, 130.7, 128.8, 128.7, 127.1, 126.9, 116.4, 116.0, 31.0, 28.2, 25.2, 20.3, 18.4, 18.1. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.7 (d, J_{PtP} = 2751 Hz, J_{PP} 398 Hz), 24.4 (d, J_{PtP} = 2668 Hz, J_{PP} = 398 Hz). ^{1}H NMR (C$_6$D$_6$): δ 8.02−7.98 (m, 4H, Ar H), 7.84 (dd, 1H, J = 6 Hz, J = 9 Hz, Ar H), 7.74 (dd, 1H, J = 4 Hz, J = 9 Hz, Ar H), 7.09 (d, 1H, J = 11 Hz, Ar H), 7.02−6.97 (m, 7H, Ar H), 6.68 (d, 1H, J = 9 Hz, Ar H), 6.72 (t, 2H, Ar H), 2.52−2.46 (m, 2H, CH(CH$_3$)$_2$), 2.13 (s, 3H, Ar CH_3), 1.93 (s, 3H, Ar CH_3), 1.42 (dd, 6H, J_{PH} = 17 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.08 (dd, 6H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 43.3 (d, J_{PtP} = 2760 Hz, J_{PP} = 402 Hz), 24.6 (d, J_{PtP} = 2685 Hz, J_{PP} = 402 Hz).

7-H. A Teflon screw cap Schlenk flask was charged with **G** (0.16 g, 0.48 mmol), toluene (15 mL), 2,4,6-trimethylaniline (0.14 mL, 0.96 mmol), acetic acid (6.0 μL, 20 mol %), molecular sieves, and a stir bar. The flask was then placed in a 110 °C oil bath for 72 h and then cooled to ambient temperature, and the volatiles were removed *in vacuo*. The remaining yellow solid was extracted in pentane and stirred vigorously over silica gel for 1 h before being filtered through a pad of Celite. The filtrate was evaporated to dryness, and the resulting oil was recrystallized in pentane at −35 °C to give **7-H** as a yellow powder (0.17 g, 0.36 mmol, 71%). ^{1}H NMR (C$_6$D$_6$): δ 11.33 (s, 1H, NH), 8.08 (s, 1H, imine CH), 7.49 (dd, 1H, J_{PH} = 4 Hz, J_{HH} = 8 Hz, Ar H), 7.33 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.28 (s, 1H, Ar H), 6.92−6.89 (m, 2H, Ar H), 6.86 (d, 3H, J_{PH} = 4 Hz, Ar H), 2.28 (s, 6H, *ortho*-CH_3), 2.19

(s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.99 (m, 2H, CH(CH$_3$)$_2$), 1.04 (dd, 6H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.88 (dd, 6H, J_{PH} = 12 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 11.33 (s, 1H, NH), 8.08 (s, 1H, imine CH), 7.49 (d, 1H, J_{HH} = 8 Hz, Ar H), 7.33 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.28 (s, 1H, Ar H), 6.92 (m, 2H, Ar H), 6.86 (d, 3H, J_{PH} = 4 Hz, Ar H), 2.28 (s, 6H, *ortho*-CH_3), 2.19 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.99 (m, 2H, CH(CH$_3$)$_2$), 1.04 (dd, 6H, J_{HH} = 7 Hz, J_{PH} = 15 Hz, CH(CH_3)$_2$), 0.88 (dd, 6H, J_{HH} = 7 Hz, J_{PH} = 12 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −5.8. ^{1}H NMR (CDCl$_3$): δ 10.63 (s, 1H, NH), 8.25 (s, 1H, imine CH), 7.35 (dd, 1H, J_{PH} = 4 Hz, J_{HH} = 8 Hz, Ar H), 7.24 (m, 1H, Ar H), 7.11 (m, 2H, Ar H), 7.02 (s, 1H, Ar H), 6.88 (s, 1H, J_{PH} = 4 Hz, Ar H), 2.28 (s, 6H, *ortho*-CH_3), 2.19 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.99 (m, 2H, CH(CH$_3$)$_2$), 1.04 (dd, 6H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.88 (dd, 6H, J_{PH} = 12 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 165.5 (s, imine CH), 148.8 (s, Ar C), 145.0 (s, Ar C), 144.1 (d, J_{CP} = 18 Hz, Ar CN), 140.3 (s, Ar C), 135.0 (s, Ar C), 134.6 (s, Ar C), 132.9 (s, Ar C), 132.5 (d, J_{CP} = 11 Hz, Ar C), 130.1 (s, Ar C), 129.0 (s, Ar C), 128.7 (s, Ar C), 127.8 (s, Ar C), 127.3 (s, Ar C), 125.6 (s, Ar C), 123.7 (s, Ar C), 122.0 (s, Ar C), 118.7 (s, Ar C), 113.9 (s, Ar C), 23.6 (d, J_{CP} = 14 Hz, CH(CH$_3$)$_2$), 21.2 (s CH$_3$), 20.5 (s, CH$_3$), 20.4 (d, J_{CP} = 5 Hz, CH(CH$_3$)$_2$), 19.6 (d, J_{CP} = 10 Hz, CH(CH$_3$)$_2$), 18.77 (s, CH$_3$), 17.72 (s, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −3.3 (s).

7-PdOAc. A 25 mL Schlenk flask was charged with **7-H** (0.15 g, 0.33 mmol) and dissolved in toluene (3 mL) under ambient temperature. Pd(OAc)$_2$ (76 mg, 0.33 mmol) was then added to the reaction mixture, resulting in an immediate color change from yellow to purple. The reaction mixture was stirred for 12 h and then the volatiles were removed *in vacuo*. The resulting red solid was then washed two times with cold pentane and dried to yield pure product (0.15 g, 76%). ^{1}H NMR (C$_6$D$_6$): δ 7.63 (d, 1H, J_{HH} = 9 Hz, imine CH), 7.38 (dd, 1H, J_{PH} = 4 Hz, J_{HH} = 9 Hz, Ar H), 7.13 (d, 1H, J_{PH} = 13 Hz, Ar H), 6.82 (s, 1H, Ar H), 6.80 (d, 1H, J_{PH} = 8 Hz, Ar H), 6.75 (d, 2H, J_{PH} = 9 Hz, Ar H), 6.67 (d, 1H, J_{HH} = 9 Hz, Ar H), 6.62 (s, 1H, Ar H), 2.74 (m, 1H, CH(CH$_3$)$_2$), 2.60 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.94 (septet, 1H, CH(CH$_3$)$_2$), 1.51 (dd, 3H, J_{PH} = 19 Hz, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.24 (dd, 3H, J_{PH} = 19 Hz, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.14 (dd, 3H, J_{PH} = 15 Hz, J_{HH} = 6 Hz, CH(CH_3)$_2$), 0.87 (dd, 3H, J_{PH} = 11 Hz, J_{HH} = 6 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.60 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.35 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.16 (s, 1H, Ar H), 7.08 (s, 1H, Ar H), 6.80 (s, 1H, Ar H), 6.77 (s, 1H, Ar H), 6.73 (s, 1H, Ar H), 6.64 (d, 1H, J_{HH} = 9 Hz, Ar H), 6.60 (s, 1H, Ar H), 2.80 (m, 1H, CH(CH$_3$)$_2$), 2.55 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.90 (m, 1H, CH(CH$_3$)$_2$), 1.50 (d, 3H, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.20 (d, 3H, J_{HH} = 6 Hz, CH(CH_3)$_2$), 1.11 (d, 3H, J_{HH} = 6 Hz, CH(CH_3)$_2$), 0.91 (d, 3H, J_{HH} = 6 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 176.3 (OAc), 163.5 (Ar CN), 163.3 (Ar CH), 150.6 (Ar C), 146.8 (Ar C), 135.3 (Ar CH), 134.8 (Ar CH), 132.7 (Ar CH), 132.7 (Ar C), 131.5 (Ar CH), 130.1 (Ar C), 128.8 (Ar CH), 127.5 (Ar C), 125.7 (Ar C), 125.4 (Ar CH), 120.8 (Ar C), 120.7 (Ar C), 120.6 (Ar C), 120.1 (Ar C), 119.7 (Ar CH), 26.8 (d, J_{CP} = 24 Hz, CH(CH$_3$)$_2$), 21.8 (d, J_{CP} = 24 Hz, CH(CH$_3$)$_2$), 20.9 (CH$_3$), 20.5 (CH$_3$), 20.1 (CH$_3$), 19.5 (broad, CH$_3$), 18.9 (broad, CH$_3$), 18.2 (broad, CH$_3$), 16.3 (CH$_3$), 16.2 (broad, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 65.6.

