Combined Experimental and Computational Studies on the Nature of Aromatic C–H Activation by Octahedral Ruthenium(II) Complexes: Evidence for $\sigma$-Bond Metathesis from Hammett Studies

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Octahedral ruthenium complexes of the type TpRu(L)(NCMe)R [Tp = hydridotris(pyrazolyl)borate; R = alkyl or aryl; L = CO or PMe$_3$] have been shown previously to initiate the C–H activation of aromatic substrates. In order to probe the nature of the C–H activation step, reaction rates have been theoretically obtained for the conversion of TpRu(L)(p$_2$-C$_6$H$_4$X)Me to TpRu(L)(p$_2$-C$_6$H$_4$X) and CH$_4$ where X is varied among Br, Cl, CN, F, NH$_2$, NO$_2$, and OMe. A linear Hammett correlation is calculated with a positive $\rho$ value of 2.6 for L = CO and 3.2 for L = PMe$_3$. Calculated kinetic data for the aromatic C–H activations indicate that an electrophilic aromatic substitution mechanism is unlikely. While experiments cannot fully replicate the entire range of calculated Hammett plots, reactivity trends are consistent with the calculations that suggest activation barriers to overall metal-mediated aren C–H bond cleavage are reduced by the presence of electron-withdrawing groups in the position para to the site of activation. Previous mechanistic studies, as well as the structure and imaginary vibrational modes of the present transition states, validate that the C–H activation for this family of TpRu complexes occurs through a $\sigma$-bond metathesis-type pathway.

Introduction

While metal-mediated reactions with aryl halides are commonly used in catalytic C–C bond formation, the creation of aryl halide starting materials often involves multistep syntheses.¹⁻⁶ These types of bond-coupling catalytic reactions also often create byproducts that may be environmentally or (in the case of pharmaceuticals) biologically problematic. In order to avoid such syntheses and their resultant byproducts, it is desirable to identify atom-efficient catalysts that directly transform C$_{arly}$=H into C$_{arly}$=E (E = C, N, and O) bonds. There has been a recent swell of success in utilizing late transition metal catalysts toward the goal of direct C–H functionalization of aromatic substrates.⁷⁻¹¹ Our research groups have completed several joint theoretical and experimental investigations on Ru(II) systems that are able to catalyze additions of aromatic and olefinic C–H bonds across olefin C=C bonds (i.e., hydroarylation and hydrovinylation of olefins)¹²⁻¹⁵ and initiate net insertion of C–N multiple bonds into Ru–R bonds¹⁶,¹⁷ with research predominantly focused on Ru(II) complexes containing the tridentate Tp ligand [Tp = hydridotris(pyrazolyl)borate]. The Tp ligand, first characterized in 1966 by Trofimenko,¹⁸,¹⁹ provides a platform for the alteration of steric and electronic properties that permit substantial flexibility with regard to modifying the chemo- and regiospecificity of the metal complex in catalytic transformations.²⁰⁻²²

Metal-mediated C–H activation is a key step in overall catalytic cycles for the addition of C–H bonds across olefin double bonds using TpRu(L)(NCMe)R systems. Computational and experimental studies of the TpRu(L)X (L = neutral, two-electron donor ligand; X = formally anionic ligand)-mediated activation of C–H bonds on both model Tab-Ru [Tab = (12) Lail, M.; Bell, C. M.; Conner, D.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. Organometallics 2004, 23, 5007.
tris(azo)borate and full Tp-Ru complexes have provided increasing evidence that the transformations traverse concerted \(\sigma\)-bond metathesis (SBM) pathways rather than oxidative addition.\(^{12,14,23-25}\) The SBM transition state was originally proposed by Bercaw, Thompson, and co-workers for early, high-valent metal complexes.\(^{26}\) The SBM reaction generally implies a concerted mechanism with a transition state possessing a “parallelogram-shaped” appearance, as depicted in Scheme 1, where \(R\) and \(R'\) can be either hydrogen, alkyl, alkenyl, aryl, alkylnyl, or a related group. The investigation of Bercaw and coauthors concluded that interactions of the metal frontier \(\pi\)-orbitals on the \(R\) group are less sterically favorable than direct attack of the metal at the \(R-H\) \(\sigma\)-bond, as the direct attack would be perpendicular to the \(\pi\)-system of the \(R\) group.\(^{26}\)

