Conversions of Ruthenium(III) Alkyl Complexes to Ruthenium(II) through Ru−C$_{alkyl}$ Bond Homolysis

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Single-electron oxidation of the Ru(II) complexes TpRu(L)(L′)(R) (L = CO, L′ = NCMe, and R = CH$_3$ or CH$_2$CH$_2$Ph; L = L′ = PMe$_3$ and R = CH$_3$) with AgOTf leads to alkyl elimination reactions that produce TpRu(L)(L′)(OTf) and organic products that likely result from Ru−C$_{alkyl}$ bond homolysis. Density functional calculations on TpRu(CO)(NCMe)(Me) and its Ru(III) cation indicate that the Ru−CH$_3$ homolytic bond dissociation enthalpy is substantially reduced (48.6 to 23.2 kcal/mol) upon oxidation.

Introduction

The reductive elimination of an organic molecule from a transition metal complex is the product-forming step in many catalytic cycles. Several mechanisms exist for the reductive elimination of metal−carbon bonds including direct C−C elimination from a single metal center, C−C elimination from two metal centers, and initial metal−carbon bond homolysis (Scheme 1). For transformations that occur from two metal centers, both intramolecular and intermolecular processes have been reported, with the former pathway being observed more frequently.[1−4] Examples of less common intermolecular pathways include C−C elimination from Mn carbonyl complexes, H−H elimination from HCo(CO)$_4$, H−H and C−H elimination from osmium carbonyl complexes, elimination of aldehydes from mixtures of alkyl and hydride complexes that possess carbonyl ligands, and the elimination of dienes from metal-vinyl complexes.[5−13] The microscopic reverse of reductive elimination, oxidative addition, has also been reported to occur across two metal centers via both intra- and intermolecular reac-

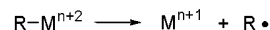## Scheme 1. Reductive Elimination of Metal−Carbon Bonds

Reductive Elimination from a Single Metal Center:

$$R\diagdown_{R\diagup} M^{n+2} \longrightarrow M^n + R-R$$

Reductive Elimination from Two Metal Centers:

$$2\ R-M^{n+2} \longrightarrow 2\ M^{n+1} + R-R$$
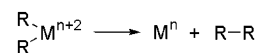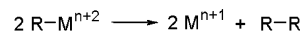
Reductive Elimination through Bond Homolysis:

$$R-M^{n+2} \longrightarrow M^{n+1} + R\bullet$$

tions.[14,15] Metal−carbon bond homolysis can also initiate the elimination of alkyl or aryl groups and results in a formal reduction of the metal center by a single electron.[16−19]

We have reported that complexes of the type TpRu(CO)(NCMe)(R) (Tp = hydridotris(pyrazolyl)borate; R = Me or aryl) serve as catalyst precursors for the hydroarylation of olefins;[20−22] however, in the presence of electron-deficient olefins the Ru(II) complexes initiate radical polymerization reactions.[23] Recent reports of intramolecular olefin hydroarylation reactions catalyzed by Ru(III) prompted us to explore single-electron oxidation sequences of the Ru(II) complexes TpRu(L)(L′)(R) (L = CO, L′ = NCMe, and R = Me or CH$_2$CH$_2$Ph; L = L′ = PMe$_3$ and R = Me).[24] Herein, we report on the

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predilection of the putative Ru(III) systems [TpRu(L)-(L′)(R)][OTf] (OTf = trifluoromethanesulfonate) to undergo reductive transformations and return to formal Ru(II) oxidation states through pathways that likely involve Ru–C$_{alkyl}$ bond homolysis.

