C−H Bond Activation by Rhodium(I) Phenoxide and Acetate Complexes: Mechanism of H−D Exchange between Arenes and Water

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New rhodium(I) complexes (PNP)Rh(X) (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) (X = OTf (**1**), OAc (**3**), OH (**8**), OCH_2CF_3 (**9**), OC_6H_5 (**10**), $OC_6H_4NO_2$ (**11**)) have been prepared. Hydroxide complex **8** and trifluoroethoxide complex **9** undergo stoichiometric activation of benzene-d_6 to form the phenyl complex (PNP)Rh(C_6D_5). Acetate and aryloxide complexes **3**, **10**, and **11** are active catalysts for H−D exchange between arenes and water. Control experiments indicate that the rhodium complexes are the active catalysts and that the observed exchange is not catalyzed by adventitious acid. Mechanistic studies of the H−D exchange reaction support a pathway involving dissociation of aryloxide or acetate ligand. The reaction is accelerated by added alcohol and, for the acetate complex, inhibited by added sodium acetate.

Introduction

The discovery of efficient catalysts for the activation and functionalization of C−H bonds could have tremendous environmental and economic impact. In particular, catalysts for the selective oxidation of organic compounds could streamline synthesis in the chemical and pharmaceutical industry, reducing energy use and waste production by allowing for direct utilization of cheaper and more available feedstocks.[1]

However, the development of alkane functionalization catalysts has proved to be a major challenge. The catalyst must be able to selectively react with alkane C−H bonds, even in the presence of functionalized products such as alcohols. Although many late transition metal complexes have been shown to activate C−H bonds, the large majority of these reactions are inhibited by or incompatible with water and alcohols.[2] This is due in part to the fact that C−H bond activation generally requires an available site at the metal center to bind alkane. Water and alcohols often bind to transition metals more effectively than arenes or alkanes, blocking the open site and suppressing the desired reactivity.[2]

For example, Labinger, Bercaw, and Tilset have studied C−H bond activation by platinum(II) diimine complexes and have shown that C−H bond activation occurs at a platinum(II) solvent complex.[3,4] In the presence of water, the platinum(II) solvent complex is in equilibrium with a water-bound complex, which does not directly activate C−H bonds.[4] Thus water serves to inhibit C−H bond activation, and rigorously water-free conditions result in higher activity for C−H bond activation.[5] Labinger and Bercaw have also shown that alcohols can bind to the metal center and be subject to C−H bond activation themselves, at rates comparable to that of alkanes.[5] This incompatibility with alcohols places limits on the potential catalytic functionalization of hydrocarbons by many metal systems.

In this context, an ideal reaction would be C−H bond activation by a metal alkoxide or hydroxide complex, breaking a C−H bond, and liberating an alcohol product in one step. The first examples of this reaction were reported in 2005 by Gunnoe and by Periana.[6,7] Gunnoe and co-workers described arene activation by (Tp)Ru(PMe_3)$_2$OH (Tp = hydridotris(pyrazoyl)borate), which exchanged deuterium into the hydroxide ligand when heated in benzene-d_6 and was demonstrated to be an active catalyst for H−D exchange between arenes and water.[6] Periana and co-workers documented the reactivity of (acac)$_2$Ir(OCH_3)py, which upon heating underwent stoichiometric benzene activation to convert to the phenyl complex (acac)$_2$Ir(C_6H_5)py and was also shown to be an active catalyst for H−D exchange between arenes and water.[7] Subsequent mechanistic studies carried out by both groups suggest similar mechanisms involving dissociation of a neutral ancillary ligand,[8] followed by a concerted C−H bond activation across the metal hydroxide or alkoxide ligand. This four-center interaction

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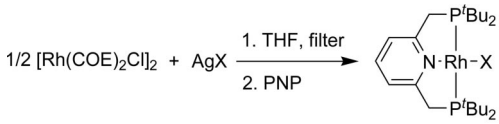
pathway involving the lone pair of the alkoxide or hydroxide group is somewhat similar to σ-bond metathesis and has been termed "internal electrophilic substitution".[9–12]

We recently reported arene activation by rhodium(I) hydroxide, trifluoroethoxide, and phenoxide complexes bearing the PNP ligand (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine).[13] The hydroxide and trifluoroethoxide complexes undergo stoichiometric benzene activation to form the rhodium(I) phenyl complex, and the phenoxide complex is an active catalyst for H−D exchange between arenes and water.[13] Rhodium(I) acetate and 4-nitrophenoxide complexes are also found to catalyze the exchange. Not only is the C−H bond activation compatible with water, but the presence of added phenol actually accelerates the reaction. While early studies suggested similarities to the reactions studied by Gunnoe and Periana,[13] new experimental evidence suggests that the H−D exchange reaction proceeds by a different mechanism than that of the ruthenium(II) and iridium(III) systems.

Results

A. Synthesis and Characterization of PNP Rhodium(I) Complexes. Rhodium(I) triflate, trifluoroacetate, and acetate complexes bearing the PNP ligand (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) were prepared by reaction of 0.5 equiv of $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) with silver triflate, silver trifluoroacetate, or silver acetate in THF, followed by filtration and addition of PNP ligand (eq 1). Complexes (PNP)Rh(X) (X = OTf (**1**), O_2CCF_3 (**2**), OAc (**3**)) were isolated in high yields (83–95%) and fully characterized. The ^{31}P NMR spectra of these compounds exhibit a doublet due to coupling to rhodium, with $^1J_{Rh-P} = 145$ Hz for **1**, $^1J_{Rh-P} = 151$ Hz for **2**, and $^1J_{Rh-P} = 156$ Hz for **3**.



X = OTf (**1**), O_2CCF_3 (**2**), OAc (**3**)

(1)

The triflate ligand of complex **1** is readily displaced; in benzene or THF solution **1** was observed to be in equilibrium with the monomeric dinitrogen complex [(PNP)Rh(N_2)]OTf (**1**-N_2). When a benzene-d_6 solution of **1** at room temperature was exposed to an atmosphere of N_2 and protected from light, quantitative conversion to **1**-N_2 occurred over the course of 6 days. Heating or subjecting a solution of **1**-N_2 to vacuum resulted in slow re-formation of **1**. The monomeric dinitrogen complex **1**-N_2 was isolated in 86% yield and fully characterized. The X-ray structure of **1**-N_2 (Figure 1) reveals that the N−N bond distance (1.116(4) Å) is only slightly elongated from that in free dinitrogen (1.09 Å).[14] The IR spectrum of **1**-N_2 shows $\nu_{N-N} = 2153$ cm^{-1}, an additional indication that the dinitrogen ligand is only weakly activated. No reaction with nitrogen was observed for trifluoroacetate complex **2** or acetate complex **3**.

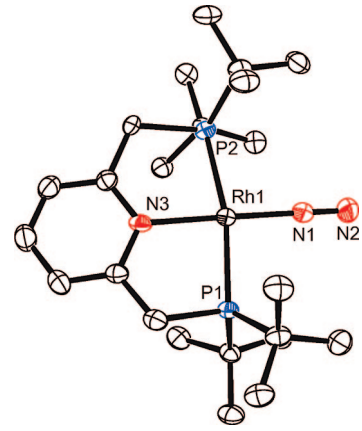
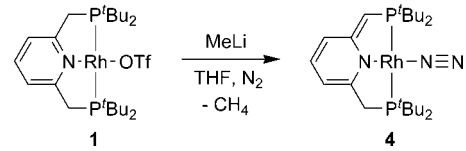


Figure 1. ORTEP drawing of the molecular cation of **1**-N_2 (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Select bond distances (Å) and angles (deg): N1−N2 = 1.116(4), Rh1−N1 = 1.898(3), Rh1−N3 = 2.074(3), Rh1−P1 = 2.304(1), Rh1−P2 = 2.297(1), P1−Rh1−P2 = 168.07(3), N1−Rh1−N3 = 178.9(1), P1−Rh1−N1 = 95.93(8), P2−Rh1−N1 = 94.71(8).

The PNP rhodium(I) methyl and hydroxide complexes could not be cleanly prepared by salt metathesis. The methylene groups on complexes **1** and **1**-N_2 are susceptible to deprotonation; reaction of **1** or **1**-N_2 with strong bases (MeLi, KO^{t}Bu, or $LiN(SiMe_3)_2$) resulted in formation of the neutral methylene-deprotonated dinitrogen complex **4** (eq 2). Neutral dinitrogen complex **4** was characterized by ^1H and ^{31}P NMR spectroscopy, IR spectroscopy, and elemental analysis. The ^{31}P NMR spectrum of **4** shows a characteristic A−B pattern of doublets at 67.74 ppm ($^2J_{P-P} = 269$ Hz, $^1J_{Rh-P} = 131$ Hz) and 63.98 ppm ($^2J_{P-P} = 269$ Hz, $^1J_{Rh-P} = 131$ Hz), indicating inequivalent phosphorus atoms. The IR spectrum of **4** shows the N−N stretch at 2122 cm^{-1}, slightly red-shifted from the N−N stretch of **1**-N_2 (2153 cm^{-1}).