Recently, access to \(C-H\) activation via \(\sigma\)-bond metathesis pathways with late transition metals has been a subject of considerable discussion.\(^{23,27-35}\) Computational studies of \(C-H\) activation mediated by late transition metals have shown different “flavors” of SBM mechanisms,\(^{12,14,23,35-38}\) which can be subdivided into two genres including one where the transition state has a “kite-shaped” geometry with a metal–hydrogen interaction [termed oxidative hydrogen migration (OHM) by Oxgaard, Goddard, and co-workers, Scheme 2]\(^{16,37,39}\) versus standard SBM, where a “parallelogram”-shaped transition state and a weak metal–hydrogen interaction are implied (Scheme 3).

1. Differences in electronic structure between the two mechanisms are perhaps only a technical point of discussion, as they describe subtle bonding characteristics of the theoretical transition states.

Further complicating matters is the possibility of an electrophilic substitution pathway, which is more commonly invoked for the activation of \(C-H\) bonds by highly electrophilic late transition metal systems.\(^{40-42}\) In this pathway, the metal serves as an electrophile to liberate \(H^+\) (depicted in Scheme 3), which is similar in some regards to the classic electrophilic aromatic substitution of organic chemistry.

The use of Hammett plots and linear free energy relationships to assist in the exploration of mechanisms is widespread experimentally and theoretically in physical organic and organometallic chemistry.\(^{43-46}\) An interesting aspect of SBM mechanisms discussed by Bercaw et al. is the relative insensitivity of substituted arenes to the electron-donating or withdrawing character of a substituent para to the \(C-H\) bond being activated, as well as roughly equal kinetic rates of meta- and para-activation for monosubstituted arenes.\(^{26}\) In this study, we will provide evidence that a linear free energy relationship exists between the calculated rates of \(C-H\) bond scission of \(C_6H_5X\) in which the substituent “\(X\)” is para to the \(C-H\) bond being activated by TpRu(L)Me (\(L = CO\) or PMe\(_3\)) and Hammett \(\rho\) values. Although experimental challenges preclude the reproduction of the full range of computational results, complementary experimental studies are shown to be consistent with the results of the calculations. Computational studies that employ Hammett relationships to model substituent effects of reactions have been reported.\(^{49-52}\) Herein, we seek to use the \(\rho\) value of a Hammett plot to discriminate between SBM and electrophilic substitution pathways for arene activation. Krogh-Jespersen, Goldman, et al. have used similar electronic effects to study oxidative addition of dihydrogen and \(C-H\) bonds to Ir(I) metals.\(^{53,54}\)

Another practical impetus for this computational Hammett study is the experimental difficulty encountered for \(C-H\) activation of functionalized arene substrates. A few experimental studies, in addition to the classic study by Bercaw et al.,\(^{26}\) employing Hammett analyses for \(C-H\) bond activating com

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**Scheme 1. Mechanism of \(C-H\) Activation by \(\sigma\)-Bond Metathesis**

\[
\text{M-R} + \text{R-H} \rightarrow \text{M-R} + \text{R-H}
\]

**Scheme 2. Mechanism of Oxidative Hydrogen Migration**

\[
\text{M-R} + \text{R-H} \rightarrow \text{M-R} + \text{R-H}
\]

**Scheme 3. Mechanism of Electrophilic Aromatic Substitution**

\[
\text{H}^+ + \text{L}_0\text{M} \rightarrow \text{L}_0\text{M}^+ + \text{H}^+
\]

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plexes (including β-hydride elimination processes) have been presented.\textsuperscript{55,59} Often, the heteroatomic groups that need to be introduced to get a significant electron-withdrawing/donating "spread" (CN, NH₂, NO₂, etc.) are incompatible with the C–H bond activating complexes and lead to decomposition. Also, in the present case (as previously discussed),\textsuperscript{12,14,15,57} the mechanism for C–H activation likely involves reversible dissociation of NCMe, reversible coordination of the arene, and rate-determining C–H activation. Thus, experimentally determined rate constants (k₀) are a combination of several individual rate constants for elementary reactions in the overall pathway, and deconvolution into individual k's for the C–H activation steps can be difficult. Hence, computational Hamnett studies of the C–H activation reactions can be a valuable adjunct, particularly when integrated with experiment, in the better understanding of the electronic factors that control the C–H activation reactions.