7-PdCl. A Schlenk flask was charged with **7-H** (0.12 mg, 0.27 mmol), Pd(COD)Cl$_2$ (78 mg, 0.27 mmol), 2,6-lutidine (31 μL, 0.27 mmol), toluene (3 mL), and a stir bar. The reaction mixture was stirred for 5 h to yield a red solution. The toluene solution was filtered through a pad of silica gel. To ensure quantitative transfer, the silica gel was washed with diethyl ether. The volatiles were then removed *in vacuo*. The resulting red solid was washed with toluene to yield **7-PdCl** as a red solid (62 mg, 0.10 mmol, 39%). ^{1}H NMR (C$_6$D$_6$): δ 7.59 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.38 (dd, 1H, J_{HH} = 9 Hz, J_{PH} = 4 Hz, Ar H), 7.21 (d, 1H, J_{PH} = 13 Hz, Ar H), 6.87−6.75 (m, 3H, Ar H), 6.70 (d, 1H, J_{PH} = 9 Hz, Ar H), 6.12 (s, 1H, Ar H), 2.58 (s, 3H, CH_3), 2.46 (m, 2H, CH(CH$_3$)$_2$), 2.36 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.40 (d, 3H, J_{PH} = 14 Hz, CH(CH_3)$_2$), 1.29

(d, 3H, J_{PH} = 14 Hz, CH(CH_3)$_2$), 1.16 (d, 3H, J_{PH} = 10 Hz, CH(CH_3)$_2$), 0.93 (d, 3H, J_{PH} = 9 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.59 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.38 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.21 (s, 1H, Ar H), 6.87−6.75 (m, 3H, Ar H), 6.70 (s, 1H, Ar H), 6.12 (s, 1H, Ar H), 2.58 (s, 3H, CH_3), 2.46 (m, 2H, CH(CH$_3$)$_2$), 2.36 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.40 (s, 3H, CH(CH_3)$_2$), 1.29 (s, 3H, CH(CH_3)$_2$), 1.16 (s, 3H, CH(CH_3)$_2$), 0.93 (s, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 163.4 (Ar C), 163.1 (d, J_{CP} = 19 Hz, Ar CN), 150.7 (Ar C), 147.9 (Ar C), 135.1 (Ar C), 134.8 (Ar C), 134.7 (Ar C), 132.9 (Ar C), 132.3 (Ar C), 131.3 (Ar C), 129.3 (Ar C), 128.8 (Ar C), 125.9 (Ar C), 125.5 (Ar C), 121.1 (Ar C), 121.0 (Ar C), 120.9 (Ar C), 119.0 (Ar C), 26.9 (d, J_{CP} = 23 Hz, CH(CH$_3$)$_2$), 24.0 (d, J_{CP} = 29 Hz, CH(CH$_3$)$_2$), 21.0 (CH$_3$), 20.5 (CH$_3$), 20.0 (CH$_3$), 19.6, (d, J_{CP} = 14 Hz, CH(CH$_3$)$_2$), 19.0 (CH$_3$), 17.9 (CH$_3$), 17.5 (CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 70.3. ^{1}H NMR (CDCl$_3$): δ 7.79 (s, 1H, Ar CH), 7.55 (s, 1H, Ar CH), 7.17 (s, 1H, Ar CH), 7.08 (s, 1H, Ar CH), 7.00 (s, 1H, Ar CH), 6.88 (s, 2H, Ar CH), 2.64 (d, J = 26 Hz, 4H, CH(CH$_3$)$_2$ overlapping with CH_3), 2.47 (s, 1H, CH(CH$_3$), 2.36 (s, 3H, CH_3), 2.27 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 1.48−1.18 (m, 12H, CH(CH)$_3$)$_2$). Elemental analysis, calculated for **7-PdCl**: C, 60.11; H, 6.39; N. Found: C, 60.06; H, 6.42.

7-RhCO. A J. Young tube was charged with **7-H** (41 mg, 90 μmol), [Rh(COD)Cl]$_2$ (46 mg, 93 μmol of Rh), 2,6-lutidine (11 μL, 90 μmol), and C$_6$D$_6$ (1 mL). The solution was then degassed and exposed to CO (1 atm). A red color change was observed, and ^{31}P NMR analysis revealed conversion to **7-RhCO**. The reaction mixture was then filtered through a pad of silica gel and washed with diethyl ether. **7-RhCO** was obtained as a red solid after removal of the volatiles *in vacuo* and recrystallization by slow diffusion of pentane into dichloromethane (26 mg, 44 μmol, 50%). ^{1}H NMR (C$_6$D$_6$): δ 7.78 (d, 1H, J = 9 Hz, Ar H), 7.47 (d, 1H, J = 9 Hz, Ar H), 6.94 (d, 1H, J = 7 Hz, Ar H), 6.85 (s, 1H, imine CH), 6.80 (d, 1H, J = 7 Hz, Ar H), 6.75−6.72 (m, 2H, Ar H), 2.51 (s, 3H, CH_3), 2.41 (m, 1H, CH(CH$_3$)$_2$), 2.37 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.90 (m, 1H, CH(CH$_3$)$_2$), 1.31−1.29 (m, 6H, CH(CH_3)$_2$), 1.11−1.04 (m, 6H, CH(CH_3)$_2$). ^{1}H NMR (CDCl$_3$): δ 7.74 (dd, J = 9.2 Hz, J = 2.3 Hz, 1H, Ar H), 7.56 (d, J = 8.9 Hz, 1H, Ar H), 7.28 (dd, J = 8.6 Hz, J = 3.9 Hz, 1H, Ar H), 7.03 (dd, J = 7.9 Hz, J = 2.2 Hz, 1H, Ar H), 6.96 (s, 1H, Ar H), 6.94−6.86 (m, 3H, Ar H), 2.45 (m, 2H, CH(CH$_3$)$_2$), 2.38 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.30−2.27 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.37−1.00 (m, 12H, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (CDCl$_3$): δ 7.74 (d, J = 2.3 Hz, 1H, Ar H), 7.56 (d, J = 8.9 Hz, 1H, Ar H), 7.28 (d, J = 8.6 Hz, 1H, Ar H), 7.03 (d, J = 2.2 Hz, 1H, Ar H), 6.96 (s, 1H, Ar H), 6.94−6.86 (m, 3H, Ar H), 2.45 (m, 2H, CH(CH$_3$)$_2$), 2.38 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.30−2.27 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.37−1.00 (m, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 192.95−191.29 (m, CO), 162.5 (s, Ar C), 162.3 (s, Ar C), 162.2 (s, Ar C), 153.60 (s, Ar C), 150.51 (s, Ar C), 134.61 (s, Ar C), 134.08 (s, Ar C), 133.39 (s, Ar C), 131.65 (s, Ar C), 131.15 (s, Ar C), 130.50 (s, Ar C), 128.59 (s, Ar C), 127.74 (s, Ar C), 124.03 (s, Ar C), 123.59 (s, Ar C), 122.91 (s, Ar C), 122.59 (s, Ar C), 119.20 (d, J_{CP} = 12.1 Hz, Ar C), 118.88 (s, Ar C), 27.43 (d, J_{CP} = 27 Hz, CH(CH$_3$)$_2$), 23.64 (d, J_{CP} = 32 Hz, CH(CH$_3$)$_2$), 21.04 (s, CH$_3$), 20.69 (s, CH$_3$), 20.19 (s, CH$_3$), 19.59 (s, CH$_3$), 18.89 (s, CH$_3$), 18.73 (s, CH$_3$), 17.95 (s, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 76.3 (d, J_{RhP} = 130 Hz). IR ν(CO) = 1942 cm^{-1}. Elemental analysis, calculated for C$_{31}$H$_{38}$N$_2$OPRh: C, 63.27; H, 6.51%. Found: C, 63.09; H, 6.38%.

