Synthesis and Reactivity of a Coordinatively Unsaturated Ruthenium(II) Parent Amido Complex: Studies of X−H Activation (X = H or C)

David Conner,[†] K. N. Jayaprakash,[†] Thomas R. Cundari,[‡] and
T. Brent Gunnoe*,[†]

*Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27695-8204, and Department of Chemistry, University of
North Texas, Box 305070, Denton, Texas 76203-5070*

The five-coordinate parent amido complex $(PCP)Ru(CO)(NH_2)$ (**2**) (PCP = 2,6-$(CH_2P$-$^tBu_2)_2C_6H_3$) has been prepared by two independent routes that involve deprotonation of Ru-(II) ammine complexes. Complex **2** reacts with phenylacetylene to yield the Ru(II) acetylide complex $(PCP)Ru(CO)(C≡CPh)$ (**5**) and ammonia. In addition, complex **2** rapidly activates dihydrogen at room temperature to yield ammonia and the previously reported hydride complex $(PCP)Ru(CO)(H)$. The ability of the amido complex **2** to cleave the H−H bond is attributed to the combination of a vacant coordination site for binding/activation of dihydrogen and a basic amido ligand. Complex **2** also undergoes an intramolecular C−H activation of a methyl group on the PCP ligand to yield ammonia and a cyclometalated complex. The reaction of $(PCP)Ru(CO)(Cl)$ with MeLi allows the isolation of $(PCP)Ru(CO)$-(Me) (**8**), and complex **8** undergoes an intramolecular C−H activation analogous to the amido complex **2** to produce methane and the cyclometalated complex. Determination of activation parameters for the intramolecular C−H activation transformations of **2** and **8** reveal identical $\Delta H^{\ddagger}$ {18(1) kcal/mol} with $\Delta S^{\ddagger} = -23(4)$ eu and $-18(4)$ eu, respectively. Density functional theory has been applied to the study of intermolecular activation of methane and dihydrogen by $(PCP')Ru(CO)(NH_2)$ to yield $(PCP')Ru(CO)(NH_3)(X)$ (X = Me or H; PCP' = 2,6-$(CH_2$-$PH_2)_2C_6H_3$). The results indicate that the activation of dihydrogen is both exoergic and exothermic. In contrast, the addition of a C−H bond of methane across the Ru−NH_2 bond has been calculated to be endoergic and endothermic. The surprising endoergic nature of the methane C−H activation has been attributed to a large and unfavorable change in Ru−N bond dissociation energy upon conversion from Ru-amido to Ru-ammine.

Introduction

Late transition metal amido complexes have been implicated as important species in catalytic processes.[1−6] Until recently, isolable examples of late transition metal complexes that possess nondative ligands were rare compared with early and middle transition elements in high oxidation states.[7−10] However, an increased interest in late metal systems has resulted in the preparation and detailed reactivity studies of amido complexes of ruthenium, rhodium, iridium, nickel, platinum, osmium, and copper.[3,11−13] Reactivity studies of such complexes have revealed that amido and related ligands bound to

metal centers with high d-electron counts can exhibit unique reactivity patterns.[3,7,8,10,11,14] For example, amido ligands bound to transition metal centers that possess filled dπ manifolds exhibit reactivity consistent with the localization of significant negative charge density on the amido nitrogen.[11,13,15−22] The highly reactive nature of such complexes has been attributed to the disruption of amido-to-metal π-donation (i.e., π-conflict) as well as the polar nature of the metal−amido bond.[7,8,11,23]

* Corresponding author. E-mail: brent_gunnoe@ncsu.edu.
† North Carolina State University.
‡ University of North Texas.

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Scheme 1. Proposed Pathway for the Activation of Nonpolar X−H (X = H or C) Bonds toward Intramolecular Deprotonation
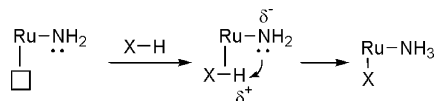
A potential synthetic application of nondative ligands bound to metal centers that possess high d-electron counts is the cleavage of carbon−hydrogen bonds. Higher oxidation states apparently increase the predilection toward hydrogen atom abstraction due to the favorable nature of metal-centered reduction, while increased ligand basicity can promote acid−base transformations for systems in lower oxidation states.[22,24−37] For example, octahedral Ru(II) (d[6]) amido complexes possess sufficient basicity to deprotonate relatively weak acids, including some C−H bonds.[22,36−38] The ability of *coordinatively and electronically saturated* Ru(II) amido complexes to deprotonate C−H bonds suggests the possibility of activating more inert bonds. Thus, by accessing Ru(II) complexes that possess an open coordination site and a nondative nitrogen-based ligand, it might be feasible to transiently bind nonpolar X−H (e.g., H−H or C−H) bonds to the metal center, thereby activating the substrate toward *intra*molecular deprotonation (Scheme 1). Similar transformations have been observed for early transition metal imido complexes.[39−42] A recent computational study of C−H addition across Ti=NR bonds suggests that increasing the Ti−N bond polarization increases the propensity toward C−H activation.[43] Complexes with nondative ligands and high d-electron counts are candidates for analogous reactions

since the inability of the nondative ligand to π-donate (due to pπ−dπ conflict) should yield highly polarized M−N bonds. In addition, due to the greater redox flexibility of metals in the mid to late portion of the transition series, accessing 1,2-additions across ruthenium−nitrogen bonds could afford synthetic opportunities not available with early transition metal systems. Herein, we report on efforts to access a coordinatively unsaturated ruthenium complex that possesses a parent amido ligand, including a combined experimental and computational study of its reactivity toward dihydrogen and carbon−hydrogen bonds.

Results and Discussion

We have previously reported that TpRu(L)(L′)(NHR) (L = L′ = P(OMe)$_3$, PMe$_3$ or L = CO and L′ = PPh$_3$) systems react to deprotonate C−H bonds. For example, TpRu(L)(L′)(NHPh) complexes exhibit acid−base equilibria with malononitrile, while TpRu(L)(L′)(NHR) (R = H or [t]Bu) complexes form ion pairs due to deprotonation of phenylacetylene.[22,38,44] However, the activation of more inert bonds (e.g., C−H bonds of alkanes/arenes or dihydrogen) by these TpRu complexes has not been attained. One possible limitation for the activation of nonpolar bonds using TpRu(L)(L′)(NHR) and related complexes is the coordinative saturation of the metal center. The Ru(II) complex (PCP)Ru(CO)(Cl) (PCP = 2,6-(CH$_2$P[t]Bu$_2$)$_2$C$_6$H$_3$) provides a precursor to a five-coordinate Ru(II) amido complex.[45] The reaction of (PCP)Ru(CO)(Cl) with ammonia yields (PCP)Ru(CO)(Cl)(NH$_3$) (**1**) (as indicated by IR and NMR spectroscopy) (eq 1); however, the lability of the ammonia ligand
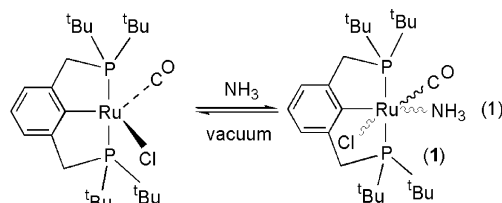
prevents the isolation of complex **1**, and quantitative reversion of **1** to (PCP)Ru(CO)(Cl) is observed upon solvent removal under reduced pressure or purging the reaction solution with dinitrogen. The precipitation of complex **1** followed by drying in the solid state under reduced pressure also results in conversion to (PCP)Ru(CO)(Cl). As delineated below, weakly coordinated ammonia is a general feature for the series of octahedral (PCP)Ru(CO)(X)(NH$_3$) systems reported herein.

