Preparation of the Octahedral d^6 Amido Complex TpRu(CO)(PPh$_3$)(NHPh) (Tp = Hydridotris(pyrazolyl)borate): Solid-State Structural Characterization and Reactivity

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The reaction of TpRu(CO)(PPh$_3$)(OTf) (**2**) with LiNHPh affords the amido complex TpRu(CO)(PPh$_3$)(NHPh) (**3**) in 88% isolated yield. The amido complex **3** has been characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, elemental analysis, cyclic voltammetry, and a solid-state X-ray diffraction study. Variable temperature NMR studies have revealed a rotational barrier around the ruthenium−amido nitrogen bond of **3** of 12 kcal/mol (transformation of the major isomer to the minor isomer). The solid-state structure of **3** discloses a pyramidal amido moiety. Heating benzene solutions of the amido complex **3** and 1,4-cyclohexadiene or 9,10-dihydroanthracene results in no observable reaction. Reaction of complex **2** with excess aniline yields [TpRu(CO)(PPh$_3$)(NH$_2$Ph)][OTf] (**4**).

Introduction

Transition metal amido moieties have been implicated in important synthetic transformations including olefin and alkyne hydroaminations as well as amination of arene and aryl halide/triflate compounds.[1−6] While numerous examples of transition metal amido complexes have been reported, examples of late metal complexes in low oxidation states are relatively rare.[7−15] Of particular relevance here are reports of monomeric octahedral amido complexes with d^6 electron counts at the metal center,[16−28] and most germane to the chemistry discussed herein are CpRu-

(PR$_3$)$_2$(amido) and (η^6-arene)Ru(PMe$_3$)(Ph)(amido) complexes.[29−31] Whereas complexes with lower coordination numbers or electron counts can stabilize the amido moiety via π-bonding (Scheme 1), octahedral/d^6 systems formally offer no such stabilization. In fact, it has been suggested that the presence of dπ electrons on a metal center in close proximity to ligand heteroatom lone electron pair(s) results in π-electron conflict that increases the reactivity of the heteroatom moiety (Scheme 2).[32,33] The *E-C* theory of bonding has also been used to rationalize enhanced reactivity of late metal−heteroatom moieties.[34] We report herein the synthesis, characterization, and preliminary reactivity of TpRu(CO)(PPh$_3$)(NHPh), including solid-state structural details.

Experimental Section

General Methods. All procedures were performed under inert atmosphere (nitrogen) in an Innovative Technologies glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer (O$_2$(g) < 15 ppm for all reactions). Methylene chloride, toluene, diethyl ether, and hexanes were purified by passage through a column of activated alumina.[35] THF was purified by passage through a column of activated alumina followed by distillation from sodium/benzophenone and storage

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Scheme 1. Illustration of Amido to Metal π-Donation To Form a Trigonal Amido and Metal−Nitrogen Double Bond

