Hydrogen–Deuterium Exchange between $\text{TpRu}(\text{PMe}_3)(\text{L})\text{X}$ ($\text{L} = \text{PMe}_3$ and $\text{X} = \text{OH}$, OPh , Me , Ph , or NHPh ; $\text{L} = \text{NCMe}$ and $\text{X} = \text{Ph}$) and Deuterated Arene Solvents: Evidence for Metal-Mediated Processes

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Abstract: At elevated temperatures (90–130 °C), complexes of the type $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}$, OPh , Me , Ph , or NHPh ; $\text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$) undergo regioselective hydrogen-deuterium (H/D) exchange with deuterated arenes. For $\text{X} = \text{OH}$ or NHPh , H/D exchange occurs at hydroxide and anilido ligands, respectively. For $\text{X} = \text{OH}$, OPh , Me , Ph , or NHPh , isotopic exchange occurs at the Tp 4-positions with only minimal deuterium incorporation at the Tp 3- or 5-positions or PMe_3 ligands. For $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$, the H/D exchange occurs at 60 °C at all three Tp positions and the phenyl ring. $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$, $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ ($\text{OTf} = \text{trifluoromethanesulfonate}$), and $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ do not initiate H/D exchange in C_6D_6 after extended periods of time at elevated temperatures. Mechanistic studies indicate that the likely pathway for the H/D exchange involves ligand dissociation (PMe_3 or NCMe), Ru-mediated activation of an aromatic C–D bond, and deuteration of basic nondative ligand (hydroxide or anilido) or Tp positions via net D^+ transfer.

Introduction

Due to the potential synthetic utility of processes for selective functionalization of hydrocarbons, transition metal-mediated activation of carbon–hydrogen bonds has been of long-standing interest.^{1–6} Efforts in this area have resulted in the identification of a variety of mechanisms by which transition metals can break C–H bonds and an increasing number of examples of metal-mediated catalytic C–H activation.^{7–14} Our group has been studying the use of $\text{TpRu}(\text{II})$ alkyl and aryl ($\text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$) complexes for the activation of aromatic C–H

bonds including catalytic hydroarylation of olefins.^{15–17} In a separate approach, we have initiated a study of the feasibility of complexes with high d-electron counts that possess nondative heteroatomic ligands to initiate C–H bond cleavage via even-electron transformations.^{18–22}

The chemistry of nondative heteroatomic ligands (e.g., amido, imido, alkoxide, aryloxide, hydroxide, and oxo ligands) bound to late transition metal centers is of increasing interest due to the likely involvement of such systems in catalytic and stoichiometric reactions.^{23–32} Our group and others have

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Scheme 1. Possible Routes for Catalytic 1,2-Addition Across Metal–Heteroatom Bonds ($\text{X} = \text{O}$ or NR)

detailed the synthesis and reactivity of $\text{Ru}(\text{II})$ complexes that possess amido ligands.^{18–20,22,33–38} Recently, we reported evidence that the $\text{Ru}(\text{II})$ hydroxide complex $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) can activate C–H(D) bonds of benzene or toluene through a pathway that likely involves phosphine dissociation, arene coordination, and net 1,2-addition of a C–H bond across the Ru-OH bond.²¹ In a closely related reaction, Periana et al. have reported that an $\text{Ir}(\text{III})$ methoxide system, which is isoelectronic to **1**, reacts with benzene to produce an $\text{Ir}(\text{III})$ phenyl complex and methanol.³⁹ These transformations are potentially related to C–H activation of hydrocarbons by early transition metal imido complexes in that they involve the net 1,2-addition of C–H bonds across a metal–heteroatom bond.^{40–43}

The incorporation of 1,2-addition of C–H bonds across transition metal heteroatom bonds into catalytic cycles would provide routes for the production of hetero-functionalized products from hydrocarbons (Scheme 1). Such catalytic cycles could be accessible through oxidation of a metal center by group transfer of “X” (e.g., $\text{X} = \text{O}$ or NR), 1,2-addition of a C–H bond, and subsequent reductive elimination of R-X-H via R-X bond formation (Route A in Scheme 1). Alternatively, oxygen/nitrene insertion into a metal–alkyl (or aryl) bond followed by 1,2-addition of a C–H bond and elimination of an alcohol or amine provides a pathway for C–H functionalization (Route B in Scheme 1). A key step in such putative catalytic cycles is net 1,2-addition of a C–H bond across a metal–oxygen or metal–nitrogen nondative bond. Although odd-electron hydrogen-atom abstraction by nondative ligands coordinated to oxidizing metal centers are known,^{44–46} to our knowledge,

Scheme 2. Proposed Pathway for H/D Exchange between **1** and C_6D_6 (80–100 °C)

examples of net 1,2-addition of C–H bonds (even-electron transformations) across M-X bonds ($\text{X} = \text{heteroatom}$) are rare for late transition metal systems in relatively low oxidation states.^{21,39,47} Herein, we report extension of our studies of hydrogen/deuterium (H/D) exchange for **1** to systems of the type $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}$, NHPh , NHPh , OPh , SH , Cl , OTf , Me , or Ph) and $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$, including the observation, for some of these systems, of H/D exchange at the nondative ligand X as well as regioselective H/D exchange between the Tp ligand and deuterated arenes.

Results and Discussion

Hydrogen/Deuterium Exchange at the Nondative Ligand X for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ { $\text{X} = \text{OH}$ (1**), NHPh (**2**), or SH (**3**)}. Synthesis and characterization of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ { $\text{X} = \text{OH}$ (**1**) or NHPh (**2**)}** have been previously reported.^{18,21} The isoelectronic hydrosulfido complex $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (**3**) can be isolated in 57% yield after reflux of the triflate complex $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (**4**) ($\text{OTf} = \text{trifluoromethanesulfonate}$) with $\text{NaSH} \cdot x\text{H}_2\text{O}$ in toluene for 24 h (eq 1). **3** is characterized by resonances for the Tp ligand that are consistent with the presence of a mirror plane of symmetry (^1H and ^{13}C NMR spectroscopy) and an upfield triplet ($^3J_{\text{PH}} = 4$ Hz, ^1H NMR) at -3.30 ppm due to the sulfido hydrogen. For a closely related $\text{Re}(\text{I})$ complex, the

resonance due to the hydrosulfido ligand (^1H NMR) has been reported at -2.43 ppm.⁴⁸

We have previously reported that heating $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) in deuterated arene solvents results in H/D exchange at the hydroxide ligand including evidence for the pathway shown in Scheme 2.²¹ The proposed H/D exchange at the hydroxide ligand is supported by the disappearance of the resonance due to the hydroxide ligand (^1H NMR) and appearance of a broad upfield resonance in the ^2H NMR (see Figure 1 below). Early in the reaction, the rate of disappearance of the protio benzene resonance equals the rate of appearance of the protio benzene resonance. In the presence of H_2O , the H/D exchange between the

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Figure 1. ^2H NMR spectrum of $(\text{Tp-}d_3)\text{Ru}(\text{PMe}_3)_2\text{OD}$ (**1-d**₄) acquired at 75 °C (note: the observation of a single Tp 4-position in the ^2H NMR is due to broad lines and overlap; resonance for benzene is due to residual C_6D_6).

hydroxide ligand and C_6D_6 becomes catalytic. For example, the combination of **1** (~ 1.6 mol %), H_2O , and C_6D_6 results in catalytic H/D exchange to produce $\text{C}_6\text{D}_x\text{H}_y$ ($x + y = 6$), as indicated by an increase in the resonance due to benzene in the ^1H NMR spectrum. After 172 h at 100 °C, a total of 10 catalytic turnovers for H/D exchange are observed with only slight catalyst decomposition. Catalysis likely occurs through the generation of Ru-OD and subsequent reaction with H_2O to produce DOH and Ru-OH . Control reactions in the absence of **1** or using $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (the synthetic precursor to **1**) do not yield H/D exchange between H_2O and C_6D_6 . Observation of catalytic H/D exchange at C–H bonds using water is relatively rare.⁴⁹

Kinetic studies reveal that H/D exchange at the hydroxide ligand of **1** in excess C_6D_6 is first-order with $k_{\text{obs}} = 8.0(2) \times 10^{-5} \text{ s}^{-1}$ (80 °C, $t_{1/2} \approx 2.4$ h). The addition of 10 mol % of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (**4**) (precursor to **1**) to a solution of **1** and C_6D_6 does not increase the rate of H/D exchange at the hydroxide ligand of **1**. Thus, small amounts of Ru impurities from starting materials are not likely to be acting as catalysts for the H/D exchange. The presence of coordinating ligands suppresses the rate of H/D exchange at the hydroxide ligand as well as the rate of catalytic H/D exchange between H_2O and C_6D_6 , which is consistent with a metal-mediated process. For example, heating a solution of **1** in C_6D_6 in the presence of 0.1 equiv (based on **1**) of PMe_3 results in no observable H/D exchange at the hydroxide ligand after 168 h at 80 °C. The addition of the “non-coordinating” base 2,6-lutidine does not increase the rate of H/D exchange at the hydroxide ligand and, in fact, slightly decreases the rate. For example, at 80 °C, H/D exchange at the hydroxide ligand occurs with $k_{\text{obs}} = 8.0(2) \times 10^{-5} \text{ s}^{-1}$, whereas the H/D exchange at the hydroxide ligand (80 °C) in the presence of 1 equiv of 2,6-lutidine occurs approximately 3.5 times slower with $k_{\text{obs}} = 2.3 \times 10^{-5} \text{ s}^{-1}$. Thus, the reaction is not likely catalyzed by basic impurities. The addition of TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) to a solution of **1** in C_6D_6 does not alter the rate of H/D exchange, which indicates that the reaction does not likely involve the generation of free radicals. Reactions in toluene- d_8 are also inconsistent with a free radical process (see below).