8-H. G (0.40 g, 1.2 mmol) was dissolved in toluene (15 mL) and treated with *tert*-butylamine (0.40 mL, 2.3 mmol) and tosylic acid (12 mg, 0.070 mmol, 10 mol %) in a Teflon screw-capped Schlenk flask. The reaction mixture was then heated in a 110 °C oil bath for 10 days while stirring over molecular sieves. The reaction was then cooled to ambient temperature, the solution decanted, and the volatiles were removed *in vacuo*. The remaining yellow oil was dissolved in pentane and stirred vigorously over silica gel for 5 min before being passed through a pad of Celite. The volatiles were removed, and the resulting yellow oil was recrystallized from fluorobenzene at −35 °C to yield **15-H** as a yellow solid (0.40 mg, 1.0 mmol, 87%). ^{1}H NMR (C$_6$D$_6$): δ 11.80 (s, 1H, NH), 8.26 (s, 1H, imine CH), 7.48 (dd, 1H, J_{PH} = 4 Hz,

J_{HH} =8 Hz, Ar H), 7.34 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.24 (s, 1H, Ar H), 6.94 (s, 1H, Ar H), 6.89 (d, 2H, J_{HH} = 8 Hz, Ar H), 2.18 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.99 (m, 2H, CH(CH$_3$)$_2$), 1.34 (s, 9H, CH_3), 1.11 (dd, 6H, J_{PH} = 15 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.99 (dd, 6H, J_{PH} = 11 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$) δ 11.80 (s, 1H, NH), 8.26 (s, 1H, imine CH), 7.48 (dd, 1H, J_{HH} = 8 Hz, Ar H), 7.34 (1H, d, J_{HH} = 9 Hz, Ar H), 7.24 (s, 1H, Ar H), 6.94 (s, 1H, Ar H), 6.89 (d, 2H, J_{HH} = 8 Hz, Ar H), 2.18 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 1.99 (m, 2H, CH(CH$_3$)$_2$), 1.34 (s, 9H, CH_3), 1.11 (dd, 6H, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.99 (dd, 6H, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 158.2 (imine C), 145.8 (d, J_{CP} = 20 Hz, Ar CN), 145.6 (Ar C), 134.6 (Ar C), 134.0 (Ar C), 131.5 (Ar C), 131.4 (Ar C), 130.3 (Ar C), 128.6 (Ar C), 25.4 (Ar C), 122.7 (Ar C), 120.3 (Ar C), 113.5 (Ar C H), 57.4 (C(CH$_3$)$_3$), 29.9 (C(CH$_3$)$_3$), 23.4 (d, J_{CP} = 13 Hz, CH(CH$_3$)$_2$), 21.0 (Ar CH$_3$), 20.5 (d, J_{CP} = 20 Hz, CH(CH$_3$)$_2$), 20.4 (Ar CH$_3$), 19.5 (d, J_{CP} = 10 Hz, CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −7.3.

8-PdOAc. A Schlenk flask was charged with **8-H** (0.10 g, 0.26 mmol), Pd(OAc)$_2$ (58 mg, 0.26 μmol), toluene (5 mL), and a stir bar. An immediate color change to a purple solution is observed. The solution was stirred for 1 h and then passed through a pad of Celite. Removal of the volatiles and washing with 3 × 5 mL of toluene yielded **8-PdOAc** as a red powder (0.11 g, 0.20 mmol, 78%). ^{1}H NMR (C$_6$D$_6$): δ 7.41 (d, 1H, J_{HH} = 5 Hz, imine CH), 7.39 (s, 1H, Ar H), 7.20 (dd, 1H, J_{PH} = 9 Hz, J_{HH} = 4 Hz, Ar H), 6.84 (d, 1H, J = 8 Hz, Ar H), 6.73 (d, 1H, J_{PH} = 9 Hz, J_{HH} = 2 Hz, Ar H), 6.67 (d, 1H, J = 9 Hz, Ar H), 6.62 (s, 1H, Ar H), 2.90 (m, 1H, CH(CH$_3$)$_2$), 2.19 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.00 (m, 1H, CH(CH$_3$)$_2$), 1.47 (dd, 3H, J_{PH} = 20 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.44 (s, 9H, C(CH_3)$_3$), 1.40 (dd, 3H, J_{PH} = 8 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.25 (dd, 3H, J_{PH} = 16 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.85 (dd, 3H, J_{PH} = 13 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 175.9 (C=O), 162.6 (d, J_{CP} = 21 Hz, N C of pincer backbone), 157.7 (Ar C), 150.3 (Ar C), 134.7 (Ar C), 133.9 (Ar C), 132.9 (Ar C), 131.2 (Ar C), 129.3 (Ar C), 125.5 (Ar C), 122.0 (Ar C), 121.9 (Ar C), 121.4 (Ar C), 118.7 (Ar C), 62.7 (C(CH$_3$)$_3$), 30.6 (C(CH$_3$)$_3$), 27.4 (d, J_{CP} = 22 Hz, CH(CH$_3$)$_2$), 24.1 (CH$_3$), 22.0 (CH$_3$), 21.8 (CH$_3$), 20.2 (CH$_3$), 19.6 (d, J_{CP} = 5 Hz, CH(CH$_3$)$_2$), 18.7 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$), 16.3 (CH$_3$), 15.9 (d, J_{CP} = 5 Hz, CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 66.3.

8-PdCl. A Schlenk flash was charged with **15-H** (51 mg, 0.13 mmol), 2,6-lutidine (15 μL, 0.13 mmol), Pd(COD)Cl$_2$ (38 mg, 0.13 mmol), toluene (5 mL) and a stir bar. The resulting red solution was then stirred overnight and then filtered through a pad of Celite. The volatiles were then removed *in vacuo*, and the solid was recrystallized in toluene to yield **15-PdCl** as a deep red powder (32 mg, 60 μmol, 50%). ^{1}H NMR (C$_6$D$_6$): δ 7.48 (d, 1H, J_{PH} = 13 Hz, imine CH), 7.32 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.22 (dd, 1H, J_{PH} = 5 Hz, J_{HH} = 9 Hz, Ar H), 6.89 (d, 1H, J_{PH} = 8 Hz, Ar H), 6.76 (d, 1H, J_{HH} = 9 Hz, Ar H), 6.69 (d, 1H J_{HH} = 9 Hz, Ar H), 6.61 (s, 1H, Ar H), 2.52 (m, 1H, CH(CH$_3$)$_2$), 2.13 (m, 1H, CH(CH$_3$)$_2$), 2.10 (s, 3H, Ar CH_3), 2.05 (s, 3H, Ar CH_3), 1.64 (s, 9H, C(CH_3)$_3$), 1.58 (dd, 3H, J_{PH} = 17 Hz, J_{HH} = 9 Hz, CH(CH_3)$_2$), 1.32 (dd, 3H, J_{PH} = 17 Hz, J_{HH} = 9 Hz, CH(CH_3)$_2$), 1.26 (dd, 3H, J_{PH} = 18 Hz, J_{HH} = 11 Hz, CH(CH_3)$_2$), 0.87 (dd, 3H, J_{PH} = 15 Hz, J_{HH} = 8 Hz, CH(CH_3)$_2$). ^{1}H{^{31}P} NMR (C$_6$D$_6$): δ 7.49 (s, 1H, imine CH), 7.32 (d, 1H, J_{HH} = 9 Hz, Ar H), 7.22 (dd, 1H, J_{HH} = 9 Hz, Ar H), 6.89 (s, 1H, Ar H), 6.76 (d, 1H, J_{HH} = 9 Hz, Ar H), 6.69 (d, 1H, J_{HH} 9 Hz, Ar H), 6.61 (s, 1H. Ar H), 2.52 (m, 1H, CH(CH$_3$)$_2$), 2.13 (m, 1H, CH(CH$_3$)$_2$), 2.10 (s, 3H, Ar CH_3), 2.05 (s, 3H, Ar CH_3), 1.64 (s, 9H, C(CH_3)$_3$), 1.57 (d, 3H, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.32 (d, 3H, J_{HH} = 7 Hz, CH(CH_3)$_2$), 1.26 (d, 3H, J_{HH} = 7 Hz, CH(CH_3)$_2$), 0.88 (d, 3H, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 162.7 (d, J_{CP} = 21 Hz, CN), 158.0 (Ar C), 150.7 (Ar C), 134.4 (Ar C), 133.8 (Ar C), 133.2 (Ar C), 131.2 (Ar C), 129.0 (d, J_{CP} = 7 Hz, Ar C), 125.6 (Ar C), 122.5 (d, J_{CP} = 16 Hz, Ar C), 122.2 (Ar C), 121.9 (Ar C), 118.1 (Ar C), 63.6 (C(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$), 26.6 (d, J_{CP} = 24 Hz, CH(CH$_3$)$_2$), 24.4 (d, J_{CP} = 30 Hz, CH(CH$_3$)$_2$), 20.5 (Ar CH_3), 2.02 (Ar CH_3), 18.9 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$), 18.3 (CH(CH$_3$)$_2$), 18.1(CH(CH$_3$)$_2$), 17.1(CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR

(C$_6$D$_6$): δ 70.4. Elemental analysis, calculated for **8-PdCl**: C, 55.87; H, 6.60; N, 5.21. Found: C, 55.72; H, 6.88; N, 5.09.

8-PdCl. A J. Young tube was charged with **8-PdOAc** (77 mg, 14 μmol) and C$_6$D$_6$ (1 mL). Me$_3$SiCl (18 μL, 14 μmol) was added to the reaction mixture via syringe. After 72 h, the volatiles were removed *in vacuo*, and the resulting solid was washed three times with toluene (1 mL). After the final wash, the volatiles were removed *in vacuo* to yield **8-PdCl** as a purple solid (63 mg, 12 μmol, 85%).

