Octahedral $[\text{TpRu}(\text{PMe}_3)_2\text{OR}]^{n+}$ Complexes (Tp = hydridotris(pyrazolyl)borate; R = H or Ph; $n = 0$ or 1): Reactions at Ru(II) and Ru(III) Oxidation States with Substrates that Possess Carbon–Hydrogen Bonds

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The Ru(II) complexes $\text{TpRu}(\text{PMe}_3)_2\text{OR}$ (R = H or Ph) react with excess phenylacetylene at elevated temperatures to produce the phenylacetylide complex $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$. Kinetic studies indicate that the reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ and phenylacetylene likely proceeds through a pathway that involves $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ as a catalyst. The reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ with 1,4-cyclohexadiene at elevated temperature forms benzene and $\text{TpRu}(\text{PMe}_3)_2\text{H}$, while $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ does not react with 1,4-cyclohexadiene even after 20 days at 85 °C. The paramagnetic Ru(III) complex $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ is formed upon single-electron oxidation of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ with AgOTf . Reactivity studies suggest that $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ initiates reactions, including hydrogen atom abstraction, with C–H bonds that have bond dissociation energy < 80 kcal/mol. Experimentally, the O–H bond strength of the Ru(II) cation $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ is estimated to be between 82 and 85 kcal/mol, while computational studies yield a BDE of 84 kcal/mol, which are in reasonable agreement with the observed reactivity of $[\text{TpRu}(\text{PMe}_3)_2\text{OH}]^+$.

Introduction

Late transition metal complexes containing alkoxide, hydroxide, and amido ligands play important roles in biological systems and catalytic reactions.^{1–9} In the past several years, efforts directed toward the synthesis of late transition metal systems with nondative heteroatomic ligands have substantially increased the number of such complexes that have been isolated and fully characterized.^{1,2,6,10–16} In low oxidation states, complexes with imido, oxo, amido, alkoxide, hydroxide, and related ligands typically display reactivity consistent with highly basic and/or

nucleophilic nondative heteroatomic ligands, and a series of detailed studies has increased the understanding of the nature of M–O/M–N bonding and its impact on reactivity.^{13,17–38} Transformations of octahedral Fe(II) and Ru(II) amido com-

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plexes, including deprotonation of C–H bonds and nucleophilic N_{amido}–C bond forming reactions, highlight the potential enhancement in reactivity due to relatively low oxidation state metals. The highly basic/nucleophilic ligand character is likely a result of the combination of polar M–O or M–N bonds and the disruption of ligand-to-metal π -donation due to filled d π atomic orbitals.^{18–21,39–51} Our group has been studying the reactivity of amido, alkoxide, aryloxide, and hydroxide moieties coordinated to ruthenium or copper with the goal of understanding and exploiting chemistry accessible when these ligands are bound to high d-electron count metal centers.^{8,18–21,47–50,52,53}

Late transition metal systems with alkoxide or amido ligands have been shown to cleave C–H bonds. These transformations typically fall into three broad categories: (a) net homolytic hydrogen atom abstraction (i.e., proton-coupled electron transfer, radical/odd-electron reaction), (b) heterolytic deprotonation (even-electron transformation), and (c) net 1,2-addition of C–H bonds across M–X bond.^{5,17–19,49,50,54–57,58} The first two processes (i.e., a and b) are *ligand-centered* and thus do not involve direct interaction of the metal with the C–H bond being broken (Scheme 1).

Late transition metal complexes in relatively high oxidation states with nondative heteroatomic ligands have been demonstrated to initiate net hydrogen atom abstraction including reactions with substrates that possess relatively weak C–H bonds.^{5,54–56} The homolytic C–H cleavage (i.e., hydrogen atom abstraction) formally reduces the metal center by one electron (Scheme 1). Thus, the predilection toward this reaction likely

Scheme 1. Two Pathways for Ligand-Centered C–H Bond Cleavage by Late Transition Metal Complexes with Nondative Heteroatomic Ligands^a

^a X = formally anionic N- or O-based ligand such as amido, hydroxide, etc.

depends on the oxidizing ability of the complex and the basicity of the nondative ligand, which reflects the formal transfer of a proton to the nondative ligand and an electron to the metal center. For example, the non-heme iron enzymes lipoygenases catalyze the oxidative conversion of 1,4-diene-containing fatty acids to alkyl hydroperoxides,⁵⁹ and these transformations likely proceed through net hydrogen atom abstraction by an Fe(III) hydroxide fragment from an allylic C–H bond (BDE $\approx$ 77 kcal/mol) to generate allyl radicals that are subsequently trapped by dioxygen.^{60,61} Stack et al. have prepared [Fe^{III}(PY₅)(OMe)]-[OTf]₂ {PY₅ = 2,6-bis(2-pyridyl)methoxymethane}pyridine} as a model for lipoygenase enzymes and have shown that it readily oxidizes cyclohexadiene to benzene and the corresponding Fe^{II}–MeOH complex.^{56,62} Studies of metal-mediated oxidation of C–H bonds by Mayer et al. using a wide range of transition metal complexes have demonstrated the prevalence of hydrogen atom transfer processes.^{58,63} Furthermore, for net hydrogen atom abstraction from C–H bonds, Mayer et al. have applied the Marcus cross relation to estimate rates of hydrogen atom transfer.⁶⁴

In contrast, heterolytic C–H bond cleavage (i.e., C–H deprotonation) depends primarily on ligand basicity since the oxidation state of the metal is not altered as a result of the transformation (Scheme 1). For example, Bergman et al. have reported a series of studies of the reactivity of *trans*-(dmpe)₂Ru-(X)(H) (X = OH or NH₂; dmpe = 1,2-dimethylphosphinoethane) that have revealed the ability of the heteroatomic ligands to break weakly acidic C–H bonds via deprotonation.^{12,17,41,42,65} In addition, our group has reported related reactivity for a series of octahedral ruthenium complexes of the type TpRu(L)(L')-(NHR) (Tp = hydridotris(pyrazolyl)borate; L = L' = P(OMe)₃ or PMe₃ or L = CO and L' = PPh₃; R = H, Ph, or ^tBu).^{18–20} We have also reported that the five-coordinate Ru(II) amido complex (PCP)Ru(CO)(NH₂) {PCP = 2,6-(CH₂^tBu)₂C₆H₃} activates dihydrogen as well as initiating intramolecular C–H activation of a ^tBu moiety of the PCP ligand and that the six-coordinate anilido complex (PCP)Ru(CO)(PMe₃)(NHPh) reacts with polar bonds including substrates that possess C–N and C–O multiple bonds (e.g., nitriles, carbodiimides, or isocyanates) as well as C–F bonds.^{21,47,48} As an extension of our studies focused on the reactivity of nondative heteroatomic ligands coordinated to Ru, we now report on the reactivity of [TpRu-

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Figure 1. Plot of k_{obs} (determined under pseudo-first-order conditions) versus concentration of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (from 0 to 15 mol % of complex **1**) for the conversion of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) (0.04 M) and phenylacetylene (0.4 M) to $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**). The plot of k_{obs} at 0 mol % of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ corresponds to the rate constant in the absence of added $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$.