According to the proposed mechanism for H/D exchange shown in Scheme 2, **1** must access a five-coordinate species on a time scale that is consistent with the observed H/D exchange at the hydroxide ligand. Monitoring the rate of exchange of PMe_3 upon combination of **1** with $\text{PMe}_3\text{-}d_9$ at 80 °C reveals $k_{\text{obs}} = 1.7(1) \times 10^{-4} \text{ s}^{-1}$. The rate of degenerate $\text{PMe}_3/\text{PMe}_3\text{-}d_9$ exchange is independent of $\text{PMe}_3\text{-}d_9$ concentration, indicating that the exchange is likely dissociative in character. The rate of PMe_3 exchange is greater than the rate of H/D exchange and indicates that external substrates (e.g., C_6D_6) should have access to the Ru coordination sphere on time scales that are more rapid than the observed H/D exchange.

The reaction of **1** with toluene- d_8 at 80 °C also results in H/D exchange of the hydroxide ligand. The kinetic selectivity (after statistical correction) for H/D exchange of **1** in toluene- d_8 is para/meta/ortho/methyl = 4.4:3.9:2.5:1.0 (eq 2). The selectivity for para and meta positions over ortho and methyl positions is consistent with a metal-mediated process and suggests that the H/D exchange does not likely involve a hydrogen atom abstraction pathway, which would preferentially occur at the benzylic position.

Another possible pathway for the isotopic exchange is the creation of a source of H^+ . For example, coordination of H_2O or the presence of an acidic impurity could provide a source of H^+ and a pathway for electrophilic aromatic substitution; however, the regioselectivity for toluene H/D exchange is inconsistent with addition of H^+ to free toluene- d_8 . For example, the para/meta/ortho selectivity for deuteration of toluene with DBr (25 °C) has been reported as approximately 1000:1:167, whereas selectivity of toluene deuteration with D_2O /perfluoroacetic acid (25 °C) has been reported as approximately 98:1:74.⁵⁰ Furthermore, the rate of H/D exchange at the hydroxide ligand upon heating a toluene- d_8 ($k_{\text{obs}} = 2.0(1) \times 10^{-5} \text{ s}^{-1}$ at 80 °C) solution of **1** is approximately 4 times slower than that observed in C_6D_6 and is inconsistent with a pathway involving production of H^+ with subsequent electrophilic aromatic substitution.

The anilido complex $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ (**2**) also initiates H/D exchange in C_6D_6 ; however, higher temperatures are required relative to the hydroxide complex **1**. The ^{15}N -labeled complex $\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NHPh})$ (**2- ^{15}N**) can be prepared starting from isotopically enriched ^{15}N -aniline. The resonance due to the amido hydrogen of **2- ^{15}N** appears as sharp doublet with $^1J_{\text{NH}} = 69$ Hz. Heating **2- ^{15}N** in C_6D_6 at 130 °C results in the disappearance of the resonance due to the amido hydrogen with $k_{\text{obs}} = 1.4(2) \times 10^{-5} \text{ s}^{-1}$ (eq 3). Similar to **1**, the rate of phosphine exchange for **2** is more rapid than H/D exchange at the anilido ligand (see below). Simultaneous to the decrease in the resonance due to the hydrogen of the anilido ligand, the resonance due to protio benzene increases. In contrast, heating $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (**3**) in C_6D_6 to 130 °C results in no observed changes in the ^1H NMR spectrum after 6 days (eq 4).

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Hydrogen/Deuterium Exchange at the Tp 4-Positions of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1). In addition to the H/D exchange at the hydroxide ligand of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1), prolonged heating of 1 in C_6D_6 results in the observation of *regioselective* H/D exchange at the Tp 4-positions (eq 5). ^2H NMR reveals only a minor amount of H/D exchange at the Tp 3/5-positions and the trimethylphosphine ligands. For example, monitoring a C_6D_6 solution of 1 at 90 °C by ^1H NMR spectroscopy for 150 h reveals the disappearance of resonances due to the Tp 4-positions without substantial change in the resonances due to the Tp 3- or 5-positions or the PMe_3 ligands.

The two resonances due to the Tp 4-positions decrease at approximately the same rate. The incorporation of deuterium at the Tp 4-positions and the hydroxide ligand (see above) has been confirmed by ^2H NMR spectroscopy (Figure 1). Only small resonances are observed due to deuterium incorporation at Tp 3/5 positions and the PMe_3 ligands, which is consistent with analysis by ^1H NMR spectroscopy for 1. In excess C_6D_6 , the H/D exchange at the Tp 4-positions follows first-order kinetics with $k_{\text{obs}} = 5.2(2) \times 10^{-6} \text{ s}^{-1}$ at 90 °C. Thus, H/D exchange at the hydroxide ligand at 80 °C ($t_{1/2} \approx 2.4 \text{ h}$) is approximately 15 times more rapid than the observed H/D exchange at the Tp 4-positions at 90 °C ($t_{1/2} \approx 37 \text{ h}$).

Consistent with the relative rates of H/D exchange at the hydroxide ligand of 1, heating 1 in toluene- d_8 results in regioselective H/D exchange at the Tp 4-positions with the rate of H/D exchange in toluene- d_8 ($k_{\text{obs}} = 1.1(3) \times 10^{-6} \text{ s}^{-1}$ at 90 °C) being approximately 4.5 times slower than the same reaction in C_6D_6 ($k_{\text{obs}} = 5.2(2) \times 10^{-6} \text{ s}^{-1}$ at 90 °C).

Attempted H/D Exchange at the Tp 4-Positions of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ (X = OPh, NH_2 , NHPh , Cl, OTf, Me, Ph, SH). To test whether the H/D exchange could be initiated by other Ru(II)–OR systems, we prepared $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5) by refluxing a toluene solution of 4 and $\text{NaOPh} \cdot 3\text{H}_2\text{O}$ (eq 6). $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5) has been characterized by a single-crystal X-ray diffraction study (Figure 2). Data collection parameters are listed in Table 1, and the ORTEP of 5 is shown in Figure 2. 5 is composed of a pseudo-octahedral coordination sphere without significant deviation from the octahedral geometry. The Ru–O bond distance is 2.102(2) Å, which is slightly longer

Figure 2. ORTEP (30% probability) of $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5) (note: hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Ru1–N1 2.069(2), Ru1–O1 2.102(2), Ru1–N3 2.145(2), Ru1–P1 2.2991(6), O1–C7 1.300(3). Selected bond angles (deg): N1–Ru1–O1 171.60(8), O1–Ru1–N3 85.09(6), O1–Ru1–P1 95.62(4), P1–Ru1–P1 103.89(3), C7–O1–Ru1 133.2(2), O1–C7–C8 125.9(3), O1–C7–C12 118.9(3).

Table 1. Selected Crystallographic Data and Collection Parameters for $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5), $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (9), and $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (10)

	complex 5	complex 9	complex 10
empirical formula	$\text{C}_{21}\text{H}_{33}\text{BN}_6\text{OP}_2\text{Ru}$	$\text{C}_{21}\text{H}_{33}\text{BN}_6\text{P}_2\text{Ru}$	$\text{C}_{20}\text{H}_{27}\text{BN}_7\text{PRu}$
formula wt	559.35	543.35	508.34
crystal system	orthorhombic	monoclinic	orthorhombic
space group	$Pnma$	$P2_1/n$	$Pna2_1$
<i>a</i> , Å	16.088(1)	10.4395(5)	18.778(2)
<i>b</i> , Å	12.981(1)	16.5658(9)	9.446(1)
<i>c</i> , Å	12.263(1)	14.5617(8)	13.149(1)
β , °		91.616(1)	
<i>V</i> (Å ³)	2561.1(4)	2517.3(2)	2332.3(4)
<i>Z</i>	4	4	4
<i>D</i> _{calc} , g cm ^{−3}	1.451	1.434	1.448
crystal size (mm)	0.18 × 0.40 × 0.40	0.10 × 0.18 × 0.20	0.16 × 0.20 × 0.27
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0246, 0.0622	0.0321, 0.0707	0.0386, 0.0883
GOF	1.064	1.025	1.040

than the Ru–O distance {2.083 Å} of 1.²¹ The bond angle P1–Ru–P1 is 103.89(3)°, which is larger than the same bond angle {93.08°} of 1, probably due to the steric profile of the phenoxide ligand compared to the small hydroxide ligand.

Heating a C_6D_6 solution of 5 to 130 °C affords the regioselective H/D exchange at the Tp 4-positions with $k_{\text{obs}} = 1.5(2) \times 10^{-6} \text{ s}^{-1}$. Having observed H/D exchange at the Tp 4-positions with 1 and 5, we extended our studies to the complexes $\text{TpRu}(\text{PMe}_3)_2\text{X}$ (X = Cl, OTf, Me, Ph, NHPh , SH, or NH_2).^{18,21,22} Table 2 summarizes the results. Upon thermolysis (90 °C) in C_6D_6 , the parent amido complex $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ (6) undergoes rapid decomposition prior to observation of evidence for H/D exchange at either the amido ligand or the Tp 4-positions. Heating $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (7), $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (4), or $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (3) in benzene- d_6 at temperatures between 90 and 130 °C for 22 days does not result in H/D exchange at the Tp 4-positions. These solutions remain un-

Table 2. Observed Rates of H/D Exchange Reaction at the 4-positions of Tp Ligands of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ Complexes^a

X	solvent	T (°C)	k_{obs} (s ⁻¹)
OH (1)	C ₆ D ₆	90	$5.2(2) \times 10^{-6}$
OH (1)	C ₆ D ₅ CD ₃	90	$1.1(3) \times 10^{-6}$
NHPh (2)	C ₆ D ₆	130	$5.6(3) \times 10^{-6}$
Me (8)	C ₆ D ₆	130	$1.1(1) \times 10^{-5}$
Me (8)	C ₆ D ₅ CD ₃	130	$4.5(5) \times 10^{-6}$
Ph (9)	C ₆ D ₆	130	$2.1(5) \times 10^{-5}$
OPh (5)	C ₆ D ₆	130	$1.5(2) \times 10^{-6}$
SH (3)	C ₆ D ₆	130	no rxn
OTf (4)	C ₆ D ₆	130	no rxn
Cl (7)	C ₆ D ₆	130	no rxn
NH ₂ (6)	C ₆ D ₆	90	decomp