Results

The reaction of TpRu(CO)(NCMe)(Me) with 1 equiv of AgOTf in methylene chloride results in the quantitative formation (by ^{1}H NMR spectroscopy) of TpRu(CO)-(NCMe)(OTf) (**1**) within 10 min at room temperature (eq 1). Complex **1** is isolated in 60% yield after workup and
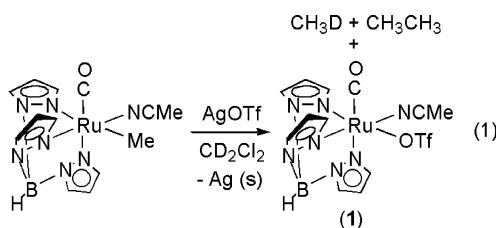
has been characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy (ν_{CO} = 1993 cm^{-1}), and elemental analysis. The overall reaction sequence involves a single-electron transfer to form Ag(s) and net loss of a methyl ligand from the putative Ru(III) intermediate [TpRu(CO)(Me)(NCMe)][OTf]. In addition to complex **1**, performing the reaction as a CD$_2$Cl$_2$ solution in a gastight NMR tube reveals the formation of CH$_3$D and ethane in a 1:9.4 molar ratio as determined by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum, a singlet due to production of ethane is observed at 0.9 ppm, while a multiplet (0.15 ppm) is observed due to the presence of CH$_3$D. In addition, sampling of the headspace from this reaction followed by analysis using mass spectrometry confirms the formation of CH$_3$D and ethane. The analogous reaction is observed in toluene-d_8 with the molar ratio of CH$_3$D to ethane in solution favoring CH$_3$D (1.8:1 ratio of CH$_3$D to CH$_3$CH$_3$). Thus, the production of methane, relative to ethane, is increased for reaction in toluene versus reaction in methylene chloride. In addition, performing the oxidation of TpRu(CO)(Me)-(NCMe) in CD$_2$Cl$_2$ in the presence of approximately 4 equiv of the radical trap 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) yields TpRu(CO)(OTf)(NCMe) (**1**) without observation of ethane or methane. Finally, analysis of several reactions of TpRu(CO)(NCMe)(Me) with AgOTf in a 1:1 molar mixture of toluene and toluene-d_8 revealed a kinetic isotope effect of 5.9(7) as determined by integration of the resonance due to CH$_4$ versus CH$_3$D in the ^{1}H NMR spectra.

Similar to the Ru(II) methyl complex, the reaction of TpRu(CO)(NCMe)(CH$_2$CH$_2$Ph) with AgOTf produces complex **1** and is complete within 5 min at room temperature (eq 2). The reaction also produces ethylbenzene, 1,4-diphenylbutane, and styrene. Although deuterium incorporation into ethylbenzene is a possibility, ^{1}H NMR spectroscopy does not allow a definitive determination whether deuterium is present. Using GC FID, the molar ratio of 1,4-diphenylbutane:styrene: ethylbenzene was determined to be 4:1:1.3.
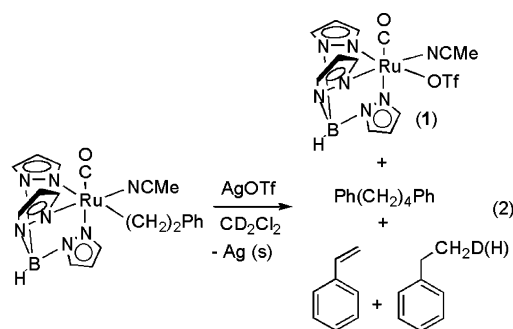
To probe the influence of the ancillary ligand set on the oxidation/reduction sequence, we sought to explore the oxidation of a complex of the type TpRuL$_2$(R). TpRu-(PMe$_3$)$_2$(Me) (**2**) is prepared by heating a solution of TpRu(PMe$_3$)$_2$Cl with Me$_2$Mg (Scheme 2), and the oxidation of TpRu(PMe$_3$)$_2$(Me) with AgOTf in CD$_2$Cl$_2$ produces CH$_3$D, ethane, and TpRu(PMe$_3$)$_2$(OTf) (**3**). The molar ratio of CH$_3$D to ethane in solution is approximately 1:10. The combination of complex **2** with AgOTf in toluene-d_8 produces complex **3** as well as CH$_3$D and ethane in an approximate 1.6:1 molar ratio. The molar ratios of methane and ethane upon oxidation of TpRu(PMe$_3$)$_2$(Me) in CD$_2$Cl$_2$ or toluene-d_8 are almost identical to those observed for analogous reactions of TpRu(CO)(NCMe)(Me).
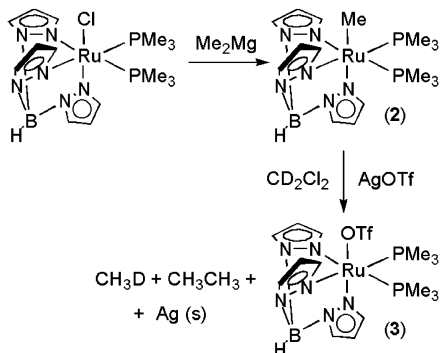
Discussion

