Organometallics **2002,** *21,* 5265−5271

Ruthenium(II) Anilido Complexes $TpRuL_2(NHPh)$: Oxidative 4,4′-Aryl Coupling Reactions (Tp = Hydridotris(pyrazolylborate); L = PMe_3, $P(OMe)_3$, or CO)

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Received August 7, 2002

Reactions of the Ru(II) amido complexes $TpRuL_2(NHPh)$ (L = CO, PMe_3, or $P(OMe)_3$) with AgOTf (OTf = trifluoromethanesulfonate) yield the binuclear complexes $[TpRuL_2NH(C_6H_4-)]_2[OTf]_2$ along with the Ru(II) amine complexes $[TpRuL_2(NH_2Ph)][OTf]$ in an approximate 1:1 molar ratio. In these reactions, the two ruthenium fragments are coupled via C−H bond cleavage and C−C bond formation at the para position of anilido ligands. A resonance structure corresponding to Ru(II) metal centers linked by a diimine ligand contributes significantly to the bonding. Evidence for such a contribution comes from the diamagnetic nature of the binuclear complexes and a solid-state X-ray crystallographic study of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$. It is proposed that the coupled products are formed via initial single-electron oxidation followed by C−C bond formation. Variable-temperature NMR spectra of the aryl-coupled complexes are consistent with two geometrical isomers around the rigid $HN-C_6H_4-C_6H_4NH$ bridges.

Introduction

Biaryl moieties are prevalent in an array of important compounds including natural products as well as compounds for nonlinear optics, helical polymers, liquid crystals, and ligands for asymmetric catalysis.[1−6] Metal-mediated routes for aryl−aryl coupling reactions include reductive coupling of aryl halides, oxidative coupling sequences, and cross-coupling reactions of aryl halides with aryl organometallic reagents.[1,4−12] Both reductive-coupling and cross-coupling methods incorporate aryl halide reagents, and cross-coupling sequences also require stoichiometric quantities of reactive organometallic aryl reagents. In addition, reductive coupling using Ullmann methods and the key oxidative addition step in Suzuki coupling reactions are inhibited by the presence of electron-donating groups.[6,13,14] Methods for oxidative coupling can offer the advantage of C−C bond formations that proceed via C−H bond cleavage. Thus, the need for stoichiometric quantities of aryl chlorides and aryl organometallic reagents is avoided. Along these lines, Yamamoto et al. have recently reported ortho coupling of phenols or anilines with aryllead compounds,[15] and copper-catalyzed oxidative couplings of binaphthyl reagents have been successful.[6,16−19]

Amido ligands of transition metal complexes have been implicated in a number of stoichiometric reactions (e.g., reactions with electrophiles and insertions) and catalytic transformations including the amination of aryl halides and triflates, hydroamination of olefins and alkynes, hydrazine reduction, C−H activation, and the synthesis of polyanilines.[20−29] The number of isolable amido ligands bound to late transition metals is few compared with early transition metal systems, and increased interest in such systems and other closely related complexes has resulted in the discovery of a

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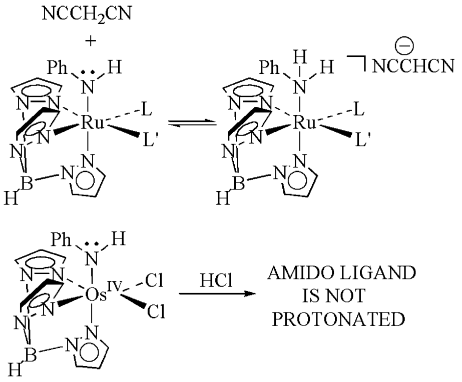
10.1021/om0206406 CCC: $22.00
Publication on Web 10/25/2002

Scheme 1. Contrasting Reactivity of d^6 Ru(II) and d^4 Os(IV) Anilido Ligands



diversity of reactivity patterns.[22,25,30,31] For example, in an interesting contrast, both parent and phenyl amido ligands of octahedral Ru(II) complexes are highly basic while an Os(IV) phenyl amido complex that is inert to protonation by HCl has been reported (Scheme 1).[32−35] It is clear that the basicities of the Ru(II) and Os(IV) anilido complexes differ by several orders of magnitude (solvent identity and ion pairing complicate a direct comparison of basicity). While the contribution of π-conflict to the heightened reactivity of late transition metal amido complexes is uncertain,[25,36] these results suggest that π-interactions can *significantly* impact the reactivity of late transition metal amido ligands. The importance of such considerations is highlighted by a recent report detailing the participation of a basic amido ligand in Ru-catalyzed ketone hydrogenation reactions.[37]

We have previously reported the synthesis and reactivity of octahedral Ru(II) phenyl amido complexes of the type TpRu(L)(L′)(NHPh) (Tp = hydridotris(pyrazolyl)borate; L = L′ = P(OMe)$_3$, PMe$_3$, or CO or L = CO and L′ = PPh$_3$).[35,38] Herein, we report that oxidation of the Ru(II) amido complexes TpRuL$_2$(NHPh) (L = CO, PMe$_3$, or P(OMe)$_3$) results in an aryl coupling reaction that proceeds via aryl C−H bond cleavage. Binuclear products with bridging C_6H_4 rings of the type [TpRuL$_2$-NH(C_6H_4−)]$_2$[OTf]$_2$ {L = CO (**2**), PMe$_3$ (**3**), or P(OMe)$_3$ (**4**)} are formed in these reactions. In addition, variable-temperature ^{1}H and ^{31}P NMR spectroscopy and details of the solid-state structure of [TpRu{P(OMe)$_3$}$_2$NH-(C_6H_4−)]$_2$[OTf]$_2$ (**4**) are presented.