^a Concentration of ruthenium complex = 0.14 mM; decomp = decomposition

Table 3. The Rates^a of PMe_3 Exchange Reactions^b for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ and Excess $\text{P}(\text{CD}_3)_3$

complex	k_{obs} (s ⁻¹)
$\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5)	$2.6(2) \times 10^{-4}$
$\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1)	$1.7(1) \times 10^{-4}$
$\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ (2)	$6.1(4) \times 10^{-5}$
$\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (9)	$4.9(3) \times 10^{-5}$
$\text{TpRu}(\text{PMe}_3)_2\text{Me}$ (8)	$2.3(1) \times 10^{-5}$
$\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (7)	$9.4(4) \times 10^{-6}$
$\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (3)	$7.3(1) \times 10^{-6}$

^a Rates determined by ¹H NMR spectroscopy. ^b Reaction conditions: 0.14 mM in C₆D₆, 15 equiv of $\text{P}(\text{CD}_3)_3$, 80 °C.

changed by ¹H NMR spectroscopy. In contrast, for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ (X = OH, NHPh, Me, Ph, or OPh), H/D exchange at the Tp 4-positions is observed, albeit at different rates. At 90 °C, $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ (**2**) does not initiate the Tp 4 H/D exchange after 4 days. However, heating a C₆D₆ solution of **2** to 130 °C results in H/D exchange at the Tp 4-positions with $k_{\text{obs}} = 5.6(3) \times 10^{-6} \text{ s}^{-1}$. Consistent with the hydroxide complex **1**, H/D exchange at the Tp ligand for **2** is slower than the rate of H/D exchange at the anilido ligand ($k_{\text{obs}} = 1.4(2) \times 10^{-5} \text{ s}^{-1}$, see above). Heating the previously reported aniline complex [$\text{TpRu}(\text{PMe}_3)_2\text{NH}_2\text{Ph}][\text{OTf}]$ in C₆D₆ results in an equilibrium with $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (**4**) and aniline ($K_{\text{eq}} = 0.11$, 130 °C) with no evidence of H/D exchange at the aniline ligand or Tp 4-positions of **4**.

With the observation that $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) undergoes H/D exchange whereas $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**) does not initiate the H/D exchange, we heated (90 °C) a 1:1 molar ratio of **1** and **7** in benzene-*d*₆. Under these conditions, the ¹H NMR resonances of the Tp 4-positions of both **1** and **7** decrease. Unfortunately, due to overlap of the resonances of the Tp 4-positions for **1** and **7**, we are unable to discern whether the rate of H/D exchange is identical or if the exchange occurs at slightly different rates. The rate of exchange must at least be *similar* for **1** and **7** because both sets of Tp 4-position resonances disappear on *approximately* the same time scale. This result seemingly indicates that the metal-mediated transfer of deuterium from C₆D₆ is an intermolecular process. That is, **1** (or a derivative thereof) activates C₆D₆, and intermolecular transfer of deuterium to the Tp ligand of another Ru system (in this experiment, a Tp ligand of *either* **1** or **7**) occurs. Thus, observed Tp H/D exchange would be dependent on the ability of the Ru complex to activate the arene rather than activation of the pyrazolyl fragment to receive the deuterium transfer. However, we cannot rule out H/D exchange exclusively at **1** followed by

Figure 3. Representative kinetic plot for the PMe_3 exchange reaction of $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ (**2**) and $\text{P}(\text{CD}_3)_3$ ($R^2 = 0.997$).

OH/Cl metathesis between **1** and **7** because such a pathway would result in apparent H/D exchange for both complexes. Heating a mixture of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) and $\text{TpRu}\{\text{P}(\text{CD}_3)_3\}_2\text{-Cl}$ (**7-d**₁₈) in C₆D₆ to 90 °C results in the appearance of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (eq 7). Thus, these experiments do not allow a differentiation between H/D exchange at the chloride complex **7** initiated by **1** and H/D exchange at **1** followed by OH/Cl metathesis. However, reaction of **1** and 1-methylpyrazole in C₆D₆ clearly indicates that intermolecular H/D exchange is possible (see below).

Rates of PMe_3 Exchange. Kinetic studies of PMe_3 exchange in the presence of excess $\text{P}(\text{CD}_3)_3$ for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ complexes were performed, and the results are shown in Table 3. The addition of 15 equiv of trimethylphosphine-*d*₉ to $\text{TpRu}(\text{PMe}_3)_2\text{X}$ (X = OPh, OH, SH, NHPh, Ph, Me, or Cl) in benzene-*d*₆ at 80 °C results in the disappearance of the resonance due to the PMe_3 ligands (¹H NMR) and an increase in the resonance due to the free PMe_3 . For **1**, the rate of exchange is independent of PMe_3 -*d*₉ concentration. A representative kinetic plot for the PMe_3 exchange reaction of $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ (**2**) is shown in Figure 3. The rate of PMe_3 exchange for $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (**4**) could not be determined due to the previously reported formation of [$\text{TpRu}(\text{PMe}_3)_3$][OTf].¹⁹ For all systems in which H/D exchange is observed, the rate of PMe_3 exchange is more rapid at 80 °C than the rate of H/D exchange at higher temperatures (90 or 130 °C). Thus, a mechanism for H/D exchange that involves dissociation of PMe_3 is feasible for all systems.

Impact of Simple Salts and Non-Coordinating Base on H/D Exchange at the Tp 4-Positions. In separate experiments, different salts (LiCl, MgCl₂, NaOTf, and CsCl) were added to C₆D₆ solutions of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**). Heating these mixtures to 100 °C for 7 days results in no change for either resonance due to the Tp 4-positions or the benzene resonance according to ¹H NMR spectroscopy. Furthermore, the addition of salts to $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**)/C₆D₆ solutions does not alter the rate of H/D exchange at the Tp 4-positions. The addition of MgCl₂ to a $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**)/C₆D₆ solution results in the formation of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**) at 90 °C, and heating for a prolonged period of time does not result in the H/D exchange.

Figure 4. Plot of k_{obs} versus equivalents (based on **1**) of 2,6-lutidine for H/D exchange at the Tp 4-positions of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) in C_6D_6 at 100°C ($R^2 = 0.96$).

The addition of the sterically hindered base 2,6-lutidine to a solution of **1** in C_6D_6 decreases the rate of H/D exchange at the hydroxide ligand (see above). The addition of 2,6-lutidine to **1** in C_6D_6 also inhibits the rate of H/D exchange at the Tp 4-positions with k_{obs} for the H/D exchange at the Tp 4-positions decreasing linearly with increasing concentrations of 2,6-lutidine (Figure 4). The rate of H/D exchange at the Tp 4-positions in the absence of 2,6-lutidine is approximately 1.5 times more rapid than in the presence of 1 equiv of 2,6-lutidine. High concentrations of 2,6-lutidine (beyond 3 equiv based on **1**) further suppress the rate of H/D exchange; however, at higher concentrations of base, the competitive decomposition of **1** to multiple uncharacterized products complicates detailed kinetic analysis.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) and 1-Methylpyrazole in C_6D_6 .** Heating **1** in C_6D_6 with 1 equiv (based on **1**) of 1-methylpyrazole results in H/D exchange at the hydroxide ligand, the Tp 4-positions and all three C–H bonds of the 1-methylpyrazole ring as determined by ^1H NMR spectroscopy (eq 8). No evidence of H/D exchange at the methyl position of 1-methylpyrazole is observed.

The rates of H/D exchange at the 4-position and 5-position of 1-methylpyrazole are similar with $k_{\text{obs}} = 1.4 \times 10^{-6}$ and $1.7 \times 10^{-6} \text{ s}^{-1}$, respectively. Due to the overlap of the resonance of the 3-position of 1-methylpyrazole with Tp resonances of **1**, the rate of H/D exchange at the 3-position of 1-methylpyrazole cannot be determined in detail (qualitatively, the rate is similar to those observed for the 4- and 5-positions). The rate of H/D exchange at the Tp 4-positions of **1** in the presence of 1-methylpyrazole ($2.6 \times 10^{-6} \text{ s}^{-1}$) is slower compared to the rate in the absence of the 1-methylpyrazole ($5.2(2) \times 10^{-6} \text{ s}^{-1}$). Heating 1-methylpyrazole in neat C_6D_6 or in C_6D_6 with catalytic quantities of AlCl_3 , BF_3 , or CuCl does not result in evidence for H/D exchange between C_6D_6 and 1-methylpyrazole. These results suggest that **1** can activate benzene for intermolecular H/D exchange with external basic (including aromatic) substrates.

Reactions in Nonaromatic Solvents. After 12 h, solutions of the hydroxide complex **1** in CD_2Cl_2 (40°C) or CDCl_3 (room temperature) yield clean formation of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**) (eq 9). Heating **1** to 130°C in $\text{THF-}d_8$ ultimately results in

Figure 5. ORTEP (30% probability) of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**) (note: hydrogen atoms omitted for clarity). Selected bond lengths ($\text{\AA}$): Ru1–N7 2.005(3), Ru1–P1 2.279(1), Ru1–C13 2.060(4), N7–C19 1.127(5), C13–C14 1.401(6), C13–C18 1.411(6). Selected bond angles (deg): Ru1–N7–C19 175.1(4), N7–C19–C20 178.6(5), C13–Ru1–N7 89.4(1), C13–Ru1–P1 92.3(1), N7–Ru1–P1 92.6(1), N7–Ru1–N1 174.7(1).

decomposition. However, prior to complete decomposition, H/D exchange occurs as indicated by an increase in the resonances (^1H NMR) of $\text{THF-}d_8$. The rate of incorporation of hydrogen into THF favors the α -position. Prior to heating, the integration of the residual protons indicates an approximate 1:1 ratio of α – β , and after 6 days of heating, the relative ratio is 1.6:1.0. After 6 days, a total of approximately 2 equiv (based on Ru) of hydrogen are incorporated into the $\text{THF-}d_8$. Heating **1** in $\text{THF-}d_8$ after decomposition is complete (6 days) results in no observed changes in the intensity of the resonances (relative to internal standard) due to the THF solvent after 4 days. These results suggest that **1** initiates H/D exchange at the sp^3 -hybridized carbons of THF but that decomposition of **1** is kinetically competitive with the activation of THF (eq 10).

