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

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The Ru(II) complexes TpRu(PMe_3)_2OR (R = H or Ph) react with excess phenylacetylene at elevated temperatures to produce the phenylacetylide complex TpRu(PMe_3)_2C≡CPh. Kinetic studies indicate that the reaction of TpRu(PMe_3)_2OH and phenylacetylene likely proceeds through a pathway that involves TpRu(PMe_3)_2OTf as a catalyst. The reaction of TpRu(PMe_3)_2OH with 1,4-cyclohexadiene at elevated temperature forms benzene and TpRu(PMe_3)_2H, while TpRu(PMe_3)_2OPh does not react with 1,4-cyclohexadiene even after 20 days at 85 °C. The paramagnetic Ru(III) complex [TpRu(PMe_3)_2OH][OTf] is formed upon single-electron oxidation of TpRu(PMe_3)_2OH with AgOTf. Reactivity studies suggest that [TpRu(PMe_3)_2OH][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 [TpRu(PMe_3)_2(Oh2)][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 [TpRu(PMe_3)_2OH]⁺.

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 complexes have been less well-characterized, and the nature of the nitrogen donor is particularly crucial. The N donors have been shown to undergo H and/or N bond formation with a variety of metal centers.16,18


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plexes, including deprotonation of C–H bonds and nucleophilic N\textsubscript{amide}–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 dσ atomic orbitals. Our group has been studying the reactivity of amido, alkoxide, arylxide, 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.

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 bonds. 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. 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 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 lipoxygenases catalyze the oxidative conversion of 1,4-diene-containing fatty acids to alkyl hydroperoxides, and these transformations likely proceed through net hydrogen atom abstraction by an Fe(III) hydroxy fragment from an allylic C–H bond (BDE ≈ 77 kcal/mol) to generate allylic radicals that are subsequently trapped by dioxygen. Stack et al. have prepared [Fe\textsuperscript{III}(PY\textsubscript{3})(OMe)]\textsuperscript{−}[OTf\textsuperscript{−}] (\textit{PYS} = 2,6-bis(2-pyridyl)methoxynitrene)pyridine) as a model for lipoxygenase enzymes and have shown that it readily oxidizes cyclohexadiene to benzene and the corresponding Fe\textsuperscript{II}–MeOH complex. 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. 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.

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)\textit{Ru}(X)(H) (X = OH or NH\textsubscript{2}; dmpe = 1,2-dimethylphosphinohexane) that have revealed the ability of the heteroligand to break weakly acidic C–H bonds via deprotonation. In addition, our group has reported related reactivity for a series of octahedral ruthenium complexes of the type \textit{TpRuL}(L\textsuperscript{′})(NHR) (\textit{Tp} = hydridotris(pyrazolyl)borate; \textit{L} = \textit{L}′ = (P\text{OMe})\textsubscript{3} or PMe\textsubscript{3} or \textit{L} = CO and \textit{L}′ = Ph\textsubscript{3}P; \textit{R} = H, Ph, or \textit{Bu}) that have reported the five-coordinate Ru(II) amido complex (PCP)\textit{Ru}(CO)(NH\textsubscript{2}) (PCP = 2,6-(CH\textsubscript{2}\textsubscript{2}Bu\textsubscript{2})\textsubscript{2}C\textsubscript{6}H\textsubscript{4}) activates dihydrogen as well as initiating intramolecular C–H activation of a \textsuperscript{1}Bu moiety of the PCP ligand and that the six-coordinate anilido complex (PCP)\textit{Ru}(CO)(PM\text{E}\textsubscript{3})(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. As an extension of our studies focused on the reactivity of nondative heteroligand coordinates to Ru, we now report on the reactivity of \textit{TpRu}...

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
| Homolytic C–H Cleavage | Heterolytic C–H Cleavage |
\hline
| M----C--H | M\textsuperscript{−}1/C--C' |
| X | X |
\hline
\end{tabular}
\caption{Two Pathways for Ligand-Centered C–H Bond Cleavage by Late Transition Metal Complexes with Nondative Heteroligands\textsuperscript{a}}
\end{table}

\textsuperscript{a} X is formally anionic N- or O-based ligand such as amido, hydroxide, etc.

