Combined Experimental and Computational Studies on the Nature of Aromatic C−H Activation by Octahedral Ruthenium(II) Complexes: Evidence for σ-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)(η^2-*C,C*-C_6H_5X)Me to TpRu(L)(*p*-C_6H_4X) and CH_4 where X is varied among Br, Cl, CN, F, H, NH_2, NO_2, and OMe. A linear Hammett correlation is calculated with a positive ρ 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 arene 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 σ-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_{aryl}−H into C_{aryl}−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 bonds[16,17] 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 =

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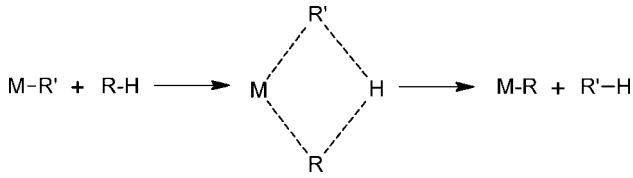
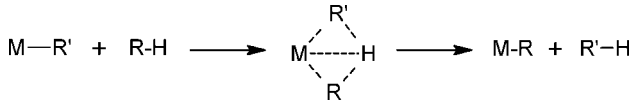
Scheme 1. Mechanism of C−H Activation by σ-Bond Metathesis



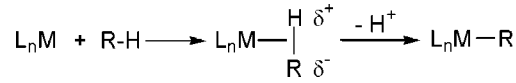
Scheme 2. Mechanism of Oxidative Hydrogen Migration



tris(azo)borate] and full Tp-Ru complexes have provided increasing evidence that the transformations traverse concerted σ-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, alkynyl, or a related group. The investigation of Bercaw and coauthors concluded that interactions of the metal frontier molecular orbitals with any π-orbitals on the R group are less sterically favorable than direct attack of the metal at the R−H σ-bond, as the direct attack would be perpendicular to the π-system of the R group.[26]

Recently, access to C−H activation via σ-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][36,37,39] versus standard SBM, where a "parallelogram"-shaped transition state and a weak metal−hydrogen interaction are implied (Scheme 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.

Scheme 3. Mechanism of Electrophilic Aromatic Substitution



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.[43–48] 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 σ_p 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 ρ 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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plexes (including β-hydride elimination processes) have been presented.[55,56] Often, the heteroatomic groups that need to be introduced to get a significant electron-withdrawing/donating "spread" (CN, NH_2, NO_2, etc.) are incompatible with the C−H bond activating complexes and lead to decomposition. Also, in the present case (as previously discussed),[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 (k_{obs}) 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 Hammett 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.

Experimental Section

Computational Methods. Quantum computations were carried out using the Gaussian03 software package.[58] Density functional theory (DFT) energies were computed using the B3LYP hybrid density functional. The Stevens relativistic effective core potentials (ECPs) and valence basis sets (VBSs) were utilized with the ruthenium atoms,[59,60] and main group elements were further augmented with a d-polarization function. The ECP/VBS combination, called SBK(d), has been shown to reliably produce a variety of computed properties.[12–14,16,61–64] At the stationary points of all investigated complexes, the Hessian was computed in order to characterize them as either minima (with no imaginary vibrational frequencies) or first-order transition states (one imaginary vibrational frequency). The quoted energies include zero-point energies (ZPE) and enthalpic and entropic thermodynamic corrections. While deficiencies in the typical approximation of the entropic contribution to gas-phase ΔG values are well-known, investigations in our laboratories have shown these approximations to be qualitatively correct.[12,14–16,24,63] Thermodynamic quantities were calculated at 298.15 K and 1 atm.