1 **4**

(2)

The rhodium(I) methyl complex (PNP)Rh(CH_3) (**5**) was prepared by transmetalation with dimethylzinc. Reaction of **1** or **1**-N_2 with dimethylzinc initially resulted in formation of a rhodium−zinc adduct, formulated as (PNP)Rh(CH_3)Zn(CH_3)O_2SOCF_3 (**6**), on the basis of NMR spectroscopy and elemental analysis. The ^1H NMR spectrum of **6** shows two virtual triplets corresponding to the *tert*-butyl groups on the ligand, indicating a low-symmetry structure. The Rh-CH_3 group exhibits a doublet of triplets at 0.71 ppm, with $^3J_{P-H} = 5.7$ Hz and $^2J_{Rh-H} = 1.8$ Hz, while the Zn-CH_3 group appears as a singlet at 0.45 ppm, integrating to 3H.

Hydrolysis of the rhodium−zinc adduct **6** resulted in re-formation of triflate complex **1**. However, reaction of **6** with 1 equiv of bipy (2,2′-bipyridyl) released rhodium(I) methyl complex **5**. The zinc products of this reaction were not characterized. Complex **5** was isolated in 67% yield by extraction into pentane and characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography.[13] The ^1H NMR spectrum of complex **5** shows a doublet of triplets for the Rh-

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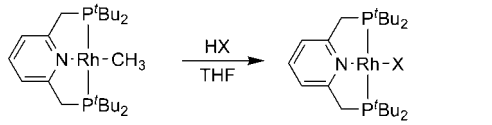
CH_3 group at 0.75 ppm, with $^3J_{P-H} = 6.0$ Hz and $^2J_{Rh-H} = 2.1$ Hz. Following an analogous procedure with **1**, treatment with diphenylzinc and then bipy allowed for isolation of the rhodium(I) phenyl complex (PNP)Rh(C_6H_5) (**7**) in 61% yield. Complex **7** was characterized by NMR spectroscopy and elemental analysis.

Rhodium(I) hydroxide, trifluoroethoxide, phenoxide, and 4-nitrophenoxide complexes (PNP)Rh(X) (X = OH (**8**), OCH_2CF_3 (**9**), OC_6H_5 (**10**), $OC_6H_4NO_2$ (**11**)) were prepared by reaction of a solution of **5** in THF with water, trifluoroethanol, phenol, or 4-nitrophenol (eq 3). However, phenoxide complex **10** and 4-nitrophenoxide complex **11** were prepared more conveniently by the reaction of 0.5 equiv of $[Rh(COD)OH]_2$ (COD = 1,5-cyclooctadiene) with 1 equiv of PNP ligand and 1 equiv of the appropriate phenol in toluene and were recrystallized from toluene or ether. Complexes **8**–**11** were characterized by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis. The ^{31}P NMR spectra of complexes **8**–**11** exhibit a doublet with coupling to rhodium of $^1J_{Rh-P} = 157$ Hz for **8**, $^1J_{Rh-P} = 161$ Hz for **9**, $^1J_{Rh-P} = 157$ Hz for **10**, and $^1J_{Rh-P} = 153$ Hz for **11**.



5 X = OH (**8**), OCH_2CF_3 (**9**), OC_6H_5 (**10**), $OC_6H_4NO_2$ (**11**)

(3)

The synthesis of phenoxide complex **10** and 4-nitrophenoxide complex **11** required use of exactly 1 equiv of phenol. Additional phenol interacted with **10** by hydrogen bonding, which could be detected by ^{1}H NMR spectroscopy and X-ray crystallography. When 1 equiv of phenol was added to a benzene-d_6 solution of **10**, the ^{1}H NMR spectrum showed a set of signals corresponding to the aryl protons on the phenoxide ligand, as well as signals arising from the hydrogen-bonded phenol at 7.16, 6.86, and 6.84 ppm, which appeared significantly downfield from the chemical shifts of free phenol in benzene-d_6 (7.04, 6.77, and 6.57 ppm). The chemical shifts of the phenoxide ligand were found to be dependent on the concentration of phenol; further increasing the concentration of phenol caused the multiplet arising from the four phenoxide aryl protons (7.40–7.29 ppm) to resolve into distinct doublet and triplet signals and shift downfield. In contrast, addition of water to a benzene-d_6 solution of **10** showed no changes in the chemical shifts of **10** nor any conversion to hydroxide complex **8**.

When crystals of **10** were grown in the presence of excess phenol, the phenoxide complex cocrystallized with 2 equiv of phenol; one molecule of phenol is oriented directly toward the phenoxide ligand in a hydrogen-bonding interaction, and the other is oriented away from the rhodium, adjacent to the ligand *tert*-butyl groups. The X-ray structure of **10**-HOC_6H_5 is shown in Figure 2. The O1−O2 distance of 2.573(2) Å is consistent with a hydrogen bond between the phenoxide ligand and the associated phenol.[15]

B. Stoichiometric Activation of Benzene by (PNP)Rh(X) Complexes. As described previously,[13] heating a benzene-d_6 solution of hydroxide complex **8** at 60 °C for 95 h resulted in formation of the deuterated phenyl complex **7**-d_5 in 60% yield (eq 4), along with formation of an intractable yellow solid precipitate. The identity of **7**-d_5 was confirmed by comparison

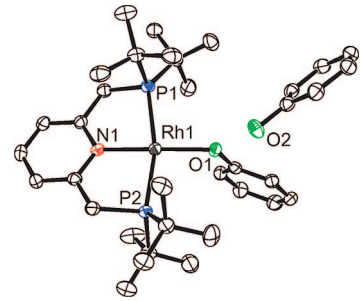
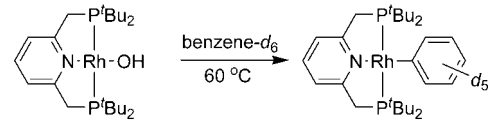


Figure 2. ORTEP drawing of **10**-HOC_6H_5 (thermal ellipsoids at 50% probability, H atoms and a second molecule of cocrystallized phenol omitted for clarity). Select bond lengths (Å) and angles (deg): Rh1−O1 = 2.1096(18), Rh1−N1 = 2.037(2), Rh1−P1 = 2.2951(7), Rh1−P2 = 2.3140(7), O1−O2 = 2.573(2), P1−Rh1−P2 = 163.68(3), N1−Rh1−O1 = 178.90(8), P1−Rh1−N1 = 82.61(6), P2−Rh1−N1 = 84.05(6).

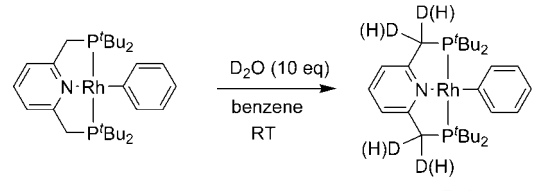
with an authentic sample of complex **7** prepared from **1** and diphenylzinc. Consistent with this finding, no reaction was observed when a benzene-d_6 solution of complex **7** was treated with water (1.6 equiv) at room temperature. Similarly, heating a benzene-d_6 solution of trifluoroethoxide complex **9** at 100 °C for 158 h resulted in partial conversion to **7**-d_5 (40%), along with unreacted starting material (40%). Some yellow solid precipitate was also observed in this reaction. When the reaction time was extended, increased decomposition was observed, with no increase in the yield of **7**-d_5.



8 **7**-d_5 (60%)

(4)

Thermolysis of complexes **8** and **9** in benzene-d_6 led to partial deuterium incorporation into the ligand methylene groups of the product **7** (40–60%). This deuterium incorporation may result from exchange with the deuterated water or trifluoroethanol product, respectively, of the reaction. In a separate experiment, approximately 75% deuterium was exchanged into the methylene positions when a benzene solution of **7** was treated with D_2O (10 equiv) for 24 h at room temperature (as determined by ^{1}H and ^{2}H NMR spectroscopy) (eq 5).[13]



7 **7**-d_n

(5)

In contrast to the reactivity observed for the hydroxide and trifluoroethoxide complexes, heating a solution of phenoxide complex **10** in benzene-d_6 resulted in no reaction. Even after heating for 1 week at 100 °C, no conversion to phenyl complex **7** was observed.[16] Consistent with this result, reaction of **7** with 2.5 equiv of phenol resulted in quantitative formation of **10** at

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(16) A small amount (ca. 15%) of deuterium incorporation into the methylene positions of the phenoxide complex **10** was observed when a solution of **10** was heated in dry benzene-d_6 at 100 °C for 118 h.