One possible pathway for the observed Ru(III)/(II) elimination sequences is Ru^{III}–R bond homolysis to generate free radical species, and the formation of CH$_3$D after the oxidation of TpRu(CO)(NCMe)(Me) or TpRu-(PMe$_3$)$_2$(Me) in CD$_2$Cl$_2$ is consistent with such a pathway. The C–H bond dissociation enthalpy (BDE) of CH$_2$Cl$_2$ is approximately 100 kcal/mol, while the C–H BDE of methane is approximately 105 kcal/mol.[25] Thus, the formation of methane from methyl radical and methylene chloride is thermodynamically favorable. The formation of ethane that results from C–C coupling of two methyl species is apparently in kinetic competition with hydrogen atom abstraction from solvent by methyl radical. Transformations that generate methyl radical should exhibit increased production of methane in solvents with weaker C–H bonds. Indeed, the oxidation of TpRu(CO)(Me)(NCMe) or TpRu(PMe$_3$)$_2$(Me) in toluene-d_8 (BDE of benzylic C–H bond approximately 88 kcal/mol) yields increased production of methane relative to ethane compared with reactions in methylene chloride. The nearly identical molar ratios of CH$_3$D:ethane for the oxidation of either TpRu(CO)(NCMe)(Me) or TpRu-(PMe$_3$)$_2$(Me) in CD$_2$Cl$_2$ or toluene-d_8 suggests that organic products are formed from a common intermediate, and these data are consistent with the formation of methyl radical for both systems. In addition, the sequestration of methyl radical prior to hydrogen atom abstraction upon addition of TEMPO to the reaction of TpRu(CO)(NCMe)(Me) and AgOTf is consistent with the intermediacy of methyl radical. The reaction of TpRu-(CO)(NCMe)(Me) with [Cp$_2$Fe][PF$_6$] at 80 °C produces a single Ru(II) complex, ferrocene, ethane, and CH$_3$D.
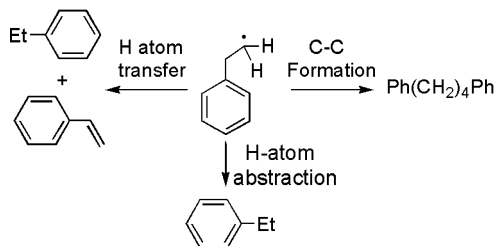
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Scheme 2.   Oxidation of TpRu(PMe$_3$)$_2$(Me) with AgOTf in CD$_2$Cl$_2$ Produces TpRu(PMe$_3$)$_2$(OTf) (3), CH$_3$D, and Ethane
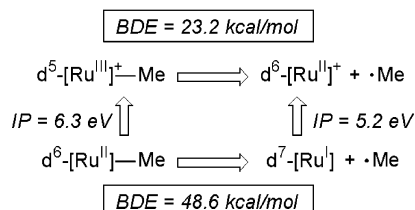

Scheme 3.   Possible Reaction Outcomes from the Generation of Ethylbenzene Radical

Figure 1. B3LYP/SBK(d)-calculated Ru−CH$_3$ BDEs enthalpies and IPs for [TpRu^{III}(CO)(NCMe)(Me)]$^+$ (top) and TpRu^{II}(CO)(NCMe)(Me) (bottom).