General Experimental Methods. Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer [$O_2(g) < 15$ ppm for all reactions]. Tetrahydrofuran was dried by distillation from sodium/benzophenone and stored over 4 Å molecular sieves. Anhydrous diethyl ether was purged with dinitrogen and stored over 4 Å molecular sieves. Substituted *m*-xylene reagents were purchased from commercial sources, distilled over CaH_2 and stored over 4 Å molecular sieves. Hexanes were purified by passage through a column of activated alumina and purged with dinitrogen. Benzene-d_6 and THF-d_8 were degassed with three freeze–pump–thaw cycles and stored under a dinitrogen atmosphere over 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer (operating frequency 75 MHz). All ^{1}H and ^{13}C NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{31}P NMR spectra were obtained on a Varian 400 MHz spectrometer and referenced against an external standard of H_3PO_4 ($\delta = 0$). Resonances due to the Tp ligand in ^{1}H NMR spectra are listed by chemical shift and multiplicity only (all coupling constants for the Tp ligand are ~2 Hz). The preparation, isolation, and characterization of TpRu(PMe_3)(NCMe)Me has been previously reported.[15] All other reagents were used as purchased from commercial sources. Elemental analyses were performed by Atlantic Microlabs, Inc. Electron ionizing (EI) mass spectrometry was carried out using a JEOL (Tokyo, Japan) HX110HF high-resolution mass spectrometer at the North Carolina State University Mass Spectrometry Laboratory using perfluorokerosene ions as a reference standard.

Reactions of Substituted *meta*-Xylene Compounds with TpRu(PMe_3)(NCMe)Me. In separate experiments, TpRu(PMe_3)(NCMe)Me was reacted with 5 equiv of 2,6-dimethylnitrobenzene, 2,6-dimethylbromobenzene, *m*-xylene, 2,6-dimethylanisole, and 2,6-dimethylaniline. A representative procedure is given for the reaction with *m*-xylene: TpRu(PMe_3)(NCMe)Me (0.011 g, 0.033 mmol), 5 equiv of *m*-xylene (0.020 mL, 0.165 mmol), and hexamethyldisiloxane (0.004 mL, 0.054 mmol) in 0.4 mL of THF-d_8 were added to a screw-cap NMR tube and heated at 60 °C in a temperature-controlled oil bath. ^{1}H NMR spectra were periodically acquired until consumption of TpRu(PMe_3)(NCMe)Me was complete. For reactions of 2,6-dimethylnitrobenzene and 2,6-dimethylbromobenzene, TpRu(PMe_3)(NCMe)(*p*-NO_2-3,5-dimethylbenzene) (**1**) and TpRu(PMe_3)(NCMe)(*p*-Br-3,5-dimethylbenzene) (**2**) were produced in 48% and 33% yields (determined by integration versus internal standard), respectively. For all other *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(PMe_3)(NCMe)Me was heated in THF-d_8 in the absence of aromatic compounds. Thus, we conclude that TpRu(PMe_3)(NCMe)Me does not react to any appreciable extent with *m*-xylene, 2,6-dimethylanisole, or 2,6-dimethylaniline.

TpRu(PMe_3)(NCMe)(*p*-NO_2-$C_6H_2Me_2$) (1). TpRu(PMe_3)(NCMe)Me (0.208 g, 0.466 mmol) was added to a mixture of 2,6-dimethylnitrobenzene (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.

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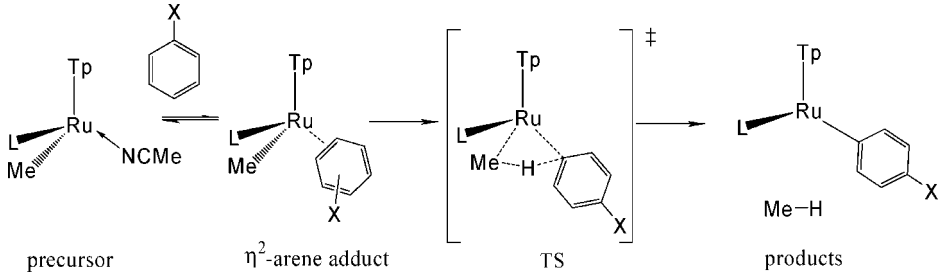
Scheme 4. General Reaction Scheme for TpRu-Mediated C−H Activation of C_6H_5X Benzene (L = PMe_3 or CO; X = CN, H, NH_2, NO_2, Br, Cl, F, or OCH_3)