8-RhCO. A J. Young tube was charged with **8-H** (42 mg, 0.11 mmol), [Rh(COD)Cl]$_2$ (52 mg, 0.11 mmol of Rh), 2,6-lutidine (13 μL, 0.11 mmol), and C$_6$D$_6$ (1 mL). Upon the addition of CO (1 atm), the solution immediately turns red. The solution was allowed to react overnight and was then passed through a pad of silica gel. The frit was washed with diethyl ether, and the volatiles were removed *in vacuo* to yield a red solid. This was then taken up in dichloromethane and stored at −35 °C to yield red crystals of **8-RhCO** (47 mg, 0.089 mmol, 84%). ^{1}H NMR (C$_6$D$_6$): δ 7.81 (d, 1H, J_{PH} = 9 Hz, imine CH), 7.53 (d, 1H, J_{HH} = 8 Hz, Ar H), 7.30 (dd, 1H, J_{PH} = 8 Hz, J_{HH} = 4 Hz, Ar H), 7.01 (d, 1H, J_{HH} = 7 Hz, Ar H), 6.80 (d, 1H, J_{HH} = 9 Hz, Ar H), 6.76 (s, 1H, Ar H), 6.75 (m, 1H, Ar H), 2.30 (m, 1H, CH(CH$_3$)$_2$), 2.14 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.46 (s, 9H, C(CH_3)$_3$), 1.32−1.19 (m, 9H, CH(CH_3)$_2$), 0.98 (dd, 3H, J_{PH} = 13 Hz, J_{HH} = 7 Hz, CH(CH_3)$_2$). ^{1}H NMR (CDCl$_3$): δ 8.25 (dd, J = 9 Hz, J = 3 Hz, 1H, imine CH), 7.50 (d, J = 3 Hz, 1H, Ar H), 7.47 (dd, J = 9 Hz, J = 3 Hz, 1H, Ar H), 7.38−7.30 (m, 2H Ar H), 7.17 (s, 1H, Ar H), 7.01 (d, J = 9 Hz, 1H, Ar H), 2.81 (m, 1H, CH(CH$_3$)$_2$), 2.50 (s, 3H, Ar CH_3), 2.48 (m, 1H, CH(CH$_3$)$_2$), 2.41 (s, 3H, Ar CH_3), 1.86 (s, 9H, C(CH_3)$_3$), 1.57 (dd, J = 16 Hz, J = 7 Hz, 3H, CH(CH_3)$_2$), 1.49 (dd, J = 15 Hz, J = 7 Hz, 6H, CH(CH_3)$_3$), 1.42 (dd, J = 14 Hz, J= 7 Hz, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 194.7 (CO), 161.6 (d, J = 21.7 Hz, Ar C), 158.2 (s), 150.1 (s), 134.2 (s), 133.1 (s), 132.0 (s), 130.8 (s), 128.6−127.3 (m), 124.6 (s), 123.5 (s), 120.50 (d, J = 13 Hz), 117.19 (d, J = 43 Hz), 63.71 (s (C(CH$_3$)$_3$), 31.95 (s, (C(CH$_3$)$_3$), 27.46 (d, J = 26 Hz, CH(CH$_3$)$_2$), 23.99 (d, J = 34 Hz, CH(CH$_3$)$_2$), 20.79 (s, CH$_3$), 20.15 (s, CH$_3$), 19.82 (s, CH$_3$), 19.13 (s, CH$_3$), 18.20 (s, CH$_3$), 17.68 (s, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.7 (d, J_{RhP} = 154 Hz). IR ν(CO) =1930 cm^{-1}.

H. A Schlenk flask was charged with **F** (0.30 g, 0.77 mmol), a stir bar, and diethyl ether. *n*-Butyllithium (0.31 mL, 0.77 mmol) was then added in a dropwise fashion. After 30 min, ClP(NMe$_2$)$_2$ (0.11 mL, 0.77 mmol) was added, and stirring was commenced for an additional 1.5 h. The ethereal solution was then filtered through a pad of Celite. Removal of the volatiles *in vacuo* and recrystallization in pentane at −35 °C resulted in isolation of **H** as colorless crystals (0.30 g, 0.59 mmol, 77%). ^{1}H NMR (C$_6$D$_6$): δ 7.93 (dd, J_{HH} = 5 Hz, J_{P1H} = 10 Hz, 1H, Ar H), 7.56 (dd, J_{HH} = 5 Hz, J_{P1H} = 10 Hz, 1H, Ar H), 7.31 (m, 1H, Ar H), 7.21 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.99 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.89 (d, J_{HH} = 5 Hz, 1H, Ar H), 2.48 (d, J_{P2H} = 10 Hz, 12H, P(N(CH_3)$_2$)$_2$), 2.15 (s, 3H, Ar CH_3), 1.93 (s, 3H, Ar CH_3), 1.90 (m, 2H, CH(CH$_3$)$_2$), 1.15 (dd, J_{HH} = 7 Hz, J_{P1H} = 15 Hz, 6H, CH(CH_3)$_2$), 0.95 (dd, J_{HH} = 7 Hz, J_{P1H} = 15 Hz, 6H, CH(CH_3)$_2$). ^{1}H{^{31}P$_1$} NMR (C$_6$D$_6$): δ 7.93 (d, J_{HH} = 5 Hz, 1H, Ar H), 7.56 (d, J_{HH} = 5 Hz, 1H, Ar H), 7.31 (m, 1H, Ar H), 7.21 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.99 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.89 (d, J_{HH} = 5 Hz, 1H, Ar H), 2.48 (d, J_{P2H} = 10 Hz, 12H, P(N(CH_3)$_2$)$_2$), 2.15 (s, 3H, Ar CH_3), 1.93 (s, 3H, Ar CH_3), 1.90 (m, 2H, CH(CH$_3$)$_2$), 1.15 (d, J_{HH} = 7 Hz, 6H, CH(CH_3)$_2$), 0.95 (d, J_{HH} = 7 Hz, 6H, CH(CH_3)$_2$). ^{1}H{^{31}P$_2$} NMR (C$_6$D$_6$): δ 7.93 (dd, J_{HH} = 5 Hz, J_{P1H} = 10 Hz, 1H, Ar H), 7.56 (dd, J_{HH} = 5 Hz, J_{P1H} = 10 Hz, 1H, Ar H), 7.31 (m, 1H, Ar H), 7.21 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.99 (d, J_{HH} = 5 Hz, 1H, Ar H), 6.89 (d, J_{HH} = 5 Hz, 1H, Ar H), 2.48 (s, 12H, P(N(CH_3)$_2$)$_2$), 2.15 (s, 3H, Ar CH_3), 1.93 (s, 3H, Ar CH_3), 1.90 (m, 2H, CH(CH$_3$)$_2$), 1.15 (dd, J_{HH} = 7 Hz, J_{P1H} = 15 Hz, 6H, CH(CH_3)$_2$), 0.95 (dd, J_{HH} = 7 Hz, J_{P1H} = 15 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 151.4 (dd, J = 17 Hz, J = 21 Hz, 3° Ar CN), 143.5 (s, 3° Ar C), 136.4 (s, Ar CH), 135.6 (dd, J = 4 Hz, J = 9 Hz, 3° Ar C), 134.5 (s, Ar CH), 134.3 (s, Ar CH), 133.8 (d, J = 22 Hz, 3° Ar C), 132.4 (s, Ar CH), 130.1 (dd, J = 6 Hz, J = 10 Hz, 3° Ar C), 129.6 (s, Ar CH), 127.4 (s, Ar CH), 124.6 (s, 3° Ar C), 38.8 (d, J = 2 Hz, N(CH_3)$_2$), 38.6 (d, J = 2 Hz, N(CH_3)$_2$), 26.8 (d, J = 5 Hz, CH(CH_3)$_2$), 26.7 (d, J = 5 Hz, CH(CH_3)$_2$), 21.9 (s, CH_3), 21.8 (s,

CH_3), 20.9 (s, CH_3), 20.6, 20.4 (s, CH_3), 20.4 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 124.5 (s, P_2, $P(NCH_3)_2$), −9.1 (s, P_1, $P(^iPr)_2$).