sp^3 pyramidal amido   sp^2 trigonal amido
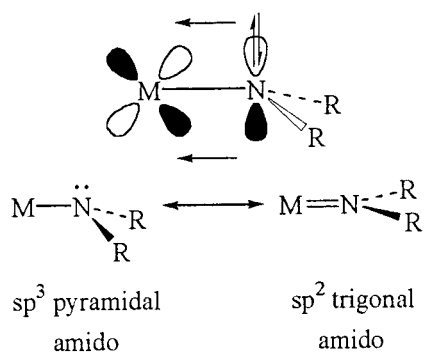
Scheme 2. Qualitative Molecular Orbital Diagram of TpRu(CO)(PPh$_3$)(NHPh) (**3**) Illustrating the π-Conflict between the Amido Ligand and Metal Center
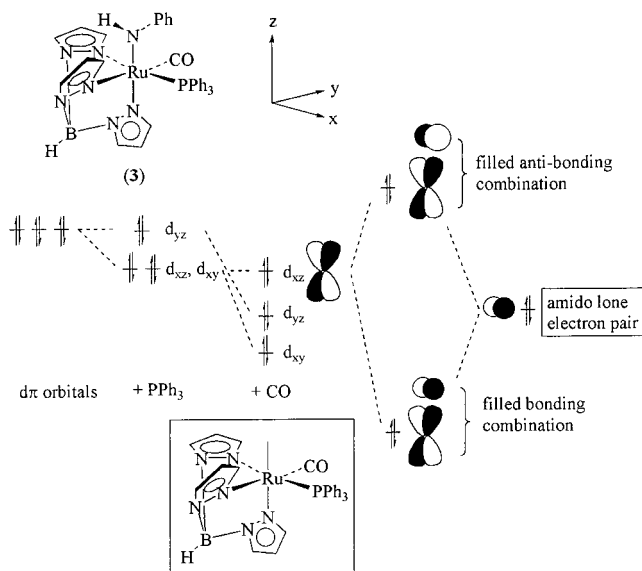
over 4 Å molecular sieves. Acetonitrile was purified by passage through a column of activated alumina followed by distillation from CaH$_2$. All solvents were purged with nitrogen for at least 10 min prior to use. Benzene-d_6 was purified by distillation from CaH$_2$, degassed, and stored over 4 Å molecular sieves. CDCl$_3$, CD$_2$Cl$_2$, and THF-d_8 were degassed and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric 300 MHz spectrometer. All ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and are referenced to tetramethylsilane using residual proton signals or to the ^{13}C signals of the deuterated solvents. ^{31}P NMR spectra were recorded on a General Electric 300 MHz instrument and are referenced against external 85% phosphoric acid. The phosphoric acid standard was referenced by adding the 85% phosphoric acid to a 2 mm insert tube contained within a standard 5 mm NMR tube with the appropriate sample (purchased from Wilmad). Peaks in the ^{1}H NMR spectra due to pyrazolyl resonances are listed by chemical shift and multiplicity only (all coupling constants are 2 Hz). Unless otherwise noted, infrared spectra were recorded on a Mattson Genesis-II spectrometer as thin films on KBr plates. 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 (TBAH) as supporting electrolyte. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) as internal standard. Mass spectra were acquired on a JEOL JMS SX-102 mass spectrometer (Duke University). Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. TpRu(CO)(PPh$_3$)(Cl) was prepared

according to a published procedure.[36] KTp was prepared according to a published procedure.[37] LiNHPh was prepared by addition of BuLi to a benzene solution of aniline. The resulting white LiNHPh salt precipitated and was isolated by vacuum filtration. All other reagents were used as purchased from commercial sources.

TpRu(CO)(PPh$_3$)(OTf) (2). To a yellow solution (1:1 v/v THF/CH$_2$Cl$_2$, 30 mL) of TpRu(CO)(PPh$_3$)(Cl) (**1**) (0.6401 g, 1.016 mmol) was added a solution of AgOTf (0.261 g, 1.016 mmol dissolved in THF). The solution was stirred at room temperature for approximately 36 h, during which time the formation of a white precipitate (AgCl) was noted. The resulting pale yellow slurry was vacuum-filtered through a fine-porosity frit in order to remove the precipitate, and the volatiles were removed from the filtrate in vacuo. The resulting yellow solid was washed with diethyl ether and hexanes, dried in vacuo, and isolated (95% yield, 0.725 g). IR (thin film on KBr plate): ν_{CO} = 1986 cm^{-1}. ^{1}H NMR (benzene-d_6, δ): 8.99, 7.41, 7.37, 7.19, 7.06, 6.43 (each 1H, each a d, Tp CH 3 and 5 position), 5.78, 5.64, 5.25 (each 1H, each a t, Tp CH 4 position), 7.33, 6.95 (15H, each a m, P(C$_6$H$_5$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, δ): 203.6 (d, $^2J_{PC}$ = 15 Hz, CO), 147.9, 146.8, 144.1 (each a s, Tp CH's), 137.5, 136.6, 135.7, 134.7, 134.5, 131.8, 131.2, 131.0, 129.1, 129.0 (resonances due to PPh$_3$, and Tp CH's, with J_{PC} to ispo, ortho, and meta PPh$_3$ carbons would expect a total of 10 lines due to 7 resonances), 107.5, 106.9 (2:1, coincidental overlap for first resonance, Tp 4 position CH's). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 39.0. CV (CH$_3$CN, TBAH, 100 mV/s): $E_{1/2}$ = 1.75 V {Ru(III/II)}. Anal. Calcd for C$_{29}$H$_{25}$BF$_3$N$_6$O$_4$PRuS: C, 46.23; H, 3.34; N, 11.15. Found: C, 46.27; H, 3.47; N, 11.12.