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%). ^{1}H NMR (C_6D_6, δ): 7.65, 7.60 (each 1H, each a d, Tp 3 or 5 positions), 7.54 (1H, dd, J_{HP} < 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*-NO_2-$C_6Me_2H_2$ aryl group), 6.12 (1H, t, Tp 4 position), 6.00 (1H, dt, J_{HP} < 1 Hz, Tp 4 position), 5.96 (1H, t, Tp 4 position), 2.41 (6H, s, C*H*$_3$'s of *p*-NO_2-$C_6Me_2H_2$ aryl group), 0.97 (9H, d, $^2J_{HP}$ = 8 Hz, P(C*H*$_3$)$_3$), 0.77 (3H, s, NCC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, δ): 191.9 (d, $^2J_{CP}$ = 13 Hz, ipso carbon of *p*-NO_2-$C_6Me_2H_2$ aryl group), 148.4, 146.2 (ortho and para positions of *p*-NO_2-$C_6Me_2H_2$ aryl group), 144.5, 143.8, 143.3, 136.9, 136.2, 135.6 (Tp 3 and 5 positions), 126.0 (meta positions of *p*-NO_2-$C_6Me_2H_2$ aryl group), 120.5 (N*C*CH$_3$), 107.0, 106.7, 106.6 (Tp 4 positions), 20.6 (*C*H$_3$ positions of *p*-NO_2-$C_6Me_2H_2$ aryl group), 17.6 (d, $^1J_{CP}$ = 26 Hz, P(*C*H$_3$)$_3$), 3.6 (NC*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 19.3 {*P*(CH$_3$)$_3$}. Anal. Calcd for $C_{22}H_{30}BN_8O_2PRu$: C, 45.45; H, 5.20; N, 19.27. Found: C, 45.79; H, 5.35; N, 18.86.

TpRu(PMe$_3$)(NCMe)(*p*-Br-C$_6$H$_2$Me$_2$) (2). TpRu(PMe_3)(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 80% diethyl ether in hexanes. The pale yellow eluent was dried to a white solid in vacuo (0.064 g, 23%). ^{1}H NMR (C_6D_6, δ): 7.67, 7.63 (each 1H, each a d, Tp 3 or 5 positions), 7.57 (1H, dd, J_{HP} < 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-$C_6Me_2H_2$ 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, C*H*$_3$'s of *p*-Br-$C_6Me_2H_2$ aryl group), 1.04 (9H, d, $^2J_{HP}$ = 8 Hz, P(C*H*$_3$)$_3$), 0.77 (3H, s, NCC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, δ): 176.8 (d, $^2J_{CP}$ = 14 Hz, ipso carbon of *p*-Br-$C_6Me_2H_2$ aryl group), 145.3 (ortho position of *p*-Br-$C_6Me_2H_2$ aryl group), 143.5, 142.9, 142.1, 135.8, 135.0, 134.4 (Tp 3 and 5 positions), 133.1 (meta or para position of *p*-Br-$C_6Me_2H_2$ aryl group), 120.8 (N*C*CH$_3$), 119.1 (meta or para position of *p*-Br-$C_6Me_2H_2$ aryl group), 105.8, 105.5, 105.5 (Tp 4 positions), 24.7 (*C*H$_3$ positions of *p*-Br-$C_6Me_2H_2$ aryl group), 16.8 (d, $^1J_{CP}$ = 25 Hz, P(*C*H$_3$)$_3$), 2.7 (NC*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 20.2 {*P*(CH$_3$)$_3$}. EI MS: *m*/*z* (%) $M_{theoretical}$ = 615.0620, M_{sample} = 615.0611 (σ = 1.5 ppm), [M^+].

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,[12,14,15,57,65] computational studies by Goddard et al.,[37] 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(PMe_3)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 π-acidic and weakly donating nature of CO, the PMe_3 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 η^2-*C,C*-arene complexes (L = CO, CNH) or, in the case of bulkier ligands (e.g., L = PMe_3, PEt_3), η^2-*C,H*-arene precursors.[15]

We have modeled TpRu(CO)(C_6H_5X)Me and TpRu(PMe_3)(C_6H_5X)Me complexes where X = CN, H, NH_2, NO_2, Br, Cl, F, or OCH_3. For all substituents X, the substituted arene is calculated to be coordinated η^2-*C,C* to the Ru(II) metal center to form TpRu(L)(η^2-*C,C*-C_6H_5X)Me systems. We have previously reported the calculated structure of TpRu(L)(C_6H_6)R systems,[15] and the calculated structures of TpRu(L)(η^2-*C,C*-C_6H_5X)Me systems are very closely related.

