Synthesis and Reactivity of the Octahedral d^6 Parent Amido Complexes $TpRu(L)(L')(NH_2)$ (Tp = Hydridotris(pyrazolyl)borate; L = L′ = PMe_3, $P(OMe)_3$; L = CO, L′ = PPh_3) and $[TpRu(PPh_3)(NH_2)_2][Li]$

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Summary: A series of octahedral ruthenium(II) parent amido complexes of the type $TpRu(L)(L')(NH_2)$ (L/L′ = neutral and two-electron-donor ligands) and $[TpRu(PPh_3)(NH_2)_2][Li]$ (Tp = hydridotris(pyrazolyl)borate) have been prepared. Preliminary reactivity studies indicate that the amido moieties are highly basic: for example, $TpRu(L)(L')(NH_2)$ complexes deprotonate phenylacetylene at room temperature to form $[TpRu(L)(L')(NH_3)][PhC_2]$ ion pairs, as determined by ^1H NMR spectroscopy.

The synthesis and reactivity of late-metal complexes with heteroatomic π-donating ligands have received significant recent attention.[1−6] Efforts in this area have been prompted in part due to the expectation that the combination of "soft" late metals with "hard" donor ligands (e.g., oxygen- and nitrogen-based ligands) can result in weak bonds and reactive ligand moieties; however, thermochemical studies of metal−heteroatom bond strengths suggest that *homolytic* bond strengths between late metals and heteroatom ligands are not inherently weak.[7,8] Additionally, it has been suggested that the scarcity of late-metal systems with π-donating ligands is due to the presence of π-conflict between filled metal dπ orbitals and lone electron pairs residing on the π-donating ligands.[1,9] Recently, application of Drago's $E-C$ bonding theory to understanding the bonding and reactivity of such complexes has been reported and raises questions as to the importance of $\pi-\pi$ repulsion in such systems.[3]

Bergman et al.'s recent reports of the synthesis and reactivity of the Ru(II) complex *trans*-$(DMPE)_2Ru(H)(NH_2)$ (DMPE = 1,2-bis(dimethylphosphinoethane)) provide a striking example of a highly reactive ruthenium amido moiety.[10,11] The parent amido ligand of this complex exhibits remarkable reactivity, including the ability to deprotonate several C−H bonds. Such extraordinary basicity and reactivity raises several questions, including the following: (1) is the enhanced basicity a general feature of such complexes and (2) what features control the amido reactivity? To begin to answer these questions, complexes with variable ancillary ligands must be accessed. We now report the synthesis and preliminary reactivity of the first example (to our knowledge) of a series of octahedral and d^6 parent amido complexes in which the ancillary ligands are systematically varied. Particularly germane here are $CpRu^{II}$ (Cp = cyclopentadienyl) phosphine complexes with amido ligands reported by Roundhill et al.[12]

{TpRu(L)(L′)} complexes have received significant recent attention.[13] These fragments offer the significant synthetic advantage of being able to systematically control the steric and electronic features of the metal coordination sphere via variation of L and L′. Reflux of the known complex $TpRu(PPh_3)_2(Cl)$[14] with excess trimethylphosphine or trimethyl phosphite in toluene yields $TpRu(PMe_3)_2(Cl)$ (**1**) and $TpRu\{P(OMe)_3\}_2(Cl)$ (**2**) in high yields (95% and 87%, respectively) after workup. Reactions of **1**, **2**, $TpRu(CO)(PPh_3)(Cl)$,[15] and $TpRu(PPh_3)_2(Cl)$ with AgOTf yield the corresponding triflate complexes $TpRu(PMe_3)_2(OTf)$ (**3**), $TpRu\{P(OMe)_3\}_2(OTf)$ (**4**), $TpRu(CO)(PPh_3)(OTf)$ (**5**), and $TpRu(PPh_3)_2(OTf)$ (**6**). Complexes **3**−**5** can be isolated cleanly, while the triphenylphosphine complex **6** has eluded isolation and is generated in situ. Reactions of complexes **3**−**6** in different solvents at variable temperatures with metal amides (e.g., $NaNH_2$ or $LiNH_2$) or metal amides in combination with ammonia result in no reaction, isolation of the corresponding ammine complexes, or decomposition.

