Inorg. Chem. **2003**, *42*, 4759–4772

Octahedral Ru(II) Amido Complexes TpRu(L)(L′)(NHR) (Tp = Hydridotris(pyrazolyl)borate; L = L′ = $P(OMe)_3$ or PMe_3 or L = CO and L′ = PPh_3; R = H, Ph, or ^{t}Bu): Synthesis, Characterization, and Reactions with Weakly Acidic C–H Bonds

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Received April 18, 2003

The octahedral Ru(II) amine complexes [TpRu(L)(L′)(NH_2R)][OTf] (L = L′ = PMe_3, $P(OMe)_3$ or L = CO and L′ = PPh_3; R = H or ^{t}Bu) have been synthesized and characterized. Deprotonation of the amine complexes [TpRu(L)(L′)(NH_3)][OTf] or [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][OTf] yields the Ru(II) amido complexes TpRu(L)(L′)(NH_2) and TpRu(PMe_3)$_2$(NH^tBu). Reactions of the parent amido complexes or TpRu(PMe_3)$_2$(NH^tBu) with phenylacetylene at room temperature result in immediate deprotonation to form ruthenium–amine/phenylacetylide ion pairs, and heating a benzene solution of the [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][PhC_2] ion pair results in the formation of the Ru(II) phenylacetylide complex TpRu(PMe_3)$_2$(C≡CPh) in >90% yield. The observation that [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][PhC_2] converts to the Ru(II) acetylide with good yield while heating the ion pairs [TpRu(L)(L′)(NH_3)][PhC_2] yields multiple products is attributed to reluctant dissociation of ammonia compared with the ^{t}butylamine ligand (i.e., different rates for acetylide/amine exchange). These results are consistent with ligand exchange reactions of Ru(II) amine complexes [TpRu(PMe_3)$_2$(NH_2R)][OTf] (R = H or ^{t}Bu) with acetonitrile. The previously reported phenyl amido complexes TpRuL_2(NHPh) {L = PMe_3 or $P(OMe)_3$} react with 10 equiv of phenylacetylene at elevated temperature to produce Ru(II) acetylide complexes TpRuL_2(C≡CPh) in quantitative yields. Kinetic studies indicate that the reaction of TpRu(PMe_3)$_2$(NHPh) with phenylacetylene occurs via a pathway that involves TpRu(PMe_3)$_2$(OTf) or [TpRu(PMe_3)$_2$(NH_2Ph)][OTf] as catalyst. Reactions of 1,4-cyclohexadiene with the Ru(II) amido complexes TpRu(L)(L′)(NH_2) (L = L′ = PMe_3 or L = CO and L′ = PPh_3) or TpRu(PMe_3)$_2$(NH^tBu) at elevated temperatures result in the formation of benzene and Ru hydride complexes. TpRu(PMe_3)$_2$(H), [Tp(PMe_3)$_2$Ru═C═C(H)Ph][OTf], [Tp(PMe_3)$_2$Ru═C(CH_2Ph){N(H)Ph}][OTf], and [TpRu(PMe_3)$_3$][OTf] have been independently prepared and characterized. Results from solid-state X-ray diffraction studies of the complexes [TpRu(CO)(PPh_3)(NH_3)][OTf], [TpRu(PMe_3)$_2$(NH_3)][OTf], and TpRu(CO)(PPh_3)(C≡CPh) are reported.

Introduction

Diverse and interesting reactivity patterns for late transition metal complexes that possess nondative heteroatomic ligands (e.g., amido, oxide, imido, or oxo ligands) have been reported.[1−10] Interest in late transition metal amido and oxide systems is derived, in part, from their importance in catalytic reactions such as olefin and alkyne hydroamination and arylamination as well as their role in C−H bond activation reactions (both biological and nonbiological),[6−8,11−19] and it

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10.1021/ic034410a CCC: $25.00
Published on Web 06/28/2003

has been demonstrated that high d-electron counts can increase the reactivity of π-donating (i.e., nondative) ligands.[9,10,20−22]

Late transition metal mediated C−H activation sequences that proceed via metal insertion into the C−H bond (oxidative addition) have received significant attention.[23−31] In contrast, many biological systems and an increasing number of synthetic models serve to activate C−H bonds remote to the metal center via ligand-based hydrogen abstraction.[13−17,19,32−41] The electronic nature and coordination environment of the metal center dictate whether the C−H activation sequences occur via hydride, hydrogen atom, or proton removal. For example, Mayer et al. have detailed a series of transition metal complexes that activate C−H bonds via initial electron transfer or hydrogen atom abstraction mechanisms and have demonstrated that competition between electron transfer and hydride abstraction mechanisms is dependent upon metal redox potentials.[17,37,42] Fe(III) hydroxide and methoxide complexes that mimic lipoxygenase enzymes and undergo odd-electron hydrogen atom abstraction have been reported.[16,38] The hydrogen atom abstraction reactions result in a change in formal metal oxidation state and are reliant upon the oxidizing ability of the transition metal center. In contrast, low valent Ru(II) amido and hydroxo complexes that cleave C−H bonds via deprotonation have been reported,[20,22,43] and the ligand-based C−H deprotonations do not alter the formal metal oxidation state. Highlighting the differences in C−H activation mechanism, Mn(III) hexafluoroacetylacetonate oxidizes 9,10-dihydroanthracene via hydrogen atom abstraction (possibly via initial single electron transfer and subsequent deprotonation) while *trans*-$(DMPE)_2$-$Ru(NH_2)(H)$ (DMPE = 1,2-dimethylphosphinoethane) converts 9,10-dihydroanthracene to anthracene via initial deprotonation.[20,37]

A thorough series of studies detailing the reactivity of octahedral Ru(II) hydroxo and parent amido complexes of the type *trans*-$(DMPE)_2Ru(X)(H)$ (X = OH or NH_2; DMPE = 1,2-dimethylphosphinoethane) has revealed the ability of the heteroatomic ligands to activate even weakly acidic C−H bonds via deprotonation reactions.[20,44,45] The basicities of the Ru−X moieties are likely derived from the lack of X to metal π-donation due to the electronically saturated metal center in combination with highly ionic Ru−X bonds.[5,9,10,46] The importance of understanding such basicity is highlighted by recent reports of nitrogen-based ligands that serve as proton reservoirs/delivery vehicles for transfer hydrogenation catalysts.[47,48] Herein, we report the synthesis and characterization of $[TpRu(L)(L')(NH_2{}^tBu)][OTf]$ (L = L′ = $P(OMe)_3$ or PMe_3 or L = CO and L′ = PPh_3), $TpRu(PMe_3)_2(NH^tBu)$, $TpRu(L)(L')(C{\equiv}CPh)$, $TpRu(PMe_3)_2(H)$, $[TpRu(PMe_3)_2(N{\equiv}CMe)][OTf]$, $[Tp(PMe_3)_2Ru{=}C(CH_2Ph)\{N(H)Ph\}][OTf]$, and $[Tp(PMe_3)_2Ru{=}C{=}C(H)Ph][OTf]$, solid-state X-ray diffraction studies of $[TpRu(CO)(PPh_3)(NH_3)][OTf]$, $[TpRu(PMe_3)_2(NH_3)][OTf]$, and $TpRu(CO)(PPh_3)(C{\equiv}CPh)$, as well as the details of the reactivity of TpRu(L)(L′)(NHR) (R = H, Ph or ^{t}Bu) with phenylacetylene and 1,4-cyclohexadiene (CHD). Also included is a linear free energy study of equilibria between aryl amido complexes upon treatment of $TpRu(PMe_3)_2(NHPh)$ with para-substituted amines of the type p-$NH_2C_6H_4$−X (X = Me, OMe, NMe_2, F, or CF_3). Portions of this work have been previously communicated.[22]

Experimental Section

General Methods. All reactions and procedures were performed under anaerobic conditions in a nitrogen filled glovebox or using

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standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and monitored by an oxygen analyzer {O_2(g) < 15 ppm for all reactions}. Acetonitrile was purified by passage through a column of activated alumina followed by distillation from CaH_2.[49] Methylene chloride was purified by passage through a column of activated alumina followed by distillation from P_2O_5. THF, hexanes, and diethyl ether were dried by distillation from sodium/benzophenone. Benzene was purified by distillation from CaH_2. CD_3CN was purified by distillation from CaH_2, degassed, and stored over 4 Å sieves. C_6D_6, $CDCl_3$, and CD_2Cl_2 were degassed via three freeze−pump−thaw cycles and stored over 4 Å sieves. THF-d_8 was distilled from Na metal, degassed via freeze−pump−thaw cycles, and stored over 4 Å sieves. ^{1}H and ^{13}C NMR spectra were obtained on Varian Mercury 300 MHz, Varian Mercury 400 MHz, and General Electric 300 MHz spectrometers. Resonances due to the Tp ligand are reported by chemical shift and multiplicity only. All $^3J_{HH}$ values for pyrazolyl rings are 2 Hz. All ^{1}H and ^{13}C NMR spectra were referenced against tetramethylsilane using 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 300 MHz spectrometer and referenced against external 85% H_3PO_4. All NMR spectra were acquired at room temperature unless otherwise noted. IR spectra were obtained on a Mattson Genesis II spectrometer either as thin films on a KBr plate or in solution using a KBr solution plate. Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon potentiostat. Cyclic voltammograms were recorded in a standard three-electrode cell from −2.00 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 or ferrocene as an internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc. Synthetic and characterization details of TpRu(PMe_3)$_2$(NHPh), TpRu{$P(OMe)_3$}$_2$(NHPh), [TpRu(L)(L′)(NH_3)][OTf], TpRu(L)(L′)(NH_2), [TpRu(L)(L′)(NH_3)][PhC_2], TpRu(CO)(PPh_3)(Cl), and [TpRu(CO)$_2$(THF)][PF_6] have been previously reported.[22,43,50−52] [Li][PhC≡C] was prepared by addition of BuLi to a benzene solution of phenylacetylene. The resulting white precipitate was collected via vacuum filtration and washed with hexanes. All other reagents were used as purchased from commercial sources.

[TpRu(CO)(PPh_3)(NH_2^{t}Bu)][OTf] (1). To a solution of TpRu(CO)(PPh_3)Cl (0.9612 g, 1.50 mmol) in approximately 50 mL of THF was added AgOTf (0.3871 g, 1.51 mmol). The resulting solution was refluxed for 18 h. During the reaction, the formation of a white precipitate (AgCl) was noted. The solution was cooled to room temperature and filtered through a fine porosity frit, and ^{t}BuNH$_2$ was added to the filtrate. The mixture was allowed to stir for an additional 24 h and was then concentrated to approximately 30 mL under reduced pressure. Diethyl ether (approximately 50 mL) was added to precipitate the product. The product was collected via vacuum filtration through a fine porosity frit and washed with diethyl ether (3 × 10 mL) to give a white solid (0.8186 g, 0.9903 mmol, 79%). The product was recrystallized from THF/hexanes. ^{1}H NMR ($CDCl_3$, δ): 7.98 (2H, overlapping d's, Tp C*H* 3 or 5 position), 7.85, 7.77, 7.72, 6.12 (4H, 1:1:1:1 integration, each a d, Tp C*H* 3 and 5 position), 7.47, 7.01 (15H, 9:6 integration, m's, PPh_3), 6.28, 6.24, 5.90 (3H, 1:1:1 integration, each a t, Tp C*H* 4 position), 3.45 (1H, d, $^2J_{HH}$ = 13 Hz, N*H*), 2.68 (1H, d, $^2J_{HH}$ = 13 Hz, N*H*), 1.02 (9H, s, $NH_2C(CH_3)_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 204.7 (*C*O, d, $^2J_{PC}$ = 14 Hz), 145.9, 145.5, 145.2, 137.8, 137.2, 137.1 (Tp 3 or 5 position), 133.6 and 129.6 (PPh_3 ortho and meta, each a d, $^2J_{PC}$ = $^3J_{PC}$ = 10 Hz), 131.5 (PPh_3 para), 129.7 (PPh_3 ipso, $^1J_{PC}$ = 44 Hz), 108.2, 107.2, 107.0 (Tp 4 position), 55.4 ($C(CH_3)_3$), 31.0 ($C(CH_3)_3$). IR (thin film on KBr): ν_{CO} = 1970 cm^{-1}, ν_{NH} = 3127, 3289 cm^{-1}, ν_{BH} = 2498 cm^{-1}. ^{31}P{^{1}H} ($CDCl_3$, δ): 39.2. Anal. Calcd for $C_{33}H_{36}BF_3N_7O_4PRuS\cdot{}^1/_2$(THF) (note that $^1/_2$ equiv of THF was confirmed via ^{1}H NMR of the analysis sample): C, 48.73; N, 11.37; H, 4.67. Found: C, 48.21; N, 11.10; H, 4.69.