The in situ reaction of the ammonia complex **1** with [Na][N(SiMe$_3$)$_2$] yields (PCP)Ru(CO)(NH$_2$) (**2**) (eq 2).

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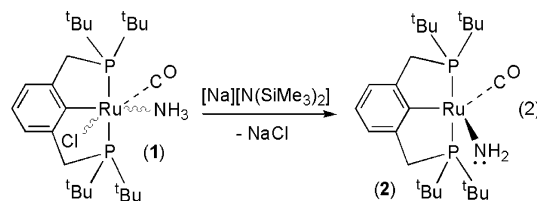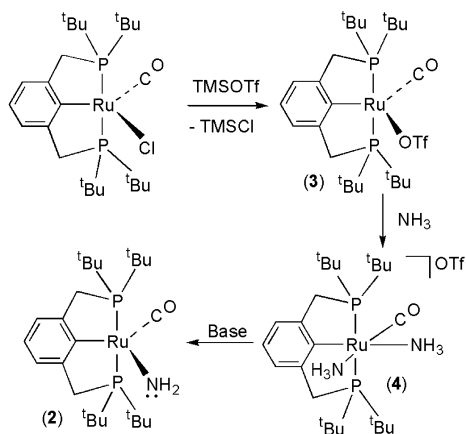(42) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903−905.
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Scheme 2. Alternative Pathway for the Synthesis of (PCP)Ru(CO)(NH₂) (2)

Scheme 3. Reaction of (PCP)Ru(CO)(NH₂) (2) and Phenylacetylene or (PCP)Ru(CO)(Cl) with [Li][C₂Ph] Yielding (PCP)Ru(CO)(C₂Ph) (5)

Complex **2** is characterized by a resonance at 72.9 ppm (^{31}P NMR) due to equivalent phosphine fragments and a triplet at 4.36 ppm (^{1}H NMR) due to the amido protons ($^3J_{PH} = 9$ Hz). The assignment of the resonance at 4.36 ppm as due to the amido hydrogens is confirmed by the absence of this resonance in the ^{1}H NMR spectrum of (PCP)Ru(CO)(ND₂) (**2**-d_2) that is synthesized by substituting ND₃ for NH₃. The IR spectrum of **2** exhibits $\nu_{CO} = 1890$ cm^{-1} as well as symmetric/asymmetric NH stretches at 3396 and 3306 cm^{-1}. The IR spectrum of (PCP)Ru(CO)(Cl) reveals $\nu_{CO} = 1923$ cm^{-1}, while the ammonia complex **1** displays $\nu_{CO} = 1900$ cm^{-1}. Thus, the {(PCP)Ru(NH₂)} system is more π-basic than the {(PCP)Ru(Cl)} and {(PCP)Ru(NH₃)}$^+$ fragments. The instability of complex **2** (see below) precludes satisfactory elemental analysis; however, high-resolution FAB mass spectrometry of **2** reveals a parent ion peak consistent with the theoretical molecular weight in addition to anticipated peaks due to molecular fragmentation. The reaction of (PCP)Ru(CO)(Cl) with TMSOTf produces (PCP)Ru(CO)(OTf) (**3**), and the bisammine complex [(PCP)Ru(CO)(NH₃)₂][OTf] (**4**) is formed upon combination of **3** and ammonia. The observation of two resonances due to bound ammonia ligands in the ^{1}H NMR spectrum (2.50 and 2.45 ppm) of **4** indicates a cis orientation of the ammine ligands. When complex **4** is synthesized using ND₃, the resonances at 2.50 and 2.45 ppm are absent in the ^{1}H NMR spectrum. Similar to the reaction of complex **1** with strong base, the treatment of **4** with [Na][N(SiMe₃)₂] results in the formation of the amido complex **2** after workup (Scheme 2).

The reaction of TpRu(L)(L′)(NHR) (R = H or ^{t}Bu) or *trans*-(DMPE)Ru(H)(NH₂) systems with phenylacetylene results in alkyne deprotonation to form the ion pairs [TpRu(L)(L′)(NH₂R)][PhC₂] and [*trans*-(DMPE)-Ru(H)(NH₃)][PhC₂], respectively.[22,36,44] The combination of amido complex **2** with phenylacetylene rapidly produces (PCP)Ru(CO)(C≡CPh) (**5**) and NH₃ (Scheme 3). Complex **5** has also been prepared by the reaction of (PCP)Ru(CO)(Cl) with [Li][PhC₂] (Scheme 3). The formation of **5** from the amido complex **2** and phenylacetylene could proceed through the initial formation of (PCP)Ru(CO)(NH₃)(C≡CPh); however, intermediates are not observed by NMR spectroscopy while monitoring the reaction of the amido complex **2** with phenylacetylene at low temperature (−78 °C).
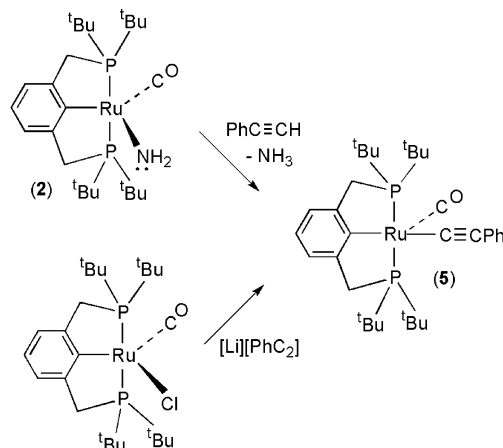
Placing a benzene solution of **2** under dihydrogen pressure yields the previously reported hydride complex (PCP)Ru(CO)(H) after workup (eq 3).[47] Prior to workup,
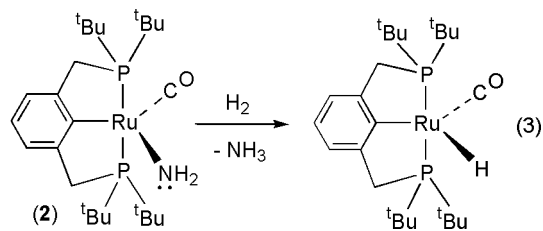
two CO absorptions are observed in the reaction mixture (1925 and 1900 cm^{-1}). The low-energy absorption at 1900 cm^{-1} is consistent with the formation of the hydride complex (PCP)Ru(CO)(H). Dissolution of (PCP)-Ru(CO)(H) in benzene and addition of H₂ result in a new CO absorption at 1925 cm^{-1}, and the high-energy CO stretching frequency is likely due to (PCP)Ru(H)₃(CO). This complex was not isolated pure, and the nature of the three hydrogen atoms is unknown.