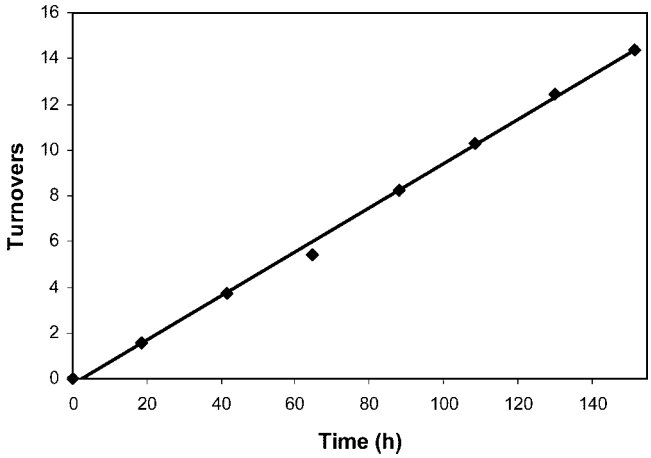
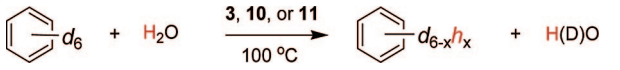


Figure 3. Plot of turnovers of the H−D exchange between benzene-d_6 and H_2O for phenoxide complex **10** vs time (h) at 100 °C.

room temperature. Like phenoxide complex **10**, rhodium(I) triflate, trifluoroacetate, acetate, and 4-nitrophenoxide complexes **1**, **2**, **3**, and **11** showed no reaction when heated in benzene at 100 °C for at least one week.

C. Catalytic H−D Exchange between Arenes and Water. As reported in a preliminary communication, phenoxide complex **10** catalyzes H−D exchange between arenes and water.[13] Acetate complex **3** and 4-nitrophenoxide complex **11** are also active catalysts for this reaction. The H−D exchange between benzene-d_6 and H_2O was conveniently monitored by ^{1}H NMR (eq 6), where the extent of the reaction was determined by integration of the residual benzene signal against an internal standard (THF or hexamethylbenzene). No intermediates were observed in the catalytic reactions; at all times the only rhodium species evident by ^{1}H NMR was **3**, **10**, or **11**.



(6)

A plot of turnovers versus time was linear for **3**, **10**, and **11** (Figure 3). The turnover frequency for each catalyst was determined by averaging three individual runs, with 0.09(2) turnovers/h for **10**, 0.10(2) turnovers/h for **11**, and 0.09(2) turnovers/h for **3**. In contrast, trifluoroacetate complex **2** and triflate complex **1** are poor catalysts for the exchange. Triflate complex **1** showed only 1.5 turnovers after 150 h at 100 °C, and trifluoroacetate complex **2** showed no exchange after 150 h at 100 °C.

Since strong acids are known to catalyze H−D exchange between arenes and water,[17] a number of control experiments were carried out to ensure that the observed H−D exchange was not catalyzed by trace acid. Control experiments with phenol, H_2O, and benzene-d_6 or toluene-d_8 (no rhodium) showed no reaction, even after 300 h at 100 °C. In addition, no exchange was observed when acetic acid (0.027 mM) was heated at 100 °C in benzene-d_6 with H_2O (no rhodium).

In toluene-d_8 with H_2O, the selectivity of the exchange catalyzed by phenoxide complex **10** could be determined. A toluene-d_8 solution of **10** was heated with H_2O at 100 °C for 360 h, and the residual toluene-*h* signals were monitored by ^{1}H NMR spectroscopy. Integration against an internal standard

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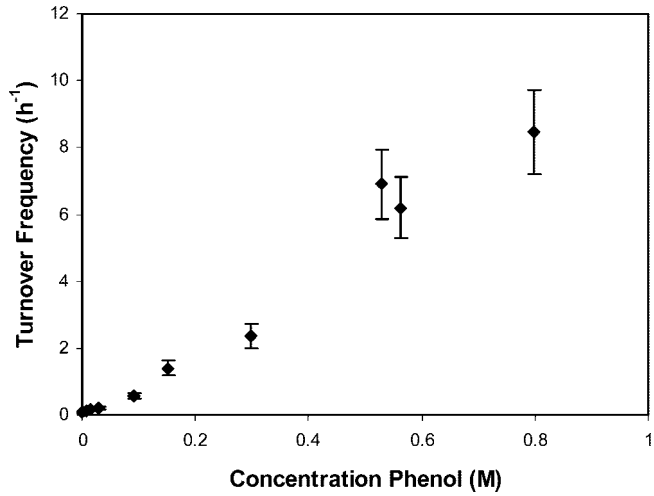

Figure 4. Plot of turnover frequency of the exchange between benzene-d_6 and H_2O for phenoxide complex **10** vs [phenol] at 100 °C.

(THF) revealed that approximately 47 turnovers had occurred, with a selectivity (statistically corrected) of 1 para:1.2 meta:0 ortho:0 CH_3.[13] Finally, when the exchange reaction between H_2O and benzene-d_6 was conducted with 4-nitrophenoxide complex **11** in the presence of the base Na_2CO_3 (18 equiv), the turnover frequency was 0.11(2) turnovers/h, the same as in the absence of added base (0.10(2) turnovers/h).

Although control experiments indicated that phenol itself does not catalyze the exchange, added phenol was found to promote the rhodium-catalyzed reaction. For the H−D exchange between benzene-d_6 and H_2O, the turnover frequency of phenoxide complex **10** was measured at concentrations of phenol ranging from 0 to 0.8 M. A plot of TOF (turnovers/h) vs [phenol] (Figure 4) reveals that the turnover frequency depends linearly on the concentration of phenol. Trifluoroethanol also serves to accelerate this reaction. The turnover frequency for catalyst **10** measured in the presence of 5 equiv of trifluoroethanol, 0.48(3) turnovers/h, is 5 times greater than the turnover frequency without added alcohol (0.09(2) turnovers/h). In contrast, the turnover frequency for catalyst **10** with added *tert*-butanol (5 equiv) (0.085(20) turnover/h) is no different from that in the absence of added alcohol.

When the H−D exchange reaction was conducted with phenoxide complex **10** in the presence of a high concentration of phenol (0.9 M), the turnover frequency was sufficiently high that after 100 h an equilibrium distribution of hydrogen and deuterium was achieved (approximately 425 turnovers), and no further increase in the residual benzene solvent signal was observed (Figure 5). Integration of the ^{1}H NMR spectrum of the reaction mixture confirmed that no catalyst decomposition had occurred, and thus the lack of increase in the residual benzene signal was due to unproductive exchanges.

Protic additives also promote the H−D exchange reaction between benzene-d_6 and H_2O when the acetate complex **3** is the catalyst. With 2 equiv of added acetic acid, the turnover frequency is 0.30(2) turnovers/h, about 3 times greater than with no additives (0.09(2) turnovers/h). Phenol also increases the catalytic activity; the turnover frequency with **3** and 2 equiv of phenol is 0.23(2) turnovers/h.

The effect of added sodium acetate on the exchange reaction with acetate complex **3** was studied. The H−D exchange between benzene-d_6 and H_2O with **3** was monitored in the presence 8, 21, and 32 equiv of NaOAc. Although determination

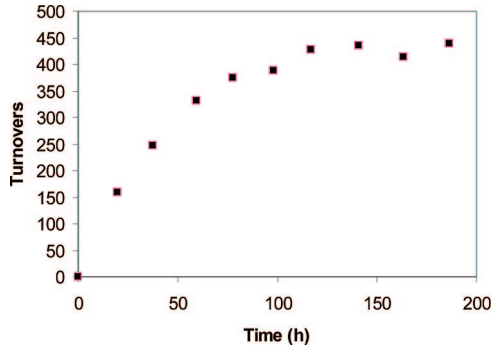

Figure 5. Equilibrium isotopic distribution reached in the exchange between benzene-d_6 and H_2O for complex **10** with 0.9 M phenol at 100 °C.