$(\text{PMe}_3)_2\text{OR}]^{n+}$ complexes at both the Ru(II) ($n = 0$) and Ru(III) ($n = 1$) oxidation states with substrates that possess C–H bonds.

Results and Discussion

Reactivity of $\text{TpRu}(\text{PMe}_3)_2\text{OR}$ ($\text{R} = \text{H}$ or Ph) with Acidic Substrates. We have previously reported the preparation of $\text{TpRu}(\text{PMe}_3)_2\text{OR}$ ($\text{R} = \text{H}$ or Ph).^{49,50} At room temperature, $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) and 10 equiv of phenylacetylene in C_6D_6 do not react after 3 days; however, heating this solution to 80 °C results in the formation of previously reported complex $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**) (eq 1). At 80 °C, the reaction requires about 100 h to achieve quantitative production (by ^1H NMR spectroscopy) of **2**.

Monitoring the reaction by ^1H NMR spectroscopy does not reveal intermediates during the conversion of **1** and phenylacetylene to **2**. Individual kinetic plots are consistent with the transformation being first-order in complex **1**. Similar to reactions of $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ and phenylacetylene,²⁰ the addition of catalytic quantities of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ to the reaction of **1** and phenylacetylene results in an increase in the rate of formation of $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**), and a plot of k_{obs} versus concentration of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ reveals a linear relationship (Figure 1). In addition, the rate of reaction of **1** and phenylacetylene increases with increasing concentration of the alkyne. These results are identical to observations made for the reaction of $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ and phenylacetylene.²⁰ Thus, we propose that the conversion of complex **1** and phenylacetylene to complex **2** in the presence of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ follows a pathway similar to that for the transformation of $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ and phenylacetylene. As previously reported for the conversion of the anilido complex $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$,²⁰ it is likely that $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ coordinates phenylacetylene and forms the vinylidene complex $[\text{TpRu}(\text{PMe}_3)_2(\text{C}=\text{CHPh})]^+$, which is not directly observed during the reaction of **1** and phenylacetylene, and subsequent deprotonation of the vinylidene complex by complex **1** yields complex **2**. The previously determined rate of conversion of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ and phe-

Scheme 2. Proposed Mechanism for the Conversion of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) and Phenylacetylene to $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**) Catalyzed by $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$

nylacetylene to the vinylidene complex is commensurate with its involvement in the conversion of **1** and phenylacetylene to complex **2**.²⁰ Ligand exchange between H_2O and phenylacetylene completes the catalytic conversion (Scheme 2). It is possible that a trace amount of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ exists in bulk samples of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**). The k_{obs} for the conversion of **1** and phenylacetylene to complex **2** in the absence of added $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ fits well on the linear plot of k_{obs} versus the mol % ($R^2 = 0.98$) of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (Figure 1). In contrast to the proposed mechanism for conversion of the Ru(II) hydroxide **1** and phenylacetylene to $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**), we have previously reported that $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ reacts with phenylacetylene at room temperature to generate the ion pair $[\text{TpRu}(\text{PMe}_3)_2(\text{NH}_3)][\text{PhC}_2]$.²⁰ Thus, it is also possible that complex **1** may react with phenylacetylene to form **2** in the absence of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$, which is implicated by the nonzero y-intercept in Figure 1.

The combination of $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ and 10 equiv of phenylacetylene in C_6D_6 does not result in a reaction at room temperature after 3 days; however, similar to complex **1**, at elevated temperature (85 °C) the formation of $\text{TpRu}(\text{PMe}_3)_2(\text{C}\equiv\text{CPh})$ (**2**) and PhOH is quantitative (^1H NMR spectroscopy) after 6 days (eq 1). The conversion of $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ and phenylacetylene to **2** and PhOH is slower than for complex **1**, which is consistent with the complexes $\text{TpRu}(\text{PMe}_3)_2\text{OR}$ ($\text{R} = \text{H}$ or Ph) reacting as Brønsted bases, and their anticipated relative basicities (i.e., $\text{Ru}-\text{OH}$ more basic than $\text{Ru}-\text{OPh}$), for the formation of **2**. Although detailed studies have not been performed, we presume that this reaction is also catalyzed by $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$.

The reaction of complex **1** with 5 equiv of 1,4-cyclohexadiene (1,4-CHD) at 85 °C results in the disappearance of the hydroxide complex (^1H NMR spectroscopy) and formation of the previously reported hydride complex $\text{TpRu}(\text{PMe}_3)_2\text{H}$ and benzene (eq 2).²⁰ In contrast to the reaction of **1** with phenylacetylene, the addition of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ does not increase the rate of this transformation. The ruthenium hydride complex $\text{TpRu}(\text{PMe}_3)_2\text{H}$ was identified on the basis of a triplet at -15.7 ppm ($^2J_{\text{PH}} = 31$ Hz) as well as resonances due to the Tp and PMe_3 ligands. $\text{TpRu}(\text{PMe}_3)_2\text{H}$ is formed in approximately 33% yield (based on complex **1**) after 9 days, as determined by integration of the hydride triplet versus an internal standard, and approximately 1 equiv of benzene is formed per equivalent of Ru hydride. Consistent with mechanistic studies of related reactions with Ru(II) parent amido systems,^{17,20} a possible pathway for

Scheme 3. Proposed Pathway for the Reaction of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) and 1,4-Cyclohexadiene

this reaction is initial deprotonation of the allylic C–H bond of 1,4-CHD to generate a transient cationic ruthenium water complex and cyclohexadienide ion pair (Scheme 3). Subsequent dissociation of water and net hydride abstraction from C_6H_7^- would afford the observed products regardless of specific mechanistic details. Alternatively, a Ru–cyclohexadienyl complex, which undergoes β -hydride elimination to generate $\text{TpRu}(\text{PMe}_3)_2\text{H}$ and benzene, could be involved. For the reaction of **1** with 1,4-CHD, isomerization of 1,4-CHD to 1,3-CHD is also observed, which is in analogy with the reactions of previously reported $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ and *trans*-(DMPE) $_2\text{Ru}(\text{NH}_2)(\text{H})$.^{17,20} However, the isomerization of 1,4-CHD is slow relative to the rate observed for $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$, and the isomerization does not reach equilibrium prior to the consumption of **1**. These observations are also consistent with the reaction pathway shown in Scheme 3.