Reactivity of TpRu(PMe₃)₂OR (R = H or Ph) with Acidic Substrates. We have previously reported the preparation of TpRu(PMe₃)₂OR (R = H or Ph).⁴⁹,⁵⁰ At room temperature, TpRu(PMe₃)₂OH (1) and 10 equiv of phenylacetylene in C₆D₆ do not react after 3 days; however, heating this solution to 80 °C results in the formation of previously reported complex TpRu(PMe₃)₂(C≡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 TpRu(PMe₃)₂NPH and phenylacetylene,²⁰ the addition of catalytic quantities of TpRu(PMe₃)₂OTf to the reaction of 1 and phenylacetylene results in an increase in the rate of formation of TpRu(PMe₃)₂(C≡CPh) (2), and a plot of kₐbs versus concentration of TpRu(PMe₃)₂OTf reveals a linear relationship (Figure 1). In addition, the rate of reaction of 1 and phenylacetylene increases with increasing concentration of the alkyn. These results are identical to observations made for the reaction of TpRu(PMe₃)₂NPH and phenylacetylene.²⁰ Thus, we propose that the conversion of complex 1 and phenylacetylene follows a similar pathway to that for the transformation of TpRu(PMe₃)₂-NPH and phenylacetylene. As previously reported for the conversion of the anilido complex TpRu(PMe₃)₂NPH,²⁰ it is likely that TpRu(PMe₃)₂OTf coordinates phenylacetylene and forms the vinylidene complex [TpRu(PMe₃)₂(C≡CPh)]⁺, 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 TpRu(PMe₃)₂OTf and phenylacetylene to the vinylidene complex is commensurate with its involvement in the conversion of 1 and phenylacetylene to complex 2.²⁰ Ligand exchange between H₂O and phenylacetylene completes the catalytic conversion (Scheme 2). It is possible that a trace amount of TpRu(PMe₃)₂OTf exists in bulk samples of TpRu(PMe₃)₂OH (1). The kₐbs for the conversion of 1 and phenylacetylene to complex 2 in the absence of added TpRu(PMe₃)₂OTf fits well on the linear plot of kₐbs versus the mol % (R² = 0.98) of TpRu(PMe₃)₂OTf (Figure 1). In contrast to the proposed mechanism for conversion of the Ru(II) hydride 1 and phenylacetylene to TpRu(PMe₃)₂C≡CPh (2), we have previously reported that TpRu(PMe₃)₂NH₂ reacts with phenylacetylene at room temperature to generate the ion pair [TpRu(PMe₃)₂(PhH)][PhC₂].²⁰ Thus, it is also possible that complex 1 may react with phenylacetylene to form 2 in the absence of TpRu(PMe₃)₂OTf, which is implicated by the nonzero y-intercept in Figure 1.

The combination of TpRu(PMe₃)₂OH and 10 equiv of phenylacetylene in C₆D₆ 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 TpRu(PMe₃)₂-C≡CPh (2) and PhOH is quantitative (¹H NMR spectroscopy) after 6 days (eq 1). The conversion of TpRu(PMe₃)₂OH and phenylacetylene to 2 and PhOH is slower than for complex 1, which is consistent with the complexes TpRu(PMe₃)₂OR (R = H or Ph) reacting as Bronsted bases, and their anticipated relative basicities (i.e., Ru−OH more basic than Ru−OPh), for the formation of 2. Although detailed studies have not been performed, we presume that this reaction is also catalyzed by TpRu(PMe₃)₂OTf.