[TpRu(PMe_3)$_2$(NH_2^{t}Bu)][OTf] (2). To a solution of TpRu(PMe_3)$_2$Cl (0.3364 g, 0.671 mmol) in approximately 30 mL of THF was added AgOTf (0.1732 g, 0.674 mmol). The resulting red solution was refluxed for 18 h. During the reaction, the formation of a white precipitate (AgCl) was noted. The solution was cooled to room temperature and filtered through a fine porosity frit. To the filtrate was added ^{t}BuNH$_2$ (0.37 g, 5.1 mmol), and the mixture was allowed to stir for an additional 24 h. The solution was concentrated to approximately 20 mL in vacuo, and diethyl ether (approximately 40 mL) was added to precipitate the product. The product was collected via vacuum filtration through a fine porosity frit and washed with diethyl ether (3 × 10 mL) to give a white solid. The solid was dried in vacuo and isolated (0.1368 g, 0.1987 mmol, 30%). ^{1}H NMR (CD_3CN, δ): 8.02, 7.91, 7.78, 7.35 (6H, 2:2:1:1 integration, each a d, Tp C*H* 3 and 5 position), 6.37, 6.17 (3H, 2:1 integration, each a t, Tp C*H* 4 position), 2.55 (2H, br s, N*H*), 1.28 (18H, vt, *N* = 6 Hz, $P(CH_3)_3$), 0.84 (9H, s, ^{t}Bu). In THF-d_8: 8.10, 7.89, 7.76, 7.40 (6H, 2:2:1:1 integration, each a d, Tp C*H* 3 and 5 position), 6.36, 6.14 (4H, 2:1 integration, each a t, Tp C*H* 4), 3.17 (2H, bs, NH_2^{t}Bu), 1.33 (18H, vt, *N* = 12 Hz, $P(CH_3)_3$), 0.89 (9H, s, NH_2^{t}Bu). ^{13}C{^{1}H} NMR (CD_3CN, δ): 148.2, 146.0, 138.7, 137.7 (Tp 3 or 5 position), 107.7, 107.1 (Tp 4 position), 53.8 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 18.7 ($P(CH_3)_3$). IR (thin film on KBr): ν_{NH} = 3262, 3114 cm^{-1}, ν_{BH} = 2522 cm^{-1}. ^{31}P{^{1}H} (CD_3CN, δ): 12.1. CV (CH_3CN, 100 mV/s): $E_{1/2}$ = 1.13 V. Anal. Calcd for $C_{20}H_{38}BF_3N_7O_3P_2RuS$: C, 34.89; N, 14.24; H, 5.71. Found: C, 34.80; N, 14.02; H, 5.78.

[TpRu{$P(OMe)_3$}$_2$(NH_2^{t}Bu)][OTf] (3). A THF (50 mL) solution of TpRu{$P(OMe)_3$}$_2$Cl (0.6747 g, 1.129 mmol) and AgOTf (0.3050 g, 1.187 mmol) was refluxed for 24 h. The mixture was allowed to cool to room temperature and passed through a plug of Celite. To the yellow filtrate was added ^{t}BuNH$_2$ (1.19 mL, 11.3 mmol). The solution was stirred at room temperature for approximately 24 h. The solvent volume was reduced in vacuo to approximately 10 mL, and 20 mL of diethyl ether was added. The resulting white precipitate was collected and washed with four 20 mL portions of diethyl ether (0.4913 g, 56% yield). ^{1}H NMR (CD_2Cl_2, δ): 7.98, 7.85, 7.72, 7.66 (6H, 2:2:1:1 integration, each a d, Tp C*H* 3 and 5 position), 6.37, 6.15 (3H, 2:1 integration, each a t, Tp C*H* 4 position), 3.41 (18H, vt, *N* = 10 Hz, $P(OCH_3)_3$), 2.59 (2H, br s, N*H*), 0.98 (9H, s, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 147.7, 144.2, 137.1, 136.5 (Tp 3 or 5 position), 106.4, 106.3 (Tp 4 position), 53.0 (d, $^2J_{PC}$ = 5 Hz, $P(OCH_3)_3$), 52.5 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$). IR (thin film on KBr): ν_{NH} = 3313, 3266 cm^{-1}; ν_{BH} = 2498 cm^{-1}. ^{31}P{^{1}H} ($CDCl_3$, δ): 138.0. CV (CH_3CN, 100 mV/s): $E_{1/2}$ = 1.45 V. Anal. Calcd for $C_{20}H_{39}BF_3N_7O_9P_2RuS$: C, 30.62; N, 12.50; H, 5.01. Found: C, 30.81; N, 12.37; H, 5.09.

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TpRu(PMe$_3$)$_2$(NH^{t}Bu) (4). To a colorless THF (5 mL) solution of [TpRu(PMe$_3$)$_2$NH$_2$^{t}Bu][OTf] (**1**) (0.0710 g, 0.103 mmol) cooled to −78 °C was added dropwise a 1.0 M THF solution of [Na][N(SiMe$_3$)$_2$] (0.103 mmol). Upon addition of base, the mixture changed color to orange and was allowed to warm to room temperature. The solvent was removed in vacuo from the reaction mixture. The resulting orange residue was stirred with benzene, and the mixture was passed through a fine porosity frit. The benzene was removed in vacuo from the filtrate yielding a solid orange product. The product was recrystallized by dissolution in benzene and addition of hexanes (0.0308 g, 56% yield). ^{1}H NMR (C$_6$D$_6$, δ): 8.36, 7.60, 7.54, 7.20 (6H, 2:2:1:1 integration, each a d, Tp C*H* 3 and 5 position), 6.04, 5.87 (3H, 2:1 integration, each a t, Tp C*H* 4 position), 1.19 (9H, s, ^{t}Bu), 1.04 (18H, vt, N = 6 Hz, P(C*H*$_3$)$_3$), −2.45 (1H, br s, N*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 145.1, 144.7, 135.2, 134.7 (Tp 3 or 5 position), 104.6, 104.0 (Tp 4 position), 53.5 (*C*(CH$_3$)$_3$), 36.1 (C(*C*H$_3$)$_3$), 18.1 (vt, N = 13 Hz, P(*C*H$_3$)$_3$). IR (THF solution): ν_{NH} = 3294 cm^{-1}; ν_{BH} = 2460 cm^{-1}. ^{31}P{^{1}H} (C$_6$D$_6$, δ): 14.8. The instability of complex **4** precludes satisfactory elemental analysis.

[TpRu(PMe$_3$)$_2$(NCMe)][OTf] (5). To a solution of TpRu(PMe$_3$)$_2$Cl (0.0976 g, 0.195 mmol) in approximately 30 mL of THF was added AgOTf (0.0512 g, 0.199 mmol). The resulting red solution was refluxed for 18 h. During the reaction, the formation of a white precipitate (AgCl) was noted. The solution was cooled to room temperature and filtered through a fine porosity frit. Approximately 5 mL of CH$_3$CN was added to the solution. The reaction was allowed to stir for an additional 4 h at room temperature. The solution was concentrated to approximately 15 mL in vacuo, and hexanes (approximately 60 mL) were added to precipitate the product. The resulting white solid was collected via vacuum filtration through a fine porosity frit and washed with hexanes (3 × 10 mL). The final product was collected in 72% yield after drying in vacuo (0.0919 g, 0.140 mmol). ^{1}H NMR (CDCl$_3$, δ): 7.75, 7.72, 7.67, 7.33 (6H, 1:2:2:1 integration, each a d, Tp C*H* 3 and 5 position), 6.25, 6.22 (3H, 2:1 integration, each a t, Tp C*H* 4 position), 2.54 (3H, NCC*H*$_3$), 1.35 (18H, vt, N = 9 Hz, P(C*H*$_3$)$_3$), 0.84 (9H, s, ^{t}Bu). ^{13}C{^{1}H} NMR (CD$_3$CN, δ): 144.8, 142.5, 136.8, 135.6 (Tp 3 or 5 position), 124.9 (Ru−N≡*C*Me), 106.3, 106.0 (Tp 4 position), 17.5 (vt, N = 29 Hz, P(*C*H$_3$)$_3$), 4.3 (Ru−N≡C*C*H$_3$). IR (CDCl$_3$ solution): ν_{CN} = 2253 cm^{-1}, ν_{BH} = 2485 cm^{-1}. ^{31}P{^{1}H} (CDCl$_3$, δ): 11.3. CV (CH$_3$CN, 100 mV/s): $E_{1/2}$ = 1.29 V. Anal. Calcd for C$_{17}$H$_{31}$BF$_3$N$_7$O$_3$P$_2$RuS·$^1/_2$(CH$_2$Cl$_2$) (note that $^1/_2$ equiv of CH$_2$Cl$_2$ was confirmed via ^{1}H NMR of the analysis sample): C, 31.80; N, 14.03; H, 4.61. Found: C, 32.33; N, 14.03; H, 4.61.

TpRu(PMe$_3$)$_2$(C≡CPh) (6). TpRu(PMe$_3$)$_2$(Cl) (0.5049 g, 1.01 mmol) was dissolved in approximately 40 mL of THF to give a pale yellow solution. To this solution was added AgOTf (0.2594 g, 1.01 mmol), and the resulting solution was refluxed for 21 h. After cooling to room temperature, the solution was filtered through a fine porosity frit, and 0.1364 g (1.26 mmol) of LiC$_2$Ph (dissolved in approximately 3 mL of THF) was added. After 5 h of reaction, the solvent was removed under reduced pressure. The products were extracted with approximately 15 mL of benzene and filtered through a fine porosity frit. The volume of the filtrate was reduced to 10 mL in vacuo, and 25 mL of hexanes was added. The resulting slurry was filtered through a fine porosity frit, and the collected solid was discarded. Volatiles were removed from the filtrate under reduced pressure to yield a beige solid. The solid was dried in vacuo to yield 0.2847 g of product (50% yield). ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.95, 7.82 (3H, 2:1 integration, each a d, Tp C*H* 3 and 5 position), 7.65 (3H, overlapping d's, Tp C*H* 3 or 5 position), 7.26 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl ortho), 7.16 (2H, t, $^3J_{HH}$ = 7 Hz, phenyl meta), 6.98 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl para), 6.28, 6.15 (3H, 1:2 integration, each a t, Tp C*H* 4 position), 1.42 (18H, vt, N = 9 Hz, P(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 144.4, 135.5, 135.0, 131.4, 130.8, 128.7, 128.0, 122.9 (Tp 3 or 5 and phenyl), 133.6 (t, $^2J_{PC}$ = 19 Hz, Ru−*C*≡CPh), 107.3 (Ru−C≡*C*Ph), 105.2, 105.0 (Tp 4 position), 19.1 (P(*C*H$_3$)$_3$). ^{31}P{^{1}H} (CD$_2$Cl$_2$, δ): 14.8. CV (CH$_3$CN, 100 mV/s): $E_{p,a}$ = 0.41 V. Anal. Calcd for C$_{23}$H$_{33}$BN$_6$P$_2$Ru: C, 48.69; N, 14.81; H, 5.86. Found: C, 48.55; N, 14.58; H, 5.77.