Similar to observations with hydroxide complex **1**, the reaction of the ruthenium parent amido $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ with 1,4-CHD at 75°C yields $\text{TpRu}(\text{PMe}_3)_2\text{H}$ and benzene in approximately 48% yield after 3 days.²⁰ The addition of PMe_3 to the reaction of $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ and 1,4-CHD does not impact the rate of the reaction, suggesting that the transformation does not involve the formation of coordinatively unsaturated complexes. The slower reaction of complex **1** and 1,4-CHD (9 days, 85°C , 33%) compared with $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$ (3 days, 75°C , 48%) is possibly due to the reduced basicity of the hydroxide ligand versus the parent amido ligand. In contrast, neither the ruthenium phenoxide complex $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ nor the anilido complex $\text{TpRu}(\text{PMe}_3)_2\text{NHPh}$ react with 1,4-CHD. For example, heating $\text{TpRu}(\text{PMe}_3)_2\text{OPh}$ (**3**) with 1,4-CHD in benzene- d_6 at 85°C for 20 days did not result in observable reaction (eq 3). These results are also consistent with the acid/base pathway shown in Scheme 3 with the decreased basicity on the nondative ligands upon going from OH to OPh or NH_2 to NHPh likely decreasing the propensity toward an acid/base reaction with 1,4-CHD. We cannot definitively eliminate a

hydrogen atom abstraction pathway from consideration;⁶³ however, the following points suggest an acid–base pathway: (a) hydrogen atom abstraction would form the 19-electron Ru(I) complex $\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)$, which is likely to be highly unfavorable; (b) other Ru(II) systems with nondative ligands have been demonstrated to initiate acid–base chemistry with weakly acidic C–H bonds;^{17,18,20,42,66} (c) the conversion of **1** and 1,4-CHD to 1,3-CHD, $\text{TpRu}(\text{PMe}_3)_2\text{H}$, and benzene is slower than the analogous reaction with $\text{TpRu}(\text{PMe}_3)_2\text{NH}_2$, a trend that is anticipated for an acid–base pathway but not necessarily for hydrogen atom abstraction; (d) the calculated O–H BDE of $\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)$ is 37 kcal/mol; and (e) to our knowledge, there are no definitive examples of d^6 octahedral complexes that initiate ligand-centered hydrogen atom abstraction reactions. The use of radical traps to probe for a radical pathway is not likely to be informative since the net hydride abstraction to form benzene and $\text{TpRu}(\text{PMe}_3)_2\text{H}$ likely involves a radical pathway. Thus, trapping of free radicals would not preclude the proposed acid/base pathway. In addition, at elevated temperatures TEMPO (2,2,6,6-tetramethylpiperidinyloxy) reacts with 1,4-CHD.

To assess the basicity of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**), weak acids (MeOH , $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_3\text{COH}$, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, and PhC_2H) were each combined with the hydroxide complex **1** in C_6D_6 . The addition of MeOH $\{\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 15.5\}$ results in the disappearance of resonances due to **1** and the appearance of new resonances that are not attributable to the previously reported complex $\text{TpRu}(\text{PMe}_3)_2\text{OMe}$.⁶⁷ Efforts to isolate and grow crystals of the products were unsuccessful. These results are consistent with the formation of $[\text{TpRu}(\text{PMe}_3)_2(\text{H}_2\text{O})][\text{OMe}]$, for which a resonance at 3.47 ppm in the ^1H NMR spectrum is consistent with the methoxide anion and a broad resonance (integration 2H) at 2.57 ppm is assigned as coordinated water. Bergman et al. have reported the addition of methanol to the ruthenium complex *trans*-(dmpe) $_2\text{Ru}(\text{H})(\text{NH}_2)$ results in immediate formation of the ion pair $[\text{trans}-(\text{dmpe})_2\text{Ru}(\text{H})(\text{NH}_3)]^+[\text{OMe}]^-$.¹⁷ Similarly, the addition of $\text{CH}_3\text{CH}_2\text{OH}$ $\{\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 15.9\}$ or Me_3COH $\{\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 18\}$ to complex **1** in C_6D_6 results in the formation of new ruthenium complexes, suggesting the formation of the ion pairs $[\text{TpRu}(\text{PMe}_3)_2(\text{H}_2\text{O})][\text{OCH}_2\text{CH}_3]$ and $[\text{TpRu}(\text{PMe}_3)_2(\text{H}_2\text{O})][\text{OC}(\text{CH}_3)_3]$, respectively (eq 4).⁶⁷ The addition of acetone $\{\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 20\}$ or PhC_2H $\{\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 25\}$ to complex **1** does not result in any reaction at room temperature. The $\text{p}K_{\text{a}}$ values for the acids ROH ($\text{R} = \text{Me}$, CH_2CH_3 , or tBu), acetone, and phenylacetylene are in water, while reactions of **1** were performed in C_6D_6 , and ion pairing is likely to be more prevalent in the latter solvent. Thus, the $\text{p}K_{\text{a}}$ range of $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)]^+$ provides only a very qualitative estimate of the basicity of complex **1**. However, we roughly estimate the acidity of $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)]^+$ to possess a $\text{p}K_{\text{a}}$ value of between 18 and 20.