TpRu(CO)(PPh$_3$)(NHPh) (3). To a yellow solution (THF, 10 mL) of TpRu(CO)(PPh$_3$)(OTf) (**2**) (0.1151 g, 0.153 mmol) was added dropwise a THF solution (5 mL) of LiNHPh (0.30 g, 0.306 mmol). The solution was stirred at room temperature for approximately 30 min, during which time the formation of a white precipitate (LiOTf) was noted and the color changed from yellow to brown. After 30 min, the volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered through a fine-porosity frit (approximately 50 mL of toluene used). The volatiles were removed in vacuo from the resulting filtrate to give a yellow-brown solid. Recrystallization by layering a toluene solution of the product with pentane yielded yellow crystals in 88% yield (0.094 g). IR (thin film on KBr plate): ν_{CO} = 1954 cm^{-1}; ν_{NH} = 3350 cm^{-1}. ^{1}H NMR (25 °C, THF-d_8, δ): 7.85, 7.72, 7.66, 7.54, 6.83, 6.38 (each 1H, each a d, Tp CH 3 and 5 position), 6.13, 5.95, 5.82 (each 1H, each a t, Tp CH 4 position), 7.35, 7.22 (15H, each a m, P(C$_6$H$_5$)$_3$), 6.52 (2H, t, $^3J_{HH}$ = 7 Hz, phenyl meta protons), 6.38 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl ortho protons), 5.88 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl para proton). ^{13}C{^{1}H} NMR (25 °C, THF-d_8, δ): 207.9 (d, $^2J_{PC}$ = 15 Hz, CO), 163.9 (s, amido phenyl ipso carbon), 146.3, 144.1, 143.9 (each a s, Tp CH's), 137.0, 136.0, 135.7, 135.6, 135.5, 131.1, 129.6, 129.3, 129.1 (Tp CH's, PPh$_3$ resonances, and meta carbon of amido phenyl), 117.7 (s, amido phenyl ortho carbon), 116.2 (s, amido phenyl para carbon), 107.0, 106.9, 106.8 (each a s, Tp 4 position CH's). ^{31}P{^{1}H} NMR (25 °C, THF-d_8, δ): 42.5. CV (CH$_3$CN, TBAH, 100 mV/s): $E_{p,a}$ = 0.11 V {Ru(III/II)}. Anal. Calcd for C$_{34}$H$_{31}$BN$_7$O$_1$PRu−C$_7$H$_8$ (note: one molecule of toluene observed in the solid-state structure of complex **3** as well as in the ^{1}H NMR of the solid used for analysis): C, 62.44; H, 4.98; N, 12.43. Found: C, 62.88; H, 5.15; N, 12.08.

[TpRu(CO)(PPh$_3$)(NH$_2$Ph)][OTf] (4). To a solution of TpRu(CO)(PPh$_3$)(OTf) (**2**) (0.24 g, 0.32 mmol) in THF (20 mL) was added aniline (0.148 g, 1.59 mmol) with stirring. The stirring was continued for approximately 24 h, and the solvent was subsequently removed under reduced pressure. The residue was redissolved in THF and precipitated with hexanes. The solid was collected via vacuum filtration through a fine frit and dried under vacuum. The solid product was collected in 91% yield (0.24 g). IR (thin film on KBr plate): ν_{CO} = 1981 cm^{-1}; ν_{NH} = 3473 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.72, 7.67, 7.56, 7.02, 6.15 (each 1H, each a d, Tp CH 3 and 5 position), 6.05, 6.00, 5.78 (each 1H, each a t, Tp CH 4 position), 7.35, 7.16 (16H, each a m, one Tp

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C*H* 3 or 5 position and P(C₆*H*₅)₃), 6.90, 6.10 (5H, m, phenyl para, meta, and ortho protons overlap), 5.35 (1H, d, N*H*(H), $^2J_{HH}$ = 12 Hz), 4.73 (1H, d, NH(*H*), $^2J_{HH}$ = 12 Hz). ^{13}C{^{1}H} NMR (CDCl₃, δ): 202.2 (d, $^2J_{PC}$ = 12 Hz, *C*O), 145.7, 145.0, 143.9 (each a s, Tp *C*H's), 142.4 (s, amine phenyl ipso carbon), 137.7, 136.6, 136.5, 133.7, 133.6, 131.5, 129.7, 129.6, 128.9, 128.6 (Tp *C*H's, PPh₃ resonances, and meta carbon of amine phenyl), 125.8, 122.0 (s, amine phenyl carbons), 107.2, 107.1, 106.2 (each a s, Tp 4 position *C*H's). ^{31}P{^{1}H} NMR (CD₂Cl₂, δ): 42.6. CV (CH₃CN, TBAH, 100 mV/s): $E_{p,a}$ = 1.14 V {Ru(III/II)}. Anal. Calcd for C₃₅H₃₂BF₃N₇O₄PSRu: C, 49.65; H, 3.81; N, 11.58. Found: C, 49.64; H, 3.79; N, 11.72. FAB-MS: *m/z* [TpRu(CO)(PPh₃)(NH₂-Ph)]⁺ calcd exact mass 698.1536, obsd 698.3041; [TpRu(CO)(PPh₃)]⁺ calcd 605.0957, obsd 605.2192.