Scheme 4.   Computational Studies Indicate Ru−CH$_3$ BDEs of 48.6 kcal/mol for Ru^{II} and 23.2 kcal/mol for Ru^{III}

suggest that the metal−alkyl bond in the Ru^{III} complex is weaker than that in the corresponding Ru^{II} complex.

Calculated Ru−Me homolytic BDEs reveal a substantial decrease of 25.4 kcal/mol upon oxidation from Ru^{II} (48.6 kcal/mol) to Ru^{III} (23.2 kcal/mol) (Scheme 4). This decrease in BDE is mirrored by the calculated ionization potentials (IPs) shown in the thermochemical cycle where the difference between the IPs of d^6-Ru^{II}−Me (6.3 eV) and d^7-Ru^{I} (5.2 eV) is 1.1 eV, which is 25.4 kcal/mol (Figure 1). Hence, the calculations support the notion that the decrease in Ru−Me BDEs arises from weakening of the Ru−C bond upon oxidation of Ru from +2 to +3 as well as stabilization of the product, i.e., its return to a d^6 configuration upon homolytic Ru−C bond scission for the Ru^{III} complex.

Understanding metal−ligand bond energies and the factors that dictate them is crucial to the rational development of synthetic methodologies as well as understanding some biological processes,[26−29] and particularly relevant to single-site organometallic catalysts are the BDEs of metal−alkyl bonds. At room temperature, the Ru-alkyl complexes TpRu(CO)(NCMe)(R) (R = Me or CH$_2$CH$_2$Ph) and TpRu(PMe$_3$)$_2$(Me) exhibit no evidence of decomposition after at least one week in solution at room temperature. In contrast, single-electron oxidation to yield the cationic Ru^{III} complexes [TpRu(L)(L′)(R)][OTf] results in rapid Ru−R bond homolysis at room temperature. For all three TpRu^{III} alkyl complexes discussed herein, the formation of organic products and TpRu(L)(L′)(OTf) through bond homolysis occurs within at least 5 min at room temperature. This observation places an upper limit on the half-life for the reactions of approximately 1 min. Thus, $k_{obs} \geq 1.1 \times 10^{-2}$ s^{-1}, which corresponds to $\Delta G^{\ddagger} \leq 20$ kcal/mol at 298 K. Since Ru−C bond homolysis is likely the rate-determining step or precedes the rate-determining step

These results are analogous to the reaction with AgOTf, suggesting that inner-sphere electron transfer upon reaction with AgOTf to produce Ag−R with subsequent Ag−C bond homolysis is an unlikely reaction pathway. Cyclic voltammetry experiments indicate a quasi-reversible oxidation of TpRu(CO)(NCMe)(Me) at 0.95 V (vs NHE).[23] Similar analyses of TpRu(CO)(NCMe)(CH$_2$CH$_2$Ph) and TpRu(PMe$_3$)$_2$Me reveal quasi-reversible oxidation waves at $E_{1/2} = 1.02$ and 0.25 V, respectively.
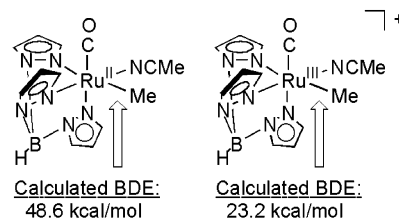
The formation of ethylbenzene and styrene in the oxidation of TpRu(CO)(NCMe)(CH$_2$CH$_2$Ph) is also consistent with the generation of alkyl radical. Thus, the formation of ethylbenzene radical can produce 1,4-diphenylbutane through C−C coupling, a 1:1 ratio of styrene and ethylbenzene through intermolecular hydrogen atom transfer, and ethylbenzene through hydrogen atom abstraction from the solvent (Scheme 3).