The pK_a of dihydrogen is ∼49 in THF;[48] however, coordination to transition metal centers has been demonstrated to increase the acidity of dihydrogen.[49,50] For example, ruthenium-bound dihydrogen complexes exhibit pK_a values as low as −5.[51] Thus, we projected that the five-coordinate Ru(II) amido complex might facilitate intramolecular H−H bond breaking due to the accessibility of an open coordination site, and the observed H−H bond cleavage likely proceeds via transient metal coordination with subsequent activation of the H−H bond (Scheme 4). In contrast, under identical reaction

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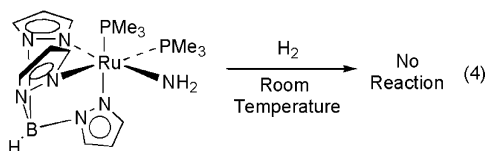(50) Jia, G.; Lau, C.-P. *Coord. Chem. Rev.* **1999**, *190−192*, 83−108.
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Scheme 4. Proposed Reaction Pathway for the Conversion of (PCP)Ru(CO)(NH₂) (2) and H₂ to (PCP)Ru(CO)(H) and NH₃
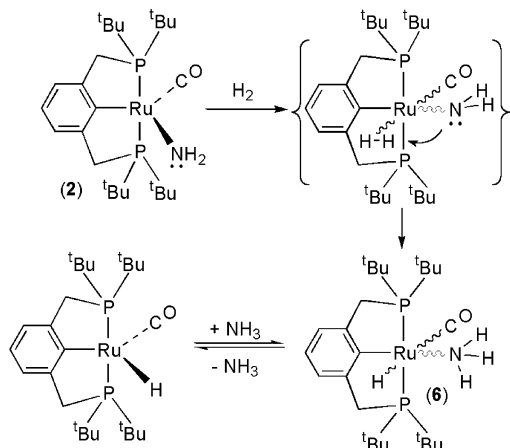
conditions the coordinatively saturated complex TpRu-(PMe₃)₂(NH₂) fails to react with dihydrogen (eq 4). The

dissolution of (PCP)Ru(CO)(H) and NH₃ in C₆D₆ yields (PCP)Ru(CO)(H)(NH₃) (**6**) as determined by NMR and IR spectroscopy. Complex **6** cannot be isolated pure due to facile loss of the coordinated ammonia; however, the formation of **6** is indicated by a new doublet in the proton-coupled ^{31}P NMR spectrum (95.7 ppm, $J_{PH} = 21$ Hz) and a new hydride resonance at −16.17 ppm (triplet, $J_{PH} = 21$ Hz). The hydride resonance of (PCP)-Ru(CO)(H) is observed at −27.9 ppm.[47] The removal of volatiles under vacuum results in the facile conversion of **6** to (PCP)Ru(CO)(H). The reaction of (PCP)Ru(CO)-(NH₂) (**2**) with dihydrogen at low temperature (−78 °C) in a sealed NMR tube allows the observation of complex **6** as a reaction intermediate by ^{1}H and ^{31}P NMR spectroscopy.

These results suggest that the coordination of dihydrogen by Ru(II) activates the H−H moiety toward intramolecular bond cleavage to yield (PCP)Ru(CO)(H)-(NH₃) (**6**), and dissociation of ammonia from **6** results in the isolation of (PCP)Ru(CO)(H) upon workup. It is also possible that oxidative addition of dihydrogen to form the Ru(IV) dihydride complex (PCP)Ru(H)₂(CO)-(NH₂) followed by reductive N−H bond formation yields (PCP)Ru(CO)(NH₃)(H) (**6**). Although examples are rare, eliminations of amine N−H bonds from d^{6} metal centers have been reported.[52,53] Morris et al. have demonstrated that the reaction of a Ru(II) amido complex with dihydrogen yields a complex in which the H−H bond is intermediate between protic-hydridic and dihydrogen bonding,[54] and the chelating amido ligand of Ru(Cl)-(PPh₃)[N(SiMe₂CH₂PPh₂)₂] deprotonates dihydrogen to yield Ru(Cl)(H)(PPh₃)[NH(SiMe₂CH₂PPh₂)₂].[55] Although

Figure 1. Kinetic plots for the conversions of (PCP)Ru-(CO)(Me) (**8**) (♦) and (PCP)Ru(CO)(NH₂) (**2**) (■) to the cyclometalated complex **7** at 50 °C.

supporting experimental evidence is not reported, the catalytic hydrogenation of carbon dioxide with a Ru(II) catalyst has been proposed to involve the addition of the H−H bond across a Ru−OH bond.[56] Siegbahn and Crabtree have reported computational studies that suggest the addition of the C−H bond of methane across a nondative Pt−Cl bond is a key step in the mechanism of the Shilov reaction.[57]

In C₆D₆, (PCP)Ru(CO)(NH₂) (**2**) undergoes intramolecular C−H activation of a methyl group of a ^{t}Bu moiety to form the cyclometalated complex **7** after workup (eq 5). A related iridium hydride complex that
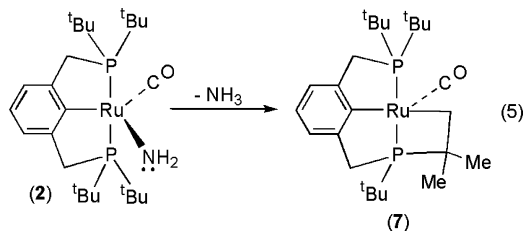
possesses a PCP "pincer" ligand has been observed in equilibrium with dihydrogen and a cyclometalated complex similar to complex **7**.[58] Monitoring the conversion of **2** to **7** by ^{1}H NMR spectroscopy reveals that the transformation is first-order in complex **2** ($k_{obs} = 6.0(3) \times 10^{-5}$ s^{-1} at 50 °C; Figure 1). The reaction mixture prior to workup contains a mixture of **7** and a small amount of another complex that is likely due to ammonia coordination to **7**. The isolation of **7** and addition of ammonia confirms that the second product is the ammonia complex. Placing the reaction solution under vacuum removes all ammonia, and ^{1}H NMR spectroscopy of the isolated solid reveals nearly quantitative formation of **7**. Complex **7** decomposes to produce uncharacterized products after approximately 2 days in the solid state under an atmosphere of dinitrogen.