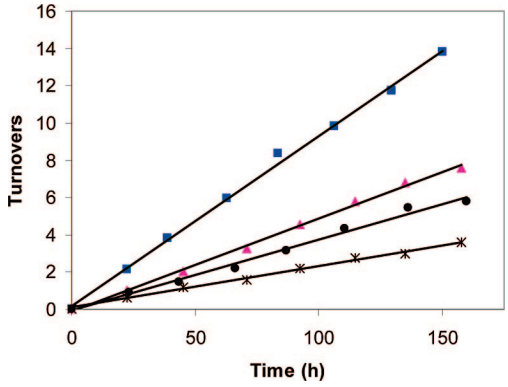

Figure 6. Plot of turnovers of the H−D exchange between benzene-d_6 and H_2O vs time (h) for acetate complex **3** in the presence of 0 (■), 8 (▲), 21 (●), and 32 (*) equiv of sodium acetate at 100 °C.

of the exact concentration of NaOAc in the benzene layer is not possible due to the biphasic nature of the reaction mixture, it was qualitatively observed that added NaOAc inhibited the exchange reaction. With 8, 21, and 32 equiv of added NaOAc, the turnover frequencies were found to be 0.05(1), 0.04(1), and 0.02(1) turnovers/h, respectively (Figure 6). An analogous experiment with phenoxide complex **10** and added potassium phenoxide could not be conducted; an equilibrium between the potassium phenoxide and water generated phenol, which could be detected in the benzene-d_6 layer by ^{1}H NMR spectroscopy and has an accelerating effect on the reaction (vide supra).

Discussion

Synthesis of Complexes 1–11. Reaction of $[Rh(COE)_2Cl]_2$ with the appropriate silver salt, followed by filtration and the addition of the PNP ligand, allowed for efficient preparation of complexes **1**−**3**. In solution, the triflate complex **1** was observed to be in equilibrium with **1**-N_2. Although there are multiple examples of neutral rhodium(I) dinitrogen complexes,[18] **1**-N_2 is a rare example of a cationic rhodium(I) dinitrogen complex. The slight elongation of the N−N bond distance of **1**-N_2 (1.116(4) Å) compared to free dinitrogen (1.09 Å) is consistent with relatively weak binding.[18] The N−N bond length of 1.116(4) is similar to the value of 1.108(3) determined for the related neutral dimeric dinitrogen complex $[(^i$PrPCP)Rh$]_2(N_2)$ (^{i}PrPCP = 1,3-bis(diisopropylphosphinomethyl)benzene).[19]

Neutral methylene-deprotonated dinitrogen complex **4** was formed from the reaction of **1** with base under a nitrogen atmosphere (eq 2). The deprotonation of ligand methylene groups has been observed before for Ru, Ir, Pd, and Pt complexes bearing similar pyridine-phosphine-based ligands.[20,21] This reactivity of the methylene groups with base prevented the synthesis of methyl complex **5** using alkylating agents such as MeLi and MeMgBr. Instead, complex **5** was prepared from the milder reagent $ZnMe_2$, which initially led to formation of the rhodium−zinc adduct **6**. Rhodium adducts of zinc,[22] mercury,[23] and aluminum[24] have been described previously. The addition of bipy to **6** allowed for the convenient separation of rhodium methyl complex **5** from the zinc byproducts, presumably due to the coordination of bipy to zinc.

Phenoxide complex **10** interacts with phenol by hydrogen bonding, which was evident in both the ^{1}H NMR spectrum and the X-ray structure of **10**-HOC_6H_5. A strong hydrogen-bonding interaction between phenol and the related rhodium(I) phenoxide complex $(PMe_3)_3Rh(OC_6H_4CH_3)$ has previously been studied by Bergman and co-workers.[25] The hydrogen bonding was detected by ^{1}H NMR spectroscopy, where the chemical shifts of both coordinated and hydrogen-bonded phenol were found to be concentration and temperature dependent. Calorimetry measurements allowed for the determination of $\Delta H = -11.4(5)$ kcal/mol for formation of the hydrogen bond in benzene.[25] The X-ray structure of $(PMe_3)_3Rh(OC_6H_4CH_3)$-$HOC_6H_4CH_3$ shows an O−O distance of 2.62 Å,[25] slightly longer than the O1−O2 distance in **10**-HOC_6H_5 (2.573(2) Å). A similar interaction has also been reported by Vrieze and co-workers, who determined by ^{1}H NMR spectroscopy that the rhodium(I) phenoxide complex (NNN)Rh(OC_6H_5) (NNN = 2,6-(CH=N^{i}Pr)$_2C_5H_3N$) forms a hydrogen-bonded adduct of the form (NNN)Rh(OC_6H_5)-HOC_6H_5 with excess phenol.[26]

Mechanism of Rhodium-Catalyzed H−D Exchange between Arenes and Water. Deuterium oxide is an inexpensive and convenient source of deuterium, and there is considerable interest in methods for labeling organic molecules with D_2O. Efficient transition metal catalysts for H−D exchange between

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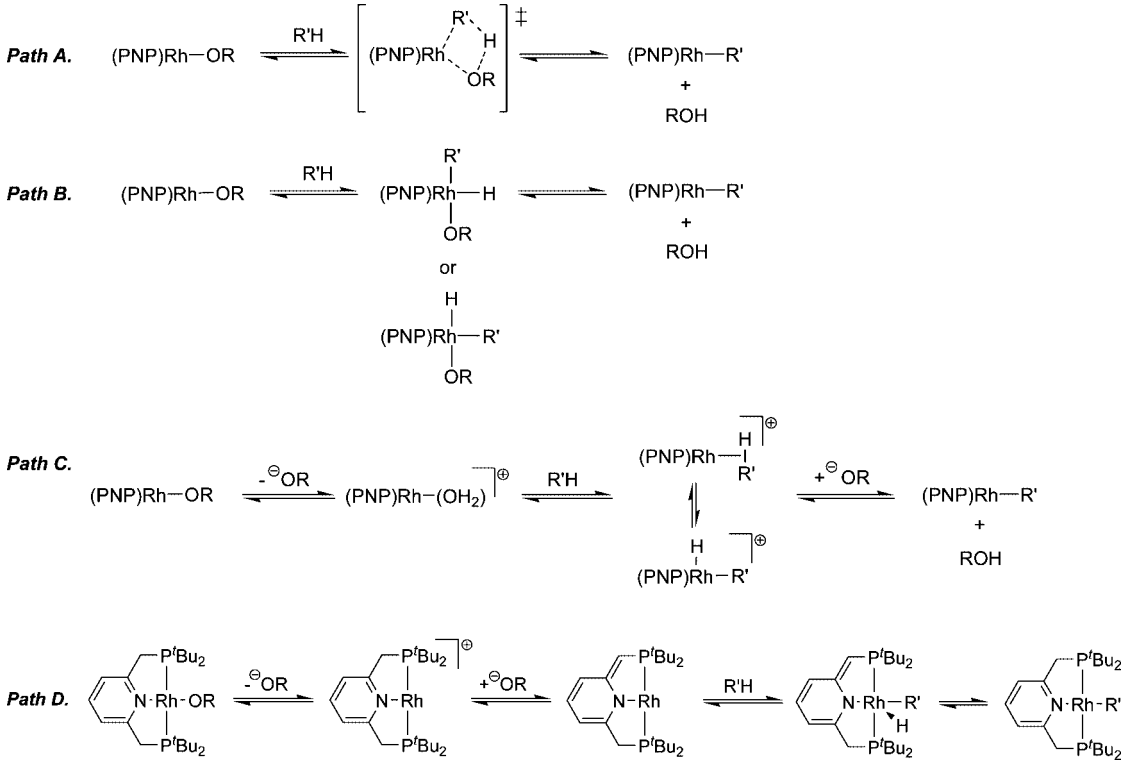
Scheme 1. Possible Mechanisms for the H−D Exchange Reaction



arenes and water are relatively rare,[27] with one of the most active examples being the iridium(III) complex $Cp^*Ir(PMe_3)Cl_2$ developed by Tilley and Bergman.[28]As described above, PNP rhodium(I) aryloxide and acetate complexes are active catalysts for the H−D exchange reaction. No intermediates are detected in this process. The reaction is accelerated by protic additives, such as phenol, trifluoroethanol, and acetic acid. For phenoxide complex **10**, the turnover frequency depends linearly on the concentration of phenol. The catalytic activity of acetate complex **3** is inhibited by added NaOAc. Complexes with more weakly basic ligands, such as triflate and trifluoroacetate, are inactive for the exchange.