The reaction of complex 1 with 5 equiv of 1,4-cyclohexadiene (1,4-CHD) at 85 °C results in the disappearance of the hydride complex (¹H NMR spectroscopy) and formation of the previously reported hydride complex TpRu(PMe₃)₂H and benzene (eq 2).²⁰ In contrast to the reaction of 1 with phenylacetylene, the addition of TpRu(PMe₃)₂OTf does not increase the rate of this transformation. The ruthenium hydride complex TpRu(PMe₃)₂H was identified on the basis of a triplet at −15.7 ppm (JₚH = 31 Hz) as well as resonances due to the Tp and PMe₃ ligands. TpRu(PMe₃)₂H 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

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**Figure 1.** Plot of kₐbs (determined under pseudo-first-order conditions) versus concentration of TpRu(PMe₃)₂OTf (from 0 to 15 mol % of complex 1) for the conversion of TpRu(PMe₃)₂OH (1) (0.04 M) and phenylacetylene (0.4 M) to TpRu(PMe₃)₂(C≡CPh) (2). The plot of kₐbs at 0 mol % of TpRu(PMe₃)₂OTf corresponds to the rate constant in the absence of added TpRu(PMe₃)₂OTf.

**Scheme 2.** Proposed Mechanism for the Conversion of TpRu(PMe₃)₂OH (1) and Phenylacetylene to TpRu(PMe₃)₂(C≡CPh) (2) Catalyzed by TpRu(PMe₃)₂OTf.
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 C6H7 complex and cyclohexadienide ion pair (Scheme 3). Subsequent

The cyclic voltammogram of [TpRu(PMe3)2(OH)]+ provides only a very qualitative estimate of the basicity of complex 1. However, we roughly estimate the acidity of [TpRu(PMe3)2(OH)]+ to possess a pKa value of between 18 and 20.

To assess the basicity of TpRu(PMe3)2OH (1), weak acids (MeOH, CH3CH2OH, (CH3)2COH, CH3C(O)CH3, and PhC2H) were each combined with the hydroxide complex 1 in C6D6. The addition of MeOH (pKa(H2O) = 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 TpRu(PMe3)2OMe. Efforts to isolate and grow crystals of the products were unsuccessful. These results are consistent with the formation of [TpRu(PMe3)2(H2O)][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)2Ru(H)(NH2) results in immediate formation of the ion pair [trans-(dmpe)2RuH(NH2)][OMe]. Similarly, the addition of CH3CH2OH (pKa(H2O) = 15.9) or Me3COH (pKa(H2O) = 18) to complex 1 in C6D6 results in the formation of new ruthenium complexes, suggesting the formation of the ion pairs [TpRu(PMe3)2(H2O)][OCH2CH3] and [TpRu(PMe3)2(H2O)][OC(CH3)2] respectively (eq 4).

Similar to observations with hydroxide complex 1, the reaction of the ruthenium parent amido TpRu(PMe3)2NH2 with 1,4-CHD at 75 °C yields TpRu(PMe3)2H and benzene in approximately 48% yield after 3 days. The addition of PMe3 to the reaction of TpRu(PMe3)2NH2 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 TpRu(PMe3)2NH2 (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 TpRu(PMe3)2OPh nor the anilido complex TpRu(PMe3)2NHPPh react with 1,4-CHD. For example, heating TpRu(PMe3)2OPh (3) with 1,4-CHD in benzene-d6 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 NH2 to NHPPh likely decreasing the propensity toward an acid/base reaction with 1,4-CHD. We cannot definitively eliminate a hydrogen atom abstraction pathway from consideration, however, the following points suggest an acid–base pathway: (a) hydrogen atom abstraction would form the 19-electron Ru(I) complex TpRu(PMe3)2(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; the conversion of 1 and 1,4-CHD to 1,3-CHD, TpRu(PMe3)2H, and benzene is slower than the analogous reaction with TpRu(PMe3)2NH2, a trend that is anticipated for an acid–base pathway but not necessarily for hydrogen atom abstraction; (d) the calculated O–H BDE of TpRu(PMe3)2(OH)2 is 37 kcal/mol; and (e) to our knowledge, there are no definitive examples of d6 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 TpRu(PMe3)2H 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-tetramethylpiperidinoxy) reacts with 1,4-CHD.
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 C₆D₆ 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 [TpRu(PMe₃)₂OH][OTf] (3) and Ag(s). The Evans NMR method was used to confirm the formation of paramagnetic Ru complex and determine that μₑffective = 1.78 μB for 3 at room temperature. This value is consistent with a single unpaired electron and close to the spin-only value of 1.73 μB, which is anticipated for an octahedral Ru(III) d⁵ species. Attempts to grow X-ray-quality crystals of 3 resulted in decomposition. In addition, after 12 h at room temperature, a C₆D₆ solution of [TpRu(PMe₃)₂OH][OTf] reveals the production of a small amount (~5% by ¹H NMR spectroscopy) of TpRu(PMe₃)₂OTf, probably due to the slow decomposition of the Ru(III) hydroxide complex 3.