Experimental Section

General Methods. All reactions and procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or using 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$_2$.[39] THF and diethyl ether were dried by distillation from sodium/benzophenone. CD$_3$CN was purified by distillation from CaH$_2$, degassed, and stored over 4 Å sieves. Me$_2$SO-d_6 was used as received. Acetone-d_6 was degassed via 3 freeze−pump−thaw cycles and stored over 4 Å sieves. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300-MHz, Varian Mercury 400-MHz, or General Electric 300-MHz spectrometer. Resonances due to the Tp ligand are reported by chemical shift and multiplicity only. All $^3J_{HH}$ 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$_3$PO$_4$. 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. Elemental analyses were performed by Atlantic Microlabs, Inc. The syntheses of TpRu(PMe$_3$)$_2$(NHPh), TpRu{P(OMe)$_3$}$_2$(NHPh), and [TpRu(CO)$_2$(THF)][PF$_6$] have been previously reported.[35,40] All other reagents were used as purchased from commercial sources.

[TpRu(CO)$_2$NH$_2$Ph][PF$_6$] (1). Aniline (0.2465 g, 2.65 mmol) was added to a THF solution of [TpRu(CO)$_2$(THF)][PF$_6$] (0.1027 g, 0.175 mmol). The resulting mixture was refluxed for 24 h, and the volatiles were removed under reduced pressure. The resulting beige solid was washed with approximately 4 × 30 mL of diethyl ether and was dried in vacuo (0.1015 g, 95%). ^{1}H NMR (acetone-d_6, δ): 8.18 (4H, overlap multiplet, Tp C*H* 3 and 5 position), 8.09, 8.03 (each 1H, each a d, Tp C*H* 3 or 5 position), 6.57, 6.42 (3H, 2:1 integration, each a t, Tp C*H* 4 position). 7.50 (4H, overlap multiplet, phenyl ortho, and meta), 7.34 (1H, t, phenyl para). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 194.5 (*C*O), 147.6, 145.0, 138.9, 138.6 (Tp 3 or 5 position), 146.5, 131.0, 127.4, 122.4 (amine phenyl), 108.7, 108.6 (Tp 4 position). IR (thin film on KBr): $\nu_{CO} = 2084, 2022$ cm^{-1}, $\nu_{NH} = 3313, 3271$ cm^{-1}, $\nu_{BH} = 2528$ cm^{-1}. Anal. Calcd for $C_{17}H_{17}BF_6N_7O_2Ru$: C, 33.57; H, 2.82; N, 16.12. Found: C, 33.82; H, 2.93; N, 15.95.

[TpRu(CO)$_2$NH(C_6H_4−)]$_2$[OTf]$_2$ (2). [TpRu(CO)$_2$(NH$_2$Ph)]-[PF$_6$] (**1**, 0.1402 g, 0.231 mmol) in approximately 50 mL of THF was cooled to −110 °C. To this solution was added sodium bis(trimethylsilyl)amide (0.253 mmol, 1.0 M in THF) dropwise via syringe. The resulting solution was pale yellow. This solution was transferred via cannula to a THF solution of AgOTf (0.1194 g, 0.465 mmol) and triethylamine (0.3511 g, 3.47 mmol) that was precooled to −110 °C. After the addition, the resulting solution was dark brown. The solution was warmed to room temperature, and a color change to dark red was noted. The volatiles were removed under reduced pressure to give a dark red solid. This solid was mixed with THF, filtered through a plug of Celite, and washed with THF until the filtrate was no longer red (approximately 50 mL of THF). The red filtrate was discarded. The remaining solids were eluted with acetonitrile until the filtrate was no longer red (approximately 100 mL of acetonitrile). The volatiles were removed under reduced pressure to give a dark purple solid (0.0763 g, 54%). Additional purification can be accomplished via recrystallization from methylene chloride and a nonpolar solvent such as hexanes or cyclohexane. ^{1}H NMR (Me$_2$SO-d_6, δ): 11.33 (2H, br s, N*H*), 8.33, 8.31, 8.24, 8.14, 7.98 (12H, 1:1:4:2:4 integration, each a d, Tp C*H* 3 and 5 position), 7.91, 7.16 (6H, 4:2 integration, overlapping d's, C_6H_4 rings), 6.49 (6H,

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overlapping t's, Tp C*H* 4 position), 5.90 (2H, overlapping d's, C_6H_4 rings). $^{13}C\{^1H\}$ NMR (Me_2SO-d_6, δ): 193.4 (*C*O), 169.7 (amido C_6H_4 ipso), 146.7, 144.6, 138.0, 137.5 (Tp 3 or 5 position), 136.4, 133.4, 122.9, 118.6, 114.4 (C_6H_4 rings), 107.9, 107.7 (Tp 4 position). IR (thin film on KBr plate): $\nu_{CO} = 2080$, 2024 cm^{-1}, $\nu_{NH} = 3437$ cm^{-1}, $\nu_{BH} = 2513$ cm^{-1}. FAB-MS: 923.1 $[TpRu(CO)_2(NHC_6H_4)]_2^+$, 647.1 $[TpRu(CO)_2NH(C_6H_4-)]_2^{2+}$, 553.1 $[TpRu(CO)_2(NHC_6H_4-C_6H_4NH)]^+$, 371.0 $[TpRu(CO)_2]^+$, 315.0 $[TpRu]^+$. Note: Consistent elemental analysis of complex **2** could not be obtained. We attribute this to the difficulty in removing solvent from the precipitated products. Even after prolonged drying in vacuo and elevated temperatures, ^1H NMR spectroscopy of **2** revealed variable mixtures of acetonitrile, methylene chloride, THF, and/or hexanes.