Reaction of **3**−**6** with excess NH_3 in THF yields the cationic ammine complexes $[TpRu(PMe_3)_2(NH_3)][OTf]$ (**7**), $[TpRu\{P(OMe)_3\}_2(NH_3)][OTf]$ (**8**), $[TpRu(CO)(PPh_3)(NH_3)][OTf]$ (**9**), and $[TpRu(PPh_3)(NH_3)_2][OTf]$ (**10**) in high yields (74−95% yield) (Scheme 1).[16] Attempts to suppress PPh_3/NH_3 ligand exchange for complex **10** to allow the isolation of $[TpRu(PPh_3)_2(NH_3)][OTf]$ have

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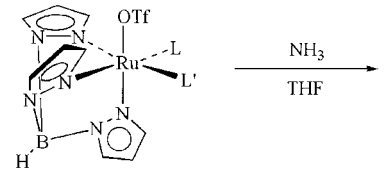
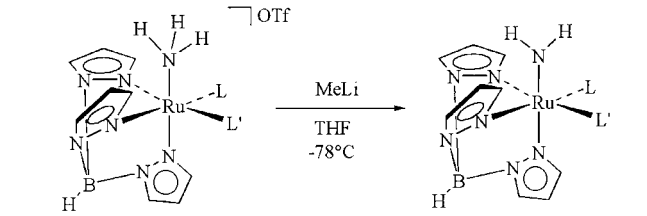
Scheme 1. Preparation of Ammine Complexes 7−10 and Amido Complexes 11−14[a]



Complex	L	L'
3	PMe_3	PMe_3
4	$P(OMe)_3$	$P(OMe)_3$
5	CO	PPh_3
6	PPh_3	PPh_3



Complex	L	L'
7	PMe_3	PMe_3
8	$P(OMe)_3$	$P(OMe)_3$
9	CO	PPh_3
10	NH_3	PPh_3

Complex	L	L'
11	PMe_3	PMe_3
12	$P(OMe)_3$	$P(OMe)_3$
13	CO	PPh_3
14	NH_2	PPh_3

[a] Note that complex **14** is anionic with a lithium counterion.

thus far failed. For example, reaction of **6** with a THF solution of NH_3 at −78 °C results in the isolation of a solid whose ^{1}H NMR spectrum is consistent with an approximately 1:1 ratio of $[TpRu(PPh_3)(NH_3)_2][OTf]$ (**10**) and $[TpRu(PPh_3)_2(NH_3)][OTf]$.

Examples of octahedral and d^6 parent amido complexes are scant compared with amido complexes with lower d-electron counts.[7,8,10−12,17,18] Reaction of the cationic ammine complexes **7**−**10** with methyllithium results in formation of the corresponding parent amido complexes $TpRu(PMe_3)_2(NH_2)$ (**11**; 95%), $TpRu\{P(OMe)_3\}_2(NH_2)$ (**12**; 57%), $TpRu(CO)(PPh_3)(NH_2)$ (**13**; 91%), and $[TpRu(PPh_3)(NH_2)_2][Li]$ (**14**; 95%) (Scheme 1).[19] Complexes **11**−**13** have been characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectroscopy as well as mass spectrometry. Under inert atmosphere in the solid state, the amido complexes are only persistent for a few days. Thus, attempts at recrystallization and clean elemental analysis were not successful. Complexes **11**−**14** display upfield chemical shifts (^{1}H NMR) for the amido protons, and the relative chemical shifts of **11**−**13** are consistent with the donating ability of L and L′ (Table 1). That is, the more donating L and L′ are, the more upfield the chemical shift for the NH_2 resonances. Given the highly reactive nature of the neutral monoamido complexes **11**−**13**, we anticipate that the amido ligands of **14** are electronically stabilized by direct interaction with the lithium cation. The ^{1}H NMR of **14** shows equivalent NH_2 ligands (broad singlet at −2.60 ppm integrated for 4H), and variable-temperature NMR reveals that this singlet decoalesces into two broad singlets (each 2H) at low temperature. The variable-temperature NMR studies are consistent with rapid exchange of the lithium cation between the two amido ligands.

Table 1. ^{1}H and ^{31}P NMR Chemical Shifts (ppm) for Complexes 11−14

complex	NH_2 resonance (^{1}H NMR)	^{31}P NMR[a]
$TpRu(PMe_3)_2(NH_2)$ (**11**)	−2.20	17.5
$TpRu\{P(OMe)_3\}_2(NH_2)$ (**12**)	−1.91	−11.3
$TpRu(CO)(PPh_3)(NH_2)$ (**13**)	−1.79	48.7
$[TpRu(PPh_3)(NH_2)_2][Li]$ (**14**)	−2.60	−3.5

[a] Referenced to external 85% phosphoric acid.