The reaction of (PCP)Ru(CO)(Cl) with MeLi yields (PCP)Ru(CO)(Me) (**8**) (Scheme 5). Complex **8** has been characterized by multinuclear NMR and IR spectros-

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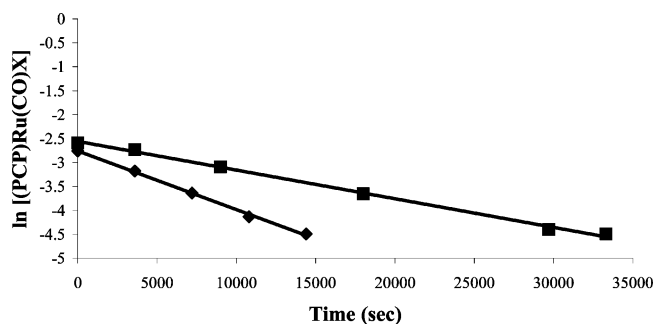
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Scheme 5. Reaction of (PCP)Ru(CO)(Cl) and MeLi Yields (PCP)Ru(CO)(Me) (8), and Complex 8 Converts to CH₄ and Complex 7

Figure 3. B3LYP/SBK(d) optimized geometry of (PCP′)-Ru(CO)(NH$_2$) (**2′**) model reactant showing pertinent bond lengths and bond angles.
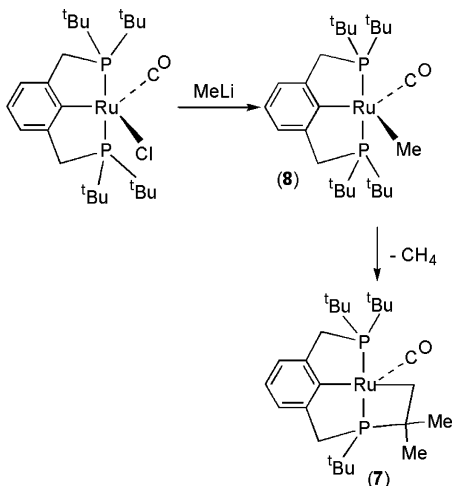
copy. Similar to the amido complex **2**, complex **8** decomposes to release methane (observed by ^{1}H NMR spectroscopy) and form the cyclometalated complex **7** (Scheme 5). The formation of methane has been confirmed using GC–MS. The rate of conversion of the methyl complex **8** to **7** is approximately 5 times faster ($k_{obs} = 3.2(1) \times 10^{-4}$ s^{-1} at 50 °C; Figure 1) than the analogous conversion with the amido complex **2** ($k_{obs} = 6.0(3) \times 10^{-5}$ s^{-1} at 50 °C; Figure 1). The determination of k_{obs} at variable temperatures for the conversions (PCP)Ru(CO)(NH$_2$) (**2**) and (PCP)Ru(CO)(Me) (**8**) to the cyclometalated complex **7** has allowed the extraction of activation parameters. Eyring plots were made over a 30 °C temperature range for both complexes (Figure 2). The $\Delta H^{\ddagger}$ for both reactions is 18(1) kcal/mol. The $\Delta S^{\ddagger}$ for the conversion of complex **2** to complex **7** and ammonia is $-23(4)$ eu, while the $\Delta S^{\ddagger}$ for the production of **7** and methane from the methyl complex **8** is $-18(4)$ eu.

The observed intramolecular C–H activation indicated the possibility of accessing intermolecular C–H addition across the Ru–amido bond of complex **2**. However, placing the amido complex (PCP)Ru(CO)(NH$_2$) (**2**) under methane pressure (50 psi) at various temperatures results in clean conversion to the cyclometalated complex **7**. The formation of **7** could occur directly from **2** (i.e., intramolecular C–H activation) or from an intermolecular reaction with methane to produce (PCP)-Ru(CO)(NH$_3$)(Me) followed by ammonia dissociation and conversion of (PCP)Ru(CO)(Me) (**8**) to complex **7**. The reaction of complex **2** with CD$_4$ could allow the differentiation between these two possibilities since the activation of methane would produce NH$_2$D, while the

intramolecular pathway would yield NH$_3$. However, a control experiment revealed that the reaction of (PCP)-Ru(CO)(NH$_2$) (**2**) with CD$_4$ could not be used to differentiate between the two possible reaction pathways. Monitoring a solution of the cyclometalated complex **7** in the presence of a mixture of CH$_4$ and ND$_3$ reveals significant isotopic scrambling to produce CH$_3$D/ND$_2$H/ CH$_4$/NH$_3$ in approximate 1:1:1:1 ratio (as determined by mass spectrometry). Therefore, production of NH$_2$D from the reaction of the amido complex **2** with CD$_4$ would not allow differentiation between direct production of NH$_2$D and isotopic scrambling between NH$_3$ and CD$_4$ to produce NH$_2$D. However, it can be stated that the lack of observation of (PCP)Ru(CO)(Me) (**8**) in the conversion of (PCP)Ru(CO)(NH$_2$) (**2**) and methane to complex **7** likely indicates that intramolecular C–H activation dominates at 50 psi of methane.

The observations of H–H activation by complex **2** and intramolecular C–H activation with failure to achieve intermolecular C–H activation of methane prompted us to incorporate DFT (density functional theory; B3LYP/ SBK(d) level of theory) studies to compare the energetics of X–H activation (X = H or CH$_3$) by (PCP′)Ru(CO)- (NH$_2$) (**2′**). PCP′ is a model of the full PCP ligand that is generated by the replacement of the phosphine ^{t}Bu substituents with hydrogen atoms. A variety of coordination isomers were investigated for the (PCP′)Ru(CO)- (NH$_2$) complex. In all cases (both square pyramidal and trigonal bipyramidal geometries) the bound carbon and phosphorus atoms of the PCP′ ligand were assumed to be meridonal (i.e., the P–C–P fragment is roughly coplanar with Ru). Two isomeric (PCP′)Ru(CO)(NH$_2$) minima were found, both of which had square pyramidal geometry. Consistent with the structures of (PCP′)Ru- (CO)(NH$_2$) determined by these computational studies, the complexes (PCP)M(CO)(Cl) (M = Ru or Os) exhibit square pyramidal structures in the solid state.[45,59] The higher energy isomer of (PCP′)Ru(CO)(NH$_2$) has CO trans to the aryl ring of the PCP′ ligand and is 15.6 kcal/ mol higher in energy (ΔG) than the lowest energy minimum found for (PCP′)Ru(CO)(NH$_2$) (**2′**), in which the coordination site trans to the aryl ring of the PCP′ ligand is vacant (Figure 3). The lower energy minimum was used in the calculation of all subsequent thermodynamic quantities.
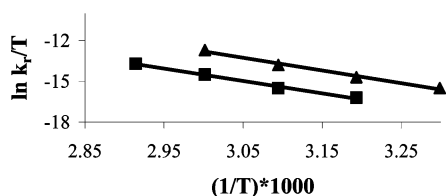