TpRu(CO)(PPh$_3$)(C≡CPh) (7). A THF solution of TpRu(CO)(PPh$_3$)(Cl) (0.1532 g, 0.2394 mmol) and LiCCPh (0.0518 g, 0.4793 mmol) was refluxed for 20 h. After this time period, volatiles were removed in vacuo. The resulting brown oil was dissolved in approximately 15 mL of benzene and filtered through a fine porosity frit. Volatiles were removed from the filtrate to yield a light brown solid. The solid was dried in vacuo and collected (0.1285 g, 76% yield). Analytically pure product was obtained by layering a methylene chloride solution with hexanes. ^{1}H NMR (CDCl$_3$, δ): 8.09, 7.71, 7.66, 7.60, 6.98, 6.58 (6H, 1:1:1:1:1:1 integration, each a d, Tp C*H* 3 and 5 position), 7.44, 7.32 (17H, overlapping m's, phenyl ortho and PPh$_3$), 7.72 (2H, t, $^3J_{HH}$ = 8 Hz, phenyl meta), 7.09 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl para), 6.20, 5.90, 5.87 (3H, 1:1:1 integration, each a t, Tp C*H* 4 position). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 203.8 (d, $^2J_{PC}$ = 16 Hz, *C*O), 144.3, 144.2, 143.9, 134.6, 134.4, 134.3, 128.2, 128.1, 127.7 (Tp 3 or 5 position and acetylide phenyl), 135.2 and 134.3 (each a d, $^2J_{PC}$ = $^3J_{PC}$ = 10 Hz, PPh$_3$ ortho and meta), 131.3 (PPh$_3$ para), 133.2 ($^1J_{PC}$ = 44 Hz, PPh$_3$ ipso), 130.0 (d, $^4J_{PC}$ = 4 Hz, acetylide phenyl ipso), 115.4 (d, $^2J_{PC}$ = 17 Hz, Ru−*C*≡CPh), 109.0 (Ru−C≡*C*Ph), 105.6 (d, $^4J_{PC}$ = 2 Hz, Tp 4 position), 105.2, 105.0 (Tp 4 position). IR (THF solution): ν_{CO} = 1966 cm^{-1}, ν_{BH} = 2103 cm^{-1}. ^{31}P{^{1}H} (CDCl$_3$, δ): 47.9. CV (CH$_3$CN, 100 mV/s): $E_{1/2}$ = 1.16 V. Anal. Calcd for C$_{36}$H$_{30}$BN$_6$OPRu·CH$_2$Cl$_2$ (note that one molecule of CH$_2$Cl$_2$ was found in the analysis sample using ^{1}H NMR spectroscopy): C, 56.22; N, 10.63; H, 4.08. Found: C, 55.85; N, 10.67; H, 4.14.

TpRu{P(OMe)$_3$}$_2$(C≡CPh) (8). A THF (50 mL) solution of TpRu{P(OMe)$_3$}$_2$Cl (0.1582 g, 0.2647 mmol) and AgOTf (0.0772 g, 0.3005 mmol) was refluxed for approximately 24 h. The mixture was allowed to cool to room temperature and passed through a plug of Celite. LiC≡CPh (0.0572 g, 0.5294 mmol) was added to the pale yellow filtrate, and the resulting solution was refluxed for 5 h. The volatiles were removed in vacuo, and the remaining brown residue was dissolved in approximately 20 mL of diethyl ether and passed through a fine porosity frit. Approximately 20 mL of hexanes was added to the filtrate. The resulting light brown precipitate was collected (0.1528 g, 87% yield). ^{1}H NMR (C$_6$D$_6$, δ): 8.34, 8.25, 7.55, 7.47 (6H, 2:1:1:2 integration, each a d, Tp C*H* 3 and 5 position), 7.50 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl ortho), 7.14 (2H, t, $^3J_{HH}$ = 7 Hz, phenyl meta), 6.96 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl para), 6.02, 5.97 (3H, 1:2 integration, each a t, Tp C*H* 4 position), 3.35 (18H, vt, N = 5 Hz, P(OC*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 146.4, 145.4, 135.5, 134.8, 131.8, 128.9, 128.5, 124.0 (Tp 3 or 5 position and acetylide phenyl), 132.3 (t, $^2J_{PC}$ = 13 Hz, Ru−*C*≡CPh), 110.4 (s, Ru−C≡*C*Ph), 105.7, 105.2 (Tp 4 position), 51.6 (br s, P(O*C*H$_3$)$_3$). ^{31}P{^{1}H} (C$_6$D$_6$, δ): 152.4. CV (CH$_3$CN, 100 mV/s): $E_{p,a}$ = 0.65 V. Anal. Calcd for C$_{23}$H$_{33}$BN$_6$O$_6$P$_2$Ru: C, 41.64; N, 12.67; H, 5.01. Found: C, 42.41; N, 12.35; H, 5.21.

TpRu(PMe$_3$)$_2$(H) (9). To a THF solution (approximately 20 mL) of TpRu(PMe$_3$)$_2$OTf (0.0541 g, 0.0879 mmol) was added lithium aluminum hydride (0.0096 g, 0.2530 mmol). The reaction was stirred for 16 H at room temperature. The volatiles were removed in vacuo, and benzene was used to extract the residue. The solution was filtered through a fine porosity frit, and the volatiles were

removed in vacuo. Additional purification of the product was achieved by column chromatography on silica gel with 80/20 benzene/THF as the eluent (0.034 g, 0.073 mmol, 81%). ^{1}H NMR (C_6D_6, δ): 7.79, 7.69, 7.66, 7.48 (6H, 1:2:1:2 integration, each a d, Tp C*H* 3 and 5 position), 6.07, 5.84 (3H, 1:2 integration, each a t, Tp C*H* 4), 1.11 (18H, vt, N = 8 Hz, P(CH_3)$_3$), −15.69 (1H, t, $^2J_{PH}$ = 31 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, δ): 146.0, 143.2, 134.4, 133.8 (each a s, Tp 3 or 5 position), 104.7, 104.2 (each a s, Tp 4 position), 22.39 (vt, N = 12 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} (C_6D_6, δ): 19.5 (s, *P*(CH$_3$)$_3$).

[TpRu(PMe$_3$)$_3$][OTf] (10). A CH_2Cl_2 (50 mL) solution of TpRu(PMe$_3$)$_2$Cl (0.1060 g, 0.2112 mmol) and AgOTf (0.0539 g, 0.2098 mmol) was refluxed for 18 h. During the reaction, the formation of a white precipitate (AgCl) was noted. To the resulting solution was added 0.3 mL of trimethylphosphine, and the reaction was allowed to stir for 6 h. The solution was concentrated to approximately 20 mL in vacuo, and diethyl ether (approximately 40 mL) was added to precipitate the product. The product was collected via vacuum filtration through a fine porosity frit and washed with diethyl ether (3 × 10 mL) to give a yellow solid (0.0845 g, 0.122 mmol, 58%). Additional purification was accomplished by dissolving the product in a minimal amount of $CHCl_3$ and cooling the solution to −20 °C, followed by vacuum filtration through a fine porosity frit. ^{1}H NMR ($CDCl_3$, δ): 7.75, 7.71 (each 3H, each a d, Tp C*H* 3 or 5), 6.31 (3H, t, Tp C*H* 4) 1.40 (27H, m, P(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 145.2, 136.7 (each a s, Tp 3 or 5 position), 106.4 (s, Tp 4 position), 21.1 (m, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 4.1 (s, *P*Me$_3$). ^{1}H and ^{13}C NMR spectra of **10** are included in the Supporting Information.

[Tp(PMe$_3$)$_2$Ru=C=C(H)Ph][OTf] (11). TpRu(PMe$_3$)$_2$(Cl) (0.3965 g, 0.7903 mmol) was dissolved in approximately 10 mL of THF. To this solution was added AgOTf (0.2030 g, 0.7901 mmol, dissolved in ∼2 mL of THF) and ∼1.0 mL of phenylacetylene (9.1 mmol), and the resulting solution was refluxed for 19 h. After cooling to room temperature, the solution was filtered through a fine porosity frit. The volatiles were removed in vacuo, and the crude reaction mixture was recrystallized from methylene chloride/hexanes. A reddish-purple solid was collected (0.2436 g, 0.3395 mmol, 43% yield). ^{1}H NMR ($CDCl_3$, δ): 7.94, 7.81, 7.70, 7.73 (6H, 1:1:2:2 integration, each a d, Tp C*H* 3 or 5 position), 7.12 (2H, t, $^3J_{HH}$ = 7 Hz, phenyl meta), 7.03 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl para), 6.72 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl ortho), 6.51, 6.23 (3H, 1:2 integration, Tp C*H* 4 position), 5.59 (1H, t, $^3J_{PH}$ = 3 Hz, Ru=C=C(*H*)Ph), 1.46 (18H, vt, N = 10 Hz, P(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 373.0 (t, $^2J_{PC}$ = 18 Hz, Ru=*C*=C(H)Ph), 143.9, 137.5, 137.0, 129.1, 126.5, 126.4 (Tp 3 or 5 position and vinylidene phenyl, two resonances are missing due to overlap), 111.5 (s, Ru=C=*C*(H)Ph), 107.6, 106.5 (Tp 4 position), 18.0 (vt, N = 28 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} (C_6D_6, δ): 2.9. CV (CH_3CN, 100 mV/s): $E_{p,a}$ = 1.39 V; $E_{p,c}$ = −1.30 V. Anal. Calcd for $C_{24}H_{34}B_1F_3N_6O_3P_2Ru_1S_1\cdot(CH_2Cl_2)_{1/2}$ (note that $^1/_2$ molecule of CH_2Cl_2 was found in the analysis sample using ^{1}H NMR spectroscopy): C, 38.72; N, 11.06; H, 4.64. Found: C, 39.53; N, 10.56; H, 4.70.

[Tp(PMe$_3$)$_2$Ru=C(CH$_2$Ph){N(H)Ph}][OTf] (12). A THF (50 mL) solution of TpRu(PMe$_3$)$_2$Cl (0.4124 g, 0.8216 mmol) and AgOTf (0.2125 g, 0.8270 mmol) was gently refluxed for 24 h. During the reaction, the formation of a white precipitate (AgCl) was noted. The solution was cooled to room temperature and filtered through a fine porosity frit. Phenylacetylene (0.2 g, 1.9 mmol) was added to the solution, and the reaction was allowed to stir for 24 h. The solution was concentrated to approximately 20 mL in vacuo, and hexanes (approximately 40 mL) were added. Formation of a brown precipitate was noted. The precipitate was collected using a fine porosity frit and then dissolved in THF (approximately 50 mL). Aniline (approximately 0.5 g) was added to the solution, and the reaction was allowed to stir for 24 h. The solution was concentrated to approximately 20 mL in vacuo, and diethyl ether (approximately 40 mL) was added to precipitate the product. The product was collected via vacuum filtration through a fine porosity frit and washed with diethyl ether (3 × 10 mL) to give a white solid (0.2576 g, 0.3178 mmol, 38%). ^{1}H NMR ($CDCl_3$, δ): 11.83 (1H, bs, N*H*Ph), 7.78, 7.71, 7.60, 7.41 (6H 1:2:1:2 integration, each a d, Tp C*H* 3 and 5 position), 7.19−7.10 (4H, m, Ph), 7.02 (1H, t, Ph para position, $^3J_{HH}$ = 7 Hz), 6.90−6.63 (5H, m, Ph) 6.30, 6.14 (3H, 1:2 integration, each a t, Tp C*H* 4 position), 4.13 (2H, s, Ru=C(CH_2-Ph)(NHPh)), 1.36 (18H, vt, J_{PH} = 8 Hz, P(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 271.1 (t, Ru=*C*(CH$_2$Ph)(NHPh), $^2J_{PC}$ = 24 Hz), 144.3, (s, Tp 3 or 5 or Ph), 144.2−144.0 (m, Tp 3 or 5 or Ph), 141.0, 136.7, 136.4, 127.5, 125.8, 125.7 (each a s, Tp 3 or 5 position or Ph), 106.8, 106.4 (each a s, Tp 4 position), 52.7 (s, Ru=C(*C*H$_2$-Ph)(NHPh)), 19.4 (m, P(*C*H$_3$)$_3$). Anal. Calcd for $C_{30}H_{41}BF_3N_7O_3P_2SRu$: C, 44.45; N, 12.10; H, 5.10. Found: C, 44.28; N, 11.87; H, 5.08.