\section*{Experimental Section}

\subsection*{Computational Methods}
Quantum computations were carried out using the Gaussian03 software package.\textsuperscript{58} Density functional theory (DFT) energies were computed using the B3LYP hybrid functional. The Stevens relativistic effective core potentials (DFT) energies were computed using the B3LYP hybrid functional. 6

\subsection*{Reactions of Substituted \textit{meta}-Xylene Compounds with TpRu(PMe₃)(NCMe)Me.}
In separate experiments, TpRu(PMe₃)(NCMe)Me was reacted with 5 equiv of 2,6-dimethyl nitrobenzene, 2,6-dimethylbromobenzene, \textit{m}-xylene, 2,6-dimethylanisole, and 2,6-dimethylaniline. A representative procedure is given for the reaction with \textit{m}-xylene: TpRu(PMe₃)(NCMe)Me (0.011 g, 0.033 mmol), 5 equiv of \textit{m}-xylene (0.020 mL, 0.165 mmol), and hexamethyldisiloxane (0.004 mL, 0.054 mmol) in 0.4 mL of THF-\textit{d₅} were added to a screw-cap NMR tube and heated at 60 °C in a temperature-controlled oil bath. TpRu(PMe₃)(NCMe)Me was completely reacted. For reactions of 2,6-dimethyl nitrobenzene and 2,6-dimethylbromobenzene, TpRu(PMe₃)(NCMe)(p-NO₂-3,5-dimethylbenzene) (1) and TpRu(PMe₃)(NCMe)(p-Br-3,5-dimethylbenzene) (2) were produced in 48% and 33% yields (determined by integration versus internal standard), respectively. For all other \textit{m}-xylene compounds, decomposition to a complicated mixture of NMR-active TpRu and NMR-silent (presumably paramagnetic) systems was observed. These mixtures are consistent with control experiments in which TpRu(PMe₃)(NCMe)Me was heated in THF-\textit{d₅} in the absence of aromatic compounds. Thus, we conclude that TpRu(PMe₃)(NCMe)Me does not react to any appreciable extent with \textit{m}-xylene, 2,6-dimethylanisole, or 2,6-dimethylaniline.

TpRu(PMe₃)(NCMe)(p-NO₂-C₆H₄Me) (1). TpRu(PMe₃)(NCMe)Me (0.208 g, 0.466 mmol) was added to a mixture of 2,6-dimethyl nitrobenzene (4 mL) and THF (2 mL) in a Schlenk tube, and the reaction was stirred for approximately 30 h at 60 °C. The red solution was dried to a film under vacuum. The resulting film was dissolved in approximately 1 mL of THF and applied to a silica gel column constituted with 40% diethyl ether in hexanes.

\begin{thebibliography}{99}
\bibitem{63} Feng, Y.; Gunnoc, T. B.; Grimes, T. V.; Cundari, T. R. \textit{Organometallics} \textbf{2006}, 25, 5456.
\end{thebibliography}
Scheme 4. General Reaction Scheme for TpRu-Mediated C–H Activation of C6H6X Benzene (L = PMe3 or CO; X = CN, H, NH2, NO2, Br, Cl, F, or OCH3)

The product was eluted and collected as the second band (red) using a gradient elution of 40% to 60% diethyl ether in hexanes. The red eluent was dried to an orange solid in vacuo (0.091 g, 33%). 1H NMR (C6D6, δ): 7.65, 7.60 (each 1H, each a d, Tp 3 or 5 positions), 7.54 (1H, dd, J♂♀ = 1 Hz, Tp 3 or 5 position), 7.47, 7.18 (each 1H, each a d, Tp 3 or 5 positions), 7.18 (1H, overlapping with solvent, Tp 3 or 5 position), 7.07 (2H, br s, ortho position of p-NO2-C6Me2H2 aryl group), 6.12 (1H, t, Tp 4 position), 6.00 (1H, dt, J♂♀ = 14 Hz, ipso carbon of p-NO2-C6Me2H2 aryl group), 1.04 (6H, s, CH3), 119.1 (meta or para position of p-Br-C6Me2H2 aryl group), 120.8 (C6Me2H2 aryl group), 148.4, 146.2 (ortho and para positions of p-NO2-C6Me2H2 aryl group), 144.5, 143.8, 136.9, 136.2, 135.6 (Tp 3 and 5 positions), 126.0 (meta positions of p-NO2-C6Me2H2 aryl group), 120.5 (NCC6H4), 107.0, 106.7, 106.6 (Tp 4 positions), 20.6 (CH3 positions of p-NO2-C6Me2H2 aryl group), 17.6 (d, 1JCp = 26 Hz, P(CH3)3), 3.6 (NCC6H4), 31P{1H} NMR (C 6D6, δ): 19.3 (P(CH3)3). Anal. Calcd for C25H30N4O6P3: C, 66.07; H, 5.20; N, 19.27. Found: C, 45.79; H, 5.35; N, 18.86.