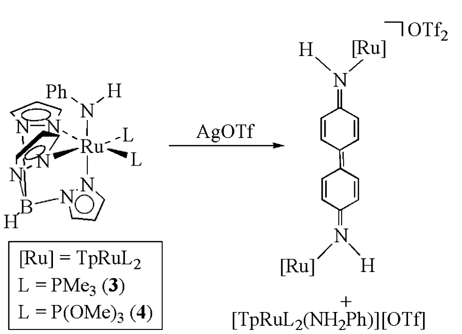
$[TpRu(PMe_3)_2NH(C_6H_4\text{-})]_2[OTf]_2$ (3). A yellow solution of $TpRu(PMe_3)_2(NHPh)$ (0.0529 g, 0.0947 mmol) in approximately 20 mL of THF was added dropwise to a solution of AgOTf (0.0452 g, 0.176 mmol) and triethylamine (0.1441 g, 1.42 mmol) in THF. Upon addition an immediate color change to dark blue-green was noted. The volatiles were removed under reduced pressure to give a dark green solid. This solid was mixed with THF, filtered through a plug of Celite, and washed with THF until the filtrate was no longer blue (approximately 50 mL of THF). The blue filtrate was discarded. The remaining solids were eluted with acetonitrile until the filtrate was no longer green (approximately 100 mL of acetonitrile). The volatiles were removed under reduced pressure to give a green solid (0.0401 g, 59%). Additional purification can be accomplished via recrystallization from methylene chloride and a nonpolar solvent such as hexanes or cyclohexane. ^1H NMR (CD_3CN, δ, 60 °C): 11.33 (2H, br s, N*H*), 7.96, 7.94, 7.78, 7.30 (12H, 2:4:2:4 integration, each a d, Tp C*H* 3 and 5 position), 7.43 (2H, d, $^3J_{HH} = 9$ Hz, C_6H_4 rings), 7.26, 7.18, 7.15, 7.06 (4H, 1:1:1:1, each a d, $^3J_{HH} = 9$ Hz, C_6H_4 rings), 6.39, 6.23 (6H, 2:4 integration, each a t, Tp C*H* 4 position), 4.99 (2H, d, $^3J_{HH} = 9$ Hz, C_6H_4 rings), 1.22 (36H, vt, N = 9 Hz, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (Me_2SO-d_6, δ): 169.5 (amido C_6H_4 ipso), 146.4, 143.1, 137.0, 136.6 (Tp 3 or 5 position), 133.5−118.5 (multiple overlapping resonances due to C_6H_4 rings), 107.1, 106.2 (Tp 4 position), 16.8 ($P(CH_3)_3$, vt, N = 29 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, δ): 8.0 (s, *P*Me$_3$). IR (thin film on KBr plate): $\nu_{NH} = 3399$ cm^{-1}, $\nu_{BH} = 2493$ cm^{-1}. FAB-MS: 649.1 $[TpRu(PMe_3)_2(NHC_6H_4-C_6H_4NH)]^+$, 573.0 $[TpRu(PMe_3)(NHC_6H_4-C_6H_4NH)]^+$, 467.1 $[TpRu(PMe_3)_2]^+$, 391.0 $[TpRu(PMe_3)]^+$, 315.0 $[TpRu]^+$. Note: Consistent elemental analysis of complex **3** could not be obtained. We attribute this to the difficulty in removing solvent from the precipitated products. Even after prolonged drying in vacuo and elevated temperatures, ^1H NMR spectroscopy of **3** revealed variable mixtures of acetonitrile, THF, methylene chloride, and/or hexanes.