Figure 2. Eyring plots for the conversions of (PCP)Ru- (CO)(Me) (**8**) (▲) and (PCP)Ru(CO)(NH$_2$) (**2**) (■) to the cyclometalated complex **7** and methane or ammonia, respectively.
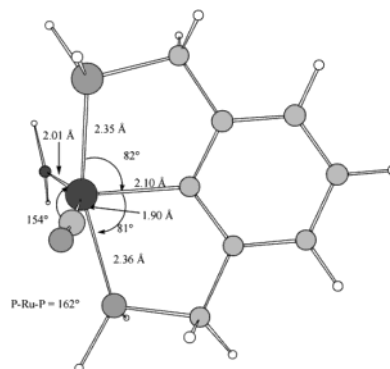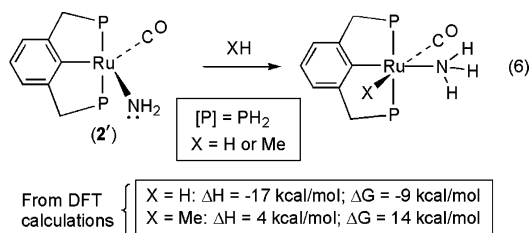
(59) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2001**, *20*, 1001−1007.

Calculations of the energies of the dihydrogen and methane activation reactions shown in eq 6 (X = H or Me) were performed. As with the calculations for **2′**, a

(6)

From DFT calculations

X = H: ΔH = -17 kcal/mol; ΔG = -9 kcal/mol
X = Me: ΔH = 4 kcal/mol; ΔG = 14 kcal/mol

variety of coordination isomers of the product (PCP′)-Ru(CO)(NH$_3$)(X) were investigated at the B3LYP/SBK-(d) level of theory for both X = methyl and hydrogen. The most stable isomers found were used in the calculation of reaction enthalpies and reaction free energies. For dihydrogen activation, the reaction in eq 6 is exothermic by 16.9 kcal/mol and exoergic by 8.9 kcal/mol. The corresponding C−H activation of methane is strikingly different, being endothermic by 3.7 and endoergic by 13.6 kcal/mol. Hence, the calculations are in qualitative agreement with experimental observations; that is, (PCP)Ru(CO)(NH$_2$) (**2**) will activate dihydrogen but not methane. In comparison to the attempted activation of methane, the entropy change for the intramolecular C−H activation to yield the metallacycle **7** should be more favorable.

Perhaps the most interesting aspect of the computational comparison of dihydrogen versus methane activation is that the methane activation is *endo*thermic rather than just less exothermic than the dihydrogen activation. To understand the calculated endothermic nature of the methane activation (eq 6), further calculations were carried out. First, the bond dissociation energies of dihydrogen and Me−H were calculated as an internal check. The enthalpies of the reactions are 105.3 kcal/mol (for H−H cleavage) and 101.9 kcal/mol (for C−H cleavage of methane). These numbers are in reasonable agreement with the experimental values in light of the small, double-ζ basis set used for hydrogen. One can estimate the enthalpy of eq 6 in terms of the appropriate bond enthalpies as shown in eq 7. Calculation of the Ru−H bond enthalpy of (PCP′)Ru(CO)(NH$_3$)-(H) yields a value of 71.6 kcal/mol.

$$\Delta H \approx BDE_{Ru-NH2} + BDE_{X-H} - BDE_{Ru-NH3} - \\ BDE_{N-H} - BDE_{Ru-X} \quad (7)$$

Consistent with known differences in metal−alkyl versus metal−hydride bond dissociation energies, the corresponding Ru−CH$_3$ bond enthalpy (47.5 kcal/mol) is 24.1 kcal/mol weaker than the ruthenium−hydride bond enthalpy. This Ru−H/Ru−Me bond enthalpy difference is consistent with the difference in enthalpies for the reactions in eq 6 ($\Delta\Delta H$ = 20.7 kcal/mol).

More relevant in the context of the present research to identify novel hydrocarbon functionalization systems is the root cause of the surprising endothermicity of methane activation by (PCP′)Ru(CO)(NH$_2$) (**2′**). Returning to eq 6, a significant enthalpic gain is expected by replacing a single C−H bond of methane with the N−H and Ru−C bonds of the (PCP)Ru(CO)(Me)(NH$_3$) product. This gain is estimated to be 31.8 kcal/mol from the

Scheme 6. DFT Calculations Reveal that the Endothermic Nature of the Reaction between (PCP)Ru(CO)(NH$_2$) and CH$_4$ Is a Result of Change in Ru−N BDE upon Conversion from Nondative Amido Ligand to Dative Ammonia Ligand ([P] = PH$_2$)
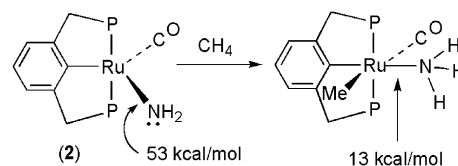
Scheme 7. Equilibrium between Complex 8 and (PCP)Ru(CO)(NH$_3$)(Me) Leads to More Rapid Conversion to Complex 7 and CH$_4$ Compared with the Direct Conversion of Complex 8 to CH$_4$ and 7
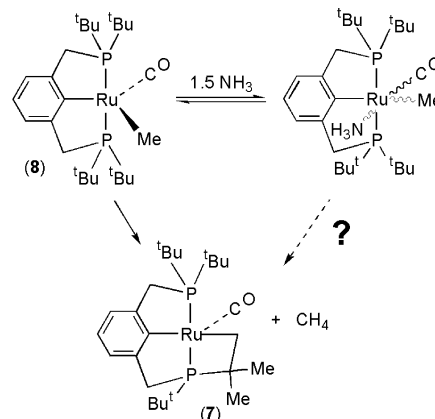
relevant B3LYP/SBK(d) bond enthalpies. The only other potential source of a significant change in enthalpy is the conversion of the ruthenium−nitrogen linkage from a nondative amido to a dative ammine bond {although minor perturbations might be anticipated, the ΔHs due to the Ru−phosphine, Ru−aryl, and Ru−CO bonds in eq 6 are unlikely to be substantial since both reactants and products are Ru(II)}. Clearly, if a change in enthalpy of the ruthenium−nitrogen bond is substantial and unfavorable, it is anticipated that methane activation would be prohibited. Indeed, calculation of the BDEs for Ru←NH$_3$ and Ru−NH$_2$ indicates that the difference is significant: BDE$_{Ru-NH2}$ = 52.5 kcal/mol; BDE$_{Ru←NH3}$ = 12.6 kcal/mol; ΔBDE = 39.9 kcal/mol (Scheme 6). The calculations of a small BDE for the Ru−NH$_3$ linkage is consistent with the general experimental observation that ammonia is weakly coordinated to the (PCP)Ru^{II}(CO)(X)(NH$_3$) systems reported herein. The loss of approximately 40 kcal/mol upon converting from an amide to ammine linkage more than cancels the approximately 32 kcal/mol gain due to breaking the methane C−H bond and forming Ru−CH$_3$ and N−H bonds and provides an explanation for the calculated endothermic nature of the methane activation.