The addition of 1 equiv of AgOTf to a C₆D₆ solution of TpRu(PMe₃)₂OH (1) and 3 equiv (based on complex 1) of 1,4-CHD (C−H BDE = 73 ± 2 kcal/mol) results in the formation of benzene (~35% based on 1), [TpRu(PMe₃)₂(OH)(H₂)][OTf] (4) (~60% yield), and TpRu(PMe₃)₂OTf (~10% yield) within 20 min at room temperature (yields were determined by ¹H NMR spectroscopy). Performing the identical reaction in toluene-d₈ results in the production of benzene, and TpRu(PMe₃)₂OTf in nearly identical yields to the reaction in C₆D₆. Complex 4 has been independently prepared upon combination of TpRu(PMe₃)₂OTf and water (see below). After 12 h, the resonances due to benzene (~50%), complex 4 (~50%), and TpRu(PMe₃)₂OTf (~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 C₆D₆ does not form benzene after 3 days. The addition of AgOTf to a C₆D₆ 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%), [TpRu(PMe₃)₂OH₂][OTf] (50%), and TpRu(PMe₃)₂OTf (50%) (all based upon complex 1) are observed by ¹H NMR spectroscopy (Scheme 5).

The addition of 2 equiv of H₂O to a C₆D₆ solution of TpRu(PMe₃)₂OTf forms [TpRu(PMe₃)₂OH₂][OTf] (4) in equilibrium with TpRuPMe₃₂OTf/H₂O. The formation of 4 is indicated by ¹H NMR and ³¹P 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 D₂O to the C₆D₆ 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 H₂O (Scheme 6).

Complex 4 has not been isolated and has been characterized in equilibrium with TpRu(PMe₃)₂OTf using ¹H and ³¹P NMR spectroscopy.


Scheme 4. Single-Electron Oxidation of TpRu(PMe₃)₂OH (1) by AgOTf to Form [TpRu(PMe₃)₂OH][OTf] (3) 

\begin{equation}
\text{OTf} \quad \text{AgOTf} \quad \text{C}_6\text{H}_{12} \quad \text{C}_6\text{H}_{12}
\end{equation}

\textbf{RT} 12 hours 

\textbf{< 5%}

* RT = room temperature.

Scheme 5. Single-Electron Oxidation of TpRu(PMe₃)₂OH (1) in the Presence of 1,4-Cyclohexadiene

\begin{equation}
\text{OTf} \quad \text{AgOTf} \quad \text{C}_6\text{H}_{12} \quad \text{C}_6\text{H}_{12}
\end{equation}

\textbf{< 50%}

* Yields taken from ¹H NMR spectroscopy.

Scheme 6. Formation [TpRu(PMe₃)₂OH₂][OTf] (4) and Equilibrium between Complex 4/D₂O and 4-d₈/H₂O

\begin{equation}
\text{OTf} \quad \text{H}_2\text{O} \quad \text{D}_2\text{O} \quad \text{H}_2\text{O}
\end{equation}