Single-Electron Oxidation of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ and Reactivity with C–H Bonds. The cyclic voltammogram of

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complex **1** displays a reversible oxidative wave at 0.01 V (vs NHE) assigned as the Ru(III/II) couple. The addition of 1 equiv of AgOTf to a C_6D_6 solution of complex **1** results in the formation of a precipitate {presumably Ag(s)} and disappearance of resonances due to **1** (^1H NMR spectroscopy). These results are consistent with the formation of the paramagnetic Ru(III) complex $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ (**3**) and Ag(s). The Evans NMR method was used to confirm the formation of paramagnetic Ru complex and determine that $\mu_{\text{eff}} = 1.78 \mu_{\text{B}}$ for **3** at room temperature.⁶⁸ This value is consistent with a single unpaired electron and close to the spin-only value of $1.73 \mu_{\text{B}}$, which is anticipated for an octahedral Ru(III) d^5 species. Attempts to grow X-ray-quality crystals of **3** resulted in decomposition. In addition, after 12 h at room temperature, a C_6D_6 solution of $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ reveals the production of a small amount ($\sim 5\%$ by ^1H NMR spectroscopy) of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$, probably due to the *slow* decomposition of the Ru(III) hydroxide complex **3**.

The addition of 1 equiv of AgOTf to a C_6D_6 solution of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) and 3 equiv (based on complex **1**) of 1,4-CHD ($\text{C}-\text{H}$ BDE = 73 ± 2 kcal/mol)⁶⁹ results in the formation of benzene ($\sim 35\%$ based on **1**), $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ (**4**) ($\sim 60\%$ yield), and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ ($\sim 10\%$ yield) within 20 min at room temperature (yields were determined by ^1H NMR spectroscopy). Performing the identical reaction in toluene- d_8 results in the production of benzene, **4**, and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ in nearly identical yields to the reaction in C_6D_6 . Complex **4** has been independently prepared upon combination of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ and water (see below). After 12 h, the resonances due to benzene ($\sim 50\%$), complex **4** ($\sim 50\%$), and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ ($\sim 50\%$) increase with no additional change after 3 days at room temperature (Scheme 5). In the absence of the ruthenium complex **1**, the reaction of 1,4-CHD and AgOTf in C_6D_6 does not form benzene after 3 days. The addition of AgOTf to a C_6D_6 solution of complex **1** and 1,4-cyclohexadiene in the presence of TEMPO results in the formation of a precipitate and broad resonances (^1H NMR). After 12 h at room temperature, resonances due to benzene (110%), $[\text{TpRu}(\text{PMe}_3)_2\text{OH}_2][\text{OTf}]$ (50%), and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ (50%) (all based upon complex **1**) are observed by ^1H NMR spectroscopy (Scheme 5).

The addition of 2 equiv of H_2O to a C_6D_6 solution of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ forms $[\text{TpRu}(\text{PMe}_3)_2\text{OH}_2][\text{OTf}]$ (**4**) in equilibrium with $\text{TpRu}(\text{PMe}_3)_2\text{OTf}/\text{H}_2\text{O}$. The formation of **4** is indicated by ^1H NMR and ^{31}P NMR spectroscopy. The resonance due to the coordinated water is observed at 4.28 ppm (^1H NMR spectroscopy). Consistent with this assignment, the addition of 2 equiv of D_2O to the C_6D_6 solution of **4** results in a decrease in the resonance due to coordinated water (4.28 ppm), a transformation that is reversible upon introduction of excess H_2O (Scheme 6). Complex **4** has not been isolated and has been characterized in equilibrium with $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ using ^1H and ^{31}P NMR spectroscopy.

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Scheme 4. Single-Electron Oxidation of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) by AgOTf to Form $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ (**3**)^a

^a RT = room temperature.

Scheme 5. Single-Electron Oxidation of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (**1**) in the Presence of 1,4-Cyclohexadiene^a

^a Yields taken from ^1H NMR spectroscopy.

Scheme 6. Formation $[\text{TpRu}(\text{PMe}_3)_2\text{OH}_2][\text{OTf}]$ (**4**) and Equilibrium between Complex **4**/ D_2O and **4**- d_2 / H_2O

The addition of AgOTf to the solution of complex **1** and 9,10-dihydroanthracene (9,10-DHA; $\text{C}-\text{H}$ BDE = 78 ± 2 kcal/mol) in C_6D_6 results in the formation of anthracene ($\sim 20\%$), anthraquinone ($\sim 6\%$), $[\text{TpRu}(\text{PMe}_3)_2\text{OH}_2][\text{OTf}]$ ($\sim 55\%$), and $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ ($\sim 40\%$) (all based on complex **1**; determined by ^1H NMR spectroscopy) after 12 h at room temperature (Scheme 7).⁷⁰ The low yields reflect low conversions of starting materials. Mayer et al. have reported that the oxidation of 9,-

Scheme 7. Single-Electron Oxidation of $\text{TpRu}(\text{PMe}_3)_2\text{OH}$ (1) in the Presence of 9,10-Dihydroanthracene

10-DHA by $[(\text{bpy})_2(\text{py})\text{Ru}^{\text{IV}}\text{O}]^{2+}$ produces a mixture of anthrone, anthraquinone, and anthracene with the distribution of products dependent on the molar ratio of Ru-oxo and 9,10-DHA.⁷¹ Anthrone was not detected by NMR spectroscopy or mass spectrometry.

The addition of AgOTf to a solution of complex **1** and fluorene (BDE = 80 ± 2 kcal/mol) in C_6D_6 results in the formation of fluorenone (eq 5). The formation of fluorenone was confirmed by both ^1H NMR and IR spectroscopy ($\nu_{\text{C=O}} = 1719\text{ cm}^{-1}$).^{70,72,73} There is no evidence (^1H NMR spectroscopy and mass spectrometry) for the formation of bifluorene. However, due to overlapping with Tp resonances of ruthenium complex, determination of the quantitative yield of fluorenone could not be determined. Based on intensities the yields are estimated as 6% for fluorenone, 29% complex **4**, and 30% $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$. As with 9,10-DHA, the low yields are a result of low conversion of starting material.

The addition of AgOTf to a C_6D_6 solution of **1** and cyclohexene (BDE = 81 ± 1 kcal/mol), cumene (BDE = 83 ± 1 kcal/mol), toluene (BDE = 88 kcal/mol), or phenylacetylene (BDE = 125 kcal/mol) results in the formation of a precipitate and disappearance of resonances due to complex **1** in the ^1H NMR spectrum.^{74–77} For each reaction a small amount ($\sim 5\%$) of $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ is observed after 12 h at room temperature, which is nearly identical to the control experiments for the reaction of complex **1** and AgOTf in the absence of added organic substrates. After 48 h at room temperature, no evidence for the formation of new organic products, $\text{TpRu}(\text{PMe}_3)_2\text{H}$, or complex **4** is obtained. Thus, we conclude that the Ru(III) complex $[\text{TpRu}(\text{PMe}_3)_2(\text{OH})][\text{OTf}]$ (**3**) does not react with cyclohexene, cumene, toluene, or phenylacetylene.