The DFT calculations suggest that (PCP)Ru(CO)-(NH$_3$)(Me) should convert to (PCP)Ru(CO)(NH$_2$) and methane. Experimentally, the addition of ammonia to (PCP)Ru(CO)(Me) (**8**) forms an equilibrium between (PCP)Ru(CO)(Me)(NH$_3$) and (PCP)Ru(CO)(Me)/NH$_3$, and the mixture converts to methane and the cyclometalated complex **7** (Scheme 7). However, whether the formation of **7** and methane is derived from complex **8** or (PCP)-Ru(CO)(Me)(NH$_3$) cannot be definitively determined.
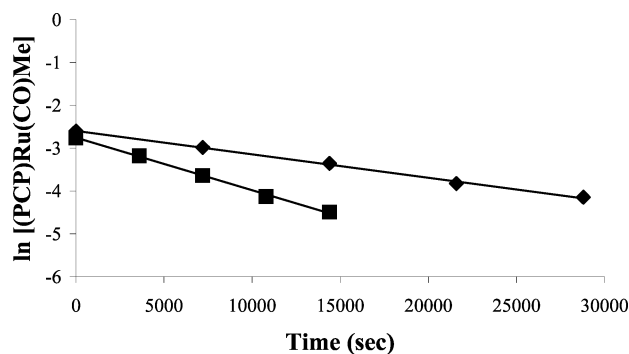
Figure 4. Kinetic plots for the conversion of (PCP)Ru(CO)-(Me) (**8**) and 1.5 equiv of NH_3 (■) to complex **7** and CH_4 as well as for the conversion of (PCP)Ru(CO)(Me) (**8**) to CH_4 in the absence of NH_3 (♦).

Isotopic labeling studies are not useful due to H/D scrambling as described above. The experimental observation that the rate of formation of **7** and methane upon addition of NH_3 to the methyl complex **8** (1.5 equiv based NMR spectroscopy) is more rapid ($k_{obs} = 1.2 \times 10^{-4}$ s^{-1} at 30 °C) than in the absence of ammonia ($k_{obs} = 5.5 \times 10^{-5}$ s^{-1} at 30 °C; Figure 4) suggests the possibility of a direct conversion of (PCP)Ru(CO)(Me)-(NH_3) to complex **7** and methane. Such a pathway would require the initial formation of (PCP)Ru(CO)(NH_2) (**2**) and methane with subsequent conversion of complex **2** to ammonia and complex **7**. However, the lack of observation of the amido complex **2** as an intermediate in this reaction precludes a definitive conclusion on the feasibility of this pathway.

It has been suggested that the observation of unexpectedly strong bonding between nondative ligands and late transition metals can be explained by a large ionic contribution (versus covalent) to the overall M—X bonding (X = amido, oxide, etc.).[23,53] This scenario also accounts for the observed high reactivity due to the localization of significant charge density on the nondative ligand. Although metal—amine bond dissociation energies can be large, the *significant* and *unfavorable* change in enthalpy upon conversion of a nondative Ru—amido bond to a dative Ru—ammine bond supports the suggestion that ionic contributions to metal—ligand bonding can dominate for these systems. Therefore, the unfavorable change in enthalpy upon conversion of the amido ligand to an ammine ligand can be explained by the loss of strong ionic bonding in the latter.

Summary and Conclusions

A coordinatively unsaturated Ru(II) parent amido complex has been prepared in anticipation that the combination of an open coordination site and a highly nucleophilic amido fragment would allow the activation of nonpolar bonds. Accordingly, complex **2** cleaves dihydrogen and activates an alkyl C—H bond in an *intra*molecular C—H activation process. The C—H activation of alkane and arene compounds has been observed at high temperatures with highly electrophilic complexes with imido ligands bound to early transition metal centers.[40,42,60−63] The observation of intramolecu-

lar C—H activation and intermolecular H—H activation indicates that such reactions are accessible with late transition metal systems. The results of DFT studies indicate that the activation of dihydrogen by complex **2** is both exoergic and exothermic, while the addition of a C—H bond of methane across the Ru—NH_2 bond has been calculated to be endoergic and endothermic. The endoergic nature of the methane C—H activation has been attributed to a large and unfavorable change in Ru—N bond dissociation energy upon conversion from Ru-amido to Ru-ammine. It is also possible that the steric bulk of the PCP fragment contributes to the inability to achieve intermolecular C—H activation. Thus, access to intermolecular C—H activations might be possible for systems that undergo reactions in which the reactive metal—ligand bond remains nondative (e.g., conversion of imido to amido or oxo to oxide as observed with early transition metal complexes).

Experimental Section

General Methods. All reactions and procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by 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}. Toluene was dried by passage through a column of activated alumina. THF and benzene were dried by distillation over sodium/benzophenone. Pentane and cyclopentane were dried by distillation over P_2O_5. Benzene-d_6 was purified by distillation from CaH_2, degassed, and stored over 4 Å sieves. $CDCl_3$, toluene-d_8, and CD_2Cl_2 were degassed via three freeze−pump−thaw cycles and stored over 4 Å sieves. Room-temperature ^1H and ^{13}C NMR spectra were obtained on a Varian Mercury 400 or 300 MHz spectrometer. All ^1H and ^{13}C NMR spectra were referenced against tetramethylsilane using residual proton signals (^1H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{31}P NMR spectra were obtained on a Varian 300 MHz (observed frequency 161 MHz) spectrometer and referenced against external 85% H_3PO_4. All variable-temperature NMR experiments were performed on a Varian 400 MHz spectrometer. IR spectra were obtained on a Mattson Genesis II spectrometer either as thin films on a KBr plate or in a solution using a NaCl solution plate. Elemental analyses were performed by Atlantic Microlabs, Inc. The syntheses of TpRu(PMe$_3$)$_2$(NH$_2$), (PCP)Ru(CO)Cl, and (PCP)Ru(CO)(H) have been previously reported.[44,45,47] [Li][C$_2$-Ph] was prepared by addition of butyllithium 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.

(PCP)Ru(CO)(NH$_3$)(Cl) (1). A screw cap NMR tube was charged with approximately 0.025 g of (PCP)Ru(CO)Cl in 1 mL of $CDCl_3$. Ammonia was bubbled through the solution until it turned from orange to pale yellow. The solution was shaken, then vented to relieve excess pressure, and NMR and IR spectra were acquired. Quantitative conversion to (PCP)Ru-(CO)(NH$_3$)Cl (1) was observed by ^1H, ^{13}C, and ^{31}P NMR and IR; however, removal of excess NH_3 by purging or placing the solution under reduced pressure results in rapid and quantitative formation of the starting material (PCP)Ru(CO)(Cl). IR (solution cell CDCl$_3$): $\nu_{CO} = 1900$ cm^{-1}. ^1H NMR (CDCl$_3$, δ):

(60) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffman, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985−2994.

(61) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131−144.

