Evidence for the Net Addition of Arene C–H Bonds across a Ru(II)–Hydroxide Bond

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The activation of C–H bonds by transition metal complexes can proceed by multiple pathways, including the 1,2-addition of C–H bonds across early transition metal imido bonds.^{1–4} Such transformations are potentially useful since subsequent N–C reductive elimination (RE) would produce a free amine; however, RE is often a high-energy reaction for early transition metals. In contrast, REs of N–C and O–C bonds form the foundation of routes to aryl amines and ethers using late transition metal catalysts.^{5,6} Thus, it is anticipated that accessing the net addition of C–H bonds (regardless of the *specific* mechanism) across late transition metal M–X bonds (X = anionic N or O-based ligand) could ultimately lead to the development of routes for hydrocarbon functionalization. Late transition metal oxo and related systems are known to initiate hydrogen atom abstraction;⁷ however, these transformations do not involve direct interaction of the metal center with the external C–H substrate. In addition, Ru–amido complexes have been demonstrated to deprotonate “acidic” C–H bonds.⁸

The previously reported complex $\text{TpRu}(\text{PMe}_3)_2(\text{OTf})$ (OTf = trifluoromethanesulfonate) reacts with $\text{CsOH} \cdot \text{H}_2\text{O}$ in refluxing toluene to produce $\text{TpRu}(\text{PMe}_3)_2(\text{OH})$ (**1**). A solid-state X-ray diffraction study of **1** has confirmed its structure as a monomeric $\text{Ru}(\text{II})$ –hydroxide complex (Figure 1, see Supporting Information).

Figure 1. ORTEP (30% probability) of $\text{TpRu}(\text{PMe}_3)_2(\text{OH})$ (**1**).

Heating **1** (80 °C) in C₆D₆ results in H/D exchange at the hydroxide ligand to produce TpRu(PMe₃)₂(OD) (**1-d**₁), as indicated by both ¹H and ²H NMR. The combination of **1** (~1.6 mol %), H₂O, and C₆D₆ results in catalytic H/D exchange to produce C₆D_xH_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. Control reactions in the absence of Ru or using TpRu(PMe₃)₂(OTf) do not yield H/D exchange between H₂O and C₆D₆. Examples of metal-catalyzed H/D exchange that incorporate water are relatively scarce.⁹

Scheme 1. Possible Pathway for H/D Exchange between **1** and C₆D₆^a

^a The scheme shows calculated ΔG (kcal/mol) for each step using the model Tab for the full Tp ligand, PH_3 for PMe_3 and C_6H_6 . Labels A–F refer to the model complexes used for the computational studies.

A possible mechanism for the H/D exchange (Scheme 1) proceeds through ligand dissociation (Scheme 1 depicts dissociation of PMe_3) and reversible addition of a benzene C–D bond across the Ru–OH bond to produce the unobserved complex $\text{TpRu}(\text{PMe}_3)_2(\text{Ph})(\text{HOD})$. The reverse of these steps would form **1** and provide a pathway for H/D scrambling between the hydroxide ligand and C_6D_6 . Consistent with the proposed pathway, the extent of disappearance of hydrogen at the hydroxide ligand is approximately matched by the rate of hydrogen incorporation into benzene as determined by ^1H NMR spectroscopy. Subsequent reaction of the Ru–OD complex with H_2O provides a route for the observed catalytic H/D exchange between H_2O and C_6D_6 .

Kinetic studies reveal that H/D exchange at the hydroxide ligand of **1** in C₆D₆ is first-order with $k_{\text{obs}} = 8.0(2) \times 10^{-5} \text{ s}^{-1}$ (80 °C, $t_{1/2} \approx 2.4 \text{ h}$). This rate of H/D exchange suggests a more active catalyst for H/D scrambling between H₂O and C₆D₆ than has been observed; however, the poor solubility of H₂O in benzene likely slows the rate of catalysis. The addition of 10 mol % of TpRu(PMe₃)₂(OTf) (precursor to **1**) to a solution of **1** and C₆D₆ does not increase the rate of H/D exchange at the hydroxide ligand of **1**. The presence of coordinating ligands suppresses the rate of H/D exchange at the hydroxide ligand as well as the rate of catalysis, which is consistent with a metal-mediated process. For example, heating a solution of complex **1** in C₆D₆ in the presence of 0.1 equiv (based on **1**) of PMe₃ 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.

In order for the proposed pathway to be viable, complex **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 PMe₃ upon combination of complex **1** with PMe₃-d₉ at 80 °C reveals that $k_{\text{obs}} = 1.7(1) \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2} \approx 68 \text{ min}$). Thus, the rate of PMe₃ exchange is greater than the rate of H/D exchange and indicates that external substrates (e.g., C₆D₆)

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should have access to the coordination sphere on time scales that are more rapid than the observed H/D exchange.

Reaction of **1** with toluene- d_8 at 80 °C also results in H/D exchange (eq 1). 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. The selectivity for para and meta positions in preference to the 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. Another possible pathway is the creation of a source of H^+ . For example, coordination of H_2O could provide a route for generation of H^+ and electrophilic aromatic substitution; however, the regioselectivity for toluene H/D exchange is inconsistent with addition of H^+ to “free” toluene. Furthermore, the rate of H/D exchange at the hydroxide ligand upon heating a toluene- d_8 ($k_{obs} = 2.0(1) \times 10^{-5} s^{-1}$) solution of **1** is slower than that observed in C_6D_6 and is inconsistent with a pathway involving production of “ H^+ ” with subsequent electrophilic aromatic substitution.