The addition of AgOTf to the solution of complex 1 and 9,-10-dihydroanthracene (9,10-DHA; C−H BDE = 78 ± 2 kcal/mol) in C₆D₆ results in the formation of anthracene (~20%), anthraquinone (~6%), [TpRu(PMe₃)₂OH₂][OTf] (~55%), and TpRu(PMe₃)₂OTf (~40%) (all based on complex 1; determined by ¹H NMR spectroscopy) after 12 h at room temperature (Scheme 7). The low yields reflect low conversions of starting materials. Mayer et al. have reported that the oxidation of 9,-
10-DHA by [(bpy)2(py)Ru IV 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 C6D6 results in the formation of fluorenone (eq 5). The formation of fluorenone was confirmed by both 1H NMR and IR spectroscopy (νC=O = 1719 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% TpRu(PMe3)2OTf. As with 9,10-DHA, the low yields are a result of low conversion of starting material.

Upon single-electron oxidation of complex 1, we suggest that the Ru(III) complex [TpRu(PMe3)2OH][OTf] reacts with substrates that possess relatively weak C–H bonds to produce [TpRu(PMe3)2(OH)2][OTf]. The latter complex then equilibrates with TpRu(PMe3)2OTf and free H2O. For example, C–H bond cleavage of 1,4-CHD (BDE = 73 ± 2 kcal/mol) via hydroxide-centered hydrogen atom abstraction would initially yield [TpRu(PMe3)2(OH)2][OTf] and cyclohexadienyl radical. Hydrogen atom abstraction from cyclohexadienyl radical by a second equivalent of [TpRu(PMe3)2OH][OTf] would produce benzene and a second equivalent of [TpRu(PMe3)2(OH)2][OTf] (Scheme 8). This pathway would produce a molar ratio of [TpRu(PMe3)2(OH)][OTf]/TpRu(PMe3)2OTf and C6H6 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 [TpRu(PMe3)2(OH)][OTf], TpRu(PMe3)2OTf, and C6H6. The addition of TEMPO to the reaction of 3 and 1,4-CHD increases the formation of benzene (relative to Ru) from ~50% (without TEMPO) to ~110% (with TEMPO). This result is consistent with initial reaction of [TpRu(PMe3)2OH][OTf] with 1,4-CHD to form [TpRu(PMe3)2(OH)2][OTf] and cyclohexadienyl radical followed by net hydrogen atom abstraction from cyclohexadienyl radical by TEMPO. Thus, with the addition of TEMPO each equivalent of C6H6 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 [TpRu(PMe3)2OH][OTf] (3) forms a mixture of anthracene and anthraquinone, while fluorene 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.72 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 complex 3 with 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,
phenylacetylene has an acidic (pKₐ = 25) yet homolytically strong C–H bond (125 kcal/mol), 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 9.²⁻,⁷⁰,⁷⁸ The redox potential of complex 1 has been determined by cyclic voltammetry (E₁/₂ = 0.01 V versus NHE, AG° = 0.23 kcal/mol). We have roughly estimated the pKₐ 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)OH][OTf]⁷⁻ 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 pKₐ 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 pKₐ 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 pKₐ of [TpRu(PMe₃)₂(OH₂)]⁺ and Ru(III/II) potential of 1 pKₐ 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)OH][OTf] can react with substrates that possess C–H bonds with BDE ≤ 80 kcal/mol. Using the B3LYP/CSDZ* level of theory, the O–H BDE of [(Tab)Ru(PH₃)₂(OH₂)]⁺ (Tab = tris(azido)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

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

<table>
<thead>
<tr>
<th>Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>[TpRu(PMe₃)₂(OH₂)]⁺ → [TpRu(PMe₃)₂OH]⁺ + H⁺ (aq) (pKₐ = 18-20)</td>
</tr>
<tr>
<td>[TpRu(PMe₃)₂OH]⁺ → [TpRu(PMe₃)₂OH]⁺ + e⁻ (E₁/₂ = 0.01 V)</td>
</tr>
<tr>
<td>1/2 H₂ (g) → H⁺ (aq)</td>
</tr>
<tr>
<td>[TpRu(PMe₃)₂(OH₂)]⁺ → [TpRu(PMe₃)₂OH]⁺ + H⁺ (aq) BDE(O-H)</td>
</tr>
</tbody>
</table>

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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]⁺

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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-d₈ was degassed by three freeze−pump−thaw cycles and stored over 4 Å molecular sieves. ³¹H 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 tetramethysilane 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

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 (I) 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 I 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),⁵⁵−⁵⁸ (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).⁵⁹,⁶⁰,⁶⁷ 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).