Control experiments indicate that the exchange is not catalyzed by adventitious acid. The turnover frequency of catalyst **11** (0.10(2) turnovers/h) is unaffected by added base (Na_2CO_3, 0.11(2) turnovers/h). The selectivity of the reaction of toluene-d_8 with H_2O catalyzed by **10** (1 para:1.2 meta:0 ortho:0 CH_3, statistically corrected) is inconsistent with an acid-catalyzed electrophilic aromatic substitution mechanism, where activation would occur preferentially at the ortho and para positions.[17]

Four possible mechanisms for the H−D exchange reaction are depicted in Scheme 1. Path A is a concerted pathway, where reaction of the C−H bond occurs in one step. In this path the oxygen lone pair is involved in forming the new O−H bond while the R−H bond is breaking.[9–12] The reverse reaction with ROD in place of ROH allows for deuterium exchange into the arene. Supporting this pathway, calculations by Oxgaard and Periana suggest that this mechanism, resembling σ-bond me-

Table 1. Crystallographic Data Collection Parameters for 1-N_2 and 10-HOC_6H_5

	1-N_2	**10**-HOC_6H_5
empirical formula	$C_{24}H_{43}F_3N_3O_3P_2RhS$	$C_{41}H_{60}NO_3P_2Rh$
fw	675.52	779.75
T (K)	130(2)	130(2)
wavelength (Å)	0.71069	0.71073
cryst descrip	prism	red prism
space group	$P2_1/n$	$P\bar{1}$
unit cell dimens (Å, deg)	a = 8.4223(2)	a = 10.3991(2)
	b = 15.6644(4)	b = 11.5735(2)
	c = 22.9973(7)	c = 18.0621(4)
	α = 90	α = 101.4002(8)
	β = 93.5385(11)	β = 91.9941(9)
	γ = 90	γ = 110.4954(9)
V (Å^3)	3028.26(14)	1983.11(7)
Z, ρ (Mg/m^3)	4, 1.482	2, 1.306
μ (mm^{-1})	0.787	0.548
F(000)	1400	824
cryst size	0.24 × 0.24 × 0.18 mm	0.43 × 0.29 × 0.22 mm
no. of reflns for indexing	502	9361
θ range (deg)	2.96 to 28.28	2.10 to 28.50
index ranges	$-11 \le h \le 11$	$-13 \le h \le 13$
	$-20 \le k \le 20$	$-15 \le k \le 15$
	$-30 \le l \le 30$	$-21 \le l \le 24$
no. of reflns collected, unique	12 566, 7169	15 112, 9364
completeness to θ	98.8%	99.3%
absorp corr	semiempirical from equivalents	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
goodness of fit on F^2	0.935	0.971
R_1	0.0450	0.0455
wR ($I > 2\sigma I$)	0.1132	0.1056

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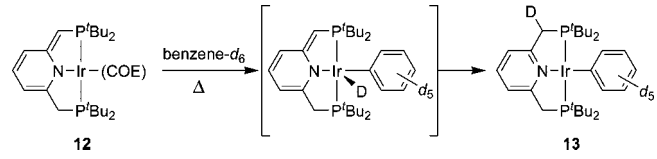
tathesis, should be accessible to metals with 6 or more d-electrons, such as the d^8 rhodium(I) center.[11] However, it is difficult to reconcile the dependence of the H−D exchange reaction on protic additives, which might be expected to inhibit the C−H bond addition by interacting with one of the lone pairs on the OR ligand.

Path B involves a direct oxidative addition of the arene C–H bond to the 16-electron rhodium(I) center. Reductive elimination of ROH, followed by oxidative addition of ROD, exchanges deuterium into the arene. The reductive elimination of ROH and oxidative addition of ROD may be concerted or stepwise eliminations and additions. Here the argument could be made that hydrogen bonding of excess phenol to the phenoxide ligand should reduce the electron density at the rhodium(I) center and increase steric crowding, making a direct oxidative addition less favorable in the presence of phenol. However, recent computational work by Goldman and Krogh-Jespersen indicates that reducing the π-electron density at the metal center may actually make C−H oxidative addition to a d^8 four-coordinate square-planar iridium(I) center more favorable.[29] Overall, though, very few examples of direct C−H bond addition to a four-coordinate square-planar iridium(I) or rhodium(I) center have been reported.[30,31] Also, a direct oxidative addition pathway cannot account for the inhibition of the acetate catalyst by sodium acetate.

In path C, the aryloxide or acetate ligand is replaced by solvent (H_2O or arene, H_2O is shown in Scheme 1). This could proceed by preliminary dissociation of $^-$OR followed by solvent coordination, or by associative substitution of $^-$OR by solvent. Once the arene has entered the coordination sphere, deprotonation of either the resulting σ-complex or phenyl hydride complex ensues. Exchange of ROH for ROD allows for incorporation of deuterium into the arene. In order to be consistent with the experimentally observed inhibition by sodium acetate, this mechanism must involve a pre-equilibrium loss of $^-$OR, followed by a rate-determining step of either displacement of H_2O by arene or oxidative addition of benzene.[32] Notably, detailed kinetic studies of the mechanism of benzene activation by the related square-planar d^8 platinum(II) diimine complexes indicate that both solvent displacement by arene and C−H oxidative addition may be rate-limiting steps, depending on the ligand substituents.[4] In addition, Tilset and co-workers have shown that for dimethyl platinum(II) diimine complexes the metal is the kinetic site of protonation, with the important implication that the microscopic reverse reaction of oxidative addition proceeds by deprotonation of a platinum(IV) alkyl hydride complex.[33]

Consistent with the experimental observations, the pre-equilibrium loss of aryloxide or acetate ligand should be favored by protic additives, as hydrogen bonding between the phenoxide ligand and added phenol could facilitate dissociation of phenoxide.[34] In addition, increasing the polarity of the reaction mixture by the addition of protic molecules would also be expected to promote anion dissociation. Finally, it is hypothesized that triflate and trifluoroacetate complexes are inactive for the exchange due to the low basicity of the triflate and trifluoroacetate anions. Attempts to test this hypothesis by conducting the exchange reaction with triflate complex **1** and base were hampered by the reaction of **1** with base, likely through the deprotonation of the methylene groups noted above.

In path D, dissociation of the aryloxide or acetate ligand is followed by deprotonation of one of the methylene groups, resulting in generation of a neutral methylene-deprotonated rhodium(I) intermediate. Activation of benzene results in formation of a neutral methylene-deprotonated rhodium(III) phenyl hydride complex, which subsequently rearranges to produce a rhodium(I) phenyl complex. Exchange of ROH for ROD allows for deuterium incorporation into the arene. A similar involvement of the methylene protons has been reported by Milstein and co-workers for the conversion of the methylene-deprotonated complex Ir(I) COE complex, **12**, to the phenyl complex (PNP)Ir(C_6D_5) (**13**) upon heating in benzene-d_6 (eq 7).[21]



(7)

Supporting the possibility that deprotonation of the methylene backbone may be involved in the PNP rhodium chemistry, as described above, partial deuteration of the methylene positions was observed upon stoichiometric benzene activation by hydroxide complex **8** and trifluoroethoxide complex **9**.[16] However, the methylene groups exchange efficiently with protic solvents at room temperature (vide supra), making differentiation between path C and path D on the basis of labeling experiments impractical. It would be difficult to distinguish the possibility that the deprotonation of the methylene groups is crucial to the mechanism from the case where it is an unrelated side reaction.

Nevertheless, path D cannot account for the observed inhibition by sodium acetate. Although this pathway also involves a pre-equilibrium loss of aryloxide or acetate ligand, the participation of the anion in the immediately following deprotonation step would be expected to offset this in the rate law and eliminate the overall rate dependence on acetate.[34,35] In order for the reaction to exhibit an inhibition by acetate, the deprotonation by acetate must occur *after* the rate-limiting step, as in path C.

Thus, the experimental evidence best supports path C. Most important in this analysis is that this pathway involves loss of $^-$OR in the first step, by either associative or dissociative substitution. A cationic rhodium(I) solvent complex is then formed, with the rate-limiting step being either displacement of H_2O by arene or C−H oxidative addition. This mechanism is distinctly different from the ruthenium(II) and iridium(III) systems studied by Gunnoe and Periana,[8] where the OR group is attached to the metal at the time of C−H bond activation, and the lone pair electrons of the OR group play a role in the actual C−H bond cleavage. Notably, pathway C bears remarkable resemblance to the mechanism believed to be operative in

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(32) Although determination of a kinetic isotope effect can implicate C−H oxidative addition as a rate-determining step, the large error associated with measuring the rate of the exchange reaction between C_6H_6 and D_2O by ^{2}H NMR prevented investigation of kinetic isotope effects in this system.

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platinum(II) Shilov chemistry, where the first step is arene or alkane coordination to a platinum(II) center, followed by deprotonation, either of a platinum(II) σ-complex or of a platinum(IV) hydrocarbyl hydride formed by oxidative addition of the C−H bond.[1b]

Conclusions

The ability to activate C−H bonds in the presence of water or alcohol will be an important characteristic of an effective catalyst for hydrocarbon oxidation. However, many of the transition metal complexes known to activate C−H bonds are incompatible with water or alcohols, which can coordinate to the metal center and suppress its reactivity toward C−H bonds. The recent discovery by Gunnoe and Periana of iridium(III) and ruthenium(II) alkoxide and hydroxide complexes capable of C−H bond activation represents a potential solution to this problem.[6,7] The addition of a C−H bond across the metal alkoxide or hydroxide ligand forms a new metal–carbon bond and releases alcohol or water in one step. The iridium(III) and ruthenium(II) complexes clearly demonstrate the ability to activate C−H bonds in the presence of water, catalyzing H−D exchange between arenes and water.