$[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (4). A yellow solution of $TpRu\{P(OMe)_3\}_2(NHPh)$ (0.1080 g, 0.165 mmol) in approximately 20 mL of THF was added dropwise to a solution of AgOTf (0.0856 g, 0.333 mmol) and triethylamine (0.2493 g, 2.46 mmol) in THF. Upon addition an immediate color change to dark blue was noted. The volatiles were removed under reduced pressure to give a dark-blue solid. The solid was mixed with THF, filtered through a plug of Celite, and washed with THF until the filtrate was no longer blue (approximately 50 mL of THF). The blue filtrate was discarded. The remaining solids were eluted with acetonitrile until the filtrate was no longer blue (approximately 100 mL of acetonitrile). The volatiles were removed under reduced pressure to give a dark-blue solid (0.0385 g, 29%). Additional purification can be accomplished via recrystallization from methylene chloride or THF and a nonpolar solvent such as hexanes or cyclohexane. ^1H NMR (CD_3CN, δ, 95 °C): 10.09 (2H, br s, amido N*H*) 8.04, 7.96, 7.91, 7.46 (12H, 2:4:2:4 integration, each a d, Tp C*H* 3 and 5 position), 7.39 (2H, d, $^3J_{HH} = 9$ Hz, amido C_6H_4 ring), 6.97 (4H, overlapping resonances, amido C_6H_4 rings), 6.34, 6.27 (6H, 2:4 integration, each a t, Tp C*H* 4 position), 4.93 (2H, d, $^3J_{HH} = 9$ Hz, amido C_6H_4 rings), 3.46 (36H, vt, N = 10 Hz, $P(OCH_3)_3$). $^{13}C\{^1H\}$ NMR (Me_2SO-d_6, δ): 169.8 (amido C_6H_4 ipso), 147.3, 144.0, 137.3, 136.5 (Tp 3 or 5 position), 136.4−122.8 (multiple overlapping resonances due to C_6H_4 rings), 106.5 (overlap, Tp 4 position), 52.2 (br s, $P(OCH_3)_3$). $^{31}P\{^1H\}$ NMR (Me_2SO-d_6, δ): 139.0 and 138.9 (each a s, *P*(OMe)$_3$). IR (thin film on KBr plate): $\nu_{NH} = 3296$ cm^{-1}, $\nu_{BH} = 2492$ cm^{-1}. FAB-MS: 745.1 $[TpRu\{P(OMe)_3\}_2(NHC_6H_4-C_6H_4NH)]^+$, 621.1 $[TpRu\{P(OMe)_3\}(NHC_6H_4-C_6H_4NH)]^+$, 654.1 $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2^{2+}$, 563.0 $[TpRu\{P(OMe)_3\}_2]^+$, 439.0 $[TpRu\{P(OMe)_3\}]^+$, 315.0 $[TpRu]^+$. Anal. Calcd for $C_{44}H_{66}B_2F_6N_{14}O_{18}P_4Ru_2S_2$−THF: C, 34.38; H, 4.45; N, 11.69. Found: C, 34.40; H, 4.36; N, 11.12.

X-ray Structure of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (4). A crystal of dimensions 0.32 × 0.14 × 0.10 mm was selected from a bulk recrystallization from a methylene chloride solution layered with cyclohexane. The sample was mounted on the end of a glass fiber using a small amount of silicon grease and was maintained at a temperature of −125 °C using a nitrogen cold stream. All X-ray measurements were made on an Enraf-Nonius CAD4-MACH diffractometer. The unit cell dimensions were determined by a fit of 25 well-centered reflections and their Friedel pairs with $26° < 2\theta < 33°$. A quadrant of unique data were acquired using the omega scan mode in a nonbisecting geometry. The adoption of a nonbisecting scan mode was accomplished by offsetting ψ by 20.00 for each data point collected. This was done to minimize the interaction of the goniometer head with the cold stream. Three standard reflections were measured every 4800 s of X-ray exposure time. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scan data was applied. The data were reduced using routines from the NRCVAX set of programs.[41] The structure was solved using SIR92.[42] All non-H atom positions were recovered from the initial *E*-map. All hydrogen atoms were placed at idealized positions and were allowed to refine isotropically. Refinement of the structure was performed using full-matrix least-squares based on *F*. All non-H atoms were allowed to refine with anisotropic displacement parameters (ADP's).

Results

Synthesis and Characterization of Binuclear Complexes. The reaction of the Ru(II) amido complexes $TpRuL_2(NHPh)$ {L = PMe_3 or $P(OMe)_3$} with 2 equivalents of AgOTf yields the binuclear coupled products $[TpRuL_2NH(C_6H_4-)]_2[OTf]_2$ {L = PMe_3 (**3**) or $P(OMe)_3$ (**4**)} (eq 1). The Ru(II) amine complexes $[TpRuL_2(NH_2Ph)][OTf]$ are also formed in these reactions, and ^1H NMR spectroscopy of the crude reaction mixture indi-



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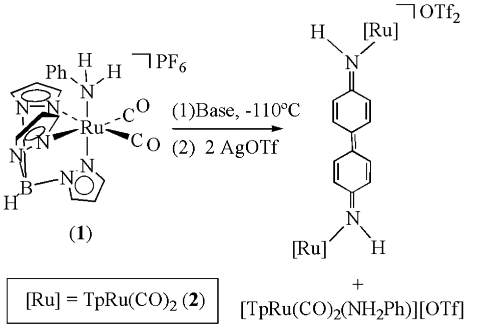
cates an approximate 1:1 molar ratio of **3** or **4** to Ru(II) amine. NMR tube reactions in CD_3CN with 1 equiv of AgOTf reveal similar results and indicate that starting material is converted to the binuclear complex and Ru(II) amine products in nearly quantitative yield. The addition of approximately 15 equiv of Et_3N to the scaled-up reaction of $TpRu(PMe_3)_2(NHPh)$ increases the molar ratio of **3** to Ru(II) amine to approximately 3:1. For the synthesis of complex **4**, the addition of Et_3N does not have a marked effect on the ratio of **4** to Ru(II) amine. Alternatively, the Ru(II) amido complexes can be generated in situ from the corresponding Ru(II) amine complexes $[TpRuL_2(NH_2Ph)][OTf]$ prior to oxidation. Complexes **3** and **4** have been characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectroscopy as well as FAB mass spectrometry. While the parent peak for binuclear complex **3** is not observed by FAB mass spectrometry, the parent peak for the dicationic complex **4** is observed as a cluster of low intensity. In addition, peaks corresponding to $[TpRuL_2(NHC_6H_4{-}C_6H_4NH)]^+$ (649.1 for **3** and 745.1 for **4**) and other expected TpRu fragments are observed. A solid-state X-ray diffraction study of complex **4** has confirmed its identity (see below). Salient NMR features for **3** and **4** include NH resonances between 10 and 11 ppm and resonances for two ring protons slightly upfield of 5 ppm in the ^1H NMR spectra. EPR spectra for complexes **3** and **4** are silent and indicate that paramagnetic systems are not present after workup. We have previously reported the binuclear complex $[TpRu(CO)(PPh_3)NH(C_6H_4-)]_2[OTf]_2$ in which it was incorrectly characterized as the monomeric amido complex.[43]