Crystal Structure of TpRu(CO)(PPh₃)(NHPh) (3). Yellow crystals were grown by slow diffusion of pentane into a toluene solution of complex **3**. A suitable crystal (0.38 × 0.30 × 0.30 mm³) was selected and mounted on the end of a glass fiber using a small amount of silicon grease and transferred to an Enraf-Nonius CAD4-MACH diffractometer. The sample was maintained at a temperature of −125 °C using a nitrogen cold stream. The unit cell dimensions were determined by a fit of 25 well centered reflections and their Friedel pairs with 34° < 2θ < 36°. A quadrant of unique data was collected using the ω 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. Data were corrected for absorption using an empirical correction based on ψ scan data for several reflections.

Structure Solution and Refinement. The data were reduced using routines from the NRCVAX set of programs.[38] The structure was solved using SIR92.[39] Most non-hydrogen atom positions were recovered from the initial E-map. The remaining non-hydrogen atom positions were recovered from subsequent difference Fourier maps. All carbon bound hydrogen atoms were placed at idealized positions and were allowed to ride on the parent carbon. A difference map contained peaks suggestive of hydrogen atom positions in the vicinity of atoms B and N(7). The peak in the vicinity of atom B was constrained to an idealized B—H bond length and allowed to ride on the parent B atom. As the hybridization of N(7) is important to the present work, the difference Fourier maps were analyzed in some detail. To increase confidence that the peak in the vicinity of N(7) was indicative of a hydrogen atom position, a series of difference Fourier map calculations were performed following the method developed by Ibers and LaPlaca and used by others.[40,41] The peak position remained in the same position relative to N(7) (see Supporting Information for full details). The peak was included as H(7n) in the refinement model, and the N(7)—H(7n) bond distance was constrained to be 0.86 Å. H(7n) was allowed to ride on the parent N(7) atom. 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 (ADPs).

Results and Discussion

{TpRu(L)(L′)} fragments have received significant recent attention.[42−54] The reaction of TpRu(CO)(PPh₃)(Cl) (**1**) with

AgOTf (OTf = trifluoromethanesulfonate) in 1:1 CH₂Cl₂/THF for approximately 36 h results in the formation of a precipitate (presumably AgCl). After filtration and workup of the yellow filtrate, TpRu(CO)(PPh₃)(OTf) (**2**) can be isolated in high yield (95%). The triflate complex **2** has been characterized by elemental analysis and cyclic voltammetry, as well as ^{1}H, ^{13}C, ^{31}P, and infrared spectroscopy. The chloride complex **1** exhibits a CO stretching frequency at 1964 cm⁻¹ in its infrared spectrum, while complex **2** shows a CO stretching frequency at 1986 cm⁻¹. The 22 cm⁻¹ increase upon substituting triflate for chloride is consistent with the weaker donating ability of triflate.[55] The ^{1}H NMR spectrum of complex **2** (as well as all other complexes reported herein) exhibits Tp resonances indicative of an asymmetric metal center. The cyclic voltammogram of **2** exhibits $E_{1/2}$ = 1.75 V {Ru(III/II), versus NHE}, while chloride complex **1** displays a reversible wave at 1.43 V.