In support of the experimental studies, B3LYP/SBK(d) calculations were carried out on full models of the methyl radical, neutral TpRu^{II}(CO)(NCMe)(Me), and {TpRu^{I}(CO)(NCMe)} complexes as well as the cationic [TpRu^{III}(CO)(NCMe)(Me)]$^+$ and [TpRu^{II}(CO)(NCMe)]$^+$ complexes to determine Ru−CH$_3$ BDEs. In general, there are no major differences in the geometries of the corresponding neutral and cationic complexes. Interestingly, the calculated Ru^{II}−Me and Ru^{III}−Me bond lengths of TpRu^{II}(CO)(NCMe)(Me) and [TpRu^{III}(CO)-(NCMe)(Me)]$^+$ were 2.15 and 2.14 Å, respectively. On the basis of available ionic radii in the literature for Ru^{II} and Ru^{III}, it is expected that bond lengths involving Ru^{III} will be 0.06 Å shorter than similar bonds involving Ru^{II}, yet the calculated ΔRu$^{III/II}$−CH$_3$ bond length is only 0.01 Å, which implies that the Ru^{III}−Me bond is weaker than the Ru^{II}−Me bond. This supposition is further supported by the Mulliken bond orbital population (BOP), which yields a value of 0.45 for the Ru^{II}−Me bond and 0.36 for the Ru^{III}−Me bond. The DFT-derived BOPs thus

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in the conversion of [TpRu(L)(L′)(R)][OTf] to TpRu(L)-(L′)(OTf), it is anticipated that the BDEs of the Ru−C bonds will be less than or similar to the magnitude of the free energy of activation. Therefore, the rapid conversions from Ru^{III} to Ru^{II} indicate that the Ru−C_{alkyl} BDEs of the Ru^{III} complexes [TpRu(L)(L′)(R)][OTf] are likely to be near 20 kcal/mol and represent a series of relatively weak metal−alkyl bonds. This estimation is consistent with the calculated Ru−C BDE of 23.2 kcal/mol for $[TpRu^{III}(CO)(NCMe)(Me)]^{+}$. Riordan and Halpern have reported that porphyrin Fe(III) alkyl BDEs range from 15 to 31 kcal/mol, and related studies have been performed on Co(III) systems.[16,17] The Ru−C BDE of a Ru^{IV} porphyrin bis-ethyl complex has been estimated at 21.7 (1.5) kcal/mol.[18] Oxidation of CpRu(PR₃)-(CO)(Me) systems yields methane and Ru(II) products.[30]

We have previously reported that the combination of TpRu(CO)(NCMe)(R) and electron-deficient olefins at elevated temperatures results in radical polymerization reactions at elevated temperatures.[23] The apparently weak Ru^{III}−C_{alkyl} bonds at the Ru(III) oxidation state of these TpRu systems are consistent with the observation of radical-initiated polymerization reactions. Thus, single-electron oxidation of TpRu(CO)(NCMe)(R) by the electron-deficient olefins, regardless of whether the electron transfer is thermodynamically favored, would provide facile access to alkyl radical species and initiate radical-based olefin polymerization. This result is key to the development of future generations of hydroarylation catalysts, as any substrate that can oxidize the TpRu(L)(L′)(R) systems would likely lead to decomposition through Ru−C bond homolysis.

A potential contributing factor to the decrease in BDEs upon oxidation to Ru(III) is the driving force to return to a d^6 electronic configuration. A comprehensive study of closely related pseudo-octahedral Cp*Fe(dppe)X complexes (Cp* = pentamethylcyclopentadienyl; dppe = 1,2-bis(diphenylphosphino)ethane; X = halide, H, or Me) BDEs has revealed that oxidation from Fe(II) to Fe(III) also decreases homolytic BDEs by 9−17 kcal/mol.[19] For the Ru−Me systems discussed herein, the calculated change in homolytic BDE upon oxidation from d^6 to d^5 is 25.4 kcal/mol, while the change is approximately 9 kcal/mol for the Cp*Fe(dppe)CH₃. Thus, decrease in BDEs for metal−ligand bonds may be general for d^6 to d^5 oxidations of octahedral or pseudo-octahedral complexes.