Preparation and Reactivity of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (10**).** Photolysis of $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**) in NCMe cleanly produces $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**) (eq 11). Complex **10** is

isolated in 75% yield, and ^1H and ^{13}C NMR spectra of **10** are consistent with an asymmetric complex. A solid-state X-ray diffraction study of **10** has confirmed its identity (Figure 5, Table 1). The structure reveals a pseudo-octahedral coordination sphere with a Ru–C(13) (ipso carbon of phenyl ligand) bond distance of 2.060(4) $\text{\AA}$. We have also performed a single-crystal X-ray diffraction study of the previously reported complex TpRu-

Figure 6. ORTEP (30% probability) of $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**) (note: hydrogen atoms omitted for clarity). Selected bond lengths (Å): Ru1–P1 2.2806(7), Ru–P2 2.2962(7), Ru1–C16 2.068(2), C16–C17 1.399(4), C16–C21 1.403(4). Selected bond angles (deg): C16–Ru1–P1 92.12(7), P1–Ru1–P2 100.49(3).

$(\text{PMe}_3)_2\text{Ph}$ (**9**) (Figure 6, Table 1). The structure of **9** is similar to that of **10** with little change in the Ru–C_{phenyl} bond distance. The cyclic voltammogram of **10** reveals a quasi-reversible Ru(IV/III) oxidation wave at 1.38 V and a reversible (if the scan is returned prior to the IV/III oxidation) Ru(III/II) oxidation wave at 0.30 V (versus NHE). In contrast, $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$ exhibits an irreversible Ru(III/II) oxidation at 0.96 V. Thus, **10** is more electron-rich than $\text{TpRu}(\text{CO})(\text{NCMe})\text{Ph}$.

The nitrile ligand of **10** undergoes exchange with NCCD_3 more rapidly than corresponding exchange of trimethylphosphine for **9**. For example, monitoring the disappearance of the resonance (^1H NMR) due to the coordinated nitrile of **10** at 60 °C in NCCD_3 reveals nitrile exchange with $k_{\text{obs}} = 1.4(2) \times 10^{-4} \text{ s}^{-1}$ ($\Delta G^\ddagger = 25.4(1) \text{ kcal/mol}$). In contrast, exchange of PMe_3 for **9** occurs at 80 °C with $k_{\text{obs}} = 4.9(3) \times 10^{-5} \text{ s}^{-1}$ ($\Delta G^\ddagger = 27.8(1) \text{ kcal/mol}$). Heating **10** to 60 °C in C_6D_6 results in H/D exchange at the phenyl ligand, H/D exchange at *all three positions of the pyrazolyl rings*, and the production of protio benzene. The rates of exchange at all three 4-positions are more rapid than the H/D exchanges at the Tp 3/5-positions. In the subset of H/D exchange reactions at the Tp 4-positions and 3/5-positions, the rates of exchange are not identical, and the minor differences are likely due to an electronic effect of the ligands trans to each pyrazolyl ring. The resonance due to the 4-position of the pyrazolyl ring trans to the PMe_3 ligand can be readily identified due to long-range coupling between the hydrogen and phosphine ligand (6.10 ppm, dt with $^5J_{\text{HP}} = 1 \text{ Hz}$). At 60 °C, this position undergoes H/D exchange less rapidly than those trans to NCMe and phenyl ligands ($k_{\text{obs}} = 7.5(5) \times 10^{-6} \text{ s}^{-1}$ versus $k_{\text{obs}} = 9.2(5) \times 10^{-6} \text{ s}^{-1}$ for the average of the pyrazolyl rings cis to PMe_3).

Incorporation of deuterium at the phenyl ligand was followed by monitoring the decrease of the resonance at 7.45 ppm due to the ortho position of phenyl ligand of **10** ($k_{\text{obs}} = 5.9(8) \times 10^{-5} \text{ s}^{-1}$ at 60 °C). Exchange of H/D can also be observed by monitoring the meta and para phenyl resonances. ^2H NMR of the product reveals resonances consistent with a phenyl- d_5 ligand of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph-}d_5$. Furthermore, heating $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph-}d_5$ in C_6H_6 and acquisition of ^2H NMR of the product reveals the disappearance of these resonances. We

Scheme 3. Likely Pathway for H/D Exchange at the Phenyl Ligand of $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**)

Table 4. $\Delta G^\ddagger$ Values (kcal/mol) of the H/D Exchange Reactions for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ and $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**)^a

X	exchange	solvent	T (°C)	$\Delta G^\ddagger$
OH (1)	OH(D)	C_6D_6	80	27.4(1)
OH (1)	OH(D)	$\text{C}_6\text{D}_5\text{CD}_3$	80	28.4(1)
OH (1)	Tp	C_6D_6	90	30.2(1)
OH (1)	Tp	$\text{C}_6\text{D}_5\text{CD}_3$	90	31.3(2)
NHPh (2)	NH(D)Ph	C_6D_6	130	32.8(1)
NHPh (2)	Tp	C_6D_6	130	33.5(1)
OPh (5)	Tp	C_6D_6	130	34.6(1)
Me (8)	Tp	C_6D_6	130	33.0(1)
Me (8)	Tp	$\text{C}_6\text{D}_5\text{CD}_3$	130	33.7(1)
Ph (9)	Tp	C_6D_6	130	32.5(2)
Ph (10)	Tp-4 trans	C_6D_6	60	28.9(1)
Ph (10)	Tp-4 cis	C_6D_6	60	27.2(1)
Ph (10)	phenyl	C_6D_6	60	26.0(1)

^a Tp-4 trans refers to pyrazolyl ring trans to PMe_3 ; Tp-4 cis refers to the average of pyrazolyl rings cis to PMe_3 .

presume that H/D exchange at the phenyl ligand occurs through C–D activation of C_6D_6 (Scheme 3).

Mechanism of H/D Exchange. For the series of complexes $\text{TpRu}(\text{PMe}_3)_2\text{X}$, two distinct H/D exchange processes have been observed. For X = OH, NHPh, Me, Ph, or OPh, extended thermolysis results in regioselective H/D exchange at the Tp 4-positions. When X = OH or NHPh, H/D exchange occurs between the deuterated arene solvent and the nondative ligand X. For both of these systems, the H/D exchange at the nondative ligand occurs more rapidly than the Tp 4-position H/D exchange. The lack of H/D exchange at the amine ligand of $[\text{TpRu}(\text{PMe}_3)_2\text{NH}_2\text{Ph}][\text{OTf}]$ is consistent with the basicity of the nondative ligand (i.e., presence of a lone pair) playing a role in the H/D exchange at the hydroxide and anilido moieties.

Table 4 shows $\Delta G^\ddagger$ values for all of the H/D exchange reactions. These results raise two important questions: (1) what is the likely mechanism for the H/D exchange processes and (2) what is the explanation for the different predilections toward H/D exchange for the closely related series of systems $\text{TpRu}(\text{PMe}_3)_2\text{X}$?

Scheme 4 depicts a pathway for the reaction of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ with C_6D_6 that accounts for the experimental observations. Dissociation of a phosphine ligand provides an open coordination site to bind and activate benzene. Consistent with the requirement of an open coordination site to observe H/D exchange, the addition of excess PMe_3 suppresses both H/D exchange reactions. It is proposed that Ru activates the benzene toward net transfer of D^+ . There are no reliable experimental data to suggest the nature of the interaction between Ru and

Scheme 4. Proposed Pathway for H/D Exchange at the Tp 4-positions and Nondative Ligand (When $\text{X} = \text{NHPH}$ or OH) for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}$, NHPH , Me , Ph , or OPh)

the C–D bond being broken; however, DFT studies suggest that activation of benzene C–H bonds by fragments of the type $\text{TpRu}(\text{L})(\text{X})$ ($\text{X} = \text{alkyl}$ or hydroxide) may occur by a σ -bond metathesis (or oxidative hydrogen migration, see below).^{16,21,39} If the ligand X possesses a lone pair (e.g., $\text{X} = \text{OH}$ or NHPH), the *intramolecular* transfer of D^+ to the nondative ligand occurs rapidly relative to intermolecular transfer of D^+ . Alternatively, the generation of D^+ can result in the intermolecular transfer to a basic site such as a pyrazolyl moiety of another Ru complex or 1-methylpyrazole. For experiments incorporating **1**, the addition of noncoordinating 2,6-lutidine sequesters D^+ in competition with transfer to the hydroxide ligand and a pyrazolyl fragment and decreases the rate of deuterium transfer to hydroxide ligand or pyrazolyl. The failure of $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (**3**) to initiate H/D exchange at the sulfido ligand or the Tp 4-positions is consistent with *both processes* (i.e., intra- and intermolecular transfer of deuterium) *having a similar origin* (i.e., *Ru-mediated activation of the deuterated arene*). For the H/D exchange at the Tp 4-positions, the rate-determining step likely precedes D^+ addition of the pyrazolyl because reaction rates are first order in the ruthenium complex.