2. Transition State Geometries: Impact of Arene Substituent "X" Calculated transition states for C−H activation from TpRu(L)(η^2-*C,C*-C_6H_5X)Me to form TpRu(L)(*p*-X-C_6H_4) and methane are similar to previously calculated transition states for C−H activation by TpRu(L)(Me)(C_6H_6) systems.[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 PMe_3 ligand. The magnitude of the imaginary vibrational frequency generally (but not linearly) increases with decreasing Hammett parameter σ_p, 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

(65) Goj, L. A.; Lail, M.; Pittard, K. A.; Riley, K. C.; Gunnoe, T. B.; Petersen, J. L. *Chem. Commun.* **2006**, 982.

(66) Vetter, A. J.; Flaschenriem, C.; Jones, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 12315.

(67) Vetter, A. J.; Jones, W. D. *Polyhedron* **2004**, *23*, 413.

(68) Wick, D. D.; Jones, W. D. *Organometallics* **1999**, *18*, 495.

Table 1. Calculated Ru−H Bond Lengths (in Å) for Transition States of C−H Activation from TpRu(L)(η^2-*C,C*-C_6H_5X)Me Based on Arene Substituent X

	L = CO	L = PMe_3
X = NO_2	1.608	1.592
X = CN	1.615	1.593
X = Br	1.638	1.596
X = Cl	1.638	1.598
X = F	1.647	1.600
X = H	1.643	1.600
X = OMe	1.665	1.611
X = NH	1.677	1.620

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 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_e(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[12,16,23,37] as well as an iridium complex studied by Goddard, Periana, et al.[36] However, the Ru−H bond distances are somewhat shorter than those obtained in the investigation of C−H activation of heteroaromatic substrates (∼1.75 Å) previously conducted in our laboratories.[14] Though we consider OHM to be a special subset of SBM, the consistently short Ru−H bonds definitely point to an OHM-type mechanism as defined by Oxgaard and Goddard.[36,37] 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 atoms in molecule (AIM) study by our groups[25,69] on transition states for C−H activation of benzene by model (Tab)Ru(PMe_3)X (X = OH, NH_2) and related complexes indicates tenuous, if any, bonding along the Ru−H axis.

3. Computational Hammett Analysis: *σ*-Bond Metathesis versus Electrophilic Aromatic Substitution. Gibbs free energies of activation for C−H bond cleavage para to the substituent "X" from TpRu(L)(η^2-*C,C*-C_6H_5X)Me adducts were calculated using standard computational methods (Table 2). Insertion of the calculated $\Delta G^{\ddagger}$ values into the Eyring equation (298.15 K) provides calculated first-order rate constants for arene C−H activation (Table 2). For the two coligands CO and PMe_3, Hammett plots using calculated rate constants are shown in Figures 1 and 2. The appropriate σ_p Hammett constants for the substituents X are listed in Table 2.[47] In both cases, the theoretical ρ 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) $\Delta G^{\ddagger}$ value is a statistical outlier, and its rate of reaction is "too large". A deviation from linearity in the ρ 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.

(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).

Table 2. Calculated Relative Rates (298 K) of C−H Activation from TpRu(L)(η^2-*C,C*-C_6H_5X)Me

L = CO				
X	$\Delta G^{\ddagger}$ (kcal mol^{-1})	k_x (s^{-1})	log(k_X/k_H)	σ_p[a]
NO_2	11.45	2.5×10^4	2.52	0.78
CN	12.33	5.7×10^3	1.87	0.66
Br	13.78	5.0×10^2	0.81	0.23
Cl	13.43	8.9×10^2	1.06	0.23
F	14.16	2.6×10^2	0.53	0.06
H	14.88	7.7×10^1	0.00	0.00
OMe	15.82	1.6×10^1	−0.69	−0.27
NH_2	16.54	4.7×10 °	−1.22	−0.66
L = PMe_3				
X	$\Delta G^{\ddagger}$ (kcal mol^{-1})	k_x (s^{-1})	log(k_X/k_H)	σ_p
NO_2	7.42	2.3×10^7	2.58	0.78
CN	8.00	8.5×10^6	2.15	0.66
Br	9.63	5.4×10^5	0.95	0.23
Cl	10.02	2.8×10^5	0.67	0.23
F	9.95	3.2×10^5	0.72	0.06
H	10.93	6.1×10^4	0.00	0.00
OMe	12.25	6.5×10^3	−0.97	−0.27
NH_2	11.31	3.2×10^4	−0.28	−0.66

[a] All substituent constants are obtained from ref 47.