Experimental Section

General Methods. All procedures were performed under an atmosphere of dry dinitrogen in a Vacuum Atmospheres glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer {$O_2(g) < 15$ ppm for all reactions}. Toluene and hexanes were purified by reflux over sodium/benzophenoneketyl followed by distillation under a dinitrogen atmosphere. Pentane and methylene chloride were refluxed over P_2O_5, followed by distillation under a dinitrogen atmosphere. Toluene-d_8, CD_2Cl_2, and $CDCl_3$ were degassed by three freeze−pump−thaw cycles and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR measurements were performed on either a Varian Mercury 300 or a 400 MHz spectrometer and were referenced against tetramethylsilane using residual proton signals (^1H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). Resonances due to the Tp ligand are reported by chemical shift and multiplicity only (all coupling constants are 2 Hz). All ^{31}P NMR spectra were recorded on a Varian Mercury instrument operating at a frequency of 161 MHz with 85% phosphoric acid (0 ppm) as external standard. ^{19}F NMR spectra were recorded on a Varian Mercury instrument operating at a frequency of 376.5 MHz with C_6F_6 (−163 ppm) as internal standard. Cyclic voltammograms were recorded in a standard three-electrode cell from −2.00 V to +2.00 V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. Tetrabutylammonium hexafluorophosphate was dried under dynamic vacuum at 110 °C for 48 h prior to use. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate as internal standard. Gas chromatography was performed on a Hewlett-Packard 5890 GC using either an HP-5 capillary column (30 m × 0.25 mm with 0.25 μm film thickness) or a J&W Scientific DB-1 capillary column (30 m × 0.25 mm with 1.00 μm film thickness) equipped with a FID detector. Chromatograms were produced using Perkin-Elmer TotalChrom 6.2 software. GC-MS was performed using a HP GCD system with a 30 m × 0.25 mm HP-5 column with 0.25 μm film thickness. Ethylbenzene, styrene, 1,4-diphenyl-butane, and decane were obtained from Sigma Aldrich Chemical Co. and used as received. Methane (99.5%) and ethane (99.5%) were received in gas lecture bottles from MWSC High-Purity Gases and used as received. All IR spectra were acquired using a Mattson Genesis II FTIR as thin films on KBr plates or as solutions. The preparation, isolation, and characterization of TpRu(CO)(NCMe)(Me), TpRu(PMe₃)₂Cl, and TpRu(PMe₃)₂(OTf) have been previously reported.[20,31]

TpRu(CO)(NCMe)(OTf) (1). TpRu(CO)(NCMe)(Me) (0.314 g, 0.79 mmol) was dissolved in 50 mL of methylene chloride in a dry Schlenk flask. To this solution was added AgOTf (0.200 g, 0.78 mmol), and the resulting mixture was stirred at room temperature for 1 h. Completion of the reaction occurred within 5 min, as indicated by a shift in ν_{CO} from 1919 to 1993 cm⁻¹ in the IR spectra. The solution was filtered through a plug of Celite. The volatiles were removed from the filtrate under reduced pressure, and the subsequent residue was washed with pentane. The resulting pale yellow solid was dried in vacuo and isolated in 60% yield (0.250 g). IR (KBr): ν_{CO} = 1993 cm⁻¹, ν_{BH} = 2504 cm⁻¹. ^1H NMR ($CDCl_3$, δ): 8.04, 7.79, 7.76, 7.71, 7.67, 7.43 (each 1H, each a d, Tp 3 or 5 position), 6.40 (1H, t, Tp 4 position), 6.23 (2H, overlapping t's, Tp 4 position), 2.47 (3H, s, Ru−NCCH_3). ^{13}C NMR ($CDCl_3$, δ): 199.8 (s, Ru−CO), 145.7, 145.3, 142.0, 137.2, 136.3, 135.3, (each a s, Tp 3 or 5 position), 124.5 (s, Ru−NCMe), 119.1 {q (due to low signal-to-noise, only the inner lines of the expected quartet were observed), $^1J_{CF}$ = 317 Hz, Ru−O_3SCF₃}, 107.3, 107.0, 106.6 (each a s, Tp 4 position), 3.9 (s, Ru−NCCH_3). ^{19}F NMR ($CDCl_3$, δ): −78.6 (s, Ru−O_3SCF_3). Anal. Calcd for $C_{13}H_{13}$-$BF_3N_7O_4Ru$: C, 29.34; H, 2.46; N, 18.42. Found: C, 29.58; H, 2.52; N, 18.33.