Scheme 8. Possible Pathway for Net Dehydrogenation of 1,4-CHD by $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ (3)

Upon single-electron oxidation of complex **1**, we suggest that the Ru(III) complex $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ reacts with substrates that possess relatively weak C–H bonds to produce $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$. The latter complex then equilibrates with $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ and free H_2O . For example, C–H bond cleavage of 1,4-CHD (BDE = 73 ± 2 kcal/mol) via hydroxide-centered hydrogen atom abstraction would initially yield $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ and cyclohexadienyl radical. Hydrogen atom abstraction from cyclohexadienyl radical by a second equivalent of $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ would produce benzene and a second equivalent of $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ (Scheme 8). This pathway would produce a molar ratio of $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ / $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$ and C_6H_6 of 2:1, which is consistent with experimental observations. For example, the reaction of **1**, AgOTf, and 1,4-CHD produces an approximate 2:1 ratio of Ru and benzene or an approximate 1:1:1 molar ratio of $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$, $\text{TpRu}(\text{PMe}_3)_2\text{OTf}$, and C_6H_6 . The addition of TEMPO to the reaction of **3** and 1,4-CHD increases the formation of benzene (relative to Ru) from $\sim 50\%$ (without TEMPO) to $\sim 110\%$ (with TEMPO). This result is consistent with initial reaction of $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ with 1,4-CHD to form $[\text{TpRu}(\text{PMe}_3)_2(\text{OH}_2)][\text{OTf}]$ and cyclohexadienyl radical followed by net hydrogen atom abstraction from cyclohexadienyl radical by TEMPO. Thus, with the addition of TEMPO each equivalent of C_6H_6 produced from 1,4-CHD consumes 1 equiv of Ru(III) hydroxide rather than the 2 equiv that are consumed in the absence of TEMPO.

The reaction of 9,10-DHA with $[\text{TpRu}(\text{PMe}_3)_2\text{OH}][\text{OTf}]$ (**3**) forms a mixture of anthracene and anthraquinone, while fluorenone is the exclusive organic product formed upon reaction of fluorene with complex **3**. While we do not know the mechanism for incorporation of oxygen, a Ru(IV)-oxo complex has been reported to initiate similar reactions.⁷¹ The relationship between reaction with C–H bonds by complex **3** and homolytic C–H BDEs is most important within the present context. For example, complex **3** reacts with 1,4-CHD, 9,10-DHA, and fluorene, all with reported C–H BDEs < 80 kcal/mol. In contrast, no evidence has been obtained for the reaction of **3** and substrates with C–H BDEs > 80 kcal/mol, including cyclohexene (BDE = 81 ± 1 kcal/mol), cumene (BDE = 83 ± 1 kcal/mol), and toluene (BDE = 88 kcal/mol). Moreover,

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Scheme 9. Calculation of the O–H Bond Strength in [TpRu(PMe₃)₂(OH₂)]⁺[OTf]

			Energy (kcal/mol)
$[\text{TpRu}^{\text{II}}(\text{PMe}_3)_2(\text{OH}_2)]^+$	$\longrightarrow$	$\text{TpRu}^{\text{II}}(\text{PMe}_3)_2\text{OH} + \text{H}^+ (\text{aq}) \quad (\text{p}K_{\text{a}} = 18\text{--}20)$	24.6–27.3
$\text{TpRu}^{\text{II}}(\text{PMe}_3)_2\text{OH}$	$\longrightarrow$	$[\text{TpRu}^{\text{III}}(\text{PMe}_3)_2\text{OH}]^+ + \text{e}^-$	$\left. \begin{array}{l} \\ \\ \end{array} \right\} \quad (\text{E}_{1/2} = 0.01 \text{ V})$
$\text{H}^+ (\text{aq}) + \text{e}^-$	$\longrightarrow$	$1/2 \text{ H}_2 (\text{g})$	
$1/2 \text{ H}_2 (\text{g})$	$\longrightarrow$	$\text{H}\cdot (\text{aq})$	
$\text{TpRu}^{\text{II}}(\text{PMe}_3)_2(\text{OH}_2)]^+$	$\longrightarrow$	$[\text{TpRu}^{\text{III}}(\text{PMe}_3)_2\text{OH}]^+ + \text{H}\cdot (\text{aq})$	$\text{BDE}(\text{O-H}) \quad 81.8\text{--}84.9$

^a See ref 79.

phenylacetylene has an acidic (pK_a = 25) yet homolytically strong C_{sp}–H bond (125 kcal/mol),^{76,77} but complex **3** does not react with phenylacetylene. The latter experiment provides evidence that the mode of reaction for **3** does not involve acid–base chemistry as is proposed for reactivity with C–H bonds for the related Ru(II) complexes (see above).

Ideally, the O–H bond dissociation energy of [TpRu(PMe₃)₂(OH₂)]⁺ can be estimated using the equations shown in Scheme 9.^{62,70,78} The redox potential of complex **1** has been determined by cyclic voltammetry (E_{1/2} = 0.01 V versus NHE, ΔG° = 0.23 kcal/mol). We have roughly estimated the pK_a of [TpRu(PMe₃)₂(OH₂)]⁺ to be between 18 and 20. Using these data, an estimated bond dissociation energy of the O–H bond of [TpRu(PMe₃)₂(OH₂)]⁺ is calculated to be between 82 and 84 kcal/mol. Consistent with this estimate, reactivity studies described above suggest that [TpRu(PMe₃)₂OH][OTf] (**3**) can react with substrates that possess C–H bonds with BDE ≤ 80 kcal/mol. There are several limitations to applying this approach to determination of the O–H BDE of [TpRu(PMe₃)₂(OH₂)]⁺. The pK_a value between 18 and 20 uses aqueous phase values, while reactions of **1** were performed in benzene. As previously discussed, the enthalpy of solution of the hydrogen atom is assumed to be equivalent to that of dihydrogen (1 kcal/mol).⁷⁹ To convert free energies from pK_a and the redox potential of **1**, it is assumed that the entropies of [TpRu(PMe₃)₂(OH₂)]⁺ and [TpRu(PMe₃)₂(OH)]⁺ are the same.⁷⁹ Despite these limitations, the estimated O–H BDE of [TpRu(PMe₃)₂(OH₂)]⁺ is consistent with observed reactivity and DFT computations (see below).