9-H. A Schlenk flask was charged with **F** (2.7 g, 6.8 mmol), a stir bar, and diethyl ether (100 mL). *n*-Butyllithium (2.7 mL, 6.8 mmol) was then added to the reaction via syringe and allowed to react for 20 min. $ClP(NMe_2)_2$ (1.0 mL, 6.8 mmol) was then added to the solution. Stirring was continued for 30 min, and then a second equivalent of *n*-butyllithium (2.7 mL, 6.8 mmol) was added to the reaction mixture. Removal of a small aliquot and analysis via ^{31}P NMR reveal conversion to **9-Li** as observed by the formation of two singlets at δ 109.5 and −3.4 ppm in diethyl ether. The addition of CF_3CH_2OH (0.49 mL, 6.8 mmol) results in immediate precipitation of $LiOCH_2CF_3$ and formation of a colorless solution. The diethyl ethereal solution was then filtered through a pad of Celite, concentrated, and stored at −35 °C. The resulting precipitate was collected and dried *in vacuo* to yield **9-H** as a colorless solid (2.4 g, 82%). ^1H NMR (C_6D_6): δ 8.55 (d, J_{P1H} = 8 Hz, 1H, N*H*), 7.43−7.33 (m, 3H, Ar *H*), 7.13 (s, 1H, Ar *H*), 6.93 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.84 (d, J_{HH} = 8 Hz, 1H, Ar *H*), 2.80 (d, J_{P2H} = 9 Hz, 12H, $P(NCH_3)_2$), 2.26 (s, 3H, Ar CH_3), 2.18 (s, 3H, Ar CH_3), 1.98−1.87 (m, 2H, $CH(CH_3)_2$), 1.09 (dd, J_{P1H} = 15 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$), 0.94 (dd, J_{P1H} = 12 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_1\}$ NMR (C_6D_6): δ 8.54 (s, 1H), 7.44−7.32 (m, 3H), 7.13 (s, 1H), 6.93 (d, J = 9 Hz, 1H), 6.84 (d, J = 8 Hz, 1H), 2.80 (d, J = 9 Hz, 12H), 2.26 (s, 3H), 2.18 (s, 3H), 1.95 (m 2H), 1.09 (d, J = 7 Hz, 6H), 0.94 (d, 6H). $^1H\{^{31}P_2\}$ NMR (C_6D_6): δ 8.55 (d, J = 8 Hz, 1H), 7.45−7.32 (m, 3H), 7.13 (s, 1H), 6.93 (d, J = 8 Hz, 1H), 6.84 (d, J = 8 Hz, 1H), 2.80 (d, J = 1 Hz, 12H), 2.26 (s, 3H), 2.18 (s, 3H), 1.95 (m, 2H), 1.09 (dd, J = 15 Hz, J = 7, 6H), 0.94 (dd, J = 12 Hz, J = 7 Hz, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.8 (d, J_{CP} = 20, Ar C*N*), 143.5 (d, J_{CP} = 18 Hz, Ar C*N*)), 133.6 (d, J_{CP} = 3 Hz, Ar *C*), 132.8 (d, J = 8 Hz, Ar *C*), 130.7 (s, Ar *C*), 130.0 (s, Ar *C*), 128.8 (s, Ar *C*), 128.5 (s, Ar *C*), 127.6 (s, Ar *C*), 122.80 (s, Ar *C*), 118.00 (d, J_{CP} = 3 Hz, Ar *C*), 117.09 (s, Ar *C*), 41.95 (dd, J_{CP} = 15 Hz, J_{CP} = 3 Hz, $P(NCH_3)_2$), 23.53 (d, J_{CP} = 11 Hz, $CH(CH_3)_2$), 21.23 (s, Ar CH_3), 20.94 (s, Ar CH_3), 20.48 (d, J = 19 Hz, $CH(CH_3)_2$), 19.28 (d, J = 9 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 98.2 (s, P, $P(NMe_2)_2$), −13.1 (s, P, $P(^iPr)_2$).

9-RhCO. A J. Young tube was charged with **9-H** (89 mg, 0.21 mmol), [Rh(COD)Cl]$_2$ (51 mg, 0.21 mmol), 2,6-lutidine (24 μL, 0.21 mmol), and C_6D_6 (1 mL). The reaction mixture was degassed and then exposed to CO (1 atm). After 30 min, the reaction was filtered through a pad of silica gel. The silica gel was washed with diethyl ether, and then the volatiles were removed *in vacuo*. Recrystallization of the product in pentane at −35 °C resulted in isolation of **9-RhCO** as a yellow powder (76 mg, 0.14 mmol, 77%). ^1H NMR (C_6D_6): δ 7.75−7.67 (m, 2H, Ar *H*), 7.23 (d, J_{P2H} = 9 Hz, 1H, Ar *H*), 6.90 (d, J_{P1H} = 8 Hz, 1H, Ar *H*), 6.83 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.79 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 2.56 (d, J_{P2H} = 12 Hz, 12H, $N(CH_3)_2$), 2.18 (s, 3H, Ar CH_3), 2.16 (s, 3H, Ar CH_3), 2.14 (m, 2H, $CH(CH_3)_2$), 1.28 (dd, J_{P1H} = 17 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$), 1.05 (dd, J_{P1H} = 15 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_1\}$ NMR (C_6D_6): δ 7.75−7.67 (m, 2H, Ar *H*), 7.23 (d, J = 9 Hz, 1H, Ar *H*), 6.90 (s, 1H, Ar *H*), 6.83 (d, J = 9 Hz, 1H, Ar *H*), 6.79 (d, J = 9 Hz, 1H, Ar *H*), 2.56 (d, J = 12 Hz, 12H, $N(CH_3)_2$), 2.18 (s, 3H, Ar CH_3), 2.16 (s, 3H, Ar CH_3), 2.14 (m, 2H, $CH(CH_3)_2$), 1.28 (dd, J_{PH} = 17 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$), 1.05 (dd, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_2\}$ NMR (C_6D_6): δ 7.75−7.67 (m, 2H, Ar *H*), 7.23 (s, 1H, Ar *H*), 6.90 (d, J = 8 Hz, 1H), 6.83 (d, J = 9 Hz, 1H, Ar *H*), 6.79 (d, J = 9 Hz, 1H, Ar *H*), 2.56 (s, 12H, $N(CH_3)_2$), 2.18 (s, 3H, Ar CH_3), 2.16 (s, 3H, Ar CH_3), 2.14 (m, 2H, $CH(CH_3)_2$), 1.28 (dd, J_{PH} = 17 Hz, J_{HH} = 7 Hz, 6H), 1.05 (dd, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.41−139.41 (m), 135.21 (s), 134.11 (s), 134.01 (s), 133.18 (s), 132.72−132.59 (m), 132.59−132.43 (m), 131.63−131.48 (m), 131.25−131.14 (m), 130.64 (s), 128.93 (d, J = 11 Hz), 117.32−116.76 (m), 116.81−116.10 (m), 25.31−25.25 (m, $CH(CH_3)_2$), 25.07 (s, $CH(CH_3)_2$), 20.39 (s, CH_3), 20.13 (s, CH_3), 18.75 (d, J = 6 Hz, $CH(CH_3)_2$), 17.98 (d, J_{CP} = 5 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 130.9 (dd, J_{PP} = 315 Hz, J_{RhP} = 163 Hz, P_2, P^{NMe2}), 58.7 (dd, J_{PP} = 315 Hz, J_{RhP} 123 Hz, P_1, P^{iPr}). IR: ν_{CO} = 1943 cm^{-1}. Elemental

analysis, calculated for $C_{25}H_{38}N_3OP_2Rh$: C, 53.48; H, 6.82%. Found: C, 53.19; H, 6.68%.