Combination of the amido complex **11** with approximately 1 equiv of phenylacetylene in an NMR tube reaction (THF-d_8) results in reaction during the time between sample preparation and ^{1}H NMR acquisition. In the ^{1}H NMR spectrum of the reaction mixture, the upfield resonance due to the amido ligand is absent, as is the characteristic acetylene proton of phenylacetylene, and a broad singlet at 2.23 ppm (3H) is observed. These observations are consistent with rapid deprotonation of phenylacetylene ($pK_a \approx 23$) by the amido ligand of **11** to yield a cationic amine complex with phenylacetylide anion as the counterion (Scheme 2).[20] The aromatic protons for the acetylide moiety are observed as multiplets at 7.25 and 7.38 ppm. Heating the reaction mixture at 80 °C for approximately 21 h results in the formation of several new intractable Tp-containing complexes. Although the rate of reaction varies, analogous results for **12** and **13** are observed. Complexes **15**−**17** are highly reactive, and all attempts at isolation have thus far failed. For the reaction of $TpRu(CO)(PPh_3)(NH_2)$ (**13**) with phenylacetylene, more than 24 h is

(16) The following is a representative procedure. $[TpRu\{P(OMe)_3\}_2(NH_3)][OTf]$ (**8**). To a solution of $TpRu\{P(OMe)_3\}_2Cl$ (**2**; 1.2549 g, 2.102 mmol) in approximately 50 mL of THF was added a solution of AgOTf (0.5413 g, 2.108 mmol, 15 mL of THF). The solution was refluxed for 20 h, cooled to room temperature, and vacuum-filtered through a fine-porosity frit. To the yellow filtrate was added a solution of ammonia in THF. The mixture was stirred for 24 h at room temperature, during which time a color change to pale pink was observed. The reaction solution was concentrated to approximately 40 mL in vacuo, and hexanes (approximately 40 mL) were added to precipitate the product. The resulting solid was collected via vacuum filtration through a fine-porosity frit and washed with hexanes (3 × 10 mL) to give a white solid (1.134 g, 74% yield). IR (thin film on KBr plate): ν_{NH} = 3359 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.79 (4H, overlapping m, Tp C*H*-3 or -5), 7.75, 7.63 (each 1H, each a d, Tp C*H*-3 or -5), 6.32 (2H, t, Tp C*H*-4), 6.17 (1H, t, Tp C*H*-4), 3.37 (18H, vt, J_{PH} = 10 Hz, $P(OCH_3)_3$), 2.09 (3H, bs, NH_3). ^{13}C{^{1}H} NMR (CD_3CN, δ): 148.7, 144.6, 138.2, 137.3 (each a s, Tp *C*H-3 or -5), 107.6, 107.5 (each a s, Tp *C*H-4), 53.2 (s, $P(OCH_3)_3$). ^{31}P{^{1}H} NMR (CD_3CN, δ): −21.0 (s, *P*$(OCH_3)_3$). CV (CH_3CN, TBAH, 100 mV/s): $E_{1/2}$ = 1.40 V (Ru(III/II)). Anal. Calcd for $C_{16}H_{31}BF_3N_7O_9P_2RuS$: C, 26.39; H, 4.29; N, 13.46; Found: C, 26.22; H, 4.23; N, 13.23.

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(19) The following is a representative procedure. $TpRu(PMe_3)_2(NH_2)$ (**11**). A solution of $[TpRu(PMe_3)_2(NH_3)][OTf]$ (**7**; 0.2423 g, 0.383 mmol) was dissolved in THF (∼15 mL) and cooled to −78 °C. MeLi (0.30 mL, 1.4 M solution in diethyl ether, 0.42 mmol) was added dropwise via a microsyringe. The solution turned immediately turned pale yellow, and stirring was continued for another 5 min at −78 °C. The slush bath was removed, and the reaction mixture was warmed to room temperature. The solvent was removed under reduced pressure to give a yellow-brown solid. The solid was dissolved in toluene (20 mL) and filtered through a fine-porosity frit. Removal of solvent from the filtrate in vacuo gave the desired product in 95% yield (0.175 g). IR (THF): ν_{BH} = 2463 cm^{-1}, ν_{NH} = 3115, 3230 cm^{-1}. ^{1}H NMR (C_6D_6, δ): 7.87, 7.55, 7.48, 7.15 (6H, 2:1:2:1 integration, each a d, Tp C*H*-3 or -5 position), 6.00, 5.88 (3H, 2:1 integration, each a t, Tp C*H*-4 position), 1.07 (18H, vt, J_{PH} = 10 Hz, $P(CH_3)_3$), −2.20 (2H, bs, NH_2). ^{13}C{^{1}H} NMR (C_6D_6, δ): 145.4, 142.8, 13.9, 135.3 (Tp 3- or 5-position), 105.8, 105.4 (Tp 4-position), 18.6 (t, J_{PC} = 12 Hz, $P(CH_3)_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 17.5 (*P*Me_3). FAB MS (*m*/*z*): 483.1 $[TpRu(PMe_3)_2(NH_2)]^+$, 467.1 $[TpRu(PMe_3)_2]^+$.