[TpRu(PMe$_3$)$_2$(NH$_2$^{t}Bu)][PhC$_2$]. In a screw cap NMR tube, TpRu(PMe$_3$)$_2$NH^{t}Bu (0.0285 g, 0.0529 mmol) was dissolved in 0.8 mL of THF-d_8. Cp_2Fe was added as an internal standard, and a ^{1}H NMR spectrum was obtained. Phenylacetylene (6.0 μL, 0.0546 mmol) was added using a microsyringe. Quantitative conversion to [TpRu(PMe$_3$)$_2$(NH$_2$^{t}Bu)][CCPh] was observed on the basis of integration. NMR spectra were obtained −50 °C. ^{1}H NMR (THF-d_8, δ): 8.14, 7.85, 7.74, 7.42 (6H, 2:2:1:1 integration, each a d, Tp C*H* 3 and 5 position), 7.34 (2H, d, J = 5 Hz, phenyl ortho), 7.24 (2H, t, J = 5 Hz, phenyl meta), 7.18 (1H, t, J = 5 Hz, phenyl para), 6.31, 6.12 (3H, 2:1 integration, each a t, Tp C*H* 4), 1.34 (18H, vt, J_{PH} = 6 Hz, P(CH_3)$_3$), 0.88 (9H, s, NH$_2$^{t}Bu). In THF-d_8, the resonance due to the amine protons is not observed; however, in C_6D_6, this resonance is observed as a broad singlet at 3.25 ppm. ^{13}C{^{1}H} NMR (THF-d_8, δ): 146.6, 144.5, 136.6, 136.5 (each a s, Tp 3 or 5 position), 132.0, 130.9, 128.9, 128.6, 127.6, 123.9 (acetylide anion), 106.5, 105.7 (each a s, Tp 4 position), 52.4 (s, NH$_2$*C*(CH$_3$)$_3$), 30.3 (s, NH$_2$C(*C*H$_3$)$_3$), 17.4 (vt, N = 10 Hz, PMe$_3$). ^{13}C{^{1}H} NMR of [PhC$_2$][Li] (THF-d_8, δ): 135.2, 131.1, 128.7, 127.6, 124.7, 114.9. ^{31}P NMR (THF-d_8, δ): 15.8.

Ligand Exchange Reactions of [TpRu(PMe$_3$)$_2$(NH$_2$R)][OTf] (R = H, Ph, or ^{t}Bu) with CD$_3$CN. The appropriate amine complex was weighed and dissolved in CD_3CN to bring the concentration to 0.06 M. A small amount of ferrocene was added as internal standard. The disappearance of resonances due to [TpRu(PMe$_3$)$_2$(NH$_2$R)][OTf] (R = H, Ph or ^{t}Bu) was monitored with respect to time using ^{1}H NMR spectroscopy. The pulse delay of the spectrometer was set to 10 s in order to ensure accurate integration. The final ^{1}H NMR spectra for R = Ph and ^{t}Bu displayed resonances consistent with the quantitative formation of [TpRu(PMe$_3$)$_2$(NCCD$_3$)][OTf] and NH$_2$R. Kinetic analysis revealed first-order transformations, and rate constants were abstracted from the slope (R^2 > 0.99). The ammonia complex [TpRu(PMe$_3$)$_2$(NH$_3$)][OTf] showed no evidence of ligand exchange even after heating at prolonged times.

Ligand Exchange Reactions of Ru(II) Phenyl Amido Complexes with Arylamines. In a representative reaction, 0.0230 g (0.0412 mmol) of TpRu(PMe$_3$)$_2$(NHPh) and 0.0059 g (0.0479 mmol) of *p*-anisidine were dissolved in approximately 0.7 mL of C_6D_6 in a screw cap NMR tube. A ^{1}H NMR spectrum was acquired with the pulse delay set to 10 s. The resulting solution was heated to approximately 100 °C. ^{1}H NMR spectra were acquired periodically until equilibrium was established (approximately 5 days). The

final distribution of $TpRu(PMe_3)_2(NHPh)$ and $TpRu(PMe_3)_2\{NH(p\text{-}C_6H_4OMe)\}$ was determined using both ^1H and ^{31}P NMR spectroscopy. Analogous procedures were used for all reactions with arylamines. The reaction with *p*-trifluoromethylaniline was slow; therefore, a catalytic (~1 mol %) amount of $TpRu(PMe_3)_2(OTf)$ was added to the reaction solution. In addition, the equilibrium constant for this reaction was confirmed by preparing $TpRu(PMe_3)_2\{NH(p\text{-}C_6H_4CF_3)\}$ and reacting it with aniline (see Supporting Information).

Reaction of $[TpRu(PMe_3)_2(NCMe)][OTf]$ (5) with NH_3. $TpRu(PMe_3)_2(NCMe)$ (**5**) (0.0183 g, 0.0279 mmol) was dissolved in ~2 mL of THF in a pressure tube. To this solution was added a THF solution saturated with NH_3. The pressure tube was sealed. After 284 h at 70 °C, the solvent was removed under reduced pressure, and ^1H NMR spectroscopy of the resulting solid ($CDCl_3$) indicated $[TpRu(PMe_3)_2(NCMe)][OTf]$ (**5**) as the only TpRu complex.

Reactions of Ru(II) Amido Complexes with 1,4-Cyclohexadiene. In a glovebox, the appropriate amount of Ru(II) amido was weighed and dissolved in 0.7−1.0 mL of C_6D_6. This solution was transferred to a screw cap NMR tube, and 1,4-CHD was added along with ferrocene (as internal standard). ^1H NMR spectra were immediately acquired with a 10 s pulse delay in order to ensure accurate integration. Reaction progress was monitored versus time by ^1H NMR spectroscopy. Percent yields of products were determined by integration versus ferrocene.

Reactions of TpRu(L)(L′)(NHR) with Phenylacetylene. In a representative reaction, 0.0224 g (0.040 mmol) of $TpRu(PMe_3)_2(NHPh)$ was weighed into a glass vial and dissolved in 1.0 mL of C_6D_6 (0.04 M solution). To the resulting solution were added 0.044 mL of phenylacetylene (0.40 mmol) and a small amount of ferrocene. The solution was transferred to a screw cap NMR tube, and a ^1H NMR spectrum was acquired with a pulse delay of 10 s. The solution was heated to approximately 80 °C in an oil bath and periodically monitored by ^1H NMR spectroscopy.

Reactions of $TpRu(PMe_3)_2(NHPh)$ with Phenylacetylene and Catalytic $TpRu(PMe_3)_2(OTf)$. These reactions were analogous to reactions in the absence of $TpRu(PMe_3)_2(OTf)$. Before heating, a known amount of $TpRu(PMe_3)_2(OTf)$ was added to the reaction mixture. The reactions were monitored by ^1H NMR spectroscopy.

Kinetic Studies for the Conversion of $[TpRu(PMe_3)_2(NH_2{}^tBu)][PhC_2]$ to $TpRu(PMe_3)_2(C{\equiv}CPh)$. In a screw cap NMR tube, a 1:1 molar mixture of $TpRu(PMe_3)_2(NH^tBu)$ and phenylacetylene was combined in THF-d_8. A ^1H NMR spectrum was acquired to confirm the clean formation of $[TpRu(PMe_3)_2(NH_2{}^tBu)][PhC_2]$. The NMR solution was taken into the glovebox, and the appropriate amount of PMe_3 or $NH_2{}^tBu$ (1−5 equiv) was added. A second ^1H NMR spectrum was acquired at room temperature. Next, the probe was heated to 90 °C, and the conversion of the ion pair to $TpRu(PMe_3)_2(C{\equiv}CPh)$ was monitored versus time. The half-lives for the all reactions were approximately 15 min and did not vary substantially upon added phosphine or amine.

Solid-State X-ray Diffraction Studies of $[TpRu(CO)(PPh_3)(NH_3)][OTf]$, $[TpRu(PMe_3)_2(NH_3)][OTf]$, and $TpRu(CO)(PPh_3)(C{\equiv}CPh)$. For details of crystal growth, X-ray data collection, and analysis, see Supporting Information.

Results

Synthesis and Characterization. Metathesis reactions of $TpRu(L)(L')(Cl)$ (L = L′ = PMe_3, $P(OMe)_3$ or L = CO and L′ = PPh_3) with AgOTf in refluxing THF yields the Ru(II) triflate complexes $TpRu(L)(L')(OTf)$.[22,43,50] The poor ligating ability of the triflate ligand allows exchange reactions with amines of the type NH_2R (R = H or ^{t}Bu), and deprotonation of the amine complexes with strong bases affords access to the corresponding amido complexes (Scheme 1). Although $TpRu(PMe_3)_2(NH^tBu)$ (**4**) can be cleanly isolated (by ^1H NMR spectroscopy), attempts to deprotonate $[TpRu(CO)(PPh_3)(NH_2{}^tBu)][OTf]$ (**2**) or $[TpRu\{P(OMe)_3\}_2(NH_2{}^tBu)][OTf]$ (**3**) result in the production of multiple TpRu complexes including the ^{t}Bu amido complexes in low yields. Evidence for the formation of the desired Ru(II) amido complexes in the reactions of $[TpRu(CO)(PPh_3)(NH_2{}^tBu)][OTf]$ or $[TpRu\{P(OMe)_3\}_2(NH_2{}^tBu)][OTf]$ with $[Na][N(SiMe_3)_2]$ comes from broad upfield resonances (−1.0 to −2.0 ppm) in the ^1H NMR spectra of the crude reaction products. However, all attempts to isolate $TpRu\{P(OMe)_3\}_2(NH^tBu)$ or $TpRu(CO)(PPh_3)(NH^tBu)$ from the product mixtures have resulted in decomposition. Other octahedral and d^6 transition metal amido systems have been reported.[20,53−65] Exposure of the parent or ^{t}Bu amido complexes to air results in rapid decomposition, and the highly reactive nature of the Ru(II) amido complexes TpRu(L)(L′)(NHR) (R = H or ^{t}Bu) precludes satisfactory elemental analysis. Conversion of the amine complexes to the corresponding amido systems results in significant upfield chemical shifts for the amido protons. For example, deprotonation of $[TpRu(PMe_3)_2(NH_2{}^tBu)][OTf]$ shifts the amine resonance from 2.55

Scheme 1. Synthesis of Parent and ^{t}Bu Amido Complexes

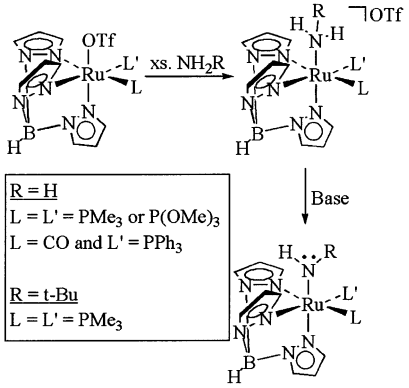

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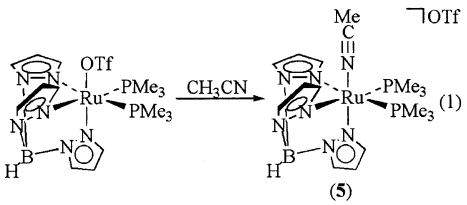
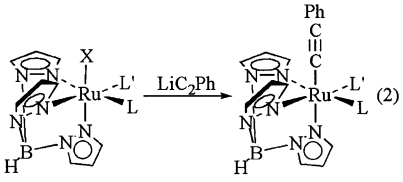
Table 1. Selected Crystallographic Data and Collection Parameters for [TpRu(CO)(PPh$_3$)(NH$_3$)][OTf], [TpRu(PMe$_3$)$_2$(NH$_3$)][OTf], and TpRu(CO)(PPh$_3$)(C≡CPh) (**7**)