10-H. A Teflon stoppered Schlenk flask was charged with **9-H** (2.00 g, 4.64 mmol), CF_3CH_2OH (1.70 mL, 23.2 mmol), toluene (15 mL), and a stir bar. The reaction mixture was then refluxed at 100 °C for 3 days. Cooling the reaction mixture to room temperature and removal of the volatiles *in vacuo* resulted in yellow oil. Recrystallization in diethyl ether yielded **10-H** as a colorless oil (2.47 g, 4.57 mmol, 98%). ^1H NMR ($CDCl_3$): δ 7.43 (d, J_{PH} = 5 Hz, 1H, N*H*), 7.19−7.17 (m, 4H, Ar *H*), 7.01 (d, J_{HH} = 10 Hz, 1H, Ar *H*), 6.89 (dd, J_{HH} = 10 Hz, J_{P1H} = 5 Hz, 1H, Ar *H*), 4.30−4.24 (m, 2H, OCH_2CF_3), 4.19−4.13 (m, 2H, OCH_2CF_3), 2.35 (s, 3H, Ar CH_3), 2.29 (s, 3H, Ar CH_3), 2.17−2.11 (m, 2H, $CH(CH_3)_2$), 1.13 (dd, J_{P1H} = 15 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$), 0.96 (dd, J_{P1H} 15 Hz, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_1\}$ NMR ($CDCl_3$): δ 7.43 (d, J_{PH} = 5 Hz, 1H, N*H*), 7.19−7.17 (m, 4H, Ar *H*), 7.01 (d, J_{HH} = 10 Hz, 1H, Ar *H*), 6.89 (d, J_{HH} = 10 Hz, J_{PH} = 5 Hz, 1H, Ar *H*), 4.30−4.24 (m, 2H, OCH_2CF_3), 4.19−4.13 (m, 2H, OCH_2CF_3), 2.35 (s, 3H, Ar CH_3), 2.29 (s, 3H, Ar CH_3), 2.17−2.11 (m, 2H, $CH(CH_3)_2$), 1.13 (d, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$), 0.96 (d, J_{HH} = 5 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.7 (d, J_{CP} = 20 Hz, C*N*), 144.7 (d, J_{CP} = 19 Hz, C*N*), 133.7 (d, J_{CP} = 5 Hz, Ar *C*), 133.4 (s, Ar *C*), 132.1 (d, J_{CP} = 3 Hz, Ar *C*), 131.5 (d, J_{CP} = 13 Hz, Ar *C*), 131.0 (s), 129.6 (s, Ar *C*), 129.5 (s, Ar *C*), 129.4 (s, Ar *C*), 121.0 (s, Ar *C*), 117.5 (d, J= 3 Hz, Ar *C*), 64.1 (m, CH_2), 23.7 (d, J_{CP} = 10 Hz, $CH(CH_3)_2$), 20.8 (d, J_{CP} = 8 Hz, $CH(CH_3)_2$), 20.4 (s, Ar CH_3), 20.3 (s, Ar CH_3), 19.2 (d, J_{CP} = 9 Hz, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 166.3 (s, $POCH_2CF_3$), −15.0 (s, P^iPr_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 167.5 (s, $POCH_2CF_3$), −14.7 (s, P^iPr_2). ^{19}F NMR (C_6D_6): δ 75.6.

10-RhCO. A J. Young tube was charged with **10-H** (0.15 g, 0.28 mmol), (Rh(COD)Cl)$_2$ (65 mg, 0.13 mmol), 2,6-lutidine (32 μL, 0.28 mmol), and C_6D_6. The mixture was degassed by freeze pump thaw techniques and then exposed to 1 atm of CO. The volatiles were then removed *in vacuo*, and the resulting red oil was taken up in pentane and filtered through a pad of Celite. Removal of the volatiles yielded **10-RhCO** as a red solid. No additional workup was conducted (0.12 mg, 0.18 mmol, 65%). ^1H NMR (C_6D_6): δ 7.60 (dd, J_{HH} = 8 Hz, J_{P1H} = 4 Hz, 1H, Ar *H*), 7.53 (t, J_{HH} = 8 Hz, 1H, Ar *H*), 7.24 (d, J_{P2H} = 11 Hz, 1H, Ar *H*), 6.83 (d, J_{P1H} = 8 Hz, 1H, Ar *H*), 6.78 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.75 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 4.57−4.20 (m, 2H, OCH_2CF_3), 3.93 (m, 2H, OCH_2CF_3), 2.14 (s, 3H, Ar CH_3), 2.09−1.99 (m, 2H, $CH(CH_3)_2$), 1.98 (s, 3H, Ar CH_3), 1.13 (dd, J_{P1H} = 17 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$), 0.92 (dd, J_{P1H} = 15 Hz, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_1\}$ NMR (C_6D_6): δ 7.60 (d, J = 9 Hz, 1H, Ar *H*), 7.53 (t, J = 8 Hz, 1H, Ar *H*), 7.24 (d, J = 11 Hz, 1H, Ar *H*), 6.83 (s, 1H, Ar *H*), 6.78 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.75 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 4.43−4.24 (m, 2H, OCH_2CF_3), 4.05−3.82 (m, 2H, OCH_2CF_3), 2.14 (s, 3H, Ar CH_3), 2.12−1.96 (m, 2H, $CH(CH_3)_2$), 1.98 (s, 3H, Ar CH_3), 1.13 (d, J_{HH} = 6.9 Hz, 6H, $CH(CH_3)_2$), 0.92 (d, J_{HH} = 6.8 Hz, 6H, $CH(CH_3)_2$). $^1H\{^{31}P_2\}$ NMR (C_6D_6): δ 7.60 (dd, J = 8 Hz, J = 4 Hz, 1H, Ar *H*), 7.53 (d, J = 9 Hz, 1H, Ar *H*), 7.24 (s, 1H, Ar *H*), 6.83 (d, J = 8 Hz, 1H, Ar *H*), 6.78 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.75 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 4.36 (m 1H, OCH_2CF_3), 3.92 (m, 1H, OCH_2CF_3), 2.14 (s, 2H, Ar CH_3), 2.09−2.01 (m, 1H, $CH(CH_3)_2$), 1.98 (s, 1H, $CH(CH_3)_2$), 1.13 (dd, J_{PH} = 17 Hz, J_{HH} = 7 Hz, 3H, $CH(CH_3)$), 0.92 (dd, J_{PH} = 15 Hz, J_{HH} = 7 Hz, 3H, $CH(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 189.3 (d, J = 71 Hz, CO), 158.8 (d, J = 19 Hz, Ar C*N*), 157.9 (d, J = 34 Hz, Ar C*N*), 135.1 (s, Ar *C*), 132.3 (s, Ar *C*), 132.1 (s, Ar *C*), 129.6 (s, Ar *C*), 126.7 (s, Ar *C*), 125.1 (br, CF_3), 123.0 (br, CF_3), 120.7 (s, Ar *C*), 120.5 (s, Ar *C*), 117.4 (s, Ar *C*), 116.5 (d, J = 14 Hz, Ar *C*), 70.9−68.0 (m, CH_2), 34.0 (d, J = 21 Hz, $CH(CH_3)_2$), 29.5 (s, CH_3), 29.0 (s, CH_3), 28.6 (s, CH_3), 27.6 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 190.7 (dd, J_{PP} = 346 Hz, J_{RhP} = 190 Hz, P_2, $P^{OCH2CF3}$), 60.1 (dd, J_{PP} = 346 Hz, J_{RhP} = 125 Hz, P_1, P^{iPr}). ^{19}F NMR (C_6D_6): δ −75.3 (t, J_{RhC} = 8 Hz, CF_3). IR ν(CO) = 1960 cm^{-1}.

10-PdCl. A Schlenk flask was charged with **10-H** (0.12 g, 0.22 mmol), Pd(COD)Cl$_2$ (62 mg, 0.22 mmol), 2,6-lutidine (25 μL, 0.22 mmol), and diethyl ether. The reaction mixture was stirred for 12 h, and then the solution was filtered through a pad of silica gel with additional diethyl ether. The ethereal solution was then concentrated

and stored at −35 °C. The resulting precipitate was collected, and the volatiles were removed *in vacuo* to yield **10-PdCl** as a purple solid (88 mg, 013 mmol, 60%). ^{1}H NMR (C$_6$D$_6$): δ 7.56−7.49 (m, 2H, Ar *H*), 7.22 (d, J_{P2} = 12 Hz, 2H, Ar *H*), 6.78−6.68 (m, 2H, Ar *H*), 6.66 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 4.67 (m, 2H, C*H*$_2$CF$_3$), 4.59−4.45 (m, 2H, C*H*$_2$CF$_3$), 2.26−2.12 (m, 2H, C*H*(CH$_3$)$_2$), 2.08 (s, 3H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 1.30 (dd, J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.02 (dd, J_{P1H} = 16 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P δ159.2} NMR (C$_6$D$_6$): δ 7.56−7.49 (m, 2H, Ar *H*), 7.22 (s, 2H), 6.78−6.68 (m, 2H), 6.66 (d, *J* = 9 Hz, 1H, Ar *H*), 4.67 (m, 2H, C*H*$_2$CF$_3$), 4.59−4.45 (m, 2H, C*H*$_2$CF$_3$), 2.26−2.12 (m, 2H, C*H*(CH$_3$)$_2$), 2.08 (s, 3H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 1.30 (dd, *J* = 18 Hz, *J* = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.02 (dd, *J* = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P δ53.5} NMR (C$_6$D$_6$): δ 7.56−7.49 (m, 2H, Ar *H*), 7.22 (s, 2H), 6.78−6.68 (m, 2H), 6.66 (d, *J* = 9 Hz, 1H, Ar *H*), 4.67 (m, 2H, C*H*$_2$CF$_3$), 4.59−4.45 (m, 2H, C*H*$_2$CF$_3$), 2.26−2.12 (m, 2H, C*H*(CH$_3$)$_2$), 2.08 (s, 3H, C*H*$_3$), 1.88 (s, 3H, C*H*$_3$), 1.30 (d, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.02 (d, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 161.3 (d, J_{CP} = 20 Hz, 3° Ar CN), 159.6 (d, J_{CP} = 38 Hz, 3° Ar CN), 137.9 (s, Ar CH), 136.1 (s, Ar CH), 133.1 (s, Ar CH), 132.5 (s, Ar CH), 130.2 (s, Ar CH), 127.7 (s, Ar CH), 125.8 (d, J_{CP} = 60 Hz, CF$_3$), 124.7 (d, J_{CP} = 9 Hz, 3° Ar C), 122.4 (d, J_{CP} = 10 Hz, 3° Ar C), 118.1 (d, J_{CP} = 42 Hz, 3° Ar C), 117.0 (d, J_{CP} = 12 H, Ar CH), 116.4 (d, 12 Hz, Ar CH), 62.5 (m, CH$_2$CF$_3$), 25.1 (d, J_{CP} = 22 Hz, CH(CH$_3$)$_2$), 20.3 (s, CH$_3$), 19.8 (s, CH$_3$), 18.5 (s, CH$_3$), 17.9 (s, CH$_3$). ^{19}F NMR (C$_6$D$_6$): δ 75.6 (d, J_{FH} = 8 Hz, CH$_2$CF$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 159.2 (dd, J_{PP} = 545 Hz, P$_2$, P(OCH$_2$CF$_3$)), 53.5 (dd, J_{PP} = 545 Hz, P$_1$, P(CH(CH$_3$)$_3$). Elemental analysis, calculated for **10-PdCl**: C, 42.25; H, 4.43; N, 2.05. Found: C, 42.32; H, 4.53; N, 1.98.