As described above, rhodium(I) hydroxide, aryloxide, and acetate complexes are also capable of C−H bond activation in the presence of water and alcohols. For the H−D exchange between benzene-d_6 and H_2O, the turnover frequency of the aryloxide and acetate complexes is actually increased by added phenol. On the surface, the reactivity observed for the rhodium complexes bears similarity to the reactions reported by Gunnoe and Periana and appears to extend the generality of the reaction. However, mechanistic studies suggest that unlike the iridium(III) and ruthenium(II) complexes, where the C−H bond adds across a coordinated OR group, the rhodium complexes react by dissociation of the aryloxide or acetate ligand and coordination of the arene to the metal. This discovery of a different pathway than previously found in related systems dramatically extends the range of C−H activation systems capable of operating in the presence of water and alcohols.

Experimental Section

General Considerations. Unless specified otherwise, all reactions were carried out under a dry nitrogen atmosphere using standard glovebox and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories, and benzene-d_6 (99.5% D), toluene-d_8, cyclohexane-d_{12}, and THF-d_8 were dried over sodium/benzophenone. Benzene-d_6 (99.96% D) was used as received and stored under N_2 at −35 °C. Dimethylzinc (10 wt% solution in hexanes), diphenylzinc (99%), and di-*tert*-butylphosphine were purchased from Strem. All other chemicals were purchased from Aldrich and used as received. THF, pentane, toluene, and benzene were dried by passage through activated alumina and molecular sieve columns. NMR spectra were obtained at room temperature on Bruker AV300, AV500 MHz, or dpx200 spectrometers, with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. $^{31}P\{^1H\}$ and ^{19}F NMR spectra were referenced externally to 85% H_3PO_4 and neat CF_3COOH (δ −78.5 ppm). $[Rh(COE)_2Cl]_2$,[36] $[Rh(COD)OH]_2$,[37] and 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (PNP)[38] were prepared according to published procedures. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

(PNP)Rh(OTf) (1). Under argon, $[Rh(COE)_2Cl]_2$ (163.0 mg, 0.227 mmol), and silver triflate (117.3 mg, 0.456 mmol) were suspended in THF (5 mL). The reaction was stirred for 10 min, resulting in the precipitation of a light gray solid (AgCl). The reaction mixture was filtered through a Teflon syringe filter, and the filter washed with THF (5 mL). Solid PNP ligand (179.3 mg, 0.454 mmol) was immediately added to the filtrate. The reaction was stirred for 10–15 min, then the solvent was removed under vacuum. The orange solid was washed with pentane (5 × 1.5 mL) and dried under vacuum. Yield: 287 mg (98%). ^1H NMR (C_6D_6, 300 MHz): δ 6.74 (t, 1H, J = 7.8 Hz, Py), 6.17 (d, 2H, J = 7.8 Hz, Py), 2.47 (vt, 4H, J = 3.3 Hz, CH_2), 1.37 (vt, 36H, J = 6.6 Hz, C(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.78 (d, 2P, $^1J_{Rh-P}$ = 145 Hz). ^{19}F NMR (C_6D_6): δ −78.05 (s). Anal. Calcd for $C_{24}H_{43}F_3NO_3P_2RhS$: C, 44.52; H, 6.69; N, 2.16. Found: C, 44.88; H, 6.88; N, 2.19.

(PNP)Rh(N_2)OTf (1-N_2). Orange solid (PNP)Rh(OTf) (282 mg, 0.435 mmol) was dissolved in THF (30 mL) under an atmosphere of nitrogen. The dark orange solution was allowed to stand at room temperature in the dark for 7 days, during which time the color changed to a pale yellow-orange. The solvent was removed under vacuum, leaving a pale yellow-orange solid, which was dried under vacuum 30 min. Yield: 261 mg (89%). ^1H NMR (C_6D_6, 300 MHz): δ 7.95 (d, 2H, J = 7.8 Hz, Py), 7.35 (t, 1H, J = 7.8 Hz, Py), 3.67 (vt, 4H, J = 4.2 Hz, CH_2), 1.11 (vt, 36H, J = 6.9 Hz, C(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 71.71 (d, 2P, $^1J_{Rh-P}$ = 125 Hz). ^{19}F NMR (C_6D_6): δ −77.86 (br s). IR (thin film): ν_{N-N} = 2153 cm^{-1}. Anal. Calcd for $C_{24}H_{43}F_3N_3O_3P_2RhS$: C, 42.67; H, 6.42; N, 6.22. Found: C, 42.91; H, 6.45; N, 6.20.

(PNP)Rh(O_2CCF_3) (2). The preparation of complex **2** from the chloride complex (PNP)Rh(Cl) and AgO_2CCF_3 has been recently reported by Milstein and co-workers.[39] Under nitrogen, $[Rh(COE)_2Cl]_2$ (139.7 mg, 0.195 mmol) and silver trifluoroacetate (86.5 mg, 0.391 mmol) were combined in THF (5 mL). The reaction mixture was stirred 10 min and then filtered through a Teflon syringe filter to remove solid AgCl. The filter was washed with THF (3 mL). To the combined filtrate was added solid PNP ligand (153.8 mg, 0.389 mmol). The resulting red solution was allowed to stand at room temperature for 30 min, and then the solvent was removed under vacuum, yielding a bright red solid. The solid was washed with pentane (3 × 2 mL) and dried under vacuum. Yield: 211.7 mg (89%). ^1H NMR (C_6D_6, 300 MHz): δ 6.79 (t, 1H, J = 7.8 Hz, Py), 6.19 (d, 2H, J = 7.8 Hz, Py), 2.52 (vt, 4H, J = 3.6 Hz, CH_2), 1.34 (vt, 36H, J = 6.3 Hz, C(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.07 (d, 2P, $^1J_{Rh-P}$ = 151 Hz). ^{19}F NMR (C_6D_6): δ −74.87 (s). Anal. Calcd for $C_{25}H_{43}F_3NO_2P_2Rh$: C, 49.11; H, 7.09; N, 2.29. Found: C, 49.31; H, 7.23; N, 2.35.

(PNP)Rh(OAc) (3). Under nitrogen, $[Rh(COE)_2Cl]_2$ (107.3 mg, 0.150 mmol) and silver acetate (50.4 mg, 0.302 mmol) were combined in THF (5 mL). The reaction mixture was stirred 10 min and then filtered through a Teflon syringe filter. The filter was washed with THF (3 mL). To the combined filtrate was added solid PNP ligand (118.1 mg, 0.299 mmol), forming a red-brown solution upon mixing. The solvent was removed under vacuum, and the resulting red-brown solid washed with pentane (2 × 3 mL). Yield: 138.5 mg (83%). ^1H NMR (C_6D_6, 500 MHz): δ 6.87 (t, 1H, J = 7.5 Hz, Py), 6.23 (d, 2H, J = 7.5 Hz, Py), 2.56 (vt, 4H, J = 3.5 Hz, CH_2), 2.28 (s, 3H, OAc), 1.44 (vt, 36H, J = 6.5 Hz, C(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 59.75 (d, 2P, $^1J_{Rh-P}$ = 156 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 50 MHz): δ 174.91 (s, OAc), 165.64 (vt, J = 6.5 Hz, Py), 130.73 (s, Py), 120.64 (vt, J = 5.5 Hz, Py), 36.40 (vt, J = 5.2 Hz, *C*H_2), 35.06 (vt, J = 5.7 Hz, *C*(CH$_3$)$_3$), 29.81 (vt, J =

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4.4 Hz, C(CH_3)$_3$), 24.87 (s, OAc). Anal. Calcd for $C_{25}H_{46}NO_2P_2Rh$: C, 53.86; H, 8.32; N, 2.51. Found: C, 53.80; H, 8.19; N, 2.48.