The reaction of **2** with LiNHPh at room temperature results in a slow color change from yellow to brown and the concomitant formation of a precipitate. The appearance of a new CO stretching frequency at 1954 cm⁻¹ and the dissipation of the CO stretching frequency at 1986 cm⁻¹ accompany this reaction. In addition, the new product exhibits $ν_{NH}$ = 3350 cm⁻¹. Workup of the brown filtrate results in isolation of TpRu(CO)-(PPh₃)(NHPh) (**3**) in 88% yield (eq 1). Complex **3** has been characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and infrared spectroscopy and cyclic voltammetry, elemental analysis, and a solid-state X-ray diffraction study (see in a following section). The cyclic voltammogram of **3** exhibits $E_{p,a}$ = 0.11 V {Ru(III/II), versus NHE}, and the irreversibility indicates that the ruthenium (III) amido [TpRu(CO)(PPh₃)(NHPh)]⁺ is unstable on the time scale of the cyclic voltammetry experiment. Restricted rotation of the amido ligand allows the possibility of rotational isomers, and the observation of a single isomer at elevated temperatures (80 °C) is the result of rapid rotation around the Ru—amido nitrogen bond on the time scale of the ^{1}H NMR experiment (see in a following section). A benzene solution of the phenylamido complex **3** shows no signs of decomposition after 48 h at room temperature.
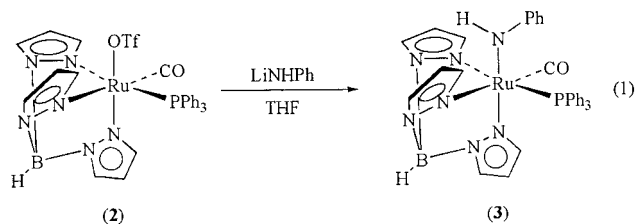
Reaction of TpRu(CO)(PPh₃)(OTf) (**2**) with excess aniline (5 equiv) allows isolation of the cationic amine complex [TpRu-

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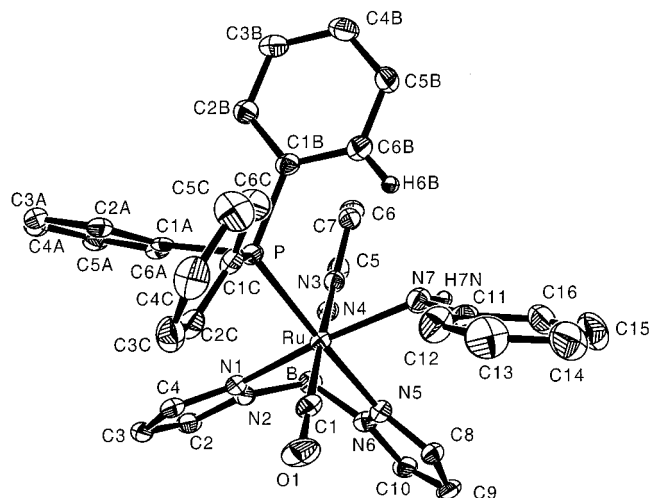
Figure 1. ORTEP diagram of TpRu(CO)(PPh₃)(NHPh) (**3**).

(CO)(PPh₃)(NH₂Ph)][OTf] (**4**) in 91% yield after workup (eq 2). Complex **4** is characterized by a CO stretching frequency at 1981 cm⁻¹ in the IR spectrum and diastereotopic amine protons with resonances (two doublets with geminal $J_{HH} = 12$ Hz) at 5.35 and 4.73 ppm in its ¹H NMR spectrum. In addition, a resonance at 42.6 ppm is observed in the ³¹P NMR spectrum of **4**, and the cyclic voltammogram reveals $E_{p,a} = 1.14$ V. While the basicity of the amido ligand of **3** has not been quantitatively determined, the formation of **4** in the presence of excess aniline indicates that **3** is at least more basic than the free amine (pK_a ≈ 4.6 in water and 3.2 in dimethyl sulfoxide for PhNH₃⁺).[56] In contrast, the amine ligand of the d⁴ and octahedral complex [Tp*W(CO)(PhC₂Me)(NH₂Ph)][OTf] (Tp* = hydridotris(3,5-dimethyl)pyrazolylborate) is deprotonated in the presence of aniline.[57]
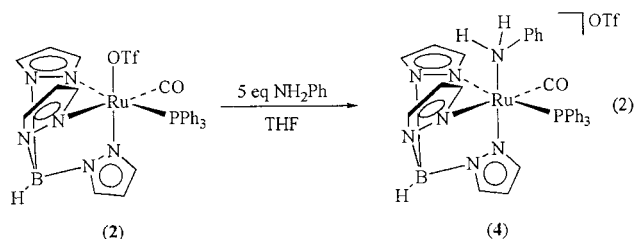
Solid-State X-ray Diffraction Study of TpRu(CO)(PPh₃)-(NHPh) (3). Recrystallization of **3** from toluene and pentane yields yellow crystals, and an X-ray diffraction study was performed. An ORTEP diagram is presented in Figure 1, selected bond distances and angles are shown in Table 1, and data collection parameters are shown in Table 2. The Ru–amido nitrogen {N(7)} bond distance is 2.076(3) Å. The Ru–amido nitrogen bond distances of *trans*-(DMPE)₂Ru(H)(NH₂) and *cis*-(PMe₃)₄Ru(H)(NHPh) are 2.191(6) Å and 2.160(4) Å, respectively.[16,25] The Ru–N bond distance of (η⁶-C₆Me₆)Ru(Ph)-(PMe₃)(NHPh) is 2.121(3) Å.[29] In comparison to the amido complexes, the Ru–amine nitrogen bond distance of [CpRu-(PPh₃)₂(NH₃)][OTf] is 2.172(3) Å.[30]