11-H. A Teflon stoppered Schlenk flask was charged with **9-H** (82 mg, 0.19 mmol) and (CF$_3$)$_2$CHOH (1 mL). The flask was placed in a 100 °C oil bath for 18 h at which point ^{31}P NMR spectroscopy demonstrated conversion to **11-H**. The following NMR data were obtained by first referencing a spectrum of pure C$_6$D$_6$. Selected ^{1}H NMR ((CF$_3$)$_2$CHOH): δ 7.79 (d, *J* = 8 Hz, 1H), 7.60 (s, 1H), 7.58−7.46 (m, 2H), 7.33 (d, *J* = 8 Hz, 1H), 6.81 (s, 1H), 6.48 (d, *J* = 8 Hz, 1H), 2.64 (s, 3H, C*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 1.56 (dd, J_{PH} = 20 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.43 (dd, J_{PH} = 14 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P 35.9} NMR ((CF$_3$)$_2$CHOH): δ 7.79 (d, *J* = 8 Hz, 1H), 7.60 (s, 1H), 7.58−7.46 (m, 2H), 7.33 (d, *J* = 8 Hz, 1H), 6.81 (s, 1H), 6.48 (d, *J* = 8 Hz, 1H), 2.64 (s, 3H), 2.46 (s, 3H), 1.56 (d, J_{HH} = 7 Hz, 6H), 1.43 (d, J_{HH} = 7 Hz, 6H). ^{31}P{^{1}H} NMR ((CF$_3$)$_2$CHOH): δ 215.2 (s, P(OCH(CH$_3$)$_2$), 35.9 (s, P(iPr)$_2$).

11-PdOAc·HOCH(CF$_3$)$_2$. A Teflon stoppered round-bottom flask was charged with **9-H** (0.20 mg, 0.46 mmol), a stir bar, and (CF$_3$)$_2$CHOH (5 mL). The reaction mixture was then stirred for 24 h in a 100 °C oil bath. Pd(OAc)$_2$ (0.11 g, 0.46 mmol) was then added to the reaction vessel. Stirring was commenced for 3 days at room temperature. The volatiles were then removed *in vacuo*, and the resulting purple solid was filtered through a pad of silica gel with diethyl ether. The volatiles were again removed, and the resulting solid was taken up in a minimal amount of pentane and recrystallized at −35 °C to yield **11-PdOAc·HOCH(CF$_3$)$_2$** as dark purple crystals (0.25 g, 0.32 mmol, 64%). ^{1}H NMR (C$_6$D$_6$): δ 7.40−7.34 (m, 2H, Ar *H*), 7.32 (d, J_{P2H} = 12 Hz, 1H, Ar *H*), 6.65 (d, J_{HH} = 9 Hz. 1H, Ar *H*), 6.63 (d, J_{P1H} = 11 Hz, 1H, Ar *H*), 6.59 (d, J_{HH} = 9 Hz, 1H, Ar *H*) 6.42 (m, 2H, POC*H*(CF$_3$)$_2$), 4.73 (s, 1H, O*H*), 3.77 (m, 1H, HOC*H*(CF$_3$)$_2$), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 2.00−1.89 (m, 2H, C*H*(CH$_3$)$_2$), 1.84 (s, 3H, OAc), 1.10 (dd, J_{P1H} = 18 Hz, J_{HH} =7 Hz, 5H), 0.88 (dd, J_{P1H} = 17 Hz, J_{HH} =7 Hz, 6H). ^{1}H{^{31}P$_1$} NMR (C$_6$D$_6$): δ 7.40−7.34 (m, 2H, Ar *H*), 7.32 (d, *J* = 12 Hz, 1H, Ar *H*), 6.65 (d, J_{HH} = 9 Hz. 1H, Ar *H*), 6.63 (s, 1H, Ar *H*), 6.59 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 6.42 (m, 2H, C*H*(CF$_3$)$_2$), 4.73 (s, 1H, O*H*), 3.77 (m, 1H, HOC*H*(CF$_3$)$_2$), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 2.00−1.89 (m, 2H, C*H*(CH$_3$)$_2$), 1.84 (s, 3H, OAc), 1.10 (dd, J_{HH} =7 Hz, 5H), 0.88 (dd, J_{HH} = 7 Hz, 6H). ^{1}H{^{31}P$_2$} NMR (C$_6$D$_6$): δ 7.40−7.34 (m, 2H, Ar *H*), 7.32 (s, 1H, Ar *H*), 6.65 (d, J_{HH} = 9 Hz. 1H, Ar *H*), 6.63 (d, J_{P1H} = 11 Hz, 1H, Ar *H*), 6.59 (d, J_{HH} =9 Hz, 1H, Ar *H*), 6.42 (m, 2H, C*H*(CF$_3$)$_2$), 4.73 (s, 1H, O*H*), 3.77 (m, 1H, HOC*H*(CF$_3$)$_2$), 2.06 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 2.00−1.89 (m, 2H, C*H*(CH$_3$)$_2$), 1.84 (s, 3H, OAc), 1.10 (dd,

J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 5H), 0.88 (dd, J_{P1H} = 17 Hz, J_{HH} = 7 Hz, 6H). ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 178.7 (OAc), 161.6 (Ar CN), 158.9 (d, J_{CP} = 40 Hz, Ar CN), 137.1 (Ar C), 133.8 (Ar C), 134.1 (Ar C), 132.8 (d, J_{CP} = 38 Hz, Ar C), 131.4 (Ar C), 130.4 (Ar C). 126.8, 126.3, 122.8, 120.3(d, J_{CP} = 30 Hz, Ar C), 118.1, 117.3 (d, J_{CP} = 17 Hz, Ar C), 116.9, 116.6, 116.2, 116.1, 73.82 (OCH(CF$_3$)$_2$), 69.53 (HOCH-(CF$_3$)$_2$), 24.82 (d, *J* = 22 Hz, CH(CH$_3$)$_2$), 21.88 (CH$_3$), 20.27 (CH$_3$), 19.81 (CH$_3$), 17.87 (CH$_3$), 17.36 (CH$_3$).^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 176.2 (d, J_{P1P2} = 517 Hz, P(OCH(CF$_3$)$_2$), 58.6 (d, J_{P1P2} = 517 Hz, P(CH(CH$_3$)$_2$). ^{19}F NMR (C$_6$D$_6$): δ −74.2 (s, CF$_3$), −74.5 (s, CF$_3$), −76.5 (m, HOCH(CF$_3$)$_2$).