(62) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591−611.

(63) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 2179−2180.

6.76 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl 3/5 position), 6.60 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl 4 position), 3.14 (4H, m, CH_2), 2.85 (3H, bs, NH_3), 1.17, 1.14 (each 18 H, each a vt, N = 12 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 207.4 (t, $^2J_{PC}$ = 13 Hz, CO), 147.7 (t, $^2J_{PC}$ = 12 Hz, PCP phenyl), 128.4, 123.9 (each a s, PCP phenyl), 122.5 (vt, N = 13 Hz, PCP phenyl), 37.4, (vt, N = 14 Hz, PC), 36.8 (vt, N = 10 Hz, PC), 36.3 (vt, N = 20 Hz, CH$_2$), 31.7, 31.2 (each a vt, N = 4 Hz, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 78.3.

(PCP)Ru(CO)(NH₂) (2). (PCP)Ru(CO)(Cl) (0.0969 g, 0.1736 mmol) was dissolved in approximately 30 mL of THF. Approximately 10 mL of a saturated solution of NH$_3$ in THF was added. Upon combination of the two solutions, a color change from dark orange to yellow was observed. Sodium bis(trimethylsilyl)amide (0.190 mmol, 1.0 M in THF) was added dropwise using a microsyringe. Upon addition of the amide, a color change to dark orange was observed. The solution was filtered through a fine porosity frit, and the volatiles were removed under reduced pressure (0.0771 g, 0.143 mmol, 82%). Orange microcrystalline product was obtained upon recrystallization from pentane at −20 °C (isolated yield of the recrystallization is approximately 50%). IR (solution cell THF): ν_{CO} = 1890 cm^{-1}, ν_{NH} = 3396, 3306 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 7.06 (2H, d, $^3J_{HH}$ = 8 Hz, phenyl 3/5 position), 6.98 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl 4 position), 4.36 (2H, br t, $^3J_{PH}$ = 9 Hz, NH_2), 3.19 (2H, dt, $^2J_{HH}$ = 17 Hz, J_{PH} = 7 Hz, CH_2), 3.09 (2H, dt, $^2J_{HH}$ = 17 Hz, J_{PH} = 9 Hz, CH_2), 1.26, 1.14 (each 18H, each vt, N = 12 Hz, CH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 212.5 (t, $^2J_{PC}$ = 11 Hz, CO), 169.1 (PCP phenyl), 149.1 (t, $^2J_{PC}$ = 7 Hz, PCP phenyl), 121.8 (s, PCP phenyl), 121.5 (vt, N = 14 Hz, PCP phenyl), 36.4 (vt, N = 22 Hz, P-CH$_2$), 36.3 (vt, N = 13 Hz, PC), 36.2 (vt, N = 13 Hz, PC), 30.1−29.9 (m, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 72.9. High-resolution FAB-MS: 539.2 (PCP)-Ru(CO)(NH$_2$), 523.2 (PCP)Ru(CO). Note: Elemental analysis could not be obtained due to instability of the product. This complex undergoes intramolecular elimination of ammonia to form the cyclometalated complex **7** in approximately 24 h.

(PCP)Ru(CO)(OTf) (3). In a 100 mL round-bottom flask, (PCP)Ru(CO)Cl (0.0675 g, 0.1209 mmol) was dissolved in approximately 40 mL of cyclopentane. Approximately 1 mL of trimethylsilyltriflate was added dropwise at room temperature. After 30 min the formation of an orange solid was observed. The reaction was stirred for 1 h. After removal of volatiles under reduced pressure, the resulting solids were dissolved in approximately 10 mL of THF, and the products were precipitated upon addition of 30 mL of cyclopentane. Orange crystals were isolated by filtration through a medium porosity frit (0.0690 g, 0.1027 mmol, 85%). IR (solution cell THF): ν_{CO} = 1936 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.09 (2H, d, $^3J_{HH}$ = 7 Hz, phenyl 3/5 position), 6.93 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl 4 position), 3.37 (4H, vt, N = 8 Hz, CH_2), 1.50 (18 H, vt, N = 14 Hz, CH_3), 1.17 (18 H, vt, N = 13 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 204.9 (t, $^2J_{PC}$ = 12 Hz, CO), 157.2 (s, phenyl 4 position), 152.7 (t, $^2J_{PC}$ = 7 Hz, phenyl ipso), 125.4 (s, phenyl 3/5 positions), 123.3 (vt, N = 16 Hz, phenyl 2/6 positions), 38.0 (vt, N = 14 Hz, PC), 36.7 (vt, N = 16 Hz, PC), 33.7 (vt, N = 22 Hz, CH$_2$), 30.1 (vt, N = 4 Hz, CH$_3$), 29.4 (vt, N = 4 Hz, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 70.0. Anal. Calcd for C$_{26}$H$_{43}$F$_3$O$_4$P$_2$-RuS: C 46.42, H 6.45. Found: C 46.28, H 6.58.

[(PCP)Ru(CO)(NH₃)₂][OTf] (4). In a 50 mL round-bottom flask, 0.0816 g (0.121 mmol) of (PCP)Ru(CO)(OTf) (**3**) was dissolved in approximately 15 mL of THF. A THF solution of ammonia was added until the solution turned from orange to colorless. The volatiles were removed under reduced pressure. The solids were dissolved in approximately 5 mL of THF, and the product was precipitated with approximately 30 mL of cyclopentane. Pale yellow crystals were isolated by filtration through a fine porosity frit (0.0439 g, 0.0621 mmol, 51%). IR (solution cell THF): ν_{CO} = 1923 cm^{-1}, ν_{NH} = 3415, 3358, 3292, 3203 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 6.95 (2H, d, $^3J_{HH}$ = 8 Hz, phenyl 3/5 positions), 6.80 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl 4

position), 3.35 (2H, dt, $^2J_{HH}$ = 16 Hz, J_{PH} = 7 Hz, CH_2), 3.23 (2H, dt, $^2J_{HH}$ = 16 Hz, J_{PH} = 7 Hz, CH_2), 2.50 (3H, bs, NH_3), 2.45 (3H, bs, NH_3), 1.33 (18H, vt, N = 13 Hz, CH$_3$), 1.26 (18H, vt, N = 12 Hz, CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 207.4 (t, $^2J_{PC}$ = 13 Hz, CO), 164.2 (s, PCP 4 position), 147.7 (t, $^2J_{PC}$ = 6 Hz, RuC), 124.3 (s, PCP 5 and 5 positions), 122.9 (vt, N = 13 Hz, PCP 2 and 6 positions), 37.3 (vt, N = 15 Hz, PC), 36.6 (vt, N = 11 Hz, PC), 36.0 (vt, N = 20 Hz, P-CH$_2$), 31.3 (vt, N = 5 Hz, CH$_3$), 31.0 (vt, N = 5 Hz, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, δ): 78.2. Note: Elemental analysis could not be obtained because drying under reduced pressure for a prolonged period of time results in the dissociation of ammonia.