Mayer et al. have recently discussed the multiple bonding between the amido ligand and Os(IV) metal center of TpOs-(NHPh)(Cl)₂ in terms of the shorter bond distance between

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Table 1. Selected Bond Distances (Å) and Angles (deg) for TpRu(CO)(PPh₃)(NHPh) (**3**)

bond distances			
Ru–P	2.3518(9)	Ru–C1	1.847(3)
Ru–N1	2.117(3)	Ru–N3	2.151(3)
Ru–N5	2.117(3)	Ru–N7	2.076(3)
C1–O1	1.152(4)	C11–C12	1.411(5)
C11–C16	1.420(5)	C12–C13	1.387(5)
C13–C14	1.393(7)	C14–C15	1.379(7)
C15–C16	1.381(5)	N7–C11	1.372(4)
N7–H7n	0.861(3)		

bond angles			
Ru–N7–C11	130.7(2)	Ru–N7–H7	106.7(2)
C11–N7–H7	109.1(3)	P–Ru–C1	93.40(10)
P–Ru–N1	95.44(7)	P–Ru–N3	92.47(7)
P–Ru–N5	176.80(7)	P–Ru–N7	93.66(8)
C1–Ru–N1	89.75(12)	C1–Ru–N3	173.36(12)
C1–Ru–N5	89.78(12)	C1–Ru–N7	96.76(13)
N1–Ru–N3	86.60(10)	N1–Ru–N5	84.97(10)
N1–Ru–N7	168.48(11)	N3–Ru–N5	84.39(10)
N3–Ru–N7	85.96(10)	N5–Ru–N7	85.56(10)
Ru–C1–O1	174.6(3)		

Table 2. Selected Crystallographic Data and Collection Parameters for TpRu(CO)(PPh₃)(NHPh) (**3**)

formula	C₄₄.₅H₄₃BN₇OPRu
mol wt	834.72
cryst syst	monoclinic
space group	$P2_{1}/c$
a, Å	12.0038(14)
b, Å	22.169(2)
c, Å	14.9766(19)
β, deg	99.292(15)
V, Å³	3933.2(8)
Z	4
D_{calcd}, g cm⁻³	1.410
total no. of reflns	6880
unique reflns	6880
R	0.037
R_w	0.039

osmium and the amido nitrogen compared with the osmium–pyrazolyl nitrogen bond distances.[58] The osmium(IV) amido complex has an empty dπ-orbital available for π-bonding with the amido ligand. In analogy, the Ru–N(7) bond distance of complex **3** is shorter than the Ru–pyrazolyl nitrogen {N(1), N(3), and N(5)} bond distances; however, the effect is *less pronounced* for complex **3** compared with TpOs(NHPh)(Cl)₂. The difference between an average of the Os–pyrazolyl nitrogen bond distances and the osmium amido bond distance is 0.105(16) Å, while the analogous difference for complex **3** is 0.052(6) Å.

The ORTEP diagram in Figure 1 shows the pyramidal nature of the amido moiety, and the pyramidal character of the amido ligand is indicated by inspection of the bond angles around the N-atom which sum to 346.5(4)°. The position of hydrogen atoms is often difficult to determine by X-ray structure analyses; however, the primary error in the position of hydrogen atoms in X-ray structure analysis is typically along the internuclear vector.[59,60] That is, atom–H bond lengths are systematically shorter because of polarization of the hydrogen's electron into a bonding orbital. Because the argument of pyramidalization relies primarily on the bond angles around N(7), the argument

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Table 3. Inverse Correlation between Ru−N$_{amido}$ and N$_{amido}$−C$_{ipso}$ Bond Distances for Octahedral Ruthenium(II) Phenylamido Complexes

| complex	Ru−N$_{amido}$^{a}	N$_{amido}$−C$_{ipso}$^{a}
TpRu(CO)(PPh$_3$)(NHPh) (**3**)	2.076(3)	1.372(4)
(η^6-C$_6$Me$_6$)Ru(PMe$_3$)(Ph)(NHPh)^b	2.121(3)	1.360(5)
cis-(PMe$_3$)$_4$Ru(H)(NHPh)^c	2.160(4)	1.340(9)
aniline^d	N/A	1.398