TpRu(PMe3)(NCMe)(p-Br-C6H4Me2H2) (2). TpRu(PMe3)(NCMe)-Me (0.205 g, 0.460 mmol) was added to a mixture of 2,6-dimethylbromobenzene (4 mL) and THF (2 mL) in a Schlenk tube, and the reaction was stirred for approximately 24 h at 60 °C. The brown solution was dried to a film under vacuum, reconstituted in approximately 1 mL of THF, and applied to a silica gel column constituted with 40% diethyl ether in hexanes. The product was eluted and collected as the second band (yellow) using a gradient elution of 40% to 60% diethyl ether in hexanes. The pale yellow eluent was dried to a white solid in vacuo (0.064 g, 23%). 1H NMR (C6D6, δ): 7.67, 7.63 (each 1H, each a d, Tp 3 or 5 positions), 7.57 (1H, dd, J♂♀ = 1 Hz, Tp 3 or 5 position), 7.50 (1H, d, Tp 3 or 5 positions), 7.31 (2H, overlapping d’s, Tp 3 or 5 position), 7.10 (2H, br s, ortho position of p-Br-C6Me2H2 aryl group) 6.13 (1H, t, Tp 4 position), 6.02 (1H, m, Tp 4 position), 5.98 (1H, t, Tp 4 position), 2.56 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3), 1.04 (6H, s, CH3). Anal. Calcd for C25H30N4O6P3: C, 66.07; H, 5.20; N, 19.27. Found: C, 45.79; H, 5.35; N, 18.86.

2. Transition State Geometries: Impact of Arene Substituent “X” Calculated transition states for C–H activation from TpRu(L)(η2-C,C6H4X)Me to form TpRu(L)(η2-C,C6H4X)Me and methane are similar to previously calculated transition states for C–H activation by TpRu(L)(Me)(C6H6) systems.2,12,15 All first-order transition states for arene C–H activation show a large, single imaginary vibrational frequency, corresponding to the removal of an arene hydrogen and its transfer to the methyl substituent. The imaginary frequencies are in the range 954 to 1264 cm⁻¹ for the CO ligand and 848 to 1104 cm⁻¹ for the PMe3 ligand. The magnitude of the imaginary vibrational frequency generally (but not linearly) increases with decreasing Hammett parameter σp, indicating some correlation of the transition state imaginary frequency with the electron-withdrawing or -donating character of the para-substituent. More importantly, the imaginary vibrational mode in all transition state computations shows little perturbation of the surrounding Ru complex. All reaction products show Ru–C σ-bonding between the aryl carbon and the Ru metal center.

A primary distinguishing feature between the SBM and OHM mechanisms is the M–H bond distance (changes in other bond lengths within the transition states as a function of X and L were less significant). Table 1 shows the Ru–H bond lengths as a function of the substituent X identity. There is some linear

Results and Discussion

1. Reaction Coordinate and Arene Adducts. Scheme 4 shows the proposed reaction sequence for aromatic C–H activation that is based on previous research by our own groups,12,14,15,31,65 computational studies by Goddard et al.,57 and experimental studies for related TpRh complexes by Jones and co-workers.66-68 The active species for arene activation are the five-coordinate 16-electron systems TpRu(CO)Me and TpRu(PMe3)Me. The two coligands, carbon monoxide and trimethylphosphine, allow the electronic and steric sensitivity of the C–H bond activation to be probed. Due to the σ-acidic and weakly donating nature of CO, the PMe3 complexes are more electron-rich as well as more sterically encumbered than their carbonyl counterparts. Previous calculations have suggested that the 16-electron complexes TpRu(L)Me activate the C–H bond of arenes through four-centered transition states that are preceded by an η2,C-arene complexes (L = CO, CNH) or, in the case of bulkier ligands (e.g., L = PMe3, PEt3), η2–η,C-H-arene precursors.15