Computational Studies or Relevant Bond Dissociation Energies. The approximate pK_a of [TpRu(PMe₃)₂(OH₂)]⁺ and Ru(III/II) potential of **1** pK_a have been used to provide an experimental estimate of the O–H BDE of [TpRu(PMe₃)₂(OH₂)]⁺ of between 82 and 85 kcal/mol. This value is consistent with observations that [TpRu(PMe₃)₂(OH)][OTf] (**3**) reacts with C–H bonds that have BDEs < 80 kcal/mol. Using the B3LYP/CSDZ* level of theory, the O–H BDE of [(Tab)Ru(PH₃)₂(OH₂)]⁺ (Tab = tris(azo)borate as a model of the full Tp) is calculated to be 84 kcal/mol in the gas phase (Chart 1), which increases confidence in the experimental estimates of the O–H BDE.

We have previously reported that single-electron oxidations of TpRu(L)(L')R (R = alkyl ligand) systems to form the Ru(III) cations [TpRu(L)(L')R]⁺ result in rapid Ru–R bond homolysis at room temperature.⁸⁰ The fast homolytic cleavage of the Ru–C bonds is attributable to a substantial decrease in

Chart 1. Computational Studies at the B3LYP/CSDZ* Level of Theory Indicate that the O–H BDE of [TpRu(PMe₃)₂(OH₂)]⁺ Is 84 kcal/mol in the Gas Phase **Chart 2.** Computational Studies {B3LYP/CSDZ*} Indicate that the Ru–OH BDE of (Tab)Ru(PH₃)₂OH (**1**) Is 74 kcal/mol and Is 50 kcal/mol for [(Tab)Ru(PH₃)₂OH]⁺

Ru–R BDE upon oxidation from Ru(II) to Ru(III). For example, B3LYP calculations reveal that conversion of the Ru(II) complex TpRu(CO)(NCMe)Me to the Ru(III) cation [TpRu(CO)(NCMe)Me]⁺ decreases the Ru–C_{Me} BDE from 49 kcal/mol to 23 kcal/mol (a 53% decrease in BDE), a result consistent with the experimentally observed reactivity of these complexes.⁴⁹ Previous experimental studies have revealed that M–OR BDEs can be greater than M–C BDEs.^{40,81–86} In contrast to [TpRu(CO)(NCMe)Me]⁺, experimental results herein indicate that the Ru–OH bond of the Ru(III) system [TpRu(PMe₃)₂OH]⁺ is relatively stable (compared with the Ru(III) alkyl bonds) at room temperature, and in the absence of reactive substrates the Ru(III) hydroxide complex **3** is persistent (only 5% decomposition is observed for **3** after 12 h in C₆D₆ at room temperature). Consistent with these observations, B3LYP/CSDZ* calculations indicate that the Ru–O_{hydroxyl} BDE of the Ru(III) system [(Tab)Ru(PH₃)₂OH]⁺ ligand is 50 kcal/mol (Chart 2), which is greater than twice the calculated value of the Ru–C_{methyl} BDE (23 kcal/mol) of the Ru(III) complex [TpRu(CO)(NCMe)Me]⁺. The calculated Ru–O_{hydroxyl} BDE of the Ru(II) complex (Tab)Ru–

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Scheme 10. Three Pathways to Cleave C–H Bonds by Late Transition Metal Systems with Nondative Heteroatomic Ligands

Hydrogen atom abstraction

Deprotonation

1,2-addition

(PH₃)₂OH is 74 kcal/mol at the same level of theory. Thus, oxidation from Ru(II) to Ru(III) is calculated to decrease the Ru–X_{hydroxyl} BDE by only 32%, a value that is proportionately less than the impact of single-electron oxidation on Ru–alkyl BDEs. A potential source of the different effect on the Ru–ligand BDE upon oxidation is the ability of the hydroxide ligand to stabilize the Ru(III) state via π -interaction and formation of some Ru–OH multiple bond character, which is not accessible at the Ru(II) oxidation state due to a filled set of $d\pi$ orbitals. Support for this conclusion can be deduced from the greater than expected shortening of the Ru–OH bond upon oxidation from Ru(II) to Ru(III) obtained from DFT geometry optimization of [(Tab)Ru(PH₃)₂(OH)]⁰⁺ models: Ru(II)–OH = 2.12 Å, Ru(III)–OH = 1.97 Å. The difference of 0.15 Å is roughly double the bond shortening expected from an increase in the formal oxidation state of ruthenium by +1 unit for a six-coordinate complex. The calculated Ru–O–H angle is larger in the Ru(III) complex than the corresponding Ru(II) hydroxide (112° versus 117°), although this difference is marginal.

Summary

At the Ru(II) oxidation state, TpRu(PMe₃)₂OR (R = H or Ph) systems exhibit reactivity with C–H bonds that is consistent with an acid/base reaction with the “OR” ligand. For example, TpRu(PMe₃)₂OH (**1**) and 1,4-CHD are converted to benzene and TpRu(PMe₃)₂H in a reaction that we propose involves initial heterolytic cleavage of an allylic C–H bond of 1,4-CHD. In contrast, single-electron oxidation of **1** to a Ru(III) complex results in reactivity indicative of a predilection toward odd-electron chemistry (i.e., net hydrogen atom abstraction of relatively weak C–H bonds). Late transition metal systems with nondative heteroatomic ligands have been demonstrated to break C–H bonds by three distinct pathways: (1) ligand-centered hydrogen atom abstraction (i.e., proton-coupled electron transfer),^{5,54–56,58} (2) ligand-centered heterolytic chemistry (i.e., C–H deprotonation),^{17–19} and (3) net 1,2-addition of C–H bonds across M–X bonds (Scheme 10).^{49,50,57} For systems with an energetically favorable $n-1$ oxidation state and inaccessible coordination sites, odd-electron and net hydrogen atom abstraction chemistry is likely to dominate. For complexes with high-energy $n-1$ oxidation states and unavailable coordination sites, heterolytic even-electron C–H cleavage (i.e., C–H deprotonation) is likely to be observed. Complexes with high energy $n-1$ oxidation states and accessible coordination sites for binding of C–H bonds are most likely to exhibit a predilection toward even-electron 1,2-addition of C–H bonds (i.e., metal-mediated C–H activation). The studies outlined here on TpRu–X (X = OH, NH₂) complexes indicate that subtle control of the activity

and selectivity within and among the different pathways for scission of C–H bonds is a delicate balance of access to open coordination sites on the metal, metal oxidation state (e.g., acid/base chemistry of Ru(II) versus odd-electron reactivity of Ru(III) complexes), and basicity of the nondative ligand (Ru–NH₂ more basic than Ru–OH complexes).