TpRu(PMe₃)₂(Me) (2). TpRu(PMe₃)₂Cl (0.187 g, 3.7 mmol) and toluene (∼50 mL) were combined in a round-bottom flask to give a homogeneous yellow solution. To this solution was added Me₂Mg (0.024 g, 4.4 mmol), and the mixture was heated to reflux for 6 h. The dark yellow solution was passed through a plug of Celite with a copious amount of diethyl ether to give a yellow filtrate. The volatiles were removed from the filtrate under reduced pressure. The white solid that remained was recrystallized by dissolving in 1 mL of methylene chloride followed by addition of 10 mL of methanol. The precipitate was collected by vacuum filtration and dried in vacuo (0.041 g, 23%). ^1H NMR ($CDCl_3$, δ): 7.71, 7.60, 7.59, 7.55 (6H total,

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1:2:2:1 integration, each a d, Tp 3 or 5 position), 6.15, 6.08 (3H total, 1:2 integration, each a t, Tp 4 position), 1.22 (18H, vt, P(CH_3)$_3$, N = 8 Hz), −0.30 (3H, t, $^3J_{HP}$ = 4 Hz, Ru−CH_3). ^{13}C NMR (CDCl$_3$, δ): 143.5, 141.7, 134.6, 134.5 (each a s, Tp 3 or 5 position), 104.4, 104.3 (each a s, Tp 4 position), 19.5 (vt, P(CH_3)$_3$, N = 25 Hz), − 9.6 (t, Ru−CH_3, $^2J_{CP}$ = 11 Hz). CV (CH$_3$CN, 100 mV/s): $E_{1/2}$ = 0.25 V (quasi-reversible). Anal. Calcd for C$_{16}$H$_{31}$BN$_6$P$_2$Ru: C, 39.93; H, 6.49; N, 17.46. Found: C, 40.21; H, 6.48; N, 16.65. ^{1}H and ^{31}P NMR spectra of complex **2** are included in the Supporting Information.

Oxidation of TpRu(L)(L′)(Me) (L = L′ = PMe$_3$ or L = CO and L′= NCMe). A sample reaction is given. A screwcap NMR tube was charged with TpRu(CO)(Me)(NCMe) (0.020 g, 0.05 mmol). The solid was dissolved in 0.5 mL of CD$_2$Cl$_2$, and a ^{1}H NMR spectrum was recorded. The NMR tube was purged into a glovebox, and AgOTf (0.013 g, 0.05 mmol) was added. Upon addition of AgOTf, conversion of the colorless homogeneous solution to a honey-colored solution with gray precipitate was observed. A ^{1}H NMR spectrum was recorded after 5 min of reaction time. In addition to resonances due to the production of TpRu(CO)(NCMe)(OTf) (**1**), the production of CH$_3$D was indicated by a multiplet at 0.15 ppm along with a singlet due to ethane at 0.9 ppm. The molar ratio of CH$_3$D and ethane in solution was determined by integration of these resonances. The assignment of the resonance due to ethane was confirmed by ^{1}H NMR spectroscopy upon bubbling commercially purchased ethane through the solution. In addition, the production of ethane and CH$_3$D was confirmed by sampling of the reaction headspace and analysis by GC-MS.