We have modeled TpRu(CO)(C6H3X)Me and TpRu(PMe3)(C6H3X)Me complexes where X = CN, H, NH2, NO2, Br, Cl, F, or OCH3. For all substituents X, the substituted arene is calculated to be coordinated η2-C,C to the Ru(II) metal center to form TpRu(L)(η2-C,C,C6H3X)Me systems. We have previously reported the calculated structure of TpRu(L)(C6H3R) systems,15 and the calculated structures of TpRu(L)(η2–η,C,C6H3X)Me systems are very closely related.

correlation ($R^2 = 0.98$ for $L = CO$ and $R^2 = 0.90$ for $L = PMe_3$) between the Ru–H bond length and the electron-withdrawing/donating character of the aryl substituent. More strongly donating “$X$” substituents result in longer Ru–H bond distances varying from 1.608 Å ($X = NO_2$) to 1.677 Å ($X = NH_2$) for $L = CO$ and from 1.592 Å ($X = NO_2$) to 1.620 Å ($X = NH_2$) for $L = PMe_3$. Overall, values of $r_c$ (Ru–H) range from 1.592 to 1.677 Å in the arene activation transition states (TSs). These bond distances closely agree with those obtained from computational studies of similar Ru complexes as an iridium complex studied by Goddard, Periana, et al. However, such results should be viewed with caution. It should be noted that a short distance alone is not prima facie evidence of a strong bond; a recent atom in molecule (AIM) study by our groups on transition states for C–H activation of benzene by model (Tab)Ru(PMe3)X ($X = OH, NH_2$) and related complexes indicates tenuous, if any, bonding along the Ru–H axis.

### Computational Hammett Analysis: $\sigma$-Bond Metathesis versus Electrophilic Aromatic Substitution

Gibbs free energies of activation for C–H bond cleavage para to the substituent “$X$” from TpRu(L)(η²-$C_6H_5X$)Me adducts were calculated using standard computational methods (Table 2). Insertion of the calculated $\Delta G^\circ$ values into the Eyring equation (298.15 K) provides calculated first-order rate constants for aryl C–H activation (Table 2). For the two coligands CO and PMe3, Hammett plots using calculated rate constants are shown in Figures 1 and 2. The appropriate $\sigma_p$, Hammett constants for the substituents X are listed in Table 2. In both cases, the theoretical $\rho$ values are positive with $\rho = 2.6$ for $L = CO$ and $\rho = 2.3$ for $L = PMe_3$. While there is a strong linear correlation ($R^2 = 0.97$) when $L = CO$, a poorer correlation ($R^2 = 0.83$) is found when $L = PMe_3$. It appears that the $X = NH_2$ ($L = PMe_3$) $\Delta G^\circ$ value is a statistical outlier, and its rate of reaction is “too large”. A deviation from linearity in the $\rho$ value is often ascribed to a change in the mechanism of the rate-determining step, but this is unlikely in the case of $L = PMe_3$ and $X = NH_2$ since the imaginary vibrational mode and calculated geometry of this TS is quite similar to that for the other substituents examined. When the $X = NH_2$ ($L = PMe_3$) data point is removed from the Hammett plot, a new value for $L = PMe_3$ of $\rho = 3.2$ is found with a much improved $R^2$ value of 0.97. The improved Hammett plot is shown in Figure 3.