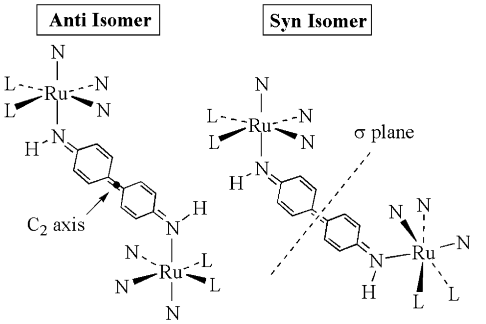
For synthesis of the dicarbonyl complex $[TpRu(CO)_2NH(C_6H_4-)]_2[OTf]_2$ (**2**) in situ generation of the Ru(II) amido complex upon treatment of $[TpRu(CO)_2NH_2Ph][OTf]$ (**1**) with $NaN(SiMe_3)_2$ at −110 °C is *required* prior to reaction with AgOTf and base (eq 2). The addition of approximately 15 equiv of Et_3N increases the molar ratio of **2** to Ru(II) amine to approximately 1.6:1 (compared with a 1:1 ratio in the absence of Et_3N). All attempts to cleanly isolate the Ru(II) amido complex $TpRu(CO)_2NHPh$ have thus far failed. It is suspected that at elevated temperatures the amido ligand of this complex undergoes CO insertion and thus eludes isolation.[44] Complex **2** has also been characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy as well as FAB mass spectroscopy.



(2)

Dynamic NMR. The ^1H NMR spectrum of a CD_3CN solution of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**) at −5 °C reveals two downfield amido NH resonances at 10.12 and 10.06 ppm ($K_{eq} \sim 1$). In addition, at low temperature (−40 °C) eight unique resonances due to C_6H_4 rings are observed, and the room temperature ^{31}P NMR spectrum reveals two resonances. Heating the solution results in line broadening and coalescence of the resonances due to the amido and ring protons (^1H NMR), and at 95 °C resonances consistent with a single isomer due to time averaging are observed. At room temperature, a single set of Tp resonances is observed. Upon cooling, the Tp resonances broaden and for some resonances decoalescence into two sets of peaks is observed. The dynamic NMR behavior is consistent with two isomers based on relative positioning of $\{TpRuL_2\}$ fragments about the bridging $HN{-}C_6H_4{-}C_6H_4{-}NH$ ligands. Thus, the relative orientation of the two $\{TpRuL_2\}$ fragments of a single binuclear complex can be "syn" or "anti" (Chart 1). For each isomer, the two $\{TpRuL_2(NHC_6H_4)\}$ fragments are symmetry equivalent. For the anti isomer, a C_2 axis renders the two Ru moieties equivalent, while a mirror plane of symmetry equilibrates the two Ru fragments of the syn isomer. Thus, *each* isomer gives rise to four C_6H_4 resonances, a single NH resonance, and a single set of Tp resonances with a 2:1 integration pattern. Consistent with the solid-state structure of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**) (see below), Chart 1 depicts an orientation with the C_6H_4 rings between two pyrazolyl rings. Whether this confirmation is present in solution has not been determined. Heating the solution results in line broadening and coalescence of the resonances due to the NH protons. The coalescence temperature (40 °C) of the two NH resonances has been used to calculate an activation barrier for isomer interconversion of 15.9 kcal/mol.

Chart 1. "Syn" and "Anti" Geometrical Isomers Due to Relative Orientations of $\{TpRuL_2\}$ Fragments about Rigid π-System



Similar to $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**), the ^1H NMR spectrum of $[TpRu(PMe_3)_2NH(C_6H_4-)]_2[OTf]_2$ (**3**) at −50 °C reveals the presence of two NH resonances at 11.56 and 11.53 ppm ($K_{eq} \sim 1$), and the dynamic NMR features of complex **3** parallel those of complex **4**. At room temperature, the ^{31}P NMR spectrum of **3** reveals a single resonance at 8.0 ppm; however, cooling the solution to −45 °C does not result in decoalescence. The inability to observe decoalescence is likely attributable to a small difference in chemical shift for the ^{31}P resonances of the two isomers. In the ^1H NMR spectra, the coalescence of the two NH resonances (−5 °C) results in a calculated barrier of 13.9 kcal/mol for isomer interconversion of complex **3**. In Me_2SO-d_6 and CD_3CN, the dicarbonyl complex $[TpRu(CO)_2NH(C_6H_4-)]_2[OTf]_2$ (**2**) exhibits a single resonance due to

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Table 1. $\Delta G^\ddagger$ for Isomer Interconversions for the Binuclear Complexes 2−4

complex	$\Delta G^\ddagger$(Ru−N), kcal/mol
$[TpRu(CO)_2NH(C_6H_4-)]_2[OTf]_2$ (**2**)	$>18.5^a$
$[TpRu(PMe_3)_2NH(C_6H_4-)]_2[OTf]_2$ (**3**)	13.9^b
$[TpRu\{P(OMe_3)\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**)	15.9^c

[a] 70 °C. [b] −5 °C. [c] 40 °C.