For the proposed pathway to be viable, the net 1,2-addition of C–H across Ru–OH or Ru–NHPH bonds must be thermodynamically disfavored because products of the type $\text{TpRu}(\text{PMe}_3)(\text{Ph})(\text{XH})$ ($\text{X} = \text{OH}$ or NHPH) and $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**) are not observed. Previously reported computational studies for the addition of a C–H bond of benzene across the Ru–OH bond of **1** are consistent with this suggestion.²¹ As anticipated on the basis of our mechanistic hypothesis, heating a mixture of $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**) and aniline in C_6D_6 (130 °C) initially results in conversion to $\text{TpRu}(\text{PMe}_3)_2\text{NHPH}$ (**2**) and benzene (eq 12); however, after this, extended heating decomposition begins to compete with the conversion and complicates a detailed analysis of the equilibrium.

Transformations involving the Tp 4-positions of the parent Tp ligand are relatively rare; however, free pyrazole is susceptible to electrophilic attack at the 3, 4, and 5-positions

Table 5. Results of Cyclic Voltammetry for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{NHPH}$, OH , OPh , SH , Me , Ph , Cl , OTf)

$\text{TpRu}(\text{PMe}_3)_2\text{X}$ complexes	$E_{1/2} \text{ Ru(III/II)} \text{ (V)}$
$\text{TpRu}(\text{PMe}_3)_2\text{NHPH}$ (2)	−0.32
$\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1)	0.01
$\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (3)	0.10
$\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (5)	0.21
$\text{TpRu}(\text{PMe}_3)_2\text{Me}$ (8)	0.23
$\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (9)	0.35
$\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (7)	0.64
$\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (4)	1.00

with addition at the 4-position typically favored kinetically.⁵¹ Thus, the regioselective H/D exchange at the Tp 4-positions is consistent with the generation of D^+ whereas the lack of regioselectivity for H/D exchange between C_6D_6 and 1-methylpyrazole is more difficult to rationalize. However, for the more active system $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**), H/D exchange is observed at all three pyrazolyl positions (3, 4, and 5) with variable rates suggesting that $\Delta\Delta G^\ddagger$'s are less pronounced for the more active Ru system.

Given the similarity of the complexes $\text{TpRu}(\text{PMe}_3)_2\text{X}$, it is intriguing that for systems with $\text{X} = \text{Cl}$ (**7**), OTf (**4**), or SH (**3**), H/D exchange at the Tp 4-positions (at temperatures up to 130 °C) is not observed. Likewise, H/D exchange is not observed at the hydrosulfido ligand of **3**. Given the impact of electron density on the predilection of metal centers to activate C–H bonds, we compared the Ru(III/II) potentials (see Table 5) with propensity toward H/D exchange. It was initially compelling that two of the systems that do not undergo H/D exchange, **7** and **4**, possess the most positive redox potentials; however, **3** is substantially more “electron-rich” and does not initiate H/D exchange. Although metal-based electron density may be important for coordination of the arene and/or activation of the C–H(D) bond toward transfer, it is not likely a “deciding factor” in whether the transformation is observed with a particular $\text{TpRu}(\text{PMe}_3)_2\text{X}$ system.

We also compared the rate of PMe_3 exchange (see Table 3) with the ability to initiate H/D exchange at the Tp 4-positions. It is perhaps noteworthy that **7** and **3** exhibit the slowest rate of PMe_3 exchange, which supports the notion that the H/D exchange is likely a metal-mediated process that requires an open coordination site. Furthermore, if data for **5** are omitted, a plot of $\Delta G^\ddagger$ versus rate of PMe_3 exchange gives a good linear

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Figure 7. Plot of $\Delta G^\ddagger$ for H/D exchange at the Tp 4-positions (at variable temperatures) versus k_{obs} for PMe_3 exchange for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ for $\text{X} = \text{OH}$, NHPh , Me , and Ph .

fit ($R^2 = 0.96$, Figure 7). There is no theoretical reason this plot should give a good fit because factors other than rate of PMe_3 dissociation certainly influence activation barriers. For example, data for **5** do not correlate well with the trend; however, the plot in Figure 7 is consistent with the suggestion that rate of PMe_3 dissociation is a substantial determinant in the rate of H/D exchange. Thus, we propose that the H/D exchange reactions are dependent on generation of the 16-electron systems $\{\text{TpRu}(\text{PMe}_3)\text{X}\}$ and subsequent coordination of C_6D_6 to yield $\text{TpRu}(\text{PMe}_3)(\eta^2\text{-C}_6\text{D}_6)\text{X}$ whereas other factors can impact the rate of the reaction including the rate of benzene coordination, strength of the bond with benzene, and activation barrier for the C–H bond breaking step. The latter factor is also likely to depend on several factors including metal-electron density and basicity of ligand “X”. Thus, although dissociation is likely required for C–H(D) activation to occur, other factors can dictate the overall activation barriers for the net reactions. For **3** and **7**, the slow rate of PMe_3 exchange suggests that formation of $\text{TpRu}(\text{PMe}_3)(\eta^2\text{-C}_6\text{D}_6)\text{X}$ is likely suppressed relative to systems where $\text{X} = \text{OH}$, NHPh , OPh , Me , or Ph , and hence C–H(D) activation is not accessed under conditions studied herein. Consistent with this proposal, $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**), which provides more rapid access to $\{\text{TpRu}(\text{PMe}_3)(\text{Ph})\}$ than does $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**), initiates H/D exchange more rapidly.

Comparison of C–H(D) Bond Cleavage with Related Ru(II) and Fe(II) Amido Complexes. Bergman et al. have accessed a series of octahedral Ru(II) and Fe(II) complexes that possess highly basic parent amido ligands. The basicity of these systems has allowed observation of heterolytic cleavage of relatively acidic C–H bonds such as phenylacetylene, fluorene, 1,4-cyclohexadiene, and the benzylic position of toluene.^{33,52–54} We have demonstrated similar reactivity for some $\text{TpRu}(\text{II})$ complexes.^{18,19,22} Experimental studies provide evidence that reactions of these complexes with C–H bonds involve *heterolytic* C–H bond cleavage (i.e., acid/base reactions) and that the C–H bond may not interact with the metal center (i.e., the C–H bond cleavage is an intermolecular process). For example, *trans*-(*dmpe*)₂Fe(H)(NH₂) (*dmpe* = 1,2-bis(dimethylphosphino)ethane) reacts with fluorene to produce an Fe(II) ammonium cation via deprotonation of the fluorene methylene group.^{22,54} Similarly, $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ (**6**) reacts with phenylacetylene to produce the directly observable (¹H NMR spectroscopy) ion pair $[\text{TpRu}(\text{PMe}_3)_2\text{NH}_3][\text{PhC}_2^-]$, and *trans*-(*dmpe*)₂Ru(H)(NH₂) reacts with Ph_3CH to form an equilibrium with $[\text{trans}-(\text{dmpe})_2\text{Ru}(\text{H})-$

Scheme 5. Comparison of Pathways for Cleavage of C–H Bonds by Late Transition Metal Complexes that Possess Nondative Heteroatomic Ligands ($\text{X} = \text{Nondative Ligand}$)

Intermolecular Heterocyclic C–H Cleavage

Intermolecular Hydrogen Atom Abstraction

Intramolecular 1,2-Addition of C–H Bond

(NH₃)] $[\text{Ph}_3\text{C}]$.^{19,22,33} We propose that these transformations are mechanistically distinct from the reactivity of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ systems reported herein (Scheme 5). A key piece of evidence involves observed reactivity with toluene-*d*₈. Although *trans*-(*dmpe*)₂Ru(H)(NH₂) reacts with toluene-*d*₈ to initiate regioselective H/D exchange at the benzylic position only (the most acidic site),³³ $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}$ or NHPh) systems react with toluene-*d*₈ to initiate H/D exchange at all four positions of toluene. Thus, we suggest that a distinguishing and important comparative feature of these reactions is whether the metal center coordinates and activates the C–H(D) bond (i.e., intramolecular 1,2-addition) or, alternatively, an intermolecular heterolytic bond cleavage occurs (Scheme 5). The two pathways will exhibit distinct selectivities and activities for different classes of C–H bonds. The proposed net 1,2-additions of C–H bonds shown in Scheme 4 are also mechanistically distinct from hydrogen atom abstraction reactions by nondative heteroatomic ligands of late transition metal systems in relatively high oxidation states (Scheme 5),^{44–46} because the latter transformations do not likely involve direct interaction of the C–H bond with the metal center (i.e., they are intermolecular in the C–H activation step) and involve single-electron reduction of the metal center.

Nature of the C–H Activation Step. The three mechanisms that generally dominate discussions of the mechanism of C–H activation are oxidative addition, σ -bond metathesis, and electrophilic substitution. The division between these processes is often unclear, as highlighted by Goddard et al.’s recent description of oxidative hydrogen migration pathway as a variant of σ -bond metathesis.^{55,56} Furthermore, it has been demonstrated that metal coordination can impart acidic character to C–H bonds and activate them toward net deprotonation.^{57,58} Thus, given that σ -bond metathesis type C–H activation and electrophilic substitution type pathways can both impart acidic character to the hydrogen being activated, it can be difficult to definitively differentiate the two mechanisms (i.e., σ -bond metathesis and electrophilic substitution) by experiment. In analogy, coordination of dihydrogen to transition metal systems often enhances acidity by several orders of magnitude.⁵⁹

Consistent with the notion that, for the Ru systems reported herein, the activated C–H(D) bond has acidic character,

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Figure 8. Calculated transition state for benzene C–H activation by $(\text{Tab})\text{Ru}(\text{PH}_3)(\text{OH})$ viewed along Ru–P axis and approximately normal to the four-centered active site with Tab and PH_3 ligands reduced to wire frame for clarity. Numbers in brackets and italics are computed values for corresponding transition state for benzene C–H activation by $(\text{Tab})\text{Ru}(\text{CO})(\text{Me})$.¹⁶

increasing the basicity of the ligand X of $\{\text{TpRu}(\text{PMe}_3)\text{X}\}$ fragments appears to reduce the barrier to net 1,2-addition of C–H(D) bonds across the Ru–X bond. For example, for $\text{TpRu}(\text{PMe}_3)_2\text{R}$ ($\text{R} = \text{Me}$ or Ph) systems in which “R” lacks a lone pair, the 1,2-addition of C–D bonds of C_6D_6 across the Ru–R bond is much slower than the rate of intermolecular transfer of D^+ to a pyrazolyl fragment. This is indicated by the lack of deuterium incorporation into the methyl and phenyl ligands of **8** and **9**, respectively, as well as the failure to produce CH_3D or $\text{C}_6\text{H}_5\text{D}$ on the time scale of intermolecular D^+ transfer to pyrazolyl rings. In contrast, for $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}$ or NHPH), the transfer of D^+ from C_6D_6 to the nondative ligand occurs *more rapidly than intermolecular transfer to a pyrazolyl group*. Given their highly basic nature,^{19,24} *the present results suggest the possibility that C–H activation events mediated by nondative, heteroatom-based ligands coordinated to late transition metals in low oxidation states possess inherently lower activation barriers than similar reactions with metal–alkyl or –aryl bonds*. The overall high activation barriers to H/D exchange at the hydroxide and amido ligands of **1** and **2** are almost certainly due to the competition for coordination to ruthenium between arene substrates and strongly coordinating PMe_3 , and systems with more labile ligands may allow access to facile C–H activation of inert substrates. Consistent with this notion, access to $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**) decreases the barrier to all H/D exchange processes, and Ru(II) hydroxide and amido complexes with more labile ligand sets will test this hypothesis.