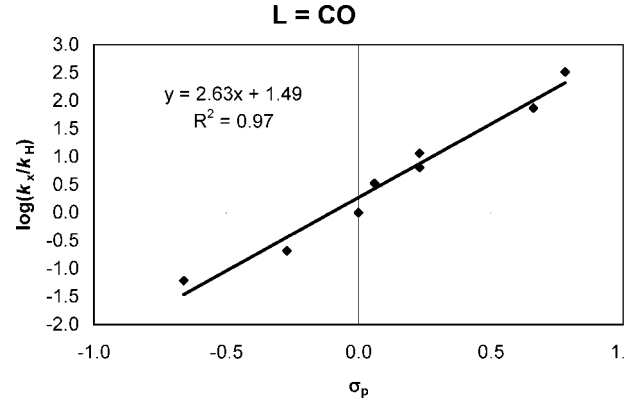


Figure 1. Hammett plot for arene C−H activation by TpRu(CO)(η^2-*C,C*-C_6H_5X)Me systems (rate constants were determined from calculated $\Delta G^{\ddagger}$'s at 298.15 K).

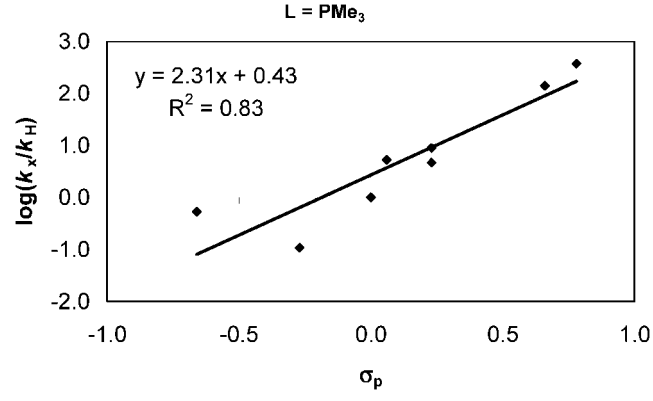


Figure 2. Hammett plot for arene C−H activation by TpRu(PMe_3)(η^2-*C,C*-C_6H_5X)Me systems (rate constants were determined from calculated $\Delta G^{\ddagger}$'s at 298.15 K).

For both L = CO and L = PMe_3 systems, the moderately large and positive ρ values and relative k_{max}/k_{min} values show that *electron-withdrawing* para-substituents are stabilizing the transition state. For L = CO, k_{max}/k_{min} is ∼5400, and when L = PMe_3, k_{max}/k_{min} is ∼3500. These calculated ratios signify that the reaction rate is less sensitive to the donating or withdrawing

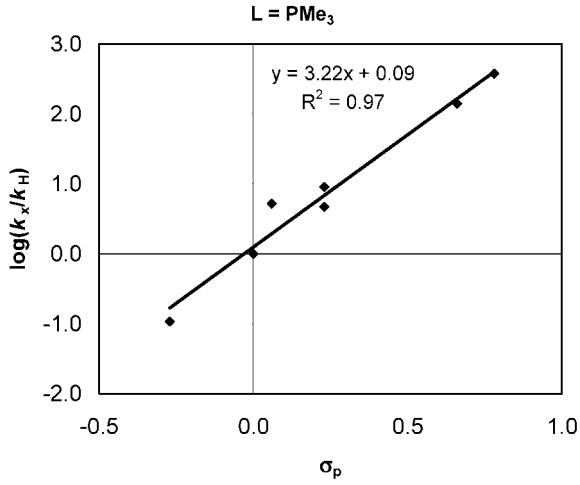


Figure 3. Hammett plot for arene C−H activation by TpRu(PMe$_3$)(η^2-*C,C*-C$_6$H$_5$X)Me systems (rate constants were determined from calculated $\Delta G^{\ddagger}$'s at 298.15 K) with X = NH$_2$ outlier removed.