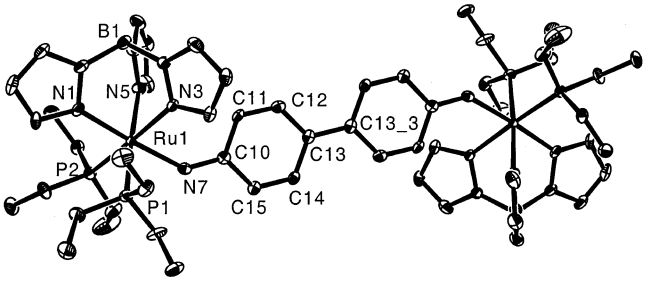

Figure 1. Partially labeled ORTEP (thermal ellipsoids at the 50% level) of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**) (solvent, hydrogen atoms, and counterions have been omitted for clarity).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (4)

atoms	bond distance	atoms	bond distance
Ru−P1	2.2459(15)	C10−C11	1.449(8)
Ru−P2	2.2406(15)	C11−C12	1.363(7)
Ru−N1	2.088(4)	C12−C13	1.435(8)
Ru−N3	2.144(4)	C13−C13_3	1.425(10)
Ru−N5	2.152(4)	C13−C14	1.440(8)
Ru−N7	2.044(4)	C14−C15	1.352(8)
N7−C10	1.315(7)	C10−C15	1.441(8)

atoms	bond angle	atoms	bond angle
P1−Ru−P2	92.38(6)	N3−Ru−N5	83.54(17)
Ru1−N7−C10	137.2(4)	N3−Ru−N7	89.91(17)
N7−C10−C11	122.8(5)	P1−Ru−N7	87.92(13)
N7−C10−C15	120.7(5)	P2−Ru−N7	90.28(13)
N1−Ru−N3	86.45(17)	N1−Ru−N7	176.33(17)
N1−Ru−N5	86.86(17)		

Table 3. Selected Crystallographic Data and Collection Parameters for $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (4)

formula	$C_{23}H_{35}BCl_2F_3N_7O_9P_2RuS$
mol wt	887.35
cryst syst	monoclinic
sp gr	$P2_1/c$
a, Å	9.6170(11)
b, Å	25.474(3)
c, Å	14.5857(18)
β, deg	92.974(8)
V, Å^3	3568.4(7)
Z	4
D_{calcd}, g cm^{-3}	1.652
total no. of reflns	6230
unique reflns	6230
R	0.046
R_w	0.049
GOF	1.47

the NH protons. However, in $CDCl_3$ two NH resonances are observed in a 2.3:1 ratio at 10.64 and 10.31 ppm ($\Delta\nu = 135$ Hz). Heating this solution to 70 °C does not result in significant line broadening; however, the addition of 3 drops of Me_2SO-d_6 results in an equilibrium shift to an approximate 1:1 ratio as well as a change in chemical shift ($\Delta\nu = 8.8$ Hz). This result indicates that K_{eq} is dependent on solvent identity perhaps due to solvent polarity and the differences in dipole of the geometrical isomers. It is also possible that ion-pairing effects play a role in the solvent-dependent K_{eq}. Heating the CD_3CN/Me_2SO-d_6 solution of **2** to 40 °C does not result in changes in chemical shift or line broadening. Thus, at room temperature the slow exchange regime has been accessed. Heating the solution to 70 °C does result in line broadening; however, coalescence is not achieved at this temperature, and increasing the temperature further is limited by the boiling point of the solvent. Using these data, $\Delta G^\ddagger$ has been calculated to be >18.5 kcal/mol (Table 1). Although access to three data points is not adequate to reliably establish a trend, it is notable that the $\Delta G^\ddagger$ values for isomer interconversion increase with decreasing donating ability of ligands "L" (i.e., for $\Delta G^\ddagger$: CO > $P(OMe)_3$ > PMe_3).

Solid-State Structure of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$. The X-ray structure of $[TpRu\{P(OMe)_3\}_2NH(C_6H_4-)]_2[OTf]_2$ (**4**) shows a binuclear complex with pseudooctahedral coordination spheres (Figure 1). Data collection parameters and selected bond distances and angles are displayed in Tables 2 and 3. The molecule resides on a crystallographic center of symmetry, and the two $\{TpRu\{P(OMe)_3\}_2(NHC_6H_4)\}$ fragments are equivalent. The C_6H_4 fragments are oriented syn to two pyrazolyl rings of the Tp ligands and are in a coplanar orientation. The Ru−N7 bond distance is 2.044(4) Å and is shorter than that observed for $TpRu^{II}(L)(L')$ amido or amine complexes.[35,38] The Ru−N7−C10 bond angle is 137.2(4)°. The N7−C10−C11 and N7−C10−C15 bond angles are 122.8(5)° and 120.7(5)°, respectively. The bond distance (1.425(10) Å) between the coupled carbon atoms (C13−C13_3) is shorter than a typical C−C single bond (1.54 Å). In addition, the N7−C10 bond distance (1.315(7) Å) is shorter than expected for a N−C single bond (1.47 Å).[45] The bond distances of the C_6H_4 rings are consistent with quinoidal localization of the π-electrons. The C11−C12 and C14−C15 bond distances (1.363(7) and 1.352(8) Å) are shorter than the bond distances between C10−C11/C10−C15 (1.449(8)/1.441(8) Å) and C13−C12/C13−C14 (1.435(8)/1.440(8) Å). A second solid-state X-ray diffraction study that revealed two independent molecules was undertaken for crystals grown from a different solvent combination (a chloroform solution layered with cyclohexane). The details of the second structure are consistent with those discussed above and are presented in the Supporting Information.