### Tables

**Table 1. Calculated Ru–H Bond Lengths (in Å) for Transition States of C–H Activation from TpRu(L)(η²-$C_6H_5X$)Me Based on Arene Substituent X**

<table>
<thead>
<tr>
<th>$X$</th>
<th>$L = CO$</th>
<th>$L = PMe_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>1.608</td>
<td>1.592</td>
</tr>
<tr>
<td>CN</td>
<td>1.615</td>
<td>1.593</td>
</tr>
<tr>
<td>Br</td>
<td>1.638</td>
<td>1.596</td>
</tr>
<tr>
<td>Cl</td>
<td>1.638</td>
<td>1.598</td>
</tr>
<tr>
<td>F</td>
<td>1.647</td>
<td>1.600</td>
</tr>
<tr>
<td>H</td>
<td>1.643</td>
<td>1.600</td>
</tr>
<tr>
<td>OMe</td>
<td>1.665</td>
<td>1.611</td>
</tr>
<tr>
<td>NH</td>
<td>1.677</td>
<td>1.620</td>
</tr>
</tbody>
</table>

**Table 2. Calculated Relative Rates (298 K) of C–H Activation from TpRu(L)(η²-$C_6H_5X$)Me**

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\Delta G^\circ$ (kcal mol$^{-1}$)</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>log($k_1/k_0$)</th>
<th>$\sigma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>11.45</td>
<td>2.5 × 10$^6$</td>
<td>2.52</td>
<td>0.78</td>
</tr>
<tr>
<td>CN</td>
<td>12.33</td>
<td>5.7 × 10$^6$</td>
<td>1.87</td>
<td>0.66</td>
</tr>
<tr>
<td>Br</td>
<td>13.78</td>
<td>5.0 × 10$^6$</td>
<td>0.81</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl</td>
<td>13.43</td>
<td>8.9 × 10$^5$</td>
<td>1.06</td>
<td>0.23</td>
</tr>
<tr>
<td>F</td>
<td>14.16</td>
<td>2.6 × 10$^5$</td>
<td>0.53</td>
<td>0.06</td>
</tr>
<tr>
<td>H</td>
<td>14.88</td>
<td>7.7 × 10$^4$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>OMe</td>
<td>15.82</td>
<td>1.6 × 10$^4$</td>
<td>−0.69</td>
<td>−0.27</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>16.54</td>
<td>4.7 × 10$^3$</td>
<td>−1.22</td>
<td>−0.66</td>
</tr>
</tbody>
</table>

*All substituent constants are obtained from ref 47.*

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(69) It must be noted that the AIM analysis also indicated differences in the bonding of activating ligands, $X$, that did (e.g., NH$_2$ and OH) and did not (e.g., Me) possess available lone pairs (see ref 25).
Hammett plot for arene C–H activation by TpRu(PMe3)(η^2-C,C-C6H3X)Me systems (rate constants were determined from calculated ΔG° values at 298.15 K) with X = NH2 outlier removed.

properties of the aryl substituent relative to an electrophilic aromatic substitution mechanism, where rates of reaction between strongly electron withdrawing and strongly electron donating X groups tend to differ by 4 to 7 orders of magnitude.26 The calculations also indicate that when the coligand (L) of the complex is PMe3, the rate-determining step is slightly less influenced by aryl substituents than when L is CO, although given the approximations made and the outlier nature of the X = NH2 (L = PMe3) ΔG° value, more definitive statements regarding the effect of L are perhaps circumstantial. First-order rate constants are larger when L = PMe3 (k_max = 2.3 × 10^7 s^-1, k_min = 6.5 × 10^1 s^-1) versus L = CO (k_max = 2.5 × 10^4 s^-1, k_min = 4.7 s^-1). These results and the calculated rate trends are clearly opposite of typical electrophilic aromatic substitution reactions, where the reaction rates are anticipated to increase upon placement of electron-donating groups on the electrophile and the Hammett analysis for an electrophilic aromatic substitution should yield a negative ρ value.46

To our knowledge, few studies have been carried out with the purpose of benchmarking aryl-substituent effects for the SBM mechanism. Surprisingly, in the initial Bercaw study of σ-bond metathesis, the cyclopentadienyl scandium complexes investigated showed a relative insensitivity to substituted arenes, σ