	[TpRu(CO)(PPh$_3$)-(NH$_3$)][OTf]	[TpRu(PMe$_3$)$_2$-(NH$_3$)][OTf]	TpRu(CO)(PPh$_3$)-(C≡CPh) (**7**)
formula	$C_{37}H_{44}BF_3N_7O_6PRuS$	$C_{20}H_{39}BF_3N_7O_4P_2RuS$	$C_{36}H_{30}BN_6OPRu$
mol wt	914.70	704.45	705.52
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
a, Å	10.8020(17)	9.4716(6)	10.9799(8)
b, Å	30.137(4)	11.6028(9)	17.0455(18)
c, Å	12.5009(12)	14.3274(16)	19.0928(19)
α, deg		88.195(8)	110.135(9)
β, deg	97.419(13)	82.610(9)	104.279(7)
γ, deg		74.679(6)	93.514(9)
V, Å^3	4035.5(9)	1506.0(2)	3209.1(5)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.506	1.554	1.460
total reflns	7030	5251	11193
unique	7030	5251	11193
R	0.035	0.035	0.027
R_w	0.039	0.045	0.033

to −2.45 ppm for the amido N*H*. In addition, the reaction of TpRu(PMe$_3$)$_2$(OTf) with CH$_3$CN results in the isolation of [TpRu(PMe$_3$)$_2$(NCMe)][OTf] (**5**) in 72% yield after workup (eq 1).



The combination of TpRu(PMe$_3$)$_2$(OTf) with LiC≡CPh at room temperature results in a metathesis reaction to yield the Ru(II) acetylide complex TpRu(PMe$_3$)$_2$(C≡CPh) (**6**) (eq 2). In contrast, the reaction of TpRu(CO)(PPh$_3$)(OTf) with



LiC≡CPh yields three new TpRu complexes. One of these reaction products is the acetylide complex TpRu(CO)(PPh$_3$)-(C≡CPh) (**7**) while the other two complexes remain uncharacterized. Reflux of the chloride complex TpRu(CO)(PPh$_3$)-(Cl) with 2 equiv of LiC≡CPh produces TpRu(CO)(PPh$_3$)-(C≡CPh) (**7**) in 76% yield after workup. TpRu{P(OMe)$_3$}$_2$-(C≡CPh) (**8**) is produced by refluxing TpRu{P(OMe)$_3$}$_2$-(OTf) with 2 equiv of LiC≡CPh in THF. The α-acetylide carbons of complexes **6**−**8** exhibit $^2J_{PC}$ between 13 and 19 Hz. Other Ru(II) acetylide complexes have been prepared and studied.[66−73]

Solid-State Characterization. The three TpRu complexes [TpRu(CO)(PPh$_3$)(NH$_3$)][OTf], [TpRu(PMe$_3$)$_2$(NH$_3$)][OTf],

Table 2. Selected Bond Distances (Å) and Angles (deg) for [TpRu(CO)(PPh$_3$)(NH$_3$)][OTf], [TpRu(PMe$_3$)$_2$(NH$_3$)][OTf], and TpRu(CO)(PPh$_3$)(C≡CPh) (**7**)

atoms	[TpRu(CO)(PPh$_3$)-(NH$_3$)][OTf]	[TpRu(PMe$_3$)$_2$-(NH$_3$)][OTf]	TpRu(CO)(PPh$_3$)-(C≡CPh) (**7**)[a]
Ru−P$_1$	2.3581(9)	2.2923(10)	2.3275(7)
Ru−P$_2$		2.2916(10)	
Ru−N$_1$	2.097(3)	2.087(3)	2.167(2)
Ru−N$_3$	2.120(3)	2.148(3)	2.1631(20)
Ru−N$_5$	2.142(3)	2.154(3)	2.1301(20)
Ru−N$_7$	2.122(3)	2.136(3)	
C$_{10}$−C$_{11}$			1.193(4)
C$_{11}$−C$_{12}$			1.454(4)
Ru−C$_{10}$	1.850(3)		2.037(3)
C$_{10}$−O$_1$	1.147(4)		
P$_1$−Ru−P$_2$		99.60(4)	
P$_1$−Ru−N$_7$	96.19(10)	93.61(10)	
P$_2$−Ru−N$_7$		93.03(11)	
OC$_{10}$−Ru−P$_1$	92.39(10)		
OC$_{10}$−Ru−N$_7$	92.63(14)		
Ru−C$_{10}$−O$_1$	173.3(3)		
Ru−C$_{10}$−C$_{11}$			177.0(2)

[a] Values for the second crystallographically independent molecule can be found in the Supporting Information.

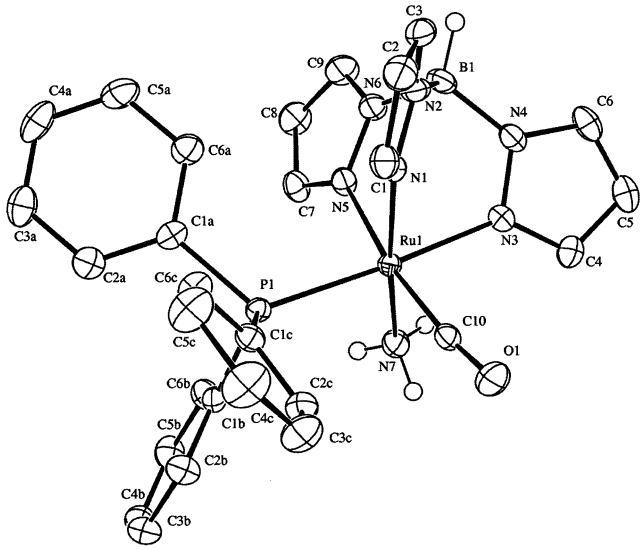


Figure 1. ORTEP diagram (50% probability) for [TpRu(CO)(PPh$_3$)(NH$_3$)]-[OTf] (the anion and most hydrogen atoms have been omitted for clarity).

and TpRu(CO)(PPh$_3$)(C≡CPh) (**7**) have been characterized by single-crystal X-ray diffraction studies. Data collection parameters are listed in Table 1, selected bond distances and angles are provided in Table 2, and the structures are shown in Figures 1−3. All three complexes are composed of pseudo-octahedral coordination spheres without significant

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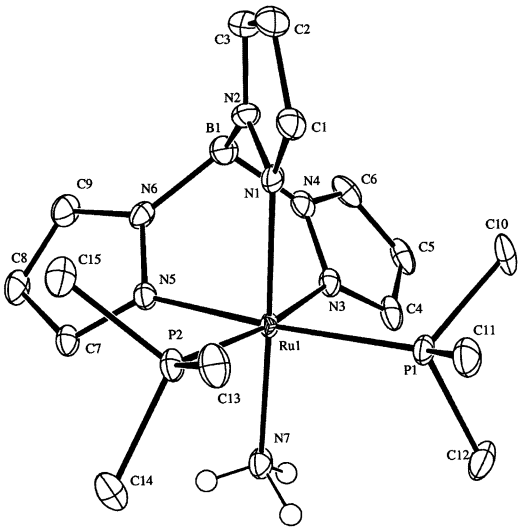


Figure 2. ORTEP diagram (50% probability) for $[TpRu(PMe_3)_2(NH_3)][OTf]$ (the anion and most hydrogen atoms have been omitted for clarity).

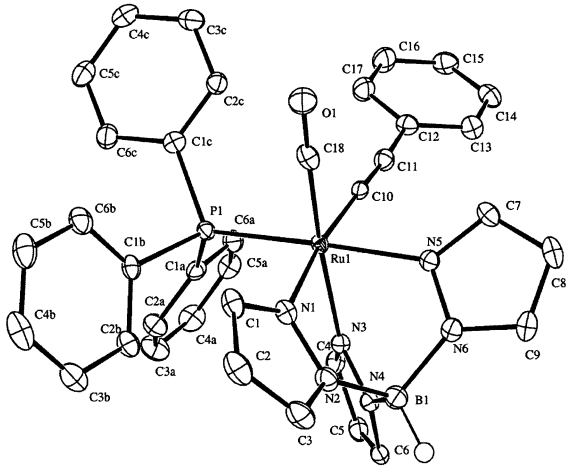


Figure 3. ORTEP diagram (50% probability) for $TpRu(CO)(PPh_3)(C{\equiv}CPh)$ (**7**).

deviation from the octahedral geometry. The Ru−N7 bond distances of complexes $[TpRu(CO)(PPh_3)(NH_3)][OTf]$ and $[TpRu(PMe_3)_2(NH_3)][OTf]$ are 2.122(3) and 2.136(3) Å, respectively, and are consistent with other Ru(II)−NH_3 bond lengths.[63] For both ammine complexes, the Ru−$N_{pyrazolyl}$ bond distances trans to the ammine ligands are shorter than the other two Ru−$N_{pyrazolyl}$ bond distances.

There are two crystallographically independent molecules in the asymmetric unit for Ru(II) phenylacetylide complex **7** due to the presence of two enantiomers of the chiral complex. At 2.037(3) Å {2.031(3) Å for the second molecule), the Ru−C10 bond distance is similar to that for related Ru(II) complexes.[69,73,74] The acetylide C≡C bond distance {C10−C11, 1.193(4) Å and C10′−C11′, 1.191(4) Å} is consistent with a C−C triple bond (1.20 Å). The C11−C12 bond distance is slightly shorter than expected for a C−C single bond at 1.454(4) Å {C11′−C12′, 1.454(4) Å}. The acetylide ligand is nearly linear with the Ru−C10−C11 bond angle of 177.0(2)°. The Ru′−C10′−C11′ bond angle is slightly reduced at 171.5(2)°. The bond distances and angles of the Ru−acetylide fragment are consistent with minimal metal to acetylide π-back-bonding, and the nearly

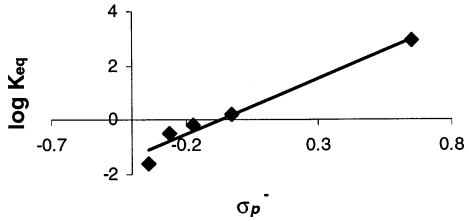
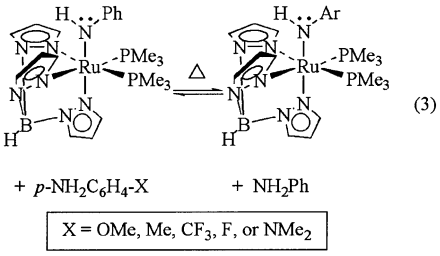


Figure 4. Hammett plot of log K_{eq} for the exchange reaction shown in eq 3 versus σ_p^- ($\rho = 4.1$).

equivalent C−C bond distances of the acetylide phenyl ring indicate the expected aromatic delocalization.