Discussion

The oxidation of $TpRuL_2(NHPh)$ complexes **2**−**4** yields aryl coupled products. Closely related to the stoichiometric Ru transformations reported herein are oxidative coupling reactions of binaphthyl reagents including a Ru complex that catalyzes the oxidative coupling of 2-naphthols under photolytic conditions.[16,18,19,46] In addition, Tolman et al. have recently detailed Cu-mediated coupling of aryloxide ligands.[47] The reactions to form the binuclear Ru complexes **2**−**4** involve C−H bond

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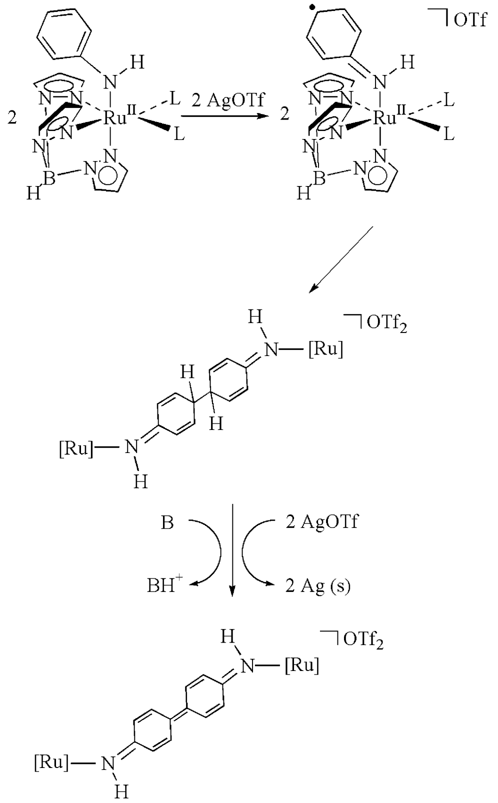
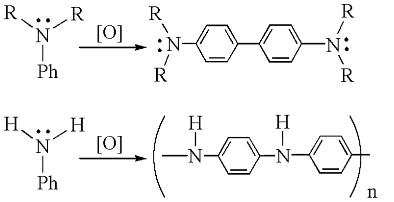
Scheme 2. Possible Route to Coupled Complexes 2−4 via C−C Bond Formation after Single-Electron Oxidation To Form a Delocalized Radical {B = base; [Ru] = TpRuL$_2$}



cleavage of two phenyl para C−H bonds via the net loss of 2 equiv of hydride. The coupling reactions proceed in the presence or absence of added Et$_3$N or 2,6-lutidine; however, the ratio of aryl coupled products **2** and **3** to Ru(II) amine increases upon addition of excess base. For example, the reaction of TpRu(PMe$_3$)$_2$(NHPh) with 2 equiv of AgOTf and 15 equiv of Et$_3$N results in the formation of the binuclear complex **3** and [TpRu(PMe$_3$)$_2$(NH$_2$Ph)][OTf] in an approximate 3:1 molar ratio (as determined by ^{1}H NMR spectroscopy of the crude reaction mixture) while the analogous reaction in the absence of base yields an approximate 1:1 molar ratio. Interestingly, the addition of Et$_3$N to the reaction of TpRu{P(OMe)$_3$}$_2$(NHPh) with 2 equiv of AgOTf yields an approximately 1.1:1 ratio of binuclear complex **4** to [TpRu{P(OMe)$_3$}$_2$(NH$_2$Ph)][OTf] and does not greatly impact the ratio of **4** to Ru(II) amine complex.

A possible route to the aryl-coupled binuclear complexes in the absence of added base involves the initial formation of the Ru(III) amido complexes [TpRuL$_2$-NHPh][OTf] to yield delocalized radical species (Scheme 2). Subsequent C−C bond formation, deprotonation by added Et$_3$N or starting Ru(II) amido complex, and a second oxidation would yield the coupled products **2**−**4**. It is also feasible that a phenyl amido radical initiates C−C bond formation by reacting with the phenyl group of a Ru(II) amido complex. Radical additions to aromatic systems are known.[48] A similar reaction has been reported with a Pt(II) phenyl amido complex, and Sharp et al. have reported the coupling of phenyl substituents of a Rh imido complex.[49−51] For the Rh imido coupling reaction, the coupled product prior to C−H bond cleavage was isolated. The observation of Ru(II) amine complexes in these reactions could result from starting material serving as a base. TpRu(L)(L′)(NHPh) complexes have been demonstrated to be basic enough to deprotonate malononitrile in methylene chloride.[35] The decreased ratio of binuclear complex to Ru(II) amine in the absence of added base could also be explained by the proposed reaction route; however, the 1:1 molar ratio of binuclear complex to Ru(II) amine is not consistent with the Ru(II) amido starting materials serving as the only proton reservoir. The mechanistic implications of these results are not yet fully understood.