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 {O₂(g) < 15 ppm for all reactions}. Benzene-*d*₆ was degassed by three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. ¹H and ¹³C 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 ¹³C NMR spectra were referenced against tetramethylsilane using resonances due to the residual protons in the deuterated solvents or the ¹³C resonances of the deuterated solvents. ³¹P NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer (operating frequency 161 MHz) and referenced against external 85% H₃PO₄. Unless otherwise noted, NMR spectra were acquired at room temperature. Unless otherwise noted, all reagents were used as purchased from commercial sources. Mass spectrometry was recorded by a JEOL HX-110 Magnetic Sector mass spectrometer. Synthetic procedures for TpRu(PMe₃)₂OH (**1**), TpRu(PMe₃)₂OTf, TpRu(PMe₃)₂OMe, TpRu(PMe₃)₂H, and TpRu(PMe₃)₂–(C≡CPh) (**2**) have been reported.^{20,49}

[TpRu(PMe₃)₂(OH₂)] [OTf] (4**).** In a glovebox, an NMR tube was charged with 0.025 g (0.04 mmol) of TpRu(PMe₃)₂OTf and 0.7 mL of C₆D₆. The NMR tube was capped with a rubber septum and removed from the glovebox, and 2 μ L of H₂O (0.11 mmol) was added using a microsyringe. The solution was shaken vigorously, and ¹H NMR spectra were acquired 10 min and 12 h after mixing. After 12 h, new resonances due to [TpRu(PMe₃)₂(OH₂)] [OTf] (**4**) appeared in equilibrium with TpRu(PMe₃)₂OTf (no further change occurred after 12 h). D₂O (2 μ L, 0.11 mmol) was added to the solution, and ¹H NMR spectra were acquired 20 min and 12 h after mixing. Resonances due to Ru-coordinated H₂O and free H₂O decreased with no change for the remaining resonances. ¹H NMR (C₆D₆, δ): 7.98, 7.43, 7.37, 6.70 (6H, 2:2:1:1 integration, each a d, Tp CH 3 and 5 positions), 6.07, 5.71 (3H, 2:1 integration, each a t, Tp CH 4 position), 4.28 (2H, broad, Ru–OH₂), 1.06 (18H, vt, $N = 8$ Hz, P(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, δ): 13.8 (s, PMe₃).

[TpRu(PMe₃)₂(OH₂)] [OMe]. In a glovebox, an NMR tube was charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**) and 1.0 mL of C₆D₆. A ¹H NMR spectrum was acquired. Methanol (1.7 μ L, 0.040 mmol) was added to the NMR solution, and the solution was shaken vigorously. Another ¹H NMR spectrum was acquired that indicated disappearance of the resonances due to complex **1** and the appearance of new resonances assigned as [TpRu(PMe₃)₂(OH₂)] [OMe]. ¹H NMR (C₆D₆, δ): 7.93, 7.54, 7.52, 7.00 (6H, 2:2:1:1 integration, each a d, Tp CH 3 and 5 positions), 5.97, 5.85 (3H, 2:1 integration, each a t, Tp CH 4 position), 3.47 (3H, s, CH₃O), 2.57 (2H, broad, Ru–OH₂), 1.11 (18H, vt, $N = 10$ Hz, P(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, δ): 18.1 (s, PMe₃).

[TpRu(PMe₃)₂(OH₂)] [OCH₂CH₃]. In a glovebox, an NMR tube was charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**) and 1.0 mL of C₆D₆. A ¹H NMR spectrum was acquired. Ethanol (2.4 μ L, 0.040 mmol) was added to the NMR solution, and the solution was shaken vigorously. Another ¹H NMR spectrum was acquired that indicated disappearance of the resonances due to complex **1** and the appearance of new resonances assigned as [TpRu(PMe₃)₂(OH₂)] [OEt]. ¹H NMR (C₆D₆, δ): 7.94, 7.55, 7.52,

7.02 (6H, 2:2:1:1 integration, each a d, Tp CH 3 and 5 positions), 5.97, 5.86 (3H, 2:1 integration, each a t, Tp CH 4 position), 3.79 (2H, q, $^3J_{\text{HH}} = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.32 (3H, t, $^3J_{\text{HH}} = 7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 1.13 (18H, vt, $N = 8$ Hz, $\text{P}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 18.4 (s, PMe_3).

[TpRu(PMe₃)₂(OH₂)][OC(CH₃)₃]. In a glovebox, an NMR tube was charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**) and 1.0 mL of C_6D_6 . A ^1H NMR spectrum was acquired. *tert*-butanol (3.9 μL , 0.040 mmol) was added to the NMR solution, and the solution was shaken vigorously. Another ^1H NMR spectrum was acquired that indicated disappearance of the resonances due to complex **1** and the appearance of new resonances assigned as [TpRu(PMe₃)₂(OH₂)][O^{*t*}Bu]. ^1H NMR (C_6D_6 , δ): 7.97, 7.57, 7.52, 7.04 (6H, 2:2:1:1 integration, each a d, Tp CH 3 and 5 positions), 5.97, 5.87 (3H, 2:1 integration, each a t, Tp CH 4 position), 1.38 (9H, s, $\text{OC}(\text{CH}_3)_3$), 1.15 (18H, vt, $N = 10$ Hz, $\text{P}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 18.9 (s, PMe_3).

Reaction of TpRu(PMe₃)₂OH (1**) with Phenylacetylene.** In a glovebox, three screw-cap NMR tubes were each charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**) and 1.0 mL of C_6D_6 . To the resulting solutions were added 0.044 mL of phenylacetylene (0.40 mmol) and a small amount of mesitylene as internal standard. A ^1H NMR spectrum was acquired with a pulse delay of 10 s in order to ensure accurate integration. The solutions were heated to approximately 80 °C in an oil bath and periodically monitored by ^1H NMR spectroscopy. The formation of TpRu(PMe₃)₂(C $\equiv$ CPh) (**2**) was observed in quantitative yield; however, multiple reactions using different batches of **1** did not produce consistent rates of reactions.