In a more recent study of C–H activation of aromatic aldehydes by Cp*Rh(L)(Me)(XC6H4(C(H)O) [L = (P(OMe)) or PMe3; X = OMe, CF3, or Me; Cp* = pentamethylcyclopentadienyl] k_X=CF/k_X=OMe values of 6 (L = PMe3) and 18 [L = P(OMe)] were determined experimentally.70 Although our computational studies did not include the perfluoromethyl group, which has a σ value of 0.54, we can compare these experimental results to our calculated results for X = OMe and X = CN (the σ value for CN is 0.66, which is the closest Hammett analogue to the CF3 group from our study). For C–H activation from the TpRu(L)(Me)(η^2-C,C-C6H3X) systems, our calculations reveal that k_X=CN/k_X=OMe = 356 for L = CO and that k_X=CN/k_X=OMe = 1307 for L = PMe3. Thus, our Hammett plots reveal a greater response to substitution than has been previously observed experimentally. We propose that the increased sensitivity of the reaction to the aryl substituent may be partially, or even primarily, due to the neglect of solvent effects in our computations. However, it could also be an indication that the reaction TS has sufficient negative charge buildup in the aryl π-cloud to possess some features of a nucleophilic substitution reaction. Of course, a direct comparison of our Ru system to the Cp*Rh system is complicated by the activation of aromatic substrates by the former and aldehyde C–H bonds by the latter.

The positive slope (ρ) of the Hammett plots and the transition state geometry (in particular, the lack of structural evidence for deaeromatization of the phenyl ring of the substrate) clearly favor a SBM (or OHM) mechanism over an electrophilic aromatic substitution. If an electrophilic aromatic substitution mechanism were occurring, a partial change of the hybridization (sp2 to sp3) would occur on the aryl carbon involved in the mechanism due to this charge buildup. For the 18 transition states investigated in this study, the aryl CC bond falls within a very narrow range from 1.41 to 1.43 Å, which are similar to the 1.42 Å CC bond length of free benzene at the all-electron B3LYP level of theory and the mean CC bond lengths of 1.42 Å for the full TpRu complexes when L = CO/PMe3, X = H. Thus, the impact on the aromatic character of the aryl ring caused by altering the para-substituent within the complex is not substantial.

4. Experimental Studies

In an effort to compare experimental Hammett plots with the calculated plots discussed above, we sought to determine the relative rate of arene C–H activation in which the site of C–H bond cleavage is para to variable functionality in a six-membered benzene ring. Such reactions have three primary requirements: (1) C–H activation must occur selectively para to the substituent “X”, (2) reactions between the metal and the functionality “X” should be suppressed, and (3) overall reactions should occur in relatively high yields. In order to direct reactivity to the C–H bond para to functionality, we probed reactions of TpRu(PMe3)(NCMe)Me with 2-substituted 1,3-dimethyl benzene (i.e., meta-xylyl) compounds. It was anticipated that the meta-methyl groups would protect the functionality “X” and serve to direct C–H activation to the position para to X (Chart 1).

TpRu(PMe3)(NCMe)Me initiates C–H activation of benzene to produce TpRu(PMe3)(NCMe)Ph and free methane.12,57 However, heating THF-d8 solutions of TpRu(PMe3)(NCMe)Me (in both the absence and presence of excess free NCMe) and 5 equiv of C6D6MeX (X = H, NH2, or OMe) results in


Figure 3. Hammett plot for arene C–H activation by TpRu(PMe3)(η^2-C,C-C6H3X)Me systems (rate constants were determined from calculated ΔG° values at 298.15 K) with X = NH2 outlier removed.
decomposition without evidence of aromatic C–H activation (eq 1). \(^1\)H NMR analysis of these reactions reveals the formation of substantial quantities of NMR-silent, and presumably para-

\[ \text{Chart 1. Use of Substituted meta-Xylyl Compounds for Probing Arene C–H Activation} \]

\[ \text{Protection of X Functionality} \]

\[ \text{Metal Directed to C-H para to} X \]

\[ \text{Blocks C-H Activation Ortho to Methyl} \]

\[ \text{Table 3. Selected Crystallographic Data for TpRu(PMe}_3(NCMe)(p-N02-C}_6H_2Me_2) \]

\[ \text{empirical formula} C_{22}H_{30}BN_8O_2PRu \]

\[ \text{fw} \]

581.39

\[ \text{cryst syst} \]

monoclinic

\[ \text{space group} \]

\[ \text{a, Å} \]

40.204(3)

\[ \text{b, Å} \]

8.5482(6)

\[ \text{c, Å} \]

15.830(1)

\[ \beta, \text{deg} \]

103.744(1)

\[ \alpha, \text{deg} \]

