Communication

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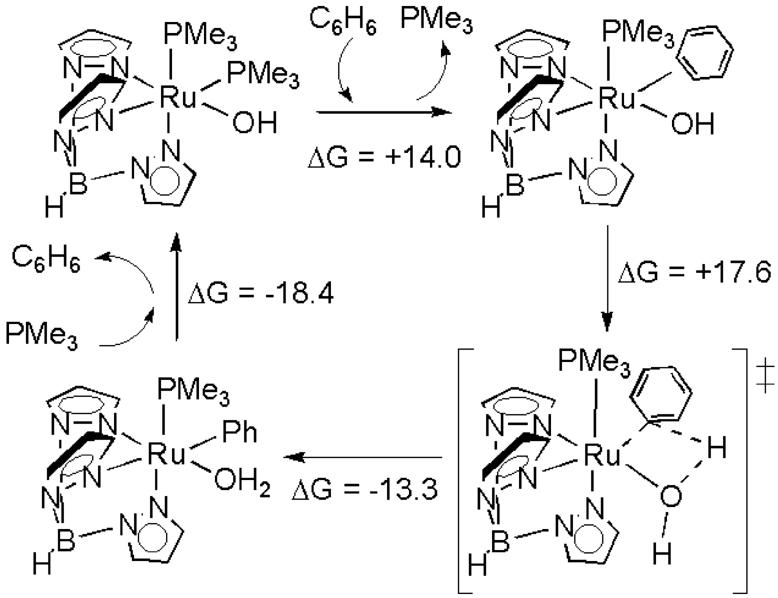

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Evidence for the Net Addition of Arene C−H Bonds across a Ru(II)−Hydroxide Bond

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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 $TpRu(PMe_3)_2(OTf)$ (OTf = trifluoromethanesulfonate) reacts with $CsOH{\cdot}H_2O$ in refluxing toluene to produce $TpRu(PMe_3)_2(OH)$ (**1**). A solid-state X-ray diffraction study of **1** has confirmed its structure as a monomeric Ru(II)−hydroxide complex (Figure 1, see Supporting Information).

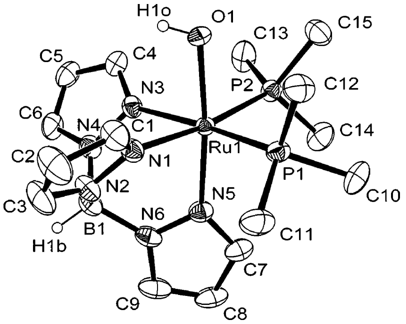
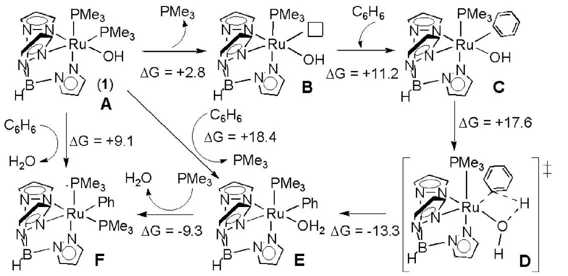


Figure 1. ORTEP (30% probability) of $TpRu(PMe_3)_2(OH)$ (**1**).

Heating **1** (80 °C) in C_6D_6 results in H/D exchange at the hydroxide ligand to produce $TpRu(PMe_3)_2(OD)$ (**1**-d_1), as indicated by both ^1H and ^2H NMR. The combination of **1** (~1.6 mol %), H_2O, and C_6D_6 results in catalytic H/D exchange to produce $C_6D_xH_y$ ($x + y = 6$), 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 $TpRu(PMe_3)_2(OTf)$ do not yield H/D exchange between H_2O and C_6D_6. 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 C_6D_6[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 $TpRu(PMe_3)(Ph)(HOD)$. 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 C_6D_6 is first-order with $k_{obs} = 8.0(2) \times 10^{-5}$ s^{-1} (80 °C, $t_{1/2} \approx 2.4$ h). This rate of H/D exchange suggests a more active catalyst for H/D scrambling between H_2O and C_6D_6 than has been observed; however, the poor solubility of H_2O in benzene likely slows the rate of catalysis. The addition of 10 mol % of $TpRu(PMe_3)_2(OTf)$ (precursor to **1**) to a solution of **1** and C_6D_6 does not increase the rate of H/D exchange at the hydroxide ligand of **1**. 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 C_6D_6 in the presence of 0.1 equiv (based on **1**) of PMe_3 results in no observable H/D exchange at the hydroxide ligand after 168 h at 80 °C. The addition of the "non-coordinating" base 2,6-lutidine does not increase the rate of H/D exchange at the hydroxide ligand.

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 PMe_3 upon combination of complex **1** with PMe_3-d_9 at 80 °C reveals that $k_{obs} = 1.7(1) \times 10^{-4}$ s^{-1} ($t_{1/2} \approx$ 68 min). Thus, the rate of PMe_3 exchange is greater than the rate of H/D exchange and indicates that external substrates (e.g., C_6D_6)

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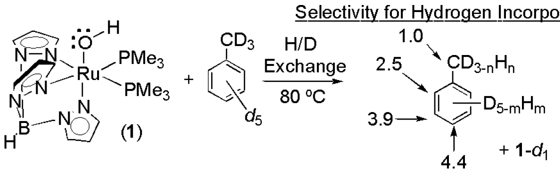
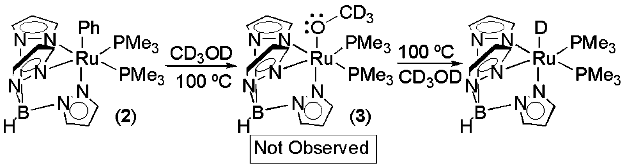
should have access to the coordination sphere on time scales that are more rapid than the observed H/D exchange.

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.



(1)

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)$_2$D as a reaction intermediate is observed. The observation of TpRu(PMe_3)$_2$D 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)$_2$D. 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.



(2)

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)(η^2-C_6H_6)(OH) (**C**) is calculated to proceed with $\Delta G = +11.2$ kcal/mol. The reaction C_6H_6 + **A** → 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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