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 PMe$_3$, 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 = NH$_2$ (L = PMe$_3$) $\Delta G^{\ddagger}$ value, more definitive statements regarding the effect of L are perhaps circumspect. First-order rate constants are larger when L = PMe$_3$ ($k_{max} = 2.3 \times 10^7$ s^{-1}, $k_{min} = 6.5 \times 10^3$ s^{-1}) versus L = CO ($k_{max} = 2.5 \times 10^4$ 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, with $k_{X=NMe2}/k_{X=H} \approx 0.97$ and $k_{X=CF3}/k_{X=H} \approx 0.42$ for C−H activation of C$_6$H$_5$X (X = H, CF$_3$ or NMe$_2$). In contrast to calculations and experiments (see below) for TpRu(L)(NCMe)Me systems in which electron-withdrawing groups appear to increase the rate of aromatic C−H activation, the electron-withdrawing perfluoromethyl group slows the rate of C−H activation relative to the parent benzene; however, the C−H activations by cyclopentadienyl scandium systems are not exclusively regioselective para to the substitution on the benzene ring.[26] In a recent study of Ru-mediated C−H activation of arylamines,[55] Yi and Yun have reported a Hammett study for substitution para to the site of C−H activation, for which a plot of $\log(k_x/k_H)$ versus σ_p revealed a slope (ρ) of −4.4, which suggests an electrophilic/carbocationic mechanism. *In contrast to the results with the Sc systems (see above), the impact of the electron-withdrawing versus electron-donating groups is opposite of the calculations/experimental results for aromatic C−H activation by the TpRu(L)(NCMe)Me systems reported herein.* However, the magnitude of the impact observed for Sc is substantially smaller than the calculated values for the Ru system.

In a more recent study of C−H activation of aromatic aldehydes by Cp*Rh(L)(Me)(XC$_6$H$_4$C(H)O) [L = P(OMe)$_3$ or PMe$_3$; X = OMe, CF$_3$ or Me; Cp* = pentamethylcyclopentadienyl] $k_{X=CF3}/k_{X=OMe}$ values of 6 (L = PMe$_3$) and 18 [L = P(OMe)$_3$] were determined experimentally.[70] Although our computational studies did not include the perfluoromethyl group, which has a σ_p value of 0.54, we can compare these experimental results to our calculated results for X = OMe and X = CN (the σ_p value for CN is 0.66, which is the closest Hammett analogue to the CF$_3$ group from our study). For C−H activation from the TpRu(L)(Me)(η^2-*C,C*-C$_6$H$_5$X) 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 = PMe$_3$. 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 dearomatization 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 (sp^2 to sp^3) 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 bonds fall 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 SBK(d) level of theory and the mean CC bond lengths of 1.42 Å for the full TpRu complexes when L = CO/PMe$_3$, 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(PMe$_3$)(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(PMe$_3$)(NCMe)Me initiates C−H activation of benzene to produce TpRu(PMe$_3$)(NCMe)Ph and free methane.[12,57] However, heating THF-d_8 solutions of TpRu(PMe$_3$)(NCMe)Me (in both the absence and presence of excess free NCMe) and 5 equiv of C$_6$H$_3$Me$_2$X (X = H, NH$_2$, or OMe) results in

(70) Corkey, B. K.; Taw, F. L.; Bergman, R. G.; Brookhart, M. *Polyhedron* **2004**, *23*, 2943.

Chart 1. Use of Substituted meta-Xylyl Compounds for Probing Arene C−H Activation

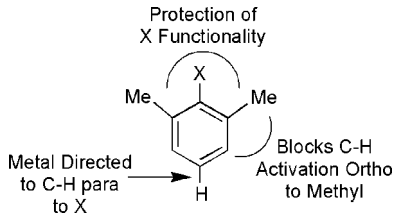
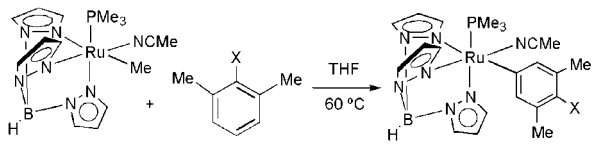