52.645(6)

\[ Z \]

8

\[ D_{\text{calc}}, \text{g/cm}^3 \]

1.462

\[ \text{cryst size (mm)} \]

0.04 × 0.06 × 0.40

\[ R_1, \text{wR}_2 \]

0.0528, 0.1326

\[ \text{GOF} \]

1.020

\[ \text{Figure 4. ORTEP of } \text{TpRu(PMe}_3(NCMe)(p-N02-C}_6H_2Me_2) \ (1) \]

(30% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru1–N7, 2.003(3); Ru1–C15, 2.059(3); Ru1–P1, 2.268(1); Ru1–N1, 2.173(2); Ru1–N3, 2.076(2); Ru1–N5, 2.139(3); N7–C10, 1.143(4); C15–C16, 1.401(4); C16–C17, 1.399(4); C17–C18, 1.385(5); C18–N8, 1.460(4); N8–O2, 1.219(4). Selected bond angles (deg): N7–Ru1–C15, 87.32(11); N7–Ru1–P1, 93.42(8); C15–Ru1–P1, 93.22(9); O1–N8–O2, 122.1(3); O2–N8–C18, 119.2(3); O1–N8–C18, 118.8(3).

of the aryl ring with an O1–N8–C18–C17 dihedral angle of approximately 52°.

The failure of TpRu(PMe}_3(NCMe)Me to undergo clean reaction with a broad range of 2-substituted meta-xylyl compounds prevents a direct comparison of calculated linear free energy correlations with experimentally determined rate constants. However, the failure of TpRu(PMe}_3(NCMe)Me to react with meta-xylyl compounds that do not possess electron-withdrawing groups while undergoing reasonably clean reaction with xylyl compounds that possess bromide and nitro groups is consistent with the computational prediction that electron-deficient arenes should undergo more facile C–H activation.

Conclusions

The impact on aromatic C–H activation of substituents para to the site of C–H bond cleavage has been examined computationally and experimentally in order to further explore the mechanism inherent to the family of TpRu(L)R systems. For C–H activation by the TpRu(L)(η\(^2\)-C\(_6\)H\(_5\)X)Me (L = CO or PMe\(_3\); X = Br, Cl, CN, F, H, NH\(_2\), NO\(_2\), or OMe) complexes, calculated gas-phase reaction rates are increased by electron-withdrawing substituents para to the C–H bond being activated, which is consistent with a σ-bond metathesis reaction pathway and inconsistent with an electrophilic aromatic substitution mechanism. The calculated structures of the aromatic rings in the TSs for C–H activation are quite similar to the structure of the rings in the η\(^2\)-arene adducts that immediately precede the C–H activation step, which also is consistent with the σ-bond metathesis reaction. However, the positive \(\rho\) values of 2.6 and 3.2 (from Hammett plots) that have been calculated are larger than those found in typical reactions with a SMB mechanism. This could be due to a lack of stabilizing solvent effects for the gas-phase calculations or due to the TpRu(L)R σ-bond metathesis mechanism being somewhat more akin to a nucleophilic aromatic substitution than systems previously investigated. All


these results point to an evolving picture for TpRu(L)R-mediated C–H activation in which the metal center coordinates the C–H bond and activates it toward an intramolecular proton transfer (Scheme 5). This model of the transition state for C–H activation is also consistent with recent studies of arene C–H activation via 1,2-addition across Ru–X (X = OH or NHPh) Ir–OMe and Rh–OAr bonds. In general, changes that enhance the basicity of the ligand receiving the activated hydrogen atom or the acidity of the C–H bond are likely to reduce the activation barrier for C–H bond cleavage. For arene substituents X, the PMe₃ ligand is calculated to provide faster reaction rates for C–H bond activation than the CO derivative, which is in agreement with previous kinetic studies of TpRu complexes, as well as a less pronounced sensitivity to aryl-substituent effects. Experimental results for reaction of TpRu(PMe₃)(NCMe)Me with 2-substituted meta-xylyl compounds are consistent with calculations that suggest enhanced reactivity for substrates that possess electron-withdrawing substituents.

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Supporting Information Available: 1H NMR spectra of complexes 1 and 2 and complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for the X-ray structure of 1. This material is available free of charge via the Internet at http://pubs.acs.org.