^{a} In Å. ^{b} See ref 29. ^{c} See ref 25. ^{d} See ref 61.

may be more confidently made than if it depended on the bond distances. The full details of X-ray analysis and location of the amido hydrogen are given in the Experimental Section and Supporting Information. To our knowledge, this is only the second example of a structurally characterized transition metal amido complex with a pyramidal amido ligand.[26,27]

The bond distance (1.372(4) Å) from the amido nitrogen {N(7)} to the phenyl ipso carbon {C(11)} of the amido moiety is shorter than that of aniline by 0.026 Å (±0.01 Å).[61] In comparison, the analogous bond distances for (η^6-C$_6$Me$_6$)Ru-(PMe$_3$)(Ph)(NHPh) and *cis*-(PMe$_3$)$_4$Ru(H)(NHPh) are 1.360(5) Å and 1.340(9) Å, respectively, while that of CpRe(NO)(PPh$_3$)-(NHPh) is 1.379(9) Å.[25,27,29] This is an inverse correlation between Ru−N$_{amido}$ and N$_{amido}$−C$_{ipso}$ (phenyl) bond distances for the series of ruthenium (II) phenyl−amido complexes TpRu-(CO)(PPh$_3$)(NHPh) (**3**), *cis*-(PMe$_3$)$_4$Ru(H)(NHPh), and (η^6-C$_6$-Me$_6$)Ru(PMe$_3$)(Ph)(NHPh) (Table 3).

Variable Temperature ^{1}H NMR Studies. Rotational isomers are possible for complex **3** because of restricted rotation around the ruthenium−amido nitrogen bond. ^{1}H NMR spectra of amido complex **3** at elevated temperatures (80 °C and above) show Tp, PPh$_3$, and amido phenyl resonances consistent with a single isomer. Cooling a THF-d_8 solution of **3** to −90 °C reveals a fluxional process. Thus, at low temperatures, resonances consistent with the presence of two isomers are observed. For example, in the range from 4 to 5 ppm, two new resonances are observed (Figure 2), and these resonances have been assigned as NH resonances for two rotational isomers (∼1.63:1 ratio at −90 °C). One of the resonances is a doublet, presumably due to coupling with phosphorus ($^3J_{PH}$ = 9 Hz). As the temperature of the NMR probe is warmed, broadening of these resonances is observed. Line broadening of the resonance due to the major isomer was used to calculate the exchange rate ($k_{rotation}$ = 4.3 s^{-1}) and rotational barrier (12 kcal/mol) at −60 °C. The rate constant and barrier to rotation correspond to the rate of conversion from the major isomer to the minor isomer. As the temperature of the solution is increased, the resonances coalesce into a doublet with J_{PH} ≈ 3 Hz (80 °C).

Comparison of the barriers to rotation around the ruthenium−amido nitrogen bond of complex **3** with Tp*W(CO)$_2$(amido) complexes provides a means to assess the impact of the filled dπ manifold of the ruthenium complexes.[62] The tungsten complexes are structurally related to the ruthenium systems; however, the tungsten(II) systems are d^4 and have an empty d-orbital of appropriate symmetry to undergo bonding with the amido lone electron pair. Tp*W(CO)$_2$(NH$_2$) has been reported to have a barrier to rotation (around the tungsten-amido nitrogen bond) of 17 kcal/mol, while Tp*W(CO)$_2$(NHPh) has barriers to rotation of 23.0 and 24.2 kcal/mol. In contrast, the corre-
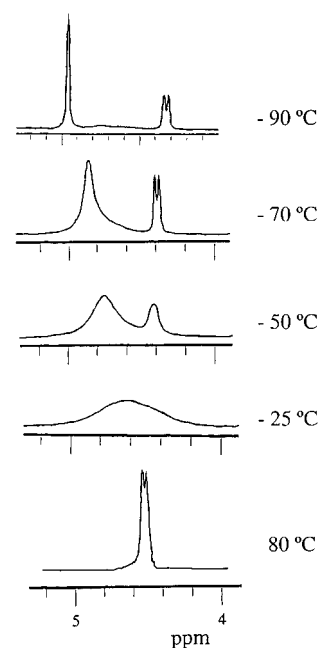
Figure 2. Variable temperature ^{1}H NMR of TpRu(CO)(PPh$_3$)(NHPh) (**3**) from approximately 4.0 to 5.2 ppm. The resonances are due to the amido proton of two rotational isomers (note: the vertical scale of the spectra at −90 °C and 80 °C are decreased relative to the other spectra).