Reaction of TpRu(PMe₃)₂OPh with Phenylacetylene. The procedure used was identical to those described above for **1** except the oil bath was set at 85 °C. The conversion to **2** was quantitative by ^1H NMR spectroscopy after 6 days.

Reaction of TpRu(PMe₃)₂OR (R = H or Ph) with 1,4-Cyclohexadiene. In a glovebox, the Ru(II) complex was weighed and dissolved in 1 mL of C_6D_6 . This solution was transferred to a screw-cap NMR tube, and 3 equiv of 1,4-CHD was added along with mesitylene (as internal standard). ^1H NMR spectra were immediately acquired with a 10 s pulse delay. The solution was then heated to 80 °C (R = H) or 85 °C (R = Ph) in temperature-regulated oil baths. Reaction progress was monitored versus time using ^1H NMR spectroscopy. Percent yields of products were determined by integration versus mesitylene. For the reaction of TpRu(PMe₃)₂OH (**1**) with 1,4-CHD, the formation of TpRu(PMe₃)₂H (33% after 9 days), 1,3-CHD, benzene, and water was observed, while the combination of TpRu(PMe₃)₂OPh and 1,4-CHD resulted in no reaction after 20 days of heating.

Reaction of TpRu(PMe₃)₂OH (1**) and Phenylacetylene with Catalytic TpRu(PMe₃)₂OTf.** Four screw-cap NMR tubes were each charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**), 0.044 mL (0.40 mmol) of phenylacetylene, and 1.0 mL of C_6D_6 . To the four separate solutions 0, 0.04, 0.07, and 0.15 equiv of TpRu(PMe₃)₂OTf (based on complex **1**) were added as well as a small amount of mesitylene as internal standard. ^1H NMR spectra were acquired using a pulse delay of 10 s in order to ensure accurate integration. The solutions were heated to approximately 80 °C in a temperature-regulated oil bath and periodically monitored by ^1H NMR spectroscopy. The formation of TpRu(PMe₃)₂(C $\equiv$ CPh) (**2**) was observed, and the rate of each reaction was determined.

[TpRu(PMe₃)₂OH][OTf] (3**).** TpRu(PMe₃)₂OH (**1**) (0.020 g, 0.040 mmol) was weighed in a glass vial and dissolved in 1.0 mL of C_6D_6 . The solution was transferred to a screw-cap NMR tube, and a ^1H NMR spectrum was acquired using a 10 s pulse delay. In a glovebox, 1 equiv of AgOTf was added to the NMR solution. The solution was mixed, and a precipitate immediately formed. A ^1H NMR spectrum revealed that all of the resonances due to complex **1** had disappeared. After 12 h at room temperature, ^1H

NMR spectroscopy showed the formation of TpRu(PMe₃)₂OTf in less than 5% yield (based on **1**).

Evans NMR Method. TpRu(PMe₃)₂OH (**1**) (0.022 g, 0.046 mmol) was dissolved in 16 mL of C_6D_6 , and this solution was divided into two 8 mL solutions, which were labeled A and B. AgOTf (0.006 g, 0.023 mmol) was added to tube A, and a precipitate formed immediately. This solution was filtered using a syringe filter. Two NMR tubes were separately charged with the filtrate from solutions A and B, each of which was charged with 2 μL of mesitylene. Two sealed capillary tubes, which were charged with 2 μL of mesitylene and 50 μL of C_6D_6 , were added into the NMR tubes containing solutions A and B. ^1H NMR spectra of each were acquired using a 10 s pulse delay. For solution A, a total of four resonances for mesitylene were observed with a chemical shift difference of 0.012 ppm (resonances at ~ 6.7 and 2.1 ppm; 300 MHz). For solution B, only a single set of resonances (two total) was observed due to mesitylene.

Reaction of [TpRu(PMe₃)₂OH][OTf] (3**) with 1,4-Cyclohexadiene, 9,10-Dihydroanthracene, Fluorene, Cyclohexene, Cumene, Toluene, or Phenylacetylene.** Six screw-cap NMR tubes were each charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**) and 1.0 mL of C_6D_6 . In a glovebox, a small amount of mesitylene (internal standard) and 3 equiv of 1,4-cyclohexadiene, 9,10-dihydroanthracene, fluorene, cyclohexene, cumene, toluene, or phenylacetylene were added to an NMR tube. A ^1H NMR spectrum was acquired using a 10 s pulse delay. One equivalent of AgOTf (based on **1**) was added to each NMR tube. ^1H NMR spectra were acquired using a 10 s pulse delay after 20 min and 12 h at room temperature. Results are described in the text. Analysis by mass spectrometry did not reveal evidence of other organic products.

Reaction of [TpRu(PMe₃)₂OH][OTf] (3**) with 1,4-Cyclohexadiene with the Addition of TEMPO.** A screw-cap NMR tube was charged with 0.020 g (0.040 mmol) of TpRu(PMe₃)₂OH (**1**), 0.007 g (0.040 mmol) of TEMPO, a small amount of mesitylene (internal standard), and 1.0 mL of C_6D_6 (0.010 g, 0.040 mmol). A ^1H NMR spectrum was acquired using a 10 s pulse delay. AgOTf (0.010 g, 0.040 mmol) was added to the NMR tube, and a ^1H NMR spectrum was acquired using a 10 s pulse delay. The formation of 50% TpRu(PMe₃)₂OTf, 50% [TpRu(PMe₃)₂(OH₂)][OTf], and 110% C_6H_6 was observed after 12 h at room temperature.

Computational Methods. All geometries were optimized in Jaguar⁸⁷ with density functional theory (DFT) using the B3LYP functional.^{88–91} The Stevens effective core potential (ECP) and valence basis sets were used,^{92,93} with a d-polarization function on heavy main group elements (termed CSDZ* in Jaguar). Each structure was confirmed as a minimum using an energy Hessian calculation; the unscaled vibrational frequencies thus obtained were used to determine enthalpic and entropic corrections at STP to the electronic energy using standard statistical thermodynamics formulas. The tris-pyrazolyl borate (Tp) ligand was replaced with tris-azo borate (Tab), the latter being shown in previous work^{49,50,94} to behave similarly in electronic and steric impact to the full Tp ligand. PMe_3 ligands were modeled with PH_3 .

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