Table 3. Selected Crystallographic Data for TpRu(PMe$_3$)(NCMe)(*p*-NO$_2$-C$_6$H$_2$Me$_2$) (1)

empirical formula	$C_{22}H_{30}BN_8O_2PRu$
fw	581.39
cryst syst	monoclinic
space group	*C2/c*
a, Å	40.204(3)
b, Å	8.5482(6)
c, Å	15.830(1)
β, deg	103.744(1)
V, Å^3	5284.5(6)
Z	8
D_{calcd}, g/cm^3	1.462
cryst size (mm)	0.04 × 0.06 × 0.40
R_1, wR_2 [$I > 2(I)$]	0.0528, 0.1326
GOF	1.020

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 paramagnetic, complexes as well as *multiple* diamagnetic TpRu(PMe$_3$) complexes. These observations are analogous to the results of heating TpRu(PMe$_3$)(NCMe)Me in THF-d_8 in the absence of added arene. Thus, the Ru(II) methyl complex TpRu(PMe$_3$)(NCMe)Me is insufficiently reactive with the xylyl compounds when X = H, NH$_2$ or OMe.



For X = H, NH$_2$, OMe: decomposition
For X = NO$_2$ (**1**): 33% isolated yield, 48% yield by NMR
For X = Br (**2**): 23% isolated yield, 33% yield by NMR

(1)

In contrast, the reactions of TpRu(PMe$_3$)(NCMe)Me with meta-xylyl compounds that have electron-withdrawing groups in the 2-position (X = NO$_2$ or Br) produce the corresponding TpRu(PMe$_3$)(NCMe)(*p*-X-C$_6$Me$_2$H$_2$) complexes (eq 1). Monitoring these reactions by ^{1}H NMR spectroscopy in THF-d_8 (60 °C) with 5 equiv of the meta-xylyl substrate reveals that TpRu(PMe$_3$)(NCMe)(*p*-NO$_2$-C$_6$H$_2$Me$_2$) (**1**) is produced in 48% yield, while TpRu(PMe$_3$)(NCMe)(*p*-Br-C$_6$H$_2$Me$_2$) (**2**) is produced in 33% yield.

An X-ray diffraction study of a single crystal of complex **1** has confirmed its identity (Table 3 and Figure 4). The Ru−C$_{phenyl}$ bond distance of 2.059(3) Å is statistically identical to the Ru−C$_{phenyl}$ bond distance of 2.060(4) Å that has been previously reported for TpRu(PMe$_3$)(NCMe)Ph.[24] Thus, for complex **1**, the presence of the two methyl groups meta and the nitro group para to the Ru−C$_{phenyl}$ bond has little impact on the metal−aryl bonding. The plane formed by the NO$_2$ group is intermediate between perpendicular and parallel to the plane

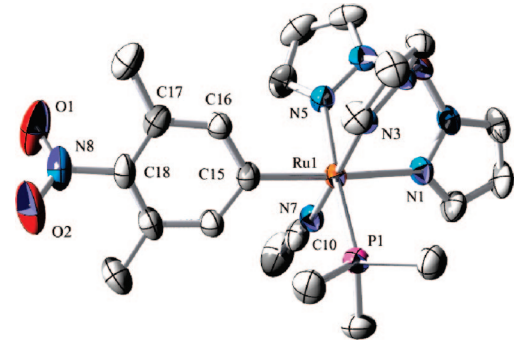


Figure 4. ORTEP of TpRu(PMe$_3$)(NCMe)(*p*-NO$_2$-C$_6$H$_2$Me$_2$) (**1**) (30% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru1−N7, 2.003(3); Ru1−C15, 2.059(3); Ru1−P1, 2.268(1); Ru1−N1, 2.173(2); Ru1−N3, 2.076(2); Ru1−N5, 2.139(3); N7−C10, 1.143(4); C15−C16, 1.401(4); C16−C17, 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,C*-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 ρ values of 2.6 and 3.2 (from Hammett plots) that have been calculated are larger than those found in typical reactions with a SBM 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

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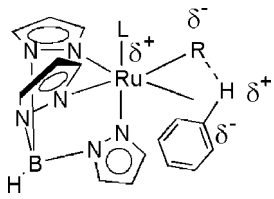
Scheme 5. Depiction of a Model for Ru(II)-Mediated C−H Activation



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.[24,38,71,72,73] 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 PMe_3 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,[15] as well as a less pronounced sensitivity to aryl-substituent effects. Experimental results for reaction of $TpRu(PMe_3)(NCMe)Me$ 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.

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