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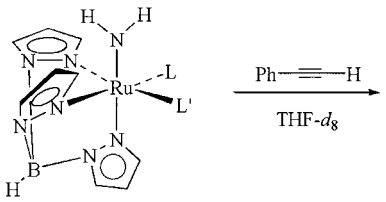
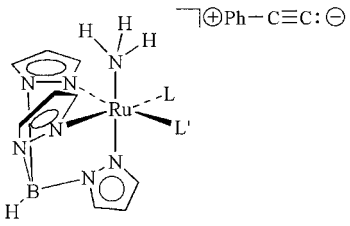
Scheme 2. Reaction of Amido Complexes 11−13 with Phenylacetylene



Complex	L	L'
11	PMe_3	PMe_3
12	$P(OMe)_3$	$P(OMe)_3$
13	CO	PPh_3



Complex	L	L'
15	PMe_3	PMe_3
16	$P(OMe)_3$	$P(OMe)_3$
17	CO	PPh_3

required to fully deprotonate phenylacetylene. The reaction of complex **12** with phenylacetylene occurs before acquisition of the ^{1}H NMR spectrum can be completed. Consistent with the case for complex **15**, heating THF-d_8 solutions of **16** and **17** results in the formation of multiple and intractable products. The qualitative kinetic trend for the deprotonation of the acetylene C−H bond corresponds to the donating abilities of the ancillary ligands (**11** ≈ **12** > **13**); however, contributions from steric factors could also be important.

The complicated reactivity product mixtures resulting from the reaction of **11**−**13** with phenylacetylene with heating contrasts with that reported for *trans*-$(DMPE)_2Ru(H)(NH_2)$, and two features likely contribute to the observed differences in reactivity. First, while deprotonation reactions by the amido ligands appear to be relatively facile, subsequent cleavage of the $Ru-NH_3$ bonds may be more difficult for the TpRu systems. Thus, while $[(DMPE)_2Ru(H)(NH_3)][X]$ undergoes relatively clean ligand exchange to form *trans*-$(DMPE)_2Ru(H)(X)$ (X = phenylacetylide, enolate) complexes, analogous ammonia dissociation (regardless of mechanistic details) may be kinetically more inert for the TpRu complexes reported herein. In addition, the presence of nonchelating phosphine ligands for **11**−**13** could afford alternative reaction pathways not readily available for *trans*-$(DMPE)_2Ru(H)(NH_2)$. Preliminary results indicate that analogous reactions with TpRu(L)(L′)(NH^tBu) (L = L′ = PMe_3, $P(OMe)_3$; L = CO, L′ = PPh_3) proceed more cleanly than for the parent amido systems, and consistent with this observation is the more labile nature of $^tBuNH_2$ ligands compared with NH_3 for the TpRu complexes discussed herein.[21] In addition, the phenyl amido complex TpRu(CO)(PPh_3)(NHPh) does not deprotonate phenylacetylene at room temperature, indicating that the phenyl substituent mitigates the basicity of the amido moiety.[22] This is consistent with the fact that ammonia is more basic than aniline; however, more thorough studies will be required to quantitatively compare the basicity differences.

The first examples of octahedral and d^6 amido complexes with variable ancillary ligands have been reported, along with initial reactivity studies. These systems exhibit a highly basic amido ligand, indicating that such reactivity could be a general feature of this class of amido complexes. A highlight of our preliminary efforts is the qualitative demonstration that the ancillary ligands impact the kinetics of amido reactivity with phenylacetylene as well as play an important role in ultimate reaction pathways.

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Supporting Information Available: Text giving complete synthetic and characterization details for complexes **1**−**17** and figures giving ^{1}H NMR spectra for complexes **11**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Conner, D.; Jayaprakash, K. N.; Gunnoe, T. B. Manuscript in preparation.

(22) (a) Jayaprakash, K. N.; Gunnoe, T. B. *Inorg. Chem.*, in press. (b) TpRu(CO)(PPh_3)(NHPh) does react with phenylacetylene at elevated temperatures. This reaction will be detailed in a future publication.