Exchange Reactions with Arylamines. Equilibria between $TpRu(PMe_3)_2(NHPh)$ and p-$NH_2C_6H_4$−X (X = OMe, Me, F, CF_3, or NMe_2) were studied to provide information about the thermodynamic preferences of the Ru(II) amido bond. Equilibria were established using NMR tube reactions in which an approximate 1:1 molar ratio mixture of $TpRu(PMe_3)_2(NHPh)$ and the arylamine was combined in C_6D_6. After acquiring initial spectra, the reaction solutions were heated for variable periods of time, and ligand exchange reactions were observed (eq 3). The reactions were monitored



periodically until equilibria were established, and equilibrium constants were determined from the final ratios of amido complexes using ^{1}H and/or ^{31}P NMR spectroscopy. The equilibrium for the reaction with p-$NH_2C_6H_4CF_3$ was confirmed by independently preparing $TpRu(PMe_3)_2\{NH(p\text{-}C_6H_4CF_3)\}$ and reacting it with aniline (see Supporting Information for details). Arylamines with electron-withdrawing groups favor binding to Ru, and the resulting equilibrium constants correlate well with σ_p^- parameters as shown in Figure 4 ($R^2 = 0.97$).[75] The Hammett plot affords a ρ value of 4.1.

Reactions with Phenylacetylene. The combination of $TpRu(PMe_3)_2(NH^tBu)$ (**4**) with phenylacetylene in THF-d_8 or C_6D_6 results in an immediate reaction at room temperature. The ^{1}H NMR spectrum of the reaction mixture is consistent with amido-based deprotonation of the phenylacetylene C−H bond to form an amine−acetylide ion pair (Scheme 2). For example, the upfield resonance due to the amido proton (−2.45 ppm) is replaced by a broad resonance consistent with an amine NH_2 fragment (3.25 ppm in C_6D_6). In addition, the resonance for the phenylacetylene PhC≡C−*H* is absent, and resonances between 7.2 and 7.4 ppm that are consistent with a phenylacetylide anion are observed. The ^{1}H NMR spectrum of the acetylide ion pair $[TpRu(PMe_3)_2(NH^tBu)]$-

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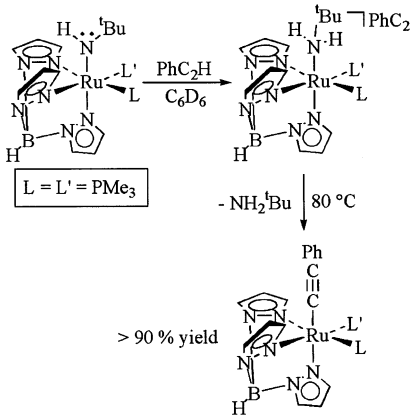
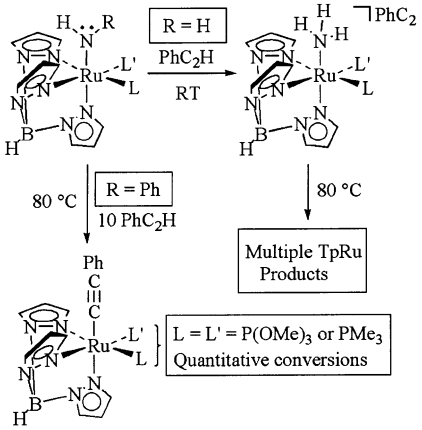
Scheme 2. Reaction of $TpRu(PMe_3)_2(NH^tBu)$ (**4**) with Phenylacetylene Yields the Ru(II) Acetylide Complex $TpRu(PMe_3)_2(C_2Ph)$ in >90% Yield



Scheme 3. Reactions of Ru(II) Amido Complexes with Phenylacetylene in THF-d_8[a]

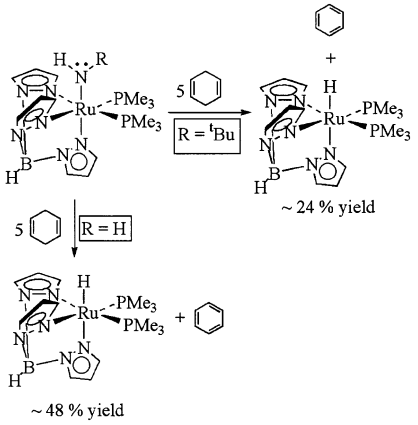


[a] RT = room temperature; $TpRu(CO)(PPh_3)(NHPh)$ does not yield $TpRu(CO)(PPh_3)(C_2Ph)$.

$[C_2Ph]$ is similar to that of $[TpRu(PMe_3)_2(NH_2{}^tBu)][OTf]$ (**2**) (see Experimental Section). All attempts to isolate the ion pair have failed. When the ion pair is heated to approximately 80 °C in C_6D_6, $TpRu(PMe_3)_2(C{\equiv}CPh)$ (**6**) is formed in approximately 90% yield as determined by ^1H NMR spectroscopy (Scheme 2).

Similar to ^{t}Bu amido complex **4**, the parent amido complexes $TpRuL_2(NH_2)$ (L = $P(OMe)_3$ or PMe_3) react immediately with phenylacetylene in THF-d_8 to yield amine−acetylide ion pairs (Scheme 3). No evidence of further reaction or decomposition is observed after 24 additional hours in sealed NMR tubes; however, all attempts to isolate the ion pairs resulted in decomposition to multiple intractable products. Heating the reaction mixture containing $[TpRu(PMe_3)_2(NH_3)][PhC_2]$ at 80 °C for approximately 21 h results in the formation of several new intractable Tp-containing complexes. Similar results are observed for the reaction of $TpRu\{P(OMe)_3\}_2(NH_2)$ with phenylacetylene. For the reaction of $TpRu(CO)(PPh_3)(NH_2)$ with phenylacetylene, more than 24 h is required to fully deprotonate phenylacetylene, and upon heating, multiple TpRu complexes are produced. Final reaction mixtures after heating are too convoluted to definitively identify $TpRu(L)(L')(C{\equiv}CPh)$ complexes.

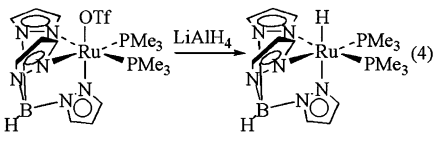
Scheme 4. Reactions of Parent and ^{t}Bu Amido Complexes with 1,4-Cyclohexadiene[a]



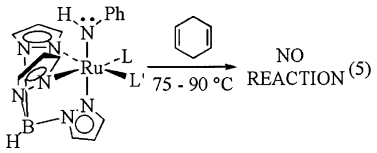
[a] Reactions are performed at 75° in THF-d_8.

In contrast to the ^{t}Bu and parent amido complexes, the phenyl amido complexes $TpRu(L)(L')(NHPh)$ show no evidence of reaction after combination with phenylacetylene at room temperature for 24 h. However, heating THF-d_8 solutions of the anilido complexes $TpRuL_2(NHPh)$ (L = PMe_3 or $P(OMe)_3$) with 10 equiv of phenylacetylene to approximately 80 °C results in the formation of Ru(II) phenylacetylide complexes $TpRuL_2(C{\equiv}CPh)$ and aniline (Scheme 3). Identical reactions in the presence of 20 and 30 equiv of phenylacetylene reveal an increase in reaction rate; however, kinetic studies using $TpRu(PMe_3)_2(NHPh)$ from different reaction batches resulted in inconsistent kinetic results (see Discussion section). The addition of 1 equiv of PMe_3 to the reaction of $TpRu(PMe_3)_2(NHPh)$ with 10 equiv of phenylacetylene results in no observed reaction after 5 days at 80 °C. The suppression of reaction upon addition of phosphine was consistently observed using ruthenium anilido from different preparation batches. The reaction of $TpRu(CO)(PPh_3)(NHPh)$ with 10 equiv of phenylacetylene results in decomposition to multiple TpRu complexes.

Reactions with 1,4-Cyclohexadiene. The reaction of $TpRu(PMe_3)_2(NH^tBu)$ with 5 equiv of 1,4-CHD at 80 °C results in the disappearance of resonances due to the amido complex and the formation of a ruthenium−hydride complex and benzene (Scheme 4). The Ru−hydride complex is assigned as $TpRu(PMe_3)_2(H)$ (**9**) on the basis of a triplet at approximately −15.7 ppm with $^2J_{PH}$ = 31 Hz. This assignment has been confirmed by independent preparation of $TpRu(PMe_3)_2(H)$ (**9**) (eq 4). Complex **9** has been characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ruthenium−hydride complex is formed in approximately 24% yield after 30 h as determined by integration of the Ru−hydride triplet versus an internal standard, and approximately 1 equiv of benzene is formed per equivalent of Ru−hydride formed. During the course of the reaction, 1,4-CHD is isomerized to



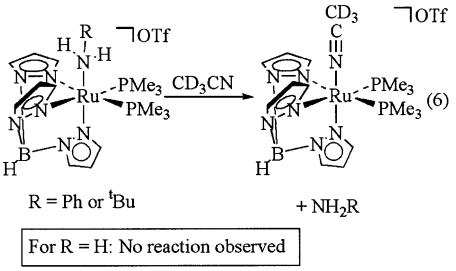
1,3-CHD. The anilido complexes TpRu(L)(L′)(NHPh) fail to react with 1,4-CHD in C_6D_6 after 24 h at approximately 75 °C and about 24 h at approximately 90 °C (eq 5). TpRu-



$(PMe_3)_2(NH_2)$ reacts with 5 equiv of 1,4-CHD at 80 °C to yield TpRu$(PMe_3)_2$(H) (**9**) (48% yield) and benzene (approximately 1.1 equiv of benzene per equivalent of Ru−hydride was observed by ^{1}H NMR integration, after 3 days of reaction). The addition of 2 equiv of trimethylphosphine to the reaction results in the formation of multiple products without observation of TpRu$(PMe_3)_2$(H) (**9**).

For reaction of TpRu$(PMe_3)_2(NH_2)$ with 1,4-CHD, the isomerization of 1,4-CHD to 1,3-CHD is observed. In analogy to the closely related reactions of *trans*-$(DMPE)_2$Ru-(NH_2)(H), we presume that these reactions occur via amido-based deprotonation reactions. It is also possible that hydrogen atom abstraction is occurring; however, the strong basicity of the ruthenium amido complexes and difficulty in accessing the Ru(I) oxidation state support an acid/base mechanism (see Discussion section). The rate of appearance of 1,3-CHD was monitored for reactions in C_6D_6 with TpRu-$(PMe_3)_2(NH_2)$. TpRu$(PMe_3)_2(NH_2)$ catalyzes complete isomerization of 1,4-CHD to 1,3-CHD within several hours at 80 °C (Figure 5). The k_1 value for the conversion of 1,4-CHD to 1,3-CHD was determined using a plot of $\ln([1,4\text{-CHD}]_t - [1,4\text{-CHD}]_{eq})$ versus time and the final equilibrium constant ($k_1 = 2.0 \times 10^{-5}$ s^{-1}). While the addition of 2 equiv of trimethylphosphine decreases the yield of TpRu$(PMe_3)_2$-(H) (**9**), the rate of 1,4-CHD to 1,3-CHD isomerization is not affected.

Ligand Exchange Reactions of [TpRu$(PMe_3)_2(NH_2R)$]-[OTf] with CH_3CN and [TpRu$(PMe_3)_2$(NCMe)][OTf] with CD_3CN. Dissolution of the Ru(II) amine complexes [TpRu$(PMe_3)_2(NH_2R)$][OTf] {R = Ph or ^{t}Bu} in CD_3CN results in ligand exchange reactions to yield [TpRu$(PMe_3)_2$-$(N{\equiv}CCD_3)$][OTf] (**7**-d_3) (eq 6). Each reaction was monitored



starting with a 0.06 M solution of the Ru(II) in CD_3CN at room temperature, and the resulting first-order kinetic plots are shown in Figure 6 ($R^2 = 0.99$ for both plots). The rate constant for the exchange reaction of the ^{t}Bu-amine complex [TpRu$(PMe_3)_2(NH_2{}^t$Bu)][OTf] is approximately an order of magnitude greater than that for [TpRu$(PMe_3)_2(NH_2$Ph)][OTf] ($k_{obs} = 1.4 \times 10^{-4}$ s^{-1} for the ^{t}Bu amine complex and 9.2×10^{-6} s^{-1} for the aniline complex at room temperature). In contrast to aniline and ^{t}Bu amine complexes, the parent ammine complex [TpRu$(PMe_3)_2(NH_3)$][OTf] shows no evidence of ligand exchange after 5 days at room temperature and 48 h at 90 °C. In order to determine if the lack of reaction between [TpRu$(PMe_3)_2(NH_3)$][OTf] and CD_3CN is due to kinetic or thermodynamic factors, [TpRu$(PMe_3)_2$(NCMe)]-[OTf] (**5**) was combined with a THF solution of ammonia in a sealed pressure tube. After approximately 12 days at approximately 70 °C, a ^{1}H NMR spectrum of the nonvolatile products revealed only starting material (i.e., no ligand exchange occurred). In addition, dissolution of [TpRu-$(PMe_3)_2(NCCH_3)$][OTf] (**5**) in CD_3CN at 80 °C for 48 h reveals no evidence of $NCCH_3/NCCD_3$ exchange. The failure of the acetonitrile ligand of complex **5** to undergo exchange with deuterated acetonitrile prevents conclusions about the inability to exchange the ammonia ligand of [TpRu$(PMe_3)_2$-(NH_3)][OTf] with CD_3CN.