In order for H/D exchange to occur by the pathway shown in Scheme 1, the conversion of **1** and benzene to free PMe_3 and $TpRu(PMe_3)(Ph)(HOD)$ and/or $TpRu(PMe_3)_2(Ph)$ (**2**) and water must be thermodynamically disfavored. Otherwise, the proposed addition of C–H bonds would afford observation of $TpRu(PMe_3)(Ph)(HOD)$ or **2**. Consistent with this notion, previous calculations and experimental results suggest that the addition of methane to (PCP)- $Ru(CO)(NH_2)$ to produce (PCP) $Ru(CO)(Me)(NH_3)$ is thermally disfavored.¹⁰ Although PMe_3 dissociation from **2** ($t_{1/2}$ for exchange with $P(CD_3)_3$ at 80 °C is ~ 235 min) is slower than for **1**, the rate of ligand exchange provides access to $\{TpRu(PMe_3)(Ph)\}$ on a time scale that is reasonable to observe reactivity; however, reactions of **2** in solvents in which water is at least partially soluble result in either decomposition of **2** (e.g., CD_2Cl_2 or $CDCl_3$) or likely competition with water for coordination (e.g., DMSO or CD_3CN). The potential reaction of **2** with methanol (in which **2** is soluble) to produce benzene and $TpRu(PMe_3)_2(OMe)$ (**3**) provides a model for the reaction of **2** with water. Although heating **2** in CD_3OD at

100 °C results in decomposition to multiple products, the formation of benzene (GC, 1H NMR) and $TpRu(PMe_3)_2D$ as a reaction intermediate is observed. The observation of $TpRu(PMe_3)_2D$ is consistent with the conversion of **2** and CD_3OD to **3**, since complex **3** in CD_3OD at 100 °C rapidly produces $TpRu(PMe_3)_2D$. Thus, it is likely that $TpRu(PMe_3)_2(Ph)$ (**2**) reacts with $MeOH$ to produce benzene and $TpRu(PMe_3)_2(OMe)$ (**3**) with subsequent conversion of **3** to $TpRu(PMe_3)_2(D)$ (eq 2). While these experiments do not provide direct evidence for the thermodynamic relationship of $2/H_2O$ and $1/C_6H_6$, they at least provide indirect evidence that $TpRu(PMe_3)_2(Ph)$ and ROH can convert to $Ru-OR$ and C_6H_6 as predicted by the pathway in Scheme 1.

DFT (B3LYP/CEP-31G(d)) calculations were performed using the model tris(azo)borate for the full Tp ligand (Scheme 1).¹¹ The calculations indicate that loss of a PH_3 ligand from $(Tab)Ru(PH_3)_2-OH$ (**A**) to form five-coordinate $(Tab)Ru(PH_3)OH$ (**B**) proceeds with $\Delta G = +2.8$ kcal/mol. The coordination of benzene to **B** to form $(Tab)Ru(PH_3)(\eta^2-C_6H_6)(OH)$ (**C**) is calculated to proceed with $\Delta G = +11.2$ kcal/mol. The reaction $C_6H_6 + A \rightarrow PH_3 + (Tab)Ru(PH_3)(Ph)(OH_2)$ (**E**) is calculated to be substantially endergonic ($\Delta G = +18.4$ kcal/mol), supporting the inference that the lack of experimental observation of **E** is a consequence of thermodynamics. Likewise, the reaction of **A** with benzene to form $(Tab)Ru(PH_3)_2(Ph)$ (**F**) and water is calculated to be endergonic, with $\Delta G = +9.1$ kcal/mol. Isolation of the transition state (**D** in Scheme 1) for C–H activation of benzene by the $Ru-OH$ bond gives a calculated free energy barrier of +17.6 kcal/mol relative to the η^2 -benzene complex (**C**). In comparison, the analogous free energy barrier for C–H activation of benzene by the $Ru-CH_3$ bond of $(Tab)Ru(CO)(Me)$ is calculated to be +21.2 kcal/mol.¹¹

The results delineated herein provide evidence for the net addition of aromatic C–H bonds across a $Ru(II)$ –hydroxide bond in a reaction sequence that is kinetically accessible yet thermodynamically unfavorable. An alternative pathway is loss of PMe_3 , hydrogen migration to yield $TpRu^{IV}(O)(H)(PMe_3)$, followed by C–H addition across the $Ru=O$ bond; however, formation of a Ru^{IV} –oxo complex is expected to rapidly produce $Me_3P=O$. The generation of a “free” acid by deprotonation of **1** to generate $[TpRu(PMe_3)_2(O)]^-$ seems unlikely since it would form a likely high-energy anionic d^6 oxo complex. Although the proposed C–H activation events are not directly observed, results reported herein suggest that late transition metal complexes with non-dative heteroatom-based ligands can be used to activate C–H bonds in a process in which the metal center is involved in the C–H cleavage step (regardless of the specific mechanism of C–H activation). Supporting this contention, in a paper in this issue, Periana et al. report the reaction of an Ir(III) methoxide complex with benzene to produce an Ir–Ph complex and $MeOH$ with calculated $\Delta H = -17.1$ kcal/mol.

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Supporting Information Available: Details of experimental (including kinetic studies and plots) and computational studies as well as details of X-ray data collection and structure solution for **1** (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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