11-PdCl. A J. Young tube was charged with **11-PdOAc·HOCH(CF$_3$)$_2$** (0.150 g, 0.18 mmol), C$_6$D$_6$ (1 mL), and Me$_3$SiCl (46 μL, 0.26 mmol). After 72 h, ^{31}P NMR analysis reveals complete conversion to the desired product. The solution was then filtered through a pad of silica gel with diethyl ether. The volatiles were removed *in vacuo*, and the product was dissolved in pentane and stored at −35 °C. After 18 h, purple needles were collected by decantation and dried to yield **11-PdCl** (0.12 g, 87 μmol, 85%). ^{1}H NMR (C$_6$D$_6$): δ 7.50−7.35 (m, 2H, Ar C*H*), 7.24 (d, J_{P2H} = 12 Hz, 1H, Ar *H*), 6.68 (d, J_{HH} = 9 Hz, 2H, Ar *H*), 6.60 (d, J_{P1H} = 9 Hz, 1H, Ar *H*), 6.58−6.46 (m, 2H, C*H*(CF$_3$)$_2$), 2.19−2.08 (m, 2H, C*H*(CH$_3$)$_2$), 2.07 (s, 3H, C*H*$_3$), 1.80 (s, 3H, C*H*$_3$), 1.23 (dd, J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.96 (dd, J_{P1H} = 16 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P$_1$} NMR (C$_6$D$_6$): δ 7.50−7.35 (m, 2H, Ar *H*), 7.24 (d, *J* = 12 Hz, 1H, Ar *H*), 6.68 (d, *J* = 9 Hz, 2H, Ar *H*), 6.60 (s, 1H, Ar *H*), 6.58−6.46 (m, 2H, C*H*(CF$_3$)$_2$), 2.19−2.08 (m, 2H, C*H*(CH$_3$)$_2$), 2.05 (s, 3H, C*H*$_3$), 1.79 (s, 3H, C*H*$_3$), 1.22 (d, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.95 (dd, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P$_2$} NMR (C$_6$D$_6$): δ 7.44 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 7.42 (m, 1H, Ar *H*), 7.24 (s, 1H, Ar *H*), 6.68 (d, *J* = 9 Hz, J_{P1H} = 4 Hz, 2H, Ar *H*), 6.60 (d, J_{P1H} = 9 Hz, 1H, Ar *H*), 6.58−6.46 (m, 2H, C*H*(CF$_3$)$_2$), 2.19−2.08 (m, 2H, C*H*(CH$_3$)$_2$), 2.07 (s, 3H, C*H*$_3$), 1.80 (s, 3H, C*H*$_3$), 1.23 (dd, J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.96 (dd, J_{P1H} = 16 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 172.3 (d, J_{PP} = 525 Hz, P$_2$, P(OCH(CF$_3$)$_2$), 57.9 (d, J_{PP} = 525 Hz, P$_1$, P(iPr)$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 161.2 (d, J_{CP} = 20 Hz, Ar CN), 160.0 (d, J_{CP} = 40 Hz, Ar CN), 137.0 (s, Ar C), 133.4 (s, Ar C),132.3 (s, Ar C), 129.8 (s, Ar C), 124.2 (m, CH(CF$_3$)$_2$), 123.7 (m, CH(CF$_3$)$_2$), 117.9 (d, J_{CP} = 3 Hz, Ar C), 117.6 (d, J_{CP} = 3 Hz, Ar C), 117.2 (d, J_{CP} = 3 Hz, Ar C), 116.9 (s, Ar C), 116.8 (s, Ar C), 116.7 (s, Ar C), 74.0 (m, CH(CF$_3$)$_2$), 25.4 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$), 25.2 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$), 20.3 (s, CH$_3$), 19.7 (s, CH$_3$), 18.2 (d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$), 17.7(d, J_{CP} = 4 Hz, CH(CH$_3$)$_2$). ^{19}F NMR (C$_6$D$_6$): δ −74.0 (s), −74.5 (s). Elemental analysis, calculated for C$_{26}$H$_{28}$ClF$_{12}$NO$_2$P$_2$Pd: C, 38.16; H, 3.45%. Found: C, 38.16; H, 3.38%.

11-RhCO. A Schlenk flask was charged with **9-H** (304 mg, 0.705 mmol), a stir bar, and (CF$_3$)$_2$CHOH (4 mL). The flask was heated at 100 °C for 18 h and then cooled to ambient temperature. [Rh(COD)Cl]$_2$ (174 mg, 0.353 mmol), 2,6-lutidine (812 μL, 0.705 mmol), and CO (1 atm) were then added to the flask. The reaction mixture was stirred for 2 h and then dried under vacuo. The resulting red solid was taken up in diethyl ether and filtered through a pad of Celite. The volatiles were again removed. **11-RhCO** was isolated as red crystals after recrystallization at −35 °C in pentane (452 mg, 0.559 mmol, 79%). ^{1}H NMR (C$_6$D$_6$): δ 7.54 (dd, J_{HH} = 9 Hz, J_{P1H} = 4 Hz, 1H, Ar *H*), 7.43 (t, J_{HH} = 8 Hz, 1H, Ar *H*), 7.35 (d, J_{HH} = 2 Hz, 1H, Ar *H*), 6.74 (d, J_{HH} = 10 Hz, 1H, Ar *H*), 6.74 (d, J_{P1H} = 10 Hz, 1H, Ar *H*), 6.68 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H, Ar *H*), 5.75 (m, 2H, C*H*(CF$_3$)$_2$), 2.11 (s, 3H, C*H*$_3$), 1.98−1.91 (m, 2H, C*H*(CH$_3$)$_2$), 1.88 (s, 3H, C*H*$_3$), 1.05 (dd, J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.83 (dd, J_{P1H} = 16 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P, P$_2$} NMR (C$_6$D$_6$): δ 7.54 (dd, J_{HH} = 9 Hz, J_{P1H} = 4 Hz, 1H, Ar *H*), 7.43 (t, J_{HH} = 8 Hz, 1H, Ar *H*), 7.35 (d, J_{HH} = 2 Hz, 1H, Ar *H*), 6.74 (d, J_{HH} = 10 Hz, 1H, Ar *H*), 6.74 (d, J_{P1H} = 10 Hz, 1H, Ar *H*), 6.68 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H, Ar *H*), 5.75 (hept, J_{HH} = 6 Hz, 2H, C*H*(CF$_3$)$_2$), 2.11 (s, 3H, C*H*$_3$), 1.98−1.91 (m, 2H, C*H*(CH$_3$)$_2$), 1.88 (s, 3H, C*H*$_3$), 1.05 (dd, J_{P1H} = 18 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$), 0.83 (dd, J_{P1H} = 16 Hz, J_{HH} = 7 Hz, 6H, CH(C*H*$_3$)$_2$). ^{1}H{^{31}P, P$_1$} NMR (C$_6$D$_6$): δ 7.54 (d, J_{HH} = 9 Hz, 1H, Ar *H*), 7.43 (t, J_{HH} = 8 Hz, 1H, Ar *H*), 7.35 (d, J_{HH}

= 2 Hz, 1H, Ar H), 6.74 (d, J_{HH} = 10 Hz, 1H, Ar H), 6.74 (s, 1H, Ar H), 6.68 (dd, J_{HH} = 9 Hz, J_{HH} = 2 Hz, 1H, Ar H), 5.75 (dp, J_{P2H} = 17 Hz, J_{HH} = 6 Hz, 2H, $CH(CF_3)_2$), 2.11 (s, 3H, CH_3), 1.98−1.91 (m, 2H, $CH(CH_3)_2$), 1.88 (s, 3H, CH_3), 1.05 (d, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$), 0.83 (d, J_{HH} = 7 Hz, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 193.8 (m, CO), 161.2 (d, J = 21 Hz, 3° Ar C), 160.3 (d, J = 40 Hz, 3° Ar C), 136.2 (d, J = 2 Hz, Ar C), 132.8 (d, J = 2 Hz, Ar C), 132.0 (s, Ar C), 129.2 (s, Ar C), 127.1 (d, J = 8 Hz, Ar C), 126.8 (d, J = 7 Hz, Ar C), 124.4 (m, CF_3), 122.2 (m, CF_3), 119.9 (m, CF_3), 118.8 (d, J = 2 Hz, Ar C), 118.4 (s, Ar C), 117.6 (m, CF_3), 116.0 (d, J = 12 Hz, Ar C), 115.4 (d, J = 18 Hz, Ar C), 74.6−72.8 (m, $CH(CF_3)_2$), 25.1 (d, J = 25 Hz, $CH(CH_3)_2$), 20.1 (s, CH_3), 19.6 (s, CH_3), 18.9 (d, J = 6 Hz, CH_3), 17.90 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 207.4 (dd, J_{P1P2} = 340 Hz, J_{P2Rh} = 195 Hz, P_2, $P(OCH(CF_3)_2)$), 59.3 (dd, J_{P1P2} = 340 Hz, J_{P1Rh} = 127 Hz, P_1, $P(^iPr)_2$). ^{19}F NMR (C_6D_6): δ −75.0 (s), −74.4 (s). IR ν(CO) = 1980 cm^{-1}. Elemental analysis, calculated for $C_{27}H_{28}F_{12}NO_3P_2Rh$: C, 40.17; H, 3.50%. Found: C, 40.28; H, 3.66%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Graphical depictions of the NMR spectra and details of the X-ray data acquisition, solution, and refinement, as well as structural information in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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