In a preliminary report,²¹ we disclosed calculated energetics for benzene C–H activation by $(\text{Tab})\text{Ru}(\text{PH}_3)_2\text{OH}$ (Tab = tris-(azo)borate as a model for the full Tp ligand). The calculated free energy of activation for the conversion of $(\text{Tab})\text{Ru}(\text{PH}_3)(\text{OH})(\eta^2\text{-C}_6\text{H}_6)$ to the C–H activation product $(\text{Tab})\text{Ru}(\text{PH}_3)(\text{OH}_2)(\text{Ph})$ is 17.6 kcal/mol. The transition state is depicted in Figure 8. We have also previously reported calculations at the same level of density functional theory on benzene C–H activation from $(\text{Tab})\text{Ru}(\text{CO})(\text{Me})(\eta^2\text{-C}_6\text{H}_6)$ that indicate a non-oxidative addition process that resembles a σ -bond metathesis transition state with a close Ru–H contact in the transition state.¹⁶ As a point of comparison, the values in brackets in Figure 8 represent the geometric details of the transition state of C–H activation for $(\text{Tab})\text{Ru}(\text{CO})(\text{Me})(\eta^2\text{-C}_6\text{H}_6)$ (i.e., transfer of a

hydrogen from $\eta^2\text{-C}_6\text{H}_6$ to the methyl ligand). For the transition state starting from $(\text{Tab})\text{Ru}(\text{PH}_3)(\text{OH})(\eta^2\text{-C}_6\text{H}_6)$ and the corresponding portion of the four-centered active site, there are differences in the metric data compared with $(\text{Tab})\text{Ru}(\text{CO})(\text{Me})(\eta^2\text{-C}_6\text{H}_6)$. The Ru– C_{ipso} distance is approximately 0.1 Å shorter and the $\text{C}_{\text{ipso}}\text{--H}$ distance is greater by a corresponding amount for the Ru–Me versus Ru–OH mediated activation. The thermodynamic driving force for the overall benzene C–H activation is more favorable for the Ru–Me complex ($\Delta G_{\text{rxn}} = -6.6$ kcal/mol) than the Ru–OH complex ($\Delta G_{\text{rxn}} = -4.3$ kcal/mol). Interestingly, the greater thermodynamic driving force for Ru–Me is not reflected in a kinetic advantage for the latter because the calculated $\Delta G_{\text{act}}^{\ddagger} = 17.6$ kcal/mol for the Ru–OH complex is less than the calculated $\Delta G_{\text{act}}^{\ddagger} = 21.2$ kcal/mol for the Ru–Me system, a difference that might result from the substitution of CO/ PH_3 and/or Me/OH. Future studies and calculations are aimed at differentiating these two ligand-based effects. Furthermore, in the two transition states, the Ru–H distance of the transannular hydrogen for the Ru–Me complex is shorter than the corresponding distance in the transition state for the Ru–OH complex by a substantial 0.3 Å, which suggests that the transition state for benzene C–H activation by $(\text{Tab})\text{Ru}(\text{PH}_3)(\text{OH})$ may possess less oxidative character than $(\text{Tab})\text{Ru}(\text{CO})(\text{Me})$. Differentiation between σ -bond metathesis and oxidative hydrogen migration on the basis of the absence or presence, respectively, of metal–hydrogen interaction in the transition state has been made.^{55,56} In light of this model for C–H activation transition states, the Ru–OH complex would seem closer to the σ -bond metathesis paradigm. Thus, *with available experimental and computational data*, we propose that the C–H(D) activation steps for $\{\text{TpRu}(\text{PMe}_3)\text{X}\}$ systems involve coordination of the C–H(D) bond to the metal center followed by a net heterolytic cleavage in a process that resembles σ -bond metathesis. For $\{\text{TpRu}(\text{L})\text{X}\}$ systems, the nature of the transition state (e.g., the extent to which the metal interacts with the transannular hydrogen, the extent of C–H bond breaking and X–H bond forming, and the extent of acidic/heterolytic character) likely depends intimately on the identity of L and X.

Summary

Experimental evidence suggests that the H/D exchange reactions occur through Ru-mediated activation of arene C–D bonds. Importantly, these results suggest that net 1,2-addition of C–H bonds across late transition metal oxygen or nitrogen nondative bonds is kinetically accessible and, for the Ru systems reported herein, is more rapid than analogous reactions with alkyl or aryl ligands. Activation barriers are likely dependent on the ability of the metal center to coordinate the hydrocarbon (herein, an arene), ability of the metal center to activate the C–H bond, *as well as the basicity of the nondative ligand*. However, the extent to which each of the various factors (e.g., metal electron density, facility with which 16-electron species are accessed, basicity of nondative ligand) impact the activation barriers for 1,2-addition of C–H bonds of late transition metal centers remains to be delineated in more detail.

There appears to be a subtle thermodynamic balance for the conversion of late transition metal nondative oxygen or nitrogen ligands and inert and covalent C–H or H–H bonds to M–R ($\text{R} = \text{H}$, alkyl, or aryl) bonds and alcohols or amines (Scheme 6). For example, a combined experimental and computational

Scheme 6. Some Examples of Equilibrium between Complexes with Nondative Ligands and Aryl or Hydride Ligands Determined by Experimental and/or Computational Studies

study suggests that the addition of H_2 across the Ru–N bond of $(PCP)Ru(CO)(NH_2)$ ($PCP = 2,6-(CH_2tBu)_2C_6H_3$) is thermally favorable, whereas the addition of a C–H bond of methane or benzene is disfavored.²⁰ Results herein suggest that addition of arene C–H bonds across Ru^{II} –OH or Ru^{II} –NHP ϕ moieties is thermally disfavored, whereas Periana et al. report that the reaction of benzene and an Ir^{III} –OMe complex to produce MeOH and Ir^{III} –Ph is favorable.³⁹ In a related result, Goldman, Hartwig et al. have reported that $K_{eq} = 105$ for the equilibrium between $(PCP)Ir(H)(Ph)/NH_2Ph$ and $(PCP)Ir(H)(NHP\phi)/C_6H_6$.⁶⁰

Experimental Section

General Methods. All procedures were performed under an inert atmosphere in either a nitrogen-filled glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer $\{O_2(g) < 15 \text{ ppm for all reactions}\}$. Toluene and hexanes were purified by reflux over sodium followed by distillation. Diethyl ether was purged with nitrogen and stored over 4 Å molecular sieves. Acetonitrile was purified by passage through a column of activated alumina followed by distillation from CaH_2 . Deuterated NMR solvents were degassed by three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. 1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz or a Varian Mercury 300 MHz spectrometer. Resonances due to the Tp ligand are listed by chemical shift and multiplicity only (all coupling constants for pyrazolyl rings are approximately 2 Hz). All 1H and ^{13}C NMR spectra were referenced against tetramethylsilane using resonances due to the residual protons in the deuterated solvents or the ^{13}C resonances of the deuterated solvents. 2H NMR spectra were recorded on a Varian 600 MHz INOVA spectrometer and referenced against TMS using the residual deuterium in perprotio benzene. ^{31}P NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer (operating frequency 161 MHz) and referenced against external 85% H_3PO_4 . Unless otherwise noted, NMR spectra were acquired at room temperature. Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in CH_3CN using a standard three-electrode cell from -2.00 to $+2.00$ V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. Tetrabutylammonium hexafluorophosphate was dried under dynamic vacuum at $110^\circ C$ for 48 h prior to use. All potentials are reported versus NHE (normal hydrogen electrode) using ferrocene or cobalto-

cenium hexafluorophosphate as the internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc. Unless otherwise noted, all other reagents were used as purchased from commercial sources. $TpRu(PMe_3)_2Cl$ (**7**), $TpRu(PMe_3)_2OTf$ (**4**), $TpRu(PMe_3)_2OH$ (**1**), $TpRu(PMe_3)_2Me$ (**8**), $TpRu(PMe_3)_2Ph$ (**9**), and $TpRu(PMe_3)_2NHP\phi$ (**2**) were prepared as previously reported.^{18,21,22} Some experimental efforts for $TpRu(PMe_3)_2OH$ (**1**) have been previously described.²¹ Details of computational studies of benzene C–H activation by $(Tab)Ru(PH_3)_2OH$ have been reported.²¹

$TpRu(PMe_3)_2SH$ (3**).** A mixture of **4** (0.48 g, 0.78 mmol) and $NaSH \cdot xH_2O$ (0.48 g, 9.62 mmol) was refluxed in approximately 40 mL of toluene for 24 h. The solution was subsequently cooled to room temperature and filtered through Celite. The filtrate was concentrated under reduced pressure to approximately 5 mL. Hexanes (20 mL) were slowly added to yield a precipitate. The resulting yellow solid was isolated and dried in vacuo (0.23 g, 57% yield). 1H NMR (C_6D_6 , δ): 8.21, 7.59, 7.50, 7.29 (6H, 2:1:2:1 integration, each a d, Tp CH 3 or 5), 5.96, 5.94 (3H, 2:1 integration, each a t, Tp CH 4), 1.13 (18H, vt, $N = 8$ Hz, $P(CH_3)_3$), -3.30 (1H, t, $^2J_{PH} = 4$ Hz, SH). $^{13}C\{^1H\}$ NMR (C_6D_6 , δ): 145.0, 144.4, 136.0, 135.1 (each a s, Tp 3 or 5 position), 105.5 (s, overlapping Tp 4 positions), 19.4 (vt, $N = 28$ Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (benzene- d_6 , δ): 13.2 (s, PMe_3). CV (CH_3CN , TBAH, 100 mV/s): $E_{1/2} = 0.10$ V $\{Ru(III/II)\}$. Anal. Calcd for $C_{16}H_{29}BN_6P_2SRu$: C, 36.08; H, 5.85; N, 16.83; Found: C, 36.53; H, 5.83; N, 16.41.