(PN$^-$P)Rh(N$_2$) (4). Under nitrogen, (PNP)Rh(OTf) (82.5 mg, 0.127 mmol) was dissolved in THF (4 mL), and the solution was cooled to −35 °C. Methyllithium (95 μL of a 1.4 M solution in diethyl ether, 0.133 mmol) was added and the solution allowed to warm to room temperature, turning a bright red color. The solvent was removed under vacuum. The remaining red residue was extracted into pentane (20 mL) and filtered through a Teflon syringe filter. The pentane was then removed under vacuum to give a bright red solid. Yield: 41.3 mg (61%). ^{1}H NMR (cyclohexane-d_{12}, 300 MHz): δ 6.26 (m, 1H, Py), 6.09 (d, 1H, J = 8.7 Hz, Py), 5.36 (d, 1H, J = 6.6 Hz, Py), 3.46 (d, 1H, J_{H-P} = 3.9 Hz, P-C*H*-Py), 3.01 (d, 2H, J_{H-P} = 8.1 Hz, P-CH_2-Py), 1.56 (m, 36H, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (cyclohexane-d_{12}): δ 67.74 (A−B pattern of doublets, 1P, $^2J_{P-P}$ = 269 Hz, $^1J_{Rh-P}$ = 131 Hz), 63.98 (A−B pattern of doublets, 1P, $^2J_{P-P}$ = 269 Hz, $^1J_{Rh-P}$ = 131 Hz). IR (thin film): ν_{N-N} = 2122 cm^{-1}. Anal. Calcd for $C_{23}H_{42}N_3P_2Rh$: C, 52.57; H, 8.06; N, 8.00. Found: C, 52.38; H, 7.93; N, 7.82.

(PNP)Rh(CH$_3$) (5). In a thick-walled glass vessel equipped with a Teflon stopcock, a solution of (PNP)Rh(OTf) (151.0 mg, 0.233 mmol) in THF (5 mL) was combined with $ZnMe_2$ (0.370 mL of a 10 wt % solution in hexanes, 0.256 mmol). The glass vessel was sealed and heated at 70 °C for 19 h. The reaction was cooled to room temperature, and the solvent was removed under vacuum, leaving a brown residue. The brown residue was dissolved in THF (5 mL), and 2,2′-bipyridyl (bipy) (36.3 mg; 0.233 mmol) was added, resulting in an immediate color change to bright pink. The solvent was removed under vacuum, and the purple solid was extracted into pentane (50 mL), leaving behind a yellow solid residue. The purple pentane solution was filtered, and the solvent was removed under vacuum to yield a dark purple solid. Yield: 80.1 mg (67%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.07 (t, 1H, J = 7.5 Hz, Py), 6.47 (d, 2H, J = 7.5 Hz, Py), 2.77 (vt, 4H, J = 3.3 Hz, CH_2), 1.39 (vt, 36H, J = 6.3 Hz, C(CH_3)$_3$), 0.75 (dt, 3H, $^3J_{P-H}$ = 6.0 Hz, $^2J_{Rh-H}$ = 2.1 Hz, Rh-CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.07 (d, 2P, $^1J_{Rh-P}$ = 169 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 50 MHz): δ 161.47 (br s, Py), 128.63 (s, Py), 119.72 (br s, Py), 38.87 (br s, *C*H$_2$), 35.12 (br s, *C*(CH$_3$)$_3$), 30.16 (br s, C(*C*H$_3$)$_3$), −22.70 (dt, $^1J_{Rh-C}$ = 25 Hz, $^2J_{P-C}$ = 12 Hz, Rh-*C*H$_3$). Anal. Calcd for $C_{24}H_{46}NP_2Rh$: C, 56.14; H, 9.03; N, 2.73. Found: C, 55.85; H, 9.00; N, 2.73.

X-ray structure determination of **5**:[13] Crystallographic data for this compound is available from the Cambridge Database CCDC #640089. Crystals were grown from a concentrated pentane solution at −35 °C. The structure was refined by full-matrix least-squares on F^2. Crystal data for (PNP)Rh(CH$_3$): $C_{24}H_{46}NP_2Rh$, MW = 513.47, orthorhombic, space group $P2_12_12_1$, T = 131(2) K, a = 13.0520(4) Å, b = 13.8410(5) Å, c = 14.5260(6) Å, β = 90°, Z = 4, R_1 = 0.0531, wR_2 = 0.1277, GOF (F^2) = 0.961, absolute structure parameter 0.01(5).

(PNP)Rh(CH$_3$)Zn(CH$_3$)OTf (6). In a thick-walled glass vessel equipped with a Teflon stopcock, (PNP)Rh(N$_2$)OTf (81.3 mg, 0.120 mmol) was dissolved in THF (5 mL). Dimethylzinc (0.260 mL of a 10 wt % solution in hexanes, 0.180 mmol) was added under nitrogen. The glass vessel was sealed and heated at 70 °C for 19 h, during which time the color changed from yellow to brown. The reaction was cooled to room temperature and the solution concentrated to 0.75 mL under vacuum. Slow diffusion of pentane into the concentrated THF solution at −35 °C yielded bright yellow crystals, which were washed with pentane (3 × 1 mL). Yield: 54.8 mg (61%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.13 (t, 1H, J = 7.5 Hz, Py), 6.81 (d, 2H, J = 7.5 Hz, Py), 3.68 (dvt, 2H, J_{H-H} = 17.7 Hz, J_{H-P} = 4.2 Hz, CH_2), 2.97 (dvt, 2H, J_{H-H} = 17.7 Hz, J_{H-P} = 4.5 Hz, CH_2), 1.23 (vt, 18 H, J = 6.9 Hz, C(CH_3)$_3$), 0.98 (vt, 18H, J = 6.0 Hz, C(CH_3)$_3$), 0.71 (dt, 3H, $^3J_{P-H}$ = 5.7 Hz, $^2J_{Rh-H}$ = 1.8 Hz, Rh-CH_3), 0.45 (s, 3H, Zn-CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 62.34 (d, 2P, $^1J_{Rh-P}$ = 124 Hz). Anal. Calcd for $C_{26}H_{49}F_3NO_3P_2RhSZn$: C, 42.03; H, 6.65; N, 1.89. Found: C, 42.00; H, 6.78; N, 1.91.

(PNP)Rh(C$_6$H$_5$) (7). In a thick-walled glass vessel fitted with a Teflon stopcock, (PNP)Rh(OTf) (43.9 mg, 0.0677 mmol) was suspended in benzene (4 mL). A suspension of solid diphenylzinc (44.6 mg, 0.203 mmol) in benzene (2 mL) was added, and the reaction mixture was heated at 60 °C for 17 h. After cooling to room temperature, 2,2′-dipyridyl (bipy) (10.7 mg, 0.0686 mmol) was added to the yellow solution, resulting in a color change to brown. The solvent was removed under vacuum, leaving a brown residue. Pentane (15 mL) was added, and the mixture was sonicated for 1 h, giving a dark brown solution and light brown-yellow solid material. The pentane solution was filtered through a Teflon syringe filter, concentrated to approximately 1 mL, and cooled to −35 °C to yield brown, solid (PNP)Rh(C$_6$H$_5$). Yield: 24.0 mg (61%). ^{1}H NMR (C_6D_6, 300 MHz): δ 8.17 (d, 2H, J = 7.5 Hz, Rh-Ph), 7.26 (t, 2H, J = 7.5 Hz, Rh-Ph), 6.98 (t, 2H, J = 7.5 Hz, Rh-Ph (1H), Py (1H)), 6.46 (d, 2H, J = 7.5 Hz, Py), 2.86 (vt, 4H, J = 3.0 Hz, CH_2), 1.26 (vt, 36H, J = 6.0 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6) δ 59.40 (d, 2P, $^1J_{Rh-P}$ = 173 Hz). ^{13}C{^{1}H} NMR (THF, 50 MHz): δ 168.70 (dt, $^1J_{Rh-C}$ = 32 Hz, $^2J_{P-C}$ = 14 Hz, Rh-*C*), 161.68 (br s, Py), 142.55 (s, Ph), 131.21 (s, Py), 123.30 (s, Ph), 118.97 (s, Py), 116.83 (s, Ph), 37.38 (br s, *C*H$_2$), 35.12 (br s, *C*(CH$_3$)$_3$), 29.11 (br s, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{29}H_{48}NP_2Rh$: C, 60.52; H, 8.41; N, 2.43. Found: C, 60.51; H, 8.31; N, 2.44.

(PNP)Rh(OH) (8). In a glass vessel equipped with a Teflon stopcock, (PNP)Rh(CH$_3$) (58.0 mg, 0.113 mmol) was dissolved in THF (1.5 mL). Approximately 10 drops of degassed, deionized water were added, and the reaction mixture was stirred for 15 min. The THF was subsequently removed under vacuum, yielding a dark pink residue. The residue was dissolved in a minimum amount of THF and crystallized by slow diffusion of pentane at −35 °C. Yield: 45.6 mg (78%). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.97 (t, 1H, J = 7.5 Hz, Py), 6.22 (d, 2H, J = 7.5 Hz, Py), 2.49 (vt, 4H, J = 3.3 Hz, CH_2), 1.45 (vt, 36H, J = 6.3 Hz, C(CH_3)$_3$), −2.03 (br s, 1H, Rh-O*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.60 (d, 2P, $^1J_{Rh-P}$ = 157 Hz). Anal. Calcd for $C_{23}H_{44}NOP_2Rh$: C, 53.59; H, 8.60; N, 2.72. Found: C, 53.63; H, 8.59; N, 2.60.