Oxidation of TpRu(CO)(NCMe)(CH$_2$CH$_2$C$_6$H$_5$). A screwcap NMR tube was charged with TpRu(CO)(NCMe)(CH$_2$-CH$_2$C$_6$H$_5$) (0.005 g, 0.01 mmol) and 0.5 mL of CD$_2$Cl$_2$ to give a homogeneous solution. A ^{1}H NMR spectrum was recorded. The addition of 1 equiv of AgOTf resulted in the formation of a gray precipitate. A ^{1}H NMR spectrum was recorded after 5 min of reaction time. The only observable TpRu system was complex **1**. The production of ethylbenzene, styrene, and 1,4-diphenylbutane was determined by ^{1}H NMR spectroscopy (confirmed by comparison to the ^{1}H NMR spectra of commercially available materials) and GC-FID. Deuterium incorporation into the methyl group of ethylbenzene is possible; however, it does not occur to an extent that allows observation by ^{1}H NMR spectroscopy. The production of styrene was indicated by resonances in the ^{1}H NMR spectrum at 6.25 ppm (dd, styrene α), 5.76 ppm (dd, styrene β), and 4.94 ppm (dd, styrene β). The production of 1,4-diphenylbutane was confirmed by resonances at 2.65 ppm {m, (PhCH_2CH$_2$)$_2$} and 1.67 ppm {m, (PhCH$_2$CH_2)$_2$}. The quantities of ethylbenzene, 1,4-diphenylbutane, and styrene were determined using GC-FID upon comparison to the added internal standard decane (after linear regression analysis of three sets of standards for each compound). The production of ethylbenzene, styrene, and 1,4-diphenylbutane was also confirmed by GC-MS analysis.

Determination of Kinetic Isotope Effect. TpRu(NCMe)-(CO)(Me) (0.050 g, 0.12 mmol) was added to a screwcap NMR tube. Toluene (0.26 mL, 2.4 mmol) and toluene-d_8 (0.25 mL, 2.4 mmol) were added to the tube to give a homogeneous solution. A ^{1}H NMR spectrum was recorded. AgOTf (0.032 g, 0.12 mmol) was added to the tube without mixing of the AgOTf with the toluene solution. The tube was sealed and then inverted to produce Ag (s). A ^{1}H NMR spectrum was recorded after 10 min of reaction time. The production of CH$_4$ was observed as a singlet at 0.23 ppm with a resonance due to CH$_3$D (1:1:1 triplet) at 0.15 ppm. Integration of the resonances

due to CH$_4$ and CH$_3$D from four separate reactions revealed a kinetic isotope effect of 5.9(7).

Computational Methods. Quantum mechanical calculations were performed using Gaussian98.[32] The calculations employed density functional theory (DFT),[33] in particular the B3LYP hybrid functional.[34−37] Ruthenium and main group elements were described with the Stevens (CEP-31G) relativistic effective core potentials (ECPs) and valence basis sets (VBSs).[38,39] The valence basis sets of main group elements (carbon, nitrogen, oxygen) were augmented with a d polarization function with an exponent of 0.8, and no polarization function was used on the boron. This combination of ECPs and VBSs, termed SBK(d), has been employed for calculations on a wide selection of transition metal complexes, including Ruscorpionates.[21,22,40,41] All stationary points for the models investigated were fully optimized to minima (i.e., no imaginary frequencies) without symmetry constraints. Open-shell molecules were calculated within the unrestricted Kohn−Sham formalism. All reported energetics include zero-point and enthalpic corrections calculated using vibrational frequencies determined at the B3LYP/SBK(d) level of theory.

Supporting Information Available: ^{1}H and ^{31}P NMR spectra of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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