sponding rotational barrier of TpRu(CO)(PPh$_3$)(NHPh) (**3**) is 12 kcal/mol (−60 °C, conversion of major isomer to minor isomer). Given that one of the small CO ligands of the tungsten complexes has been replaced by a bulky PPh$_3$ in the ruthenium system, the smaller barrier to rotation for the ruthenium complex (cf. the tungsten systems) is likely due to the high d-electron count of the ruthenium complex. However, the role of sterics is complicated by the presence of the more sterically imposing Tp* ligand of the Tp*W(CO)$_2$(NHR) systems. In comparison, the barrier to amido rotation for the isoelectronic CpRe(NO)-(PPh$_3$)(NMe$_2$) (i.e., isoelectronic with **3**) complex has been determined to be 7.8 kcal/mol.[27] The difference in activation barriers to amido rotation of 3.7−3.9 kcal/mol between **3** and CpRe(NO)(PPh$_3$)(NMe$_2$) is likely a result of the larger steric profile of the Tp ligand versus the Cp ligand.[63]

Reactivity. Bergman et al.'s intriguing reports of deprotonation of 1,4-cyclohexadiene, 9,10-dihydroanthracene, and toluene with *trans*-(DMPE)$_2$Ru(NH$_2$)(H) led us to consider the generality of these reactions. That is, is the high basicity of the amido ligand of *trans*-(DMPE)$_2$Ru(NH$_2$)(H) a general property of octahedral ruthenium(II) amido complexes, and what factors control the amido basicity? Heating benzene-d_6 solutions (70 °C) of amido complex **3** with excess 1,4-cyclohexadiene or 9,10-dihydroanthracene results in no reaction after 72 h. Thus, complex **3** fails to demonstrate basicity similar to *trans*-(DMPE)$_2$Ru(NH$_2$)(H). However, the failure of aniline to deprotonate [TpRu(CO)(PPh$_3$)(NH$_2$Ph)][OTf] (**4**) in THF indicates that TpRu(CO)(PPh$_3$)(NHPh) (**3**) is basic enough to deprotonate PhNH$_3^+$ (see previously). We have recently learned that parent amido complexes of the type TpRu(L)(L′)(NH$_2$) (L = L′ = PMe$_3$, P(OMe)$_3$ or L = CO and L′ = PPh$_3$) react with 1,4-cyclohexadiene to yield benzene, TpRu−hydride complexes, and other uncharacterized TpRu complexes.[64] In addition, the TpRu-(L)(L′)(NH$_2$) complexes deprotonate phenylacetylene (pK_a ≈

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23) at room temperature.[65] These reactions are similar to those reported for *trans*-(DMPE)$_2$Ru(H)(NH$_2$). Thus, the reactivity differences between TpRu(CO)(PPh$_3$)(NHPh) (**3**) and the octahedral ruthenium(II) parent amido complexes are attributed to the presence of the amido phenyl ring. It is suggested that the amido phenyl substituent mitigates the amido basicity via delocalization of the amido lone electron pair, and the solid-state structure of **3** supports this notion (see previously). We are presently exploring the reactivity of a series of TpRu(L)-(L′)(NHR) (R = H, ^{t}Bu or Ph; L, L′ = CO, PPh$_3$, P(OMe)$_3$, or PMe$_3$) complexes to help delineate the factors which control amido basicity including the extent of influence of amido substituents and ancillary ligands.

Summary

Because of the potential for novel structural patterns and reactivity, interest in metal systems which simultaneously possess π-donating ligands and high d-electron counts is increasing.[32−34,66−68] Along these lines, we have reported the synthesis and characterization of the octahedral d^6 amido complex TpRu(CO)(PPh$_3$)(NHPh) (**3**). Complex **3** has been structurally characterized by an X-ray diffraction study, and evidence for the influence of the filled dπ manifold has been observed. In addition, the lack of reactivity of **3** with 1,4-cyclohexadiene or 9,10-dihydroanthracene has been discussed in terms of the ability of the amido phenyl substituent to delocalize the amido lone electron pair.

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

IC010785P

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