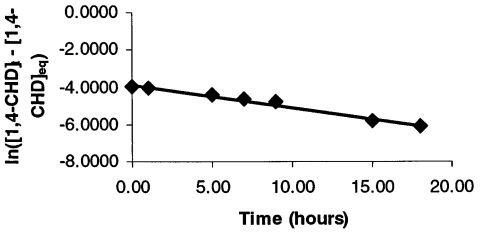


Figure 5. Conversion of 1,4-cyclohexadiene to 1,3-cyclohexadiene catalyzed by the parent amido complex TpRu$(PMe_3)_2(NH_2)$.

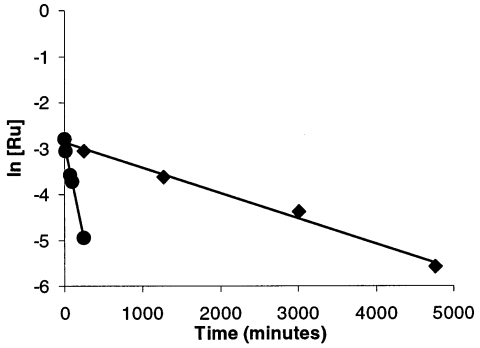


Figure 6. Kinetic plots of ligand exchange reactions of [TpRu$(PMe_3)_2$-(NH_2R)][OTf] {R = Ph (◆) or ^{t}Bu (●)} with CD_3CN at room temperature.

Discussion

The room temperature reactions of TpRu(L)(L′)(NH_2) or TpRu$(PMe_3)_2(NH^t$Bu) (**4**) with phenylacetylene result in simple acid/base transformations to yield amine/acetylide ion pairs. In contrast, no evidence of analogous acid/base transformations is observed upon combination of the anilido complexes TpRu(L)(L′)(NHPh) with phenylacetylene (at room temperature). These observations are explained by the attenuated basicity of the anilido complexes due to delocalization of the amido lone pair into the phenyl π^*, and evidence for such an interaction in the form of reduced $N_{amido}-C_{phenyl}$ bond lengths and restricted $N_{amido}-C_{phenyl}$ bond rotation has been reported.[43,76] Additional confirmation of electron delocalization into the amido phenyl substituent is derived from the Hammett plot of TpRu$(PMe_3)_2$(NHPh)/NH_2-Ar equilibria (Figure 4). The ρ value of 4.1 (versus σ_p^-)

indicates the delocalization of electron density into the amido phenyl ring. Bergman et al. have reported a similar result in which Cp*Ni(PEt_3)(NHPh)/NH_2Ar equilibrium constants plotted against σ_p^- parameters yield $\rho = 3.4$.[77] In contrast, a study of four-coordinate Re(III) aryloxides equilibria revealed correlation with Hammett σ parameters with $\rho = 0.7$.[78]

The combination of TpRu(PMe_3)$_2$(NH^{t}Bu) and phenylacetylene yields [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][PhC_2], and heating the ion pair in C_6D_6 produces TpRu(PMe_3)$_2$(C≡CPh) in approximately 90% yield. These results are consistent with amine dissociation and coordination of the acetylide anion. In contrast to the reaction of TpRu(PMe_3)$_2$(NHPh) with phenylacetylene, the addition of excess trimethylphosphine (1−5 equiv) has no impact on the rate of the conversion. In addition, heating [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][PhC_2] in the presence of excess $NH_2{}^t$Bu (1−5 equiv) has no impact on the rate of conversion ($t_{1/2}$ = 15(2) min). These results are consistent with a simple amine/acetylide ligand exchange reaction in which the amine dissociation is irreversible. It is surprising that the rate of ligand exchange between bound $NH_2{}^t$Bu and free acetonitrile of [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][OTf] is facile at room temperature while amine/acetylide exchange for [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][PhC_2] appears to occur more slowly (i.e., not observed at room temperature). However, studies of ammonia displacement with anions "X" for *trans*-[(DMPE)$_2$Ru(NH_3)(H)][X] complexes indicate that more basic anions undergo slower ammonia displacement reactions.[20] In contrast to the ^{t}Bu amido system, the ion pairs that result from the parent amido complexes and phenylacetylene {i.e., [TpRu(L)(L′)(NH_3)][PhC_2]} do not undergo clean reaction to yield Ru(II) acetylide complexes. We suspected that these observed reactivity differences might be explained by the facility with which the amines dissociate from the Ru(II) coordination sphere. Thus, for the ^{t}Bu amido system, the relatively facile amine dissociation (compared with the corresponding ammonia complex) possibly accounts for conversion to Ru(II) acetylide complexes in high yield (approximately 90%). In contrast, tightly bound ammonia ligands may result in alternative reaction pathways to yield various and intractable products. Ligand exchange reactions of [TpRu(PMe_3)$_2$(NH_2R)][OTf] (R = ^{t}Bu, Ph or H) with CD_3CN are consistent with this proposal (eq 6 and Figure 6). While [TpRu(PMe_3)$_2$($NH_2{}^t$Bu)][OTf] undergoes ligand exchange at room temperature, the ammine complex [TpRu(PMe_3)$_2$(NH_3)][OTf] does not undergo similar ligand exchange even after prolonged heating at 90 °C. Although the studies of amine dissociation from [TpRu(PMe_3)$_2$(NH_2R)][OTf] complexes cannot be directly compared to net amine/acetylide ligand exchange for [TpRu(L)(L′)(NH_2R)][PhC_2] ion pairs, the relative ease of amine substitution for R = H or ^{t}Bu is consistent with the observed reactivity of the parent and ^{t}Bu amido systems.

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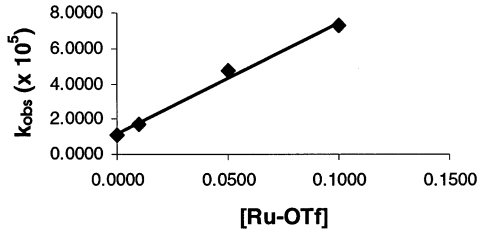
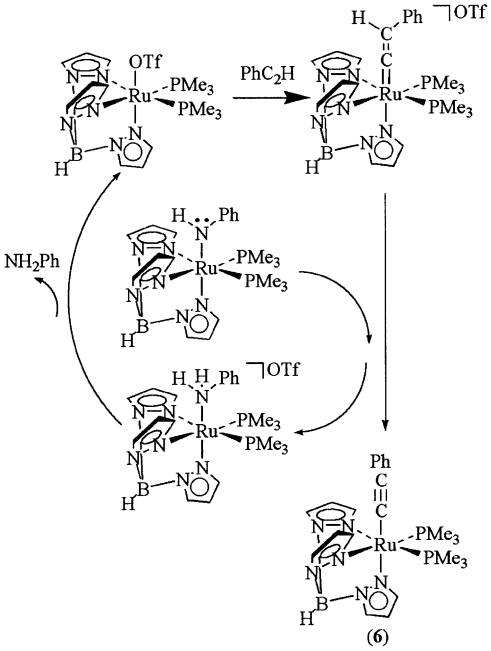


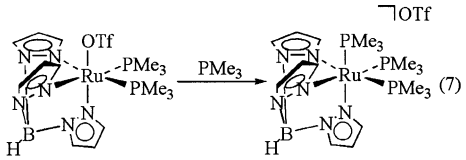
Figure 7. Plot of k_{obs} versus concentration of TpRu(PMe_3)$_2$(OTf) for the conversion of TpRu(PMe_3)$_2$(NHPh) and phenylacetylene to aniline and TpRu(PMe_3)$_2$(C≡CPh) (**6**). The plot of k_{obs} at zero concentration corresponds to the rate constant in the absence of added TpRu(PMe_3)$_2$(OTf) {[Ru−OTf] = TpRu(PMe_3)$_2$(OTf)}.

Scheme 5. Possible Reaction Pathway for the Conversion of TpRu(PMe_3)$_2$(NHPh) and Phenylacetylene to the Ru(II) Acetylide Complex TpRu(PMe_3)$_2$(C_2Ph) (**6**)



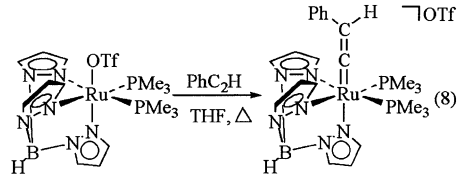
In THF-d_8, TpRuL$_2$(NHPh) complexes (L = PMe_3 or P(OMe)$_3$) react with 10 equiv of phenylacetylene to quantitatively yield TpRuL$_2$(C≡CPh) products. In contrast to TpRuL$_2$(NHR) (R = H or ^{t}Bu), ion pairs resulting from phenylacetylene deprotonation are not observed for the anilido complexes. Inconsistent kinetic data for the reaction of TpRu(PMe_3)$_2$(NHPh) with excess phenylacetylene indicated the possibility of an impurity catalyzing the transformation. The addition of TpRu(PMe_3)$_2$(OTf) results in an increase in the rate of formation of TpRu(PMe_3)$_2$(C≡CPh) (**6**), and a linear dependence is observed for a plot of k_{obs} versus concentration of TpRu(PMe_3)$_2$(OTf) (Figure 7). The addition of PMe_3 (1 equiv based on ruthenium anilido) suppresses the conversion. For example, the combination of TpRu(PMe_3)$_2$(NHPh), 10 equiv of phenylacetylene, 1 equiv of trimethylphosphine, and 1 mol % (based on ruthenium anilido) of TpRu(PMe_3)$_2$(OTf) at 80 °C results in no observed reaction after 24 h. These results are consistent with the ruthenium triflate complex catalyzing the conversion of the amido complex TpRu(PMe_3)$_2$(NHPh) and phenylacetylene to the acetylide complex **6** and aniline, and a plausible reaction pathway is shown in Scheme 5 (note: the amine complex [TpRu(PMe_3)$_2$(NH_2Ph)][OTf] could react directly

with phenylacetylene to produce the vinylidene complex **11**). In addition, [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] could serve as the catalytic impurity rather than TpRu(PMe$_3$)$_2$(OTf). The catalytic reaction is likely suppressed upon addition of PMe$_3$ due to the formation of [TpRu(PMe$_3$)$_3$][OTf] (**10**) from TpRu(PMe$_3$)$_2$(OTf) (or [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf]). In a separate experiment, TpRu(PMe$_3$)$_2$(OTf) was shown to quickly react with PMe$_3$ to form [TpRu(PMe$_3$)$_3$][OTf] (**10**) (eq 7).