(PNP)Rh(OCH$_2$CF$_3$) (9). (PNP)Rh(CH$_3$) (22.1 mg, 0.0431 mmol) was added to a glass vessel equipped with a Teflon stopcock containing a solution of trifluoroethanol (0.3 mL) in THF (1 mL). The solvent was removed under vacuum. The remaining red residue was dissolved in toluene (1 mL), and the toluene was removed under vacuum. The red solid product was then recrystallized from pentane at –35 °C. Yield: 12.8 mg (50%). ^{1}H NMR (C_6D_6, 300 MHz): δ 6.85 (t, 1H, J = 7.5 Hz, Py), 6.19 (d, 2H, J = 7.5 Hz, Py), 4.48 (q, 2H, $^3J_{H-F}$ = 10.5 Hz, −OCH_2CF$_3$), 2.48 (vt, 4H, J = 3.3 Hz, CH_2), 1.38 (vt, 36H, J = 6.6 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.57 (d, 2P, $^1J_{Rh-P}$ = 161 Hz). ^{19}F NMR (C_6D_6): δ −76.64 (t, 3F, $^3J_{H-F}$ = 10.2 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 50 MHz): δ 165.31 (vt, J = 5.6 Hz, Py), 129.86 (s, Py), 127.92 (q, $^1J_{C-F}$ = 284.9 Hz, −OCH$_2$*C*F$_3$), 120.45 (vt, J = 5.1 Hz, Py), 76.68 (q vt, $^2J_{C-F}$ = 29.9 Hz, J = 2.6 Hz, −O*C*H$_2$CF$_3$), 36.73 (vt, J = 6.8 Hz, *C*H$_2$), 35.14 (vt, J = 5.1 Hz, *C*(CH$_3$)$_3$), 29.71 (vt, J = 4.9 Hz, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{25}H_{45}NF_3OP_2Rh$: C, 50.26; H, 7.59; N, 2.34. Found: C, 50.41; H, 7.84; N, 2.43.

(PNP)Rh(OC$_6$H$_5$) (10). A solution of phenol (7.6 mg, 0.0809 mmol) in THF (1 mL) was added to a glass vial containing (PNP)Rh(CH$_3$) (41.5 mg, 0.0809 mmol), forming a deep red solution. The solvent was removed under vacuum, and the remaining red solid washed with cold pentane (1 mL). Yield: 37.7 mg (79%).

Alternate Preparation of 10. In a glass vessel equipped with a Teflon stopcock, [Rh(COD)OH]$_2$ (65.4 mg, 0.1434 mmol), PNP ligand (112.7 mg, 0.2853 mmol), and phenol (26.5 mg, 0.2819 mmol) were dissolved in toluene (6 mL). The reaction was heated at 100 °C for 24 h, then cooled to room temperature. The solvent

was removed under vacuum, leaving a red residue. The red solid was recrystallized from diethyl ether at −35 °C, giving dark purple crystals of **10**, which were washed with pentane (2 × 1 mL). Yield: 90.6 mg (54%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.40–7.29 (m, 4H, phenoxide), 6.85 (t, 1H, J = 7.8 Hz, Py), 6.70 (t, 1H, J = 6.9 Hz, phenoxide), 6.22 (d, 2H, J = 7.8 Hz, Py), 2.57 (vt, 4H, J = 3.0 Hz, CH_2), 1.34 (vt, 36H, J = 5.7 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 57.71 (d, 2P, $^1J_{Rh-P}$ = 157 Hz). Anal. Calcd for $C_{29}H_{48}NOP_2Rh$: C, 58.88; H, 8.17; N, 2.37. Found: C, 58.30; H, 8.17; N, 2.39.

(PNP)Rh(OC$_6$H$_4$NO$_2$) (11). In a dry glass vial, [Rh(COD)OH]$_2$ (50.0 mg, 0.110 mmol), PNP ligand (86.6 mg, 0.219 mmol), and 4-nitrophenol (30.2 mg, 0.217 mmol) were combined. Toluene (3.5 mL) was added, and the reaction mixture was allowed to stand undisturbed for 3 days at room temperature, during which time large red crystals grew in the vial. The supernatant was removed, and the crystals were washed with pentane (3 × 2 mL). Yield: 123.5 mg (89%). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.41 (d, 2H, J = 9.0 Hz, aryloxide), 6.89 (d, 2H, J = 9.0 Hz, aryloxide), 6.81 (t, 1H, J = 8.0 Hz, Py), 6.22 (d, 2H, J = 8.0 Hz, Py), 2.53 (vt, 4H, J = 3.5 Hz, CH_2), 1.20 (vt, 36H, J = 6.0 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 59.19 (d, 2P, $^1J_{Rh-P}$ = 153 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 50 MHz): δ 180.79 (s, aryloxide), 166.20 (vt, J = 5.0 Hz, Py), 133.94 (s, aryloxide), 132.47 (s, Py), 126.06 (s, aryloxide), 121.55 (s, aryloxide), 120.89 (vt, J = 5.7 Hz, Py), 36.21 (vt, J = 6.4 Hz, CH$_2$), 35.16 (vt, J = 7.2 Hz, C(CH$_3$)$_3$), 29.90 (vt, J = 3.4 Hz, C(CH$_3$)$_3$). Anal. Calcd for $C_{29}H_{47}N_2O_3P_2Rh$: C, 54.72; H, 7.44; N, 4.40. Found: C, 55.05; H, 7.51; N, 4.36.

General Procedure for the H−D Exchange Reactions. In an NMR tube fitted to a vacuum adaptor, the rhodium catalyst (ca. 3 mg, 0.005 mmol) was dissolved in benzene-d_6 (99.96% D, 350 μL) containing THF or hexamethylbenzene as an internal standard. Deionized water (20 μL, 1.11 mmol) was added, and the NMR tube was flame-sealed under active vacuum. The tube was heated submerged in a steel jacket in a Neslab Exacal EX-250 HT oil bath at 100 °C. The reaction was monitored at intervals over the course of 150 h, with the extent of the exchange being determined by integration of the residual benzene signal against the internal standard. ^{1}H NMR spectra were recorded using a 360 s delay (one scan) to ensure accurate integration of the benzene. For the reactions conducted with high concentrations of phenol (0.5–0.8 M), the rate of exchange was determined from the first 20 h of reaction time; at longer times the rate slowed as the reaction approached an equilibrium distribution of hydrogen and deuterium (approximately 425 turnovers).

H−D Exchange between Toluene-d_8 and H$_2$O. A resealable Teflon-capped NMR tube was charged with deionized H_2O (33 μL) and toluene-d_8 (0.30 mL). The mixture was degassed by three freeze–pump–thaw cycles. (PNP)Rh(OC_6H_5) (2.9 mg, 0.00491 mmol) and THF (0.00455 mmol) were added, and the tube was placed under argon. The NMR tube was heated in a stainless steel jacket in a Neslab Exacal EX-250 HT oil bath at 100 °C and monitored by ^{1}H NMR spectroscopy. The residual toluene meta and para signals increased, but no increase in the ortho and CH_3 positions was observed. After 336 h, a total of 47 turnovers had occurred, with a selectivity of 1.2 meta:1 para:0 ortho:0 CH_3 (statistically corrected) determined from the integrals of the residual toluene signals (versus the THF internal standard). A control reaction with phenol (3.1 mg, 0.0330 mmol) and no rhodium showed no detectible increase in the residual toluene signals after 360 h.

Deuterium Exchange into the Methylene Protons of (PNP)Rh(C$_6$H$_5$) from D$_2$O. (PNP)Rh(C_6H_5) (3.0 mg; 0.00521 mmol) was dissolved in benzene (0.25 mL). D_2O (1 μL; 0.0550 mmol) was added and the mixture allowed to react for 24 h at room temperature. Examination of the reaction mixture by ^{2}H NMR showed a broad signal at 2.8 ppm, indicating deuterium had exchanged into the methylene positions. The volatiles were removed under vacuum, and upon examination by ^{1}H NMR (benzene-d_6), the methylene signal integrated at only 25% of its normal intensity.

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Supporting Information Available: CIF files for **1**-N_2, **5**, and **10**-HOC_6H_5. This material is available free of charge via the Internet at http://pubs.acs.org.

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