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

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen atom abstraction</td>
<td>M⁰ + H → M⁻ + H²⁺</td>
</tr>
<tr>
<td>Deprotonation</td>
<td>M⁺ + C → M⁻ + C⁻</td>
</tr>
<tr>
<td>1,2-addition</td>
<td>M⁻ + C → M⁻⁻ + C⁻⁻</td>
</tr>
</tbody>
</table>

(Response text)
In a glovebox, 1 equiv of AgOTf was added to the NMR solution. tert-butanol (3.9 \(\mu\)L, 0.046 mmol) was added to complex [TpRu(PMe3)2(OH)]2[O-tBu]. 1 H NMR (C\textsubscript{6}D\textsubscript{6}, 5.97, 5.87 (3H, 2:1 integration, each a t, Tp C(3)) 3), 1.15 (18H, vt, \(J\) 8 Hz, P(C\textsubscript{6}H\textsubscript{5}) \(\beta\)). 31 P NMR (C\textsubscript{6}D\textsubscript{6}, 29.0 ppm) showed the formation of TpRu(PMe\textsubscript{3})\textsubscript{2}OTf in less than 5% yield (based on 1).

**Evans NMR Method.** TpRu(PMe\textsubscript{3})\textsubscript{2}OH (1) (0.022 g, 0.046 mmol) was dissolved in 16 mL of C\textsubscript{6}D\textsubscript{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 \(\mu\)L of mesitylene. Two sealed capillary tubes, which were charged with 2 \(\mu\)L of mesitylene and 50 \(\mu\)L of C\textsubscript{6}D\textsubscript{6}, were added into the NMR tubes containing solutions A and B. 1 H 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 \(-6.7, 2.1, 300\) MHz). For solution B, only a single set of resonances (two total) was observed due to mesitylene.

**Reaction of** [TpRu(PMe\textsubscript{3})\textsubscript{2}OH][OTf] (3) **with 1,4-Cyclohexadiene.** Six screw-cap NMR tubes were each charged with 0.020 g (0.040 mmol) of TpRu(PMe\textsubscript{3})\textsubscript{2}OH (1) and 1.0 mL of C\textsubscript{6}D\textsubscript{6}. To the resulting solutions were added 0.044 mL of phenylacetylene (based on \(\text{TPR=0.046}\) mmol) and a small amount of mesitylene as internal standard. A 1 H 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 1 H NMR spectrum was 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(PMe\textsubscript{3})\textsubscript{2}OH][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(PMe\textsubscript{3})\textsubscript{2}OH (1) (0.007 g (0.040 mmol) of TEMPO, a small amount of mesitylene (internal standard), and 1.0 mL of C\textsubscript{6}D\textsubscript{6}. A 1 H 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 1 H NMR spectrum was acquired using a 10 s pulse delay. The formation of 50% TpRu-(PMe\textsubscript{3})\textsubscript{2}OTf, 50% [TpRu(PMe\textsubscript{3})\textsubscript{2}OH][OTf], and 110% C\textsubscript{6}H\textsubscript{5} was observed after 12 h at room temperature.

**Computational Methods.** All geometries were optimized in Jaguar\textsuperscript{90} with density functional theory (DFT) using the B3LYP functional.96–98 The Stevens effective core potential (ECP) and valence basis sets were used.99\textsuperscript{–}103 With a d-polarization function on heavy main group elements (CSDZ\textsuperscript* 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-azano borate (Tab), the latter being shown in previous work.49,50,54 to behave similarly in electronic and steric impact to the full Tp ligand. PMe\textsubscript{3} ligands were modeled with PH\textsubscript{3}.

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(87) Jaguar, version 5.5; Schrodinger, Inc.; Portland.
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