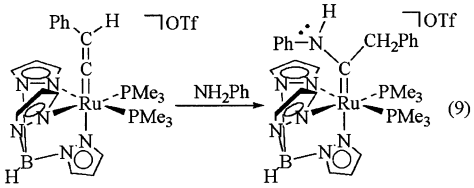
(**10**)

The formation of **10** is complete (at room temperature) within 10 min. Complex **10** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Monitoring the reaction of 10 mol % TpRu(PMe$_3$)$_2$(OTf) with TpRu(PMe$_3$)$_2$(NHPh) and phenylacetylene by ^{1}H NMR spectroscopy reveals the presence of a mixture of species during the course of the reaction. For example, after approximately 50% conversion, aniline, TpRu(PMe$_3$)$_2$(C≡CPh) (**6**), and [Tp(PMe$_3$)$_2$Ru=C=C(H)Ph][OTf] (**11**) are all observed along with a set of broadened Tp and PMe$_3$ resonances. Vinylidene complex **11** has been independently prepared and characterized (eq 8). The broad



(**11**)

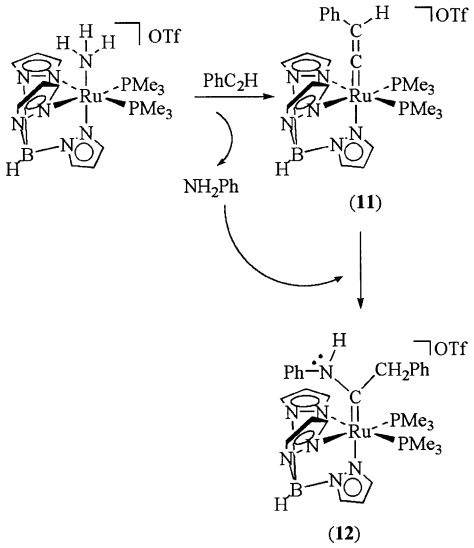
resonances are consistent with the presence of both [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] and TpRu(PMe$_3$)$_2$(NHPh) in which rapid proton transfer results in line broadening. The combination of [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] and TpRu(PMe$_3$)$_2$(NHPh) in C$_6$D$_6$ confirms that the broadened resonances could be due to an amine/amido mixture (i.e., similarly broadened resonances are observed). In addition, toward the end of the reaction, a new TpRu complex that exhibits a downfield singlet at 11.83 ppm (^{1}H NMR) is observed in small quantities. This complex has been identified as [Tp(PMe$_3$)$_2$Ru=C(CH$_2$Ph){N(H)Ph}][OTf] (**12**) and is formed upon reaction of [Tp(PMe$_3$)$_2$Ru=C=C(H)Ph][OTf] (**11**) and aniline (eq 9). Spectroscopic data for complex **12** reveal 2:1



(**9**) (**12**)

integration patterns for the Tp resonances that are consistent with the presence of mirror symmetry. Thus, either the

Scheme 6. Reaction of [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] with Phenylacetylene Initially Yields [Tp(PMe$_3$)$_2$Ru=C=C(H)Ph)][OTf] (**11**) Followed by [Tp(PMe$_3$)$_2$Ru=C(CH$_2$Ph){N(H)Ph}][OTf] (**12**)



carbene C−C−N plane is oriented to bisect the P−Ru−P bond or the Ru−carbene bond is capable of rapid rotation on the NMR time scale. The carbene carbon resonates as a triplet at 271.1 ppm in the ^{13}C NMR spectrum of **12**. The combination of [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] and phenylacetylene at 80 °C results in the formation of [Tp(PMe$_3$)$_2$Ru=C=C(H)Ph)][OTf] (**11**) and aniline with the ultimate product being [Tp(PMe$_3$)$_2$Ru=C(CH$_2$Ph){N(H)Ph}][OTf] (**12**) (Scheme 6). These results demonstrate that amine/phenylacetylene ligand exchange is feasible.

It is possible either that (1) contamination of TpRu(PMe$_3$)$_2$(NHPh) with undetectable amounts of TpRu(PMe$_3$)$_2$(OTf) (or [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf]) catalyzes the reaction of the amido complex with phenylacetylene or that (2) the conversion in the absence of added TpRu(PMe$_3$)$_2$(OTf) proceeds via a distinct reaction pathway. The k_{obs} value for a reaction in the absence of added TpRu(PMe$_3$)$_2$(OTf) (Figure 7) is consistent with a small amount of ruthenium(II) triflate (or aniline) complex serving as catalyst. The observation of a ruthenium impurity serving as catalyst is similar to the insertion of ethylene into an iridium hydroxide bond.[79]

The mechanisms for activation of C−H bonds by late and middle transition metal complexes with nondative heteroatomic ligands are dependent upon the oxidation state of the transition metal center. For systems capable of facile single-electron reduction, hydrogen atom abstraction mechanisms (odd-electron reactions) appear to dominate. Examples include Mn(III) hexafluoroacetylacetonate (see Introduction section), Mn(III) acetate for oxidative cyclization reactions, and biological systems such as lipoxygenases, methane-monooxygenase (calculations indicate a redox-based hydrogen abstraction by a bridging oxo ligand), and the chemistry of vitamin E.[16,37−39,80,81] In addition, Meyer et al. have recently reported that the mechanism of Ru^{IV}=O oxidation of cyclohexenol to cyclohexenone involves the initial

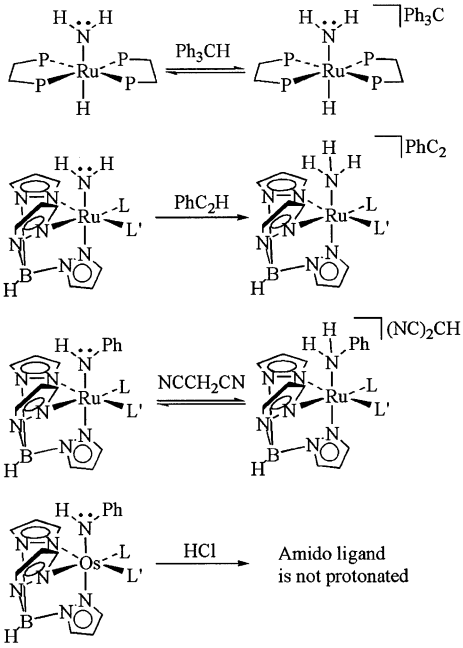
(79) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 2580−2581.

conversion of Ru^{IV}−oxo to Ru^{III}−hydroxide.[82] In contrast, Bergman et al. have demonstrated that reactions of *trans*-$(DMPE)_2Ru(NH_2)(H)$ with 1,4-CHD to yield *trans*-$(DMPE)_2Ru(H)_2$ and benzene proceed via an initial deprotonation to form a cationic Ru(II)−NH_3 complex and cyclohexadienide.[20] This mechanism is in contrast to late transition metal alkoxide complexes that activate C−H bonds of 1,4-cyclohexadiene via hydrogen atom removal (i.e., metal reduction).[16,17]

$TpRu(PMe_3)_2(NH_2)$ reacts with 1,4-CHD to yield 1,3-CHD. Similar to observations made for *cis*-$(PMe_3)_4Ru(H)(NH_2)$, the addition of trimethylphosphine does not impact the rate of isomerization.[83] Thus, phosphine dissociation is not likely to be involved in the isomerization reaction. Ultimately, these reactions produce benzene and $TpRu(PMe_3)_2(H)$ (**9**) in approximately 50% yield, and in analogy to reactions observed with other parent amido ruthenium(II) complexes, we suggest an acid−base reaction mechanism to account for these results.[20] Phosphine dissociation appears to be important to the formation of $TpRu(PMe_3)_2(H)$ (**9**) since the addition of 2 equiv of trimethylphosphine results in no observation of complex **9**. Stack et al. have prepared an octahedral Fe(III) methoxide complex that dehydrogenates 1,4-CHD via a hydrogen atom abstraction mechanism that yields 2 equiv of Fe(II) methanol product, and the favorable Fe(III/II) reduction (E_{red} = 0.73 V) plays a key role in the C−H activation capability of the Fe(III) methoxide complex.[38] In contrast, the Ru(II) amido complexes reported herein are not reduced to −2.0 V (vs NHE). Thus, although hydrogen atom abstraction is a possible reaction pathway, it is a seemingly less likely mechanism for the Ru amido systems. In addition, if hydrogen atom abstraction were occurring, it might be anticipated that the resulting Ru(II/I) reduction would render the reaction more favorable for the anilido complexes TpRu(L)(L′)(NHPh) than for the more electron-rich complex $TpRu(PMe_3)_2(NH_2)$. However, the Ru(II) anilido complexes fail to react with 1,4-CHD. These results in combination with the extensive studies of *trans*-$(DMPE)_2Ru(NH_2)(H)$ and *cis*-$(PMe_3)_4Ru(H)(NH_2)$ support an acid−base pathway.[20,83]

Recent work with Ru and Os amido complexes has revealed a remarkable breadth of reactivity (Scheme 7). For example, Bergman et al. have reported that *trans*-$(DMPE)_2Ru(NH_2)(H)$ deprotonates triphenylmethane.[20] Isoelectronic $TpRu(L)(L')(NH_2)$ complexes do not react with triphenylmethane; however, they have been observed to fully deprotonate phenylacetylene. The Ru(II) anilido complexes TpRu(L)(L′)(NHPh) form acid−base equilibria with malononitrile,[43] and Mayer et al. have reported that the anilido ligand of the d^4 osmium complex $TpOs(NHPh)Cl_2$ is not protonated by HCl.[84] Thus, octahedral group 8 amido complexes with Tp ligands exhibit basicities that span several orders of magnitude (direct comparisons are complicated by ion pairing and studies in different solvents).

Scheme 7. Basicities of Closely Related Octahedral Group 8 Amido Complexes Span Approximately 28 Orders of Magnitude[a]



[a] See refs 22, 45, and 84.

Summary

The reactivity of TpRu(L)(L′)(NHR) (R = H, ^{t}Bu, or Ph) complexes with phenylacetylene is highly dependent on the amido substituent. The highly basic amido ligands for R = H or ^{t}Bu yield intermolecular acid/base reactions to form ion pairs. In contrast, reaction of the anilido complex $TpRu(PMe_3)_2(NHPh)$ with phenylacetylene is catalyzed by the presence of $TpRu(PMe_3)_2(OTf)$ (or $[TpRu(PMe_3)_2(NH_2Ph)][OTf]$) impurity. The highly basic parent and ^{t}Bu amido complexes react with 1,4-CHD to yield benzene and ruthenium−hydride products. In contrast, the less basic anilido systems TpRu(L)(L′)(NHPh) fail to react with 1,4-CHD. The ability of the parent and ^{t}Bu amido complexes TpRu(L)(L′)(NHR) (R = H or ^{t}Bu) to deprotonate phenylacetylene, the high basicity of *trans*-$(DMPE)_2Ru(NH_2)(H)$, the decreased basicity of TpRu(L)(L′)(NHPh) relative to the Ru(II) parent amido complexes, and the highly inert anilido ligand of $TpOsCl_2(NHPh)$ (inert to protonation by HCl) reveal a large range of reactivity for closely related octahedral amido complexes bound to group 8 metal centers.[20,22,43,84]

Acknowledgment is made to the donors of the Petroleum Research Fund (administered by the American Chemical Society) and to North Carolina State University for support of this research. In addition, this work was supported in part by the National Science Foundation (CAREER Award; CHE 0238167). The authors also wish to thank the National Science Foundation (NSF) for funding (CHE-9509532) to obtain the X-ray diffractometer and for support of Selena Manzer under the Chemistry Research Experiences for Undergraduates Program (CHE-0097485).

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for $[TpRu(CO)(PPh_3)(NH_3)][OTf]$, $[TpRu(PMe_3)_2(NH_3)][OTf]$, and $TpRu(CO)(PPh_3)(C{\equiv}CPh)$ (**7**). Procedures for the preparation of $[TpRu(PMe_3)_2\{NH_2(p\text{-}C_6H_4CF_3)\}][OTf]$ and $TpRu(PMe_3)_2\{NH(p\text{-}C_6H_4CF_3)\}$ and ^1H NMR spectra of these systems as well as NMR spectra for **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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