Scheme 3. Oxidation of Bisalkylaryl-Amines Leads to C−C Bond Formation while the Oxidation of Aniline Results in N−C Bond Formation and the Synthesis of Polyaniline



While oxidation of bisalkyl−aryl (R$_2$NAr) and trisarylamines (Ar$_3$N) at electrode surfaces can lead to biaryls via C−C bond formation, similar oxidation of aniline yields oligomerized products (Scheme 3).[52−54] A study of aniline oxidation using fast scan cyclic voltammetry has revealed that benzidine is only a minor product of the reaction that occurs upon oxidation of aniline.[55] In the proposed route for the Ru-mediated aryl coupling, Ru(III) likely serves as an electron reservoir to allow delocalization of the radical into the aryl ring. This is reminiscent of recently invoked Cu(I) phenoxyl resonance structures to explain the reactivity of Cu(II) phenoxide systems.[56] The Ru(III/II) oxidation potentials for TpRuL$_2$(NHPh) {L = PMe$_3$ or P(OMe)$_3$} are −0.25 and −0.28 V, respectively, and the Ru(III/II) potential for TpRu(CO)(PPh$_3$)(NHPh) is 0.11 V (versus NHE).[35,38] Thus, the Ru(II) resonance structure of the oxidized complex allows radical reactivity at the amido ligand, and the Ru metal center serves as a protecting group to prevent the N−C bond formation that occurs upon oxidation of free aniline.[52] In a closely related system, Mayer et al. have reported that coordination of a phenyl amido moiety to TpOs^{IV}Cl$_2$ activates the phenyl ring toward nucleophilic substitution reactions.[57] In these reactions Os(IV) serves both to activate the phenyl ring

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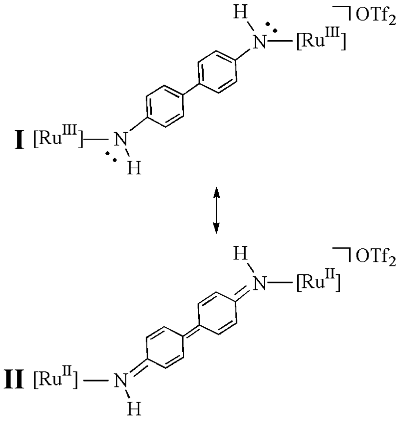
Scheme 4. Resonance Structures for Complexes 2−4 Corresponding to Ru(III) Amido and Ru(II) Imine Systems



toward nucleophilic attack and also as a strong oxidant. It is apparent that the reactivity of nondative heteroatomic ligands bound to late transition metals can be significantly impacted by the metal d-electron count. Several low oxidation state/high d-electron count transition metal amido and imido complexes that display highly nucleophilic and/or basic reactivity have been reported. In contrast, late transition metals in high oxidation states can serve as electron reservoirs and activate normally electron-rich phenyl amido species toward nucleophilic attack or radical coupling reactions.

The binuclear complexes **2**−**4** could be described as $\{TpRu^{III}L_2\}$ fragments bridged by aryl coupled amido ligands; however, a resonance structure corresponding to $\{TpRu^{II}L_2\}$ fragments bridged by coupled imine ligands can also be drawn (Scheme 4). Features of the solid-state structure of complex **4** (see above) are consistent with a significant contribution from the imine resonance structure. For example, localized bonding of the aryl moieties, multiple bonding between the C−C bond of the biaryl linkage, and a short N−C bond are all consistent with the quinoidal resonance structure **II** (Scheme 4). In addition, upfield chemical shifts (<5.0 ppm) for protons of the C_6H_4 rings are consistent with the imine resonance structure **II**. Contribution of this resonance structure explains the diamagnetic nature {Ru(II)} of complexes **2**−**4**. The contribution of resonance structure **II** results in dearomatization of the biaryl system, and it might be anticipated that the reduction of Ru(III) to Ru(II) provides a driving force for electron delocalization; however, the Ru(III/II) oxidation potentials do not indicate that the Ru(III) systems are strongly oxidizing (see above).

Summary

The oxidation of a series of Ru(II) phenyl amido complexes results in aryl−aryl coupling reactions via C−H bond cleavage. A possible route for the C−C bond formation is the creation of radical complexes via single-electron oxidation. Delocalization of the radical into the amido aryl rings provides a pathway for C−C bond formation. Subsequent deprotonation and oxidation (regardless of specific mechanistic details) yields the binuclear products. The observation of aryl−aryl coupling with the three Ru systems reported herein, as well as similar reactions with Pt(II) phenyl amido and Rh phenyl imido complexes, indicates that such coupling sequences may be a general feature of oxidizing late transition metal complexes with nondative heteroatom ligands that possess aryl substituents.

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. We also thank the Shultz group (North Carolina State University) for assistance with EPR experiments. The authors also wish to thank the National Science Foundation (NSF) for funding (CHE 9509532) to obtain the X-ray diffractometer.

Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for **4**; ^1H NMR spectra of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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