$TpRu(PMe_3)_2OPh$ (5**).** A mixture of **4** (0.50 g, 0.81 mmol) and $NaOPh \cdot 3H_2O$ (0.52 g, 3.1 mmol) was refluxed in approximately 40 mL of toluene for 24 h. The solution was subsequently allowed to cool to room temperature and was filtered through Celite. The filtrate was concentrated under reduced pressure to approximately 15 mL. Hexanes (40 mL) were added, and a yellow-green precipitate formed. The resulting mixture was filtered, and the solid was washed with hexane and diethyl ether. The product was isolated and dried in vacuo (0.38 g, 83% yield). 1H NMR ($CDCl_3$, δ): 7.73, 7.70, 7.60, 7.20 (6H, 2:1:2:1 integration, each a d, Tp CH 3 or 5), 6.72 (2H, t, $^3J_{HH} = 7$ Hz, phenyl meta), 6.16 (1H, t, $^3J_{HH} = 7$ Hz, phenyl para), 6.10, 6.08 (3H, 2:1 integration, each a t, Tp CH 4), 5.80 (2H, d, $^3J_{HH} = 7$ Hz, phenyl ortho), 1.30 (18H, vt, $N = 10$ Hz, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 171.8 (s, phenyl ipso), 145.8, 142.6, 136.1, 135.2 (each a s, Tp 3 or 5 position), 128.1, 120.8, 110.3 (each a s, phenyl ortho, meta, and para), 105.5, 105.4 (each a s, Tp 4 position), 17.6 (vt, $N = 26$ Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (benzene- d_6 , δ): 19.9 (s, PMe_3). CV (CH_3CN , TBAH, 100 mV/s): $E_{1/2} = 0.21$ V $\{Ru(III/II)\}$. Anal. Calcd for $C_{21}H_{33}BN_6OP_2Ru$: C, 45.09; H, 5.95; N, 15.02; Found: C, 45.06, H, 5.99; N, 14.86.

$TpRu(PMe_3)(NCMe)Ph$ (10**).** $TpRu(PMe_3)_2Ph$ (**9**) (0.498 g, 0.92 mmol) was added to acetonitrile (~ 90 mL) in a 100 mL thick-walled

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pressure tube with a Teflon stopper to give a light-yellow heterogeneous solution. The mixture was irradiated with UV-vis light, generated by a 450W power supply (Mode #17830, Ace Glass, Inc.) equipped with a water-cooled 450W 5 inch arc IMMER UV-vis lamp (Model #7825-34, Ace Glass, Inc.), while stirring for a total of 38 h. The solution was concentrated to ~5 mL under reduced pressure to produce a white precipitate. Approximately 40 mL of methanol was added to the slurry to produce additional precipitate. The precipitate was collected on a fine porosity frit and dried in vacuo (0.348 g, 0.64 mmol, 75%). ^1H NMR (C_6D_6 , δ): 7.69, 7.62 (1H and each a dd, $^4J_{\text{CH}} = 1$ Hz, Tp 3 or 5 position), 7.59 (1H, ddd, $^4J_{\text{CH}} \approx J_{\text{HP}} = 1$ Hz, Tp 3 or 5 position), 7.53 (1H, d, Tp 3 or 5 position), 7.45 (2H, d, $^3J_{\text{HH}} = 8$ Hz, ortho phenyl), 7.34 (1H, d, Tp 3 or 5 position), 7.32 (1H, d, Tp 3 or 5 position), 7.27 (2H, t, $^3J_{\text{HH}} = 8$ Hz, meta phenyl), 7.20 (1H, tt, $^3J_{\text{HH}} = 8$ Hz, $^5J_{\text{HH}} = 1$ Hz, para phenyl), 6.15 (1H, t, Tp 4 position), 6.01 (1H, dt, $^5J_{\text{HP}} = 1$ Hz, Tp 4 position), 5.94 (1H, t, Tp 4 position), 1.07 (9H, d, $^2J_{\text{HP}} = 6$ Hz, $\text{P}(\text{CH}_3)_3$), 0.75 (3H, s, NCCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 177.4 (d, $^2J_{\text{CP}} = 13$ Hz, ipso carbon of phenyl), 144.9, 142.7, 142.5, 141.6, 135.1, 134.5, 133.7 (Tp 3 and 5 positions and phenyl resonance), 125.2, 119.4, 118.4 (phenyl and NCMe), 105.3, 105.0, 104.9 (Tp 4 positions), 16.4 (d, $\text{P}(\text{CH}_3)_3$, $^1J_{\text{CP}} = 26$ Hz), 2.2 (NCCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , δ): 21.7 ($\text{P}(\text{CH}_3)_3$). CV (CH_3CN , TBAH, 100 mV/s): $E_{1/2} = 0.30$ V {Ru(III/II)}, 1.38 V {Ru(IV/III), quasi-reversible}. Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{BN}_7\text{PRu}$: C, 47.16; H, 5.43; N, 19.26. Found: C, 47.37; H, 5.31; N, 19.29.

[$\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NH}_2\text{Ph})\text{[OTf]}$]. [$\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NH}_2\text{Ph})\text{[OTf]}$] was prepared following a previously reported procedure for [$\text{TpRu}(\text{PMe}_3)_2(\text{NH}_2\text{Ph})\text{[OTf]}$] except that isotopically labeled ^{15}N -aniline was used.¹⁸ ^1H NMR spectroscopy (CD_3CN) confirmed the identity of the product with resonances identical to [$\text{TpRu}(\text{PMe}_3)_2(\text{NH}_2\text{Ph})\text{[OTf]}$] except for the amine resonance, which is observed as a doublet at 4.77 ppm (2H, d, $^1J_{\text{NH}} = 70$ Hz).

$\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NHPH})$ (2- ^{15}N). $\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NHPH})$ (2- ^{15}N) was prepared following the previously reported procedure for $\text{TpRu}(\text{PMe}_3)_2\text{-NHPH}$ except that [$\text{TpRu}(\text{PMe}_3)_2(^{15}\text{NH}_2\text{Ph})\text{[OTf]}$] was used as the starting material.¹⁸ ^1H NMR (C_6D_6 , δ): 7.68, 7.52, 7.48, 6.90 (6H, 2:1:2:1 integration, each a d, Tp CH 3 or 5), 7.24 (2H, t, $^3J_{\text{HH}} = 7$ Hz, phenyl meta), 6.47 (1H, t, $^3J_{\text{HH}} = 7$ Hz, phenyl para), 6.26 (2H, br, phenyl ortho), 5.90, 5.86 (3H, 2:1 integration, each a t, Tp CH 4), 2.19 (1H, d, $^1J_{\text{NH}} = 69$ Hz, NHPH), 1.30 (18H, vt, $N = 8$ Hz, $\text{P}(\text{CH}_3)_3$).

$\text{TpRu}\{\text{P}(\text{CD}_3)_3\}_2\text{Cl}$ (7- d_{18}). The preparation of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (7) has been reported.²² 7- d_{18} was prepared using an analogous method with $\text{P}(\text{CD}_3)_3$ substituted for PMe_3 . ^1H NMR spectroscopy revealed identical resonances to 7 with the exception that the virtual triplet due to the phosphine ligands is absent.

H/D Exchange Reactions for 1–9. All reactions probing H/D exchange followed the same general procedure. Inside a nitrogen-filled glovebox, a screw-cap NMR tube was charged with a known amount of the appropriate ruthenium complex in C_6D_6 . The NMR tube was sealed, vigorously shaken, and a ^1H NMR spectrum was acquired (for ^1H NMR data acquisition, the delay time was set to 10 s). The solution was heated (90, 130, or 150 °C) in an oil bath. The reaction progress was monitored periodically using ^1H NMR spectroscopy and the change in integration of the resonances due to Tp 4-position as compared to the resonances of the Tp 3- and 5-positions. In control experiments, heating solutions with an internal standard (e.g., C_6Me_6) revealed no substantial change in the integration for the resonances due to Tp 3- or 5-positions relative to the internal standard. Under the various reaction temperatures, with the exception of $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ (6), no evidence of decomposition was observed. For all reactions, the integration of the resonance due to benzene increases, whereas the intensities of resonances due to the Tp 4-positions decrease versus time for 1, 2, 5, 8, and 9. For 8 and 9, there was no evidence of deuterium incorporation into the Me or Ph ligands. Multiple experiments using different batches of complexes revealed consistent k_{obs} for the disappearance of reso-

nances due to the Tp 4-positions. There is no change of the resonances due to the Tp 4-positions for 3, 4, and 7.

H/D Exchange for $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (10) in C_6D_6 . A solution of 10 (7.3 mg, 0.0143 mmol) in 2 mL of C_6D_6 (23 mmol) with a small amount of hexamethylbenzene (as an internal standard) was divided among three screw-cap NMR tubes. A ^1H NMR spectrum was acquired of each reaction mixture with the delay time set to 10 s. The set of NMR tubes were each heated at 60 °C with thermoregulatory control in a Varian Mercury 400 MHz NMR. ^1H NMR spectra recorded every 10 min and compiled into an array until 3 half-lives were achieved (~12 h). H/D exchange was followed by integration of the phenyl resonance of 10 (7.45 ppm) relative to the internal standard hexamethylbenzene.

Catalytic H/D Exchange between C_6D_6 and H_2O . In a typical experiment, a J. Young NMR tube was charged with $\text{TpRu}(\text{PMe}_3)_2\text{-}(\text{OH})$ (1) (0.030 g, 0.062 mmol) in benzene- d_6 (0.35 mL, 3.8 mmol) and 10 equiv (based on 1) of degassed H_2O (11 μL , 0.62 mmol). The tube was sealed, vigorously shaken, and heated to 100 °C. The reaction progress was monitored periodically using ^1H NMR spectroscopy by following the increase in integration of the resonance due to benzene (7.16 ppm) as compared to the resonances of Tp 3 and 5 positions. Heating 1 at 100 °C for up to 7 days yields no evidence of decomposition. The intensity of the benzene resonance increases, whereas intensity of OH resonance decreases versus time. *The decrease in integration for the hydroxide resonance equals the magnitude of increase in the integration for the benzene resonance.*

A plot of TON (turnover number, TON is defined as one mole of hydrogen incorporated into benzene per mole of ruthenium complex 1) versus time is nearly linear and reproducible using different batches of 1. Samples plots have been previously reported.²¹ After 172 h of reaction, a total of 10 TONs is observed.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (9) with Aniline in C_6D_6 . Three screw-cap NMR tubes were each charged with 0.025 g of 9 (0.046 mmol) and 0.5 mL of C_6D_6 (7 mmol). To each solution was added 6 equiv of aniline (based on 9) using a microsyringe (25 μL , 0.276 mmol). All the solutions were heated to 130 °C and periodically monitored by ^1H NMR spectroscopy. The formation of $\text{TpRu}(\text{PMe}_3)_2\text{NHPH}$ (2) was initially observed except for the resonances at Tp 4-positions. The resonances due to Tp 4-positions of $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ disappear due to H/D exchange. The formation of benzene was confirmed by the increase of the benzene resonance at 7.16 ppm. Ultimately, decomposition is competitive with the conversion of 9 to 2, and K_{eq} could not be determined.

Reaction of [$\text{TpRu}(\text{PMe}_3)_2\text{NH}_2\text{Ph}\text{[OTf]}$] in C_6D_6 . A screw-cap NMR tube was charged with [$\text{TpRu}(\text{PMe}_3)_2\text{NH}_2\text{Ph}\text{[OTf]}$] (0.023 g) and C_6D_6 (0.5 mL). The NMR tube was sealed, vigorously shaken, and heated to 130 °C in an oil bath. The reaction progress was monitored periodically using ^1H NMR spectroscopy. An equilibrium between [$\text{TpRu}(\text{PMe}_3)_2\text{NH}_2\text{Ph}\text{[OTf]}$] and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ /aniline was observed with $K_{\text{eq}} = 0.11$.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (7) with Added Salts in C_6D_6 . Four screw-cap NMR tubes were each charged with 7 (0.030 g) and C_6D_6 (0.5 mL). To each tube was added 10 mg of a different salt (LiCl , MgCl_2 , NaOTf , or CsCl). The NMR tubes were sealed, vigorously shaken, and heated to 130 °C in an oil bath. The reaction progress was monitored periodically using ^1H NMR spectroscopy. Heating the solutions for 7 days did not provide evidence of decomposition nor H/D exchange.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1) with Added Salts (CsCl , MgCl_2 , or NaOTf) in C_6D_6 . Three screw-cap NMR tubes were each charged with 1 (0.025 g) and C_6D_6 (0.5 mL). To each tube was added 10 mg of a different salt (CsCl , MgCl_2 , or NaOTf). The solutions were sealed, vigorously shaken, and heated to 90 °C in an oil bath. The reaction progress was monitored periodically using ^1H NMR spectroscopy. The addition of CsCl does not alter the rate of H/D exchange at the Tp 4-positions for 1. The addition of MgCl_2 results in the formation of

$\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**), and prolonged heating does not result in H/D exchange at the Tp 4-positions of **7**. $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) reacts with NaOTf to form a new complex that is uncharacterized.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) with Added $\text{P}(\text{CH}_3)_3$ in C_6D_6 .** To a vial containing 0.030 g of **1** (0.062 mmol) was added 0.6 mL of C_6D_6 (7 mmol). To this solution was added 1 equiv of PMe_3 (based on **1**) using a microsyringe ($\sim 6 \mu\text{L}$, 0.06 mmol). The solution was transferred to a J. Young NMR tube and heated to 90 °C. The solution was periodically monitored by ^1H NMR spectroscopy. After 4 days, no evidence of H/D exchange was observed.

Rate of PMe_3 Exchange for $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**), $\text{TpRu}(\text{PMe}_3)_2\text{NHPH}$ (**2**), $\text{TpRu}(\text{PMe}_3)_2\text{SH}$ (**3**), $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (**5**), $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**), $\text{TpRu}(\text{PMe}_3)_2\text{Me}$ (**8**), and $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**).** All reactions followed the same general procedure. To a vial of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{Cl}, \text{SH}, \text{OH}, \text{OPh}, \text{Me}, \text{Ph}, \text{or NHPH}$) (0.062 mmol) was added 0.6 mL of C_6D_6 (7 mmol). To this solution were added 15 equiv of PMe_3 (based on ruthenium complex) using a microsyringe ($96 \mu\text{L}$, 0.93 mmol). The solution was transferred to a J. Young NMR tube, heated to 80 °C, and periodically monitored by ^1H NMR spectroscopy. The rate of disappearance of the resonance due to the PMe_3 ligand of $\text{TpRu}(\text{PMe}_3)_2\text{X}$ was determined by integration of the PMe_3 resonance with the delay time for data acquisition set at 10 s. In addition, the appearance of a resonance consistent with the formation for free PMe_3 was observed. For all systems, multiple experiments using different batches of ruthenium complexes revealed consistent values for k_{obs} .

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) and $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**) in C_6D_6 .** A J. Young NMR tube was charged with **1** (0.025 g, 0.05 mmol) and $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$ (**7**) (0.026 g, 0.05 mmol) in C_6D_6 (0.5 mL, 5 mmol). The solution was heated to 90 °C and periodically monitored by ^1H NMR spectroscopy. Resonances due to **7** were observed separately from resonances due to **1** prior to heating. Heating resulted in the disappearance of Tp 4 resonances for both **7** and **1**.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) in C_6D_6 with 1-Methylpyrazole.** A screw-cap NMR tube was charged with **1** (0.025 g, 0.05 mmol) and 1-methylpyrazole ($\sim 6 \mu\text{L}$, 0.05 mmol) in C_6D_6 (0.5 mL, 5 mmol). The solution was heated to 100 °C and periodically monitored by ^1H NMR spectroscopy. Heating resulted in the disappearance of Tp 4 resonances for **1** and the resonance due to the 4- and 5-positions of 1-methylpyrazole. The resonance due to the 3-position of 1-methylpyrazole also decreases in intensity and eventually cannot be detected; however, overlap of this resonance with the Tp 3- or 5-position protons at approximately 7.6 ppm complicates a detailed kinetic analysis.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) in C_6D_6 with TEMPO.** Two J. Young NMR tubes were each charged with **1** (0.025 g, 0.05 mmol) and C_6D_6 (0.5 mL, 5 mmol). TEMPO (0.016 g, 0.10 mmol) was added to one of these tubes. Both solutions were heated to 90 °C and periodically monitored by ^1H NMR spectroscopy. The reactions occur at the same rate.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) in C_6D_6 with 2,6-Lutidine.** Four J. Young NMR tubes were each charged with **1** (0.025 g, 0.05 mmol)

and C_6D_6 (0.5 mL, 5 mmol). To each solution was added 0, 1 ($\sim 7 \mu\text{L}$, 0.05 mmol), 3 ($\sim 21 \mu\text{L}$, 0.15 mmol), and 6 equiv ($\sim 42 \mu\text{L}$, 0.30 mmol) of 2,6-lutidine. All of the solutions were heated to 100 °C and periodically monitored by ^1H NMR spectroscopy. Adding 2,6-lutidine suppresses the rate of H/D exchange at Tp 4-positions of **1**.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) in CDCl_3 .** A screw-cap NMR tube was charged with $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) (0.025 g) and CDCl_3 (0.5 mL). The NMR tube was sealed and vigorously shaken. After 12 h at room temperature, ^1H NMR spectroscopy revealed quantitative conversion to $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) in CD_2Cl_2 .** A screw-cap NMR tube was charged with $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) (0.025 g) and CD_2Cl_2 (0.5 mL). The NMR tube was sealed and vigorously shaken. After 12 h at 40 °C, ^1H NMR spectroscopy revealed quantitative conversion to $\text{TpRu}(\text{PMe}_3)_2\text{Cl}$.

Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1**) with THF- d_8 .** A screw-cap NMR tube was charged with $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) (0.025 g), THF- d_8 (0.5 mL), and C_6Me_6 as internal standard. The NMR tube was sealed, vigorously shaken, and heated to 130 °C in an oil bath. The reaction progress was monitored periodically using ^1H NMR spectroscopy. Ultimately, the formation of several new uncharacterized ruthenium complexes is observed. Prior to decomposition of **1**, the intensities of the resonances due to protio-THF increased relative to the internal standard.

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (**5**), $\text{TpRu}(\text{PMe}_3)_2\text{Ph}$ (**9**), and $\text{TpRu}(\text{PMe}_3)(\text{NCMe})\text{Ph}$ (**10**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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