(PCP)Ru(CO)(C≡CPh) (5). Method A. (PCP)Ru(CO)(Cl) (0.1096 g, 0.1964 mmol) was dissolved in approximately 30 mL of THF. Approximately 10 mL of a saturated solution of NH$_3$ in THF were added. Upon addition of the ammonia solution, a color change from dark orange to yellow was observed. Sodium bis(trimethylsilyl)amide (0.216 mmol, 1.0 M in THF) was added dropwise using a microsyringe, and a change in color to dark orange was observed. The solution was filtered through a fine porosity frit, and the volatiles were removed under reduced pressure. Approximately 25 mL of THF was added to dissolve all solids. Phenylacetylene (24 μL, 0.219 mmol) was added using a microsyringe. Upon addition, a color change to dark red orange was observed. The volatiles were removed under reduced pressure to yield a dark red product (0.1112 g, 0.1781 mmol, 91%).

Method B. (PCP)Ru(CO)(Cl) (0.0977 g, 0.1750 mmol) was dissolved in approximately 30 mL of toluene. The solution was cooled to −78 °C. The salt [Li][C$_2$Ph] (0.021 g, 0.194 mmol) was added to the solution of (PCP)Ru(CO)(Cl). A color change to dark red-orange was observed upon addition of the lithium acetylide salt. The volatiles were removed under reduced pressure, and the product was extracted with cyclopentane and filtered through a fine porosity frit. Removal of volatiles from the resulting filtrate allowed the isolation of a dark red solid (0.0850 g, 0.1362 mmol, 78%). This procedure yields product that is pure by NMR spectroscopy; however, additional purification can be achieved by column chromatography on silica gel with THF as eluent. IR (solution cell THF): ν_{CO} = 1915 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.29 (2H, t, $^3J_{HH}$ = 8 Hz, acetylide phenyl meta position), 7.23−7.17 (4H, m, overlapping PCP and acetylide phenyl), 7.09 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl para/4 position), 6.95 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl para/4 position), 3.63 (4H, vt, N = 8 Hz, PCP CH_2), 1.53, 1.18 (each 18H, each a vt, N = 14 Hz, CH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 209.0 (t, $^2J_{PC}$ = 13 Hz, CO), 179.4 (t, $^2J_{PC}$ = 3 Hz, ipso phenyl), 152.5 (vt, N = 15 Hz, PCP 3,5 or 2,6 position), 131.7 (t, $^2J_{PC}$ = 11 Hz CCPh), 130.3 (t, N =1.4 Hz, PCP 4 or Ph o, m, p), 129.8 (t, $^4J_{PC}$ = 0.8 Hz, Ph ipso), 128.1 (s, PCP 4 or Ph o, m, p), 127.8 (t, $^3J_{PC}$ = 1.1 Hz, CCPh), 124.5 (s, PCP 4 or Ph o, m, p), 124.4 (s, PCP 4 or Ph o, m, p), 121.8 (vt, N = 15 Hz, PCP 3,5- or 2,6-position), 37.9 (vt, N = 23 Hz, CH$_2$), 37.8 (vt, N = 15 Hz, PC), 37.0 (vt, N = 17 Hz, PC), 30.0, 29.8 (each a vt, N = 5 Hz, CH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): 80.0. Anal. Calcd for C$_{33}$H$_{48}$-OP$_2$Ru: C 63.54, H 7.76. Found: C 63.52, H 7.74.

(PCP)Ru(CO)(NH₃)(H) (6). A screw cap NMR tube was charged with approximately 0.025 g of (PCP)Ru(CO)(H) and 1 mL of C$_6$D$_6$. Ammonia was gently bubbled through the solution until it turned from orange to pale yellow. The solution was vigorously mixed and vented to relieve excess pressure, and NMR and IR spectra were acquired. Quantitative conversion to (PCP)Ru(CO)(NH$_3$)(H) (**6**) was observed by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy; however, removal of excess ammonia by purging the solution with dinitrogen or placing the solution under reduced pressure results in the rapid formation of the starting material (PCP)Ru(CO)(H). IR (solution cell THF): ν_{CO} = 1905 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 7.07 (2H, d, $^3J_{HH}$ = 9 Hz, phenyl 3/5 position), 6.98 (1H, t, $^3J_{HH}$ = 9 Hz, phenyl 4 position), 3.26 (2H, dt, $^2J_{HH}$ = 16 Hz, J_{PH} = 8 Hz, CH_2), 3.19 (2H, dt, $^2J_{HH}$ = 17 Hz, J_{PH} = 6 Hz, CH_2), 1.18, 1.06

(each 18 H, each a vt, N = 12 Hz, CH$_3$), −16.17 (1H, t, $^2J_{PH}$ = 21 Hz). The resonance due to bound NH$_3$ is not observed possibly due to overlap with a ^{t}Bu resonance. ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 208.1 (t, $^2J_{PC}$ = 13 Hz, CO), 149.9 (t, $^2J_{PC}$ = 11 Hz, PCP phenyl), 123.4 (s, PCP phenyl), 122.5 (vt, N = 16 Hz, PCP phenyl), 39.4, (vt, N = 14 Hz, PC), 36.8 (vt, N = 9 Hz, PC), 36.5 (vt, N = 21 Hz, CH$_2$), 30.0−29.7 (m, overlapping CH$_3$); note: missing one PCP phenyl resonance possibly due to coincidental overlap. ^{31}P NMR (hydrogen coupled; C$_6$D$_6$, δ): 95.7 (d, $^2J_{PH}$ = 21 Hz).

Ru(CO){C$_6$H$_3$-2-(CH$_2$P^{t}Bu$_2$)-6-(CH$_2$P(^{t}Bu)(CMe$_2$CH$_2$} (7). In a 100 mL round-bottom flask, (PCP)Ru(CO)Cl (0.3837 g, 0.6876 mmol) was dissolved in approximately 50 mL of THF. Methyllithium (1.6 M in THF, 0.907 mmol) was added dropwise using a microsyringe. The volatiles were removed under reduced pressure, and the solids were dissolved in benzene. The solution was allowed to stir at room temperature for 48 h. Filtration of the solution through a fine porosity frit and removal of the volatiles under reduced pressure yielded a brown solid (0.3337 g, 0.6404 mmol, 93%). IR (solution cell benzene): ν_{CO} = 1897 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 7.37 (1H, d, $^3J_{HH}$ = 7 Hz, phenyl 3/5 position), 7.34 (1H, d, $^3J_{HH}$ = 7 Hz, phenyl 3/5 position), 7.22 (1H, t, $^3J_{HH}$ = 7 Hz, phenyl 4 position), 3.67 (2H, d, $^2J_{PH}$ = 8 Hz CH$_2$), 3.47 (1H, dd, $^2J_{HH}$ = 17 Hz, $^2J_{PH}$ = 10 Hz, P−CH$_2$), 3.37 (1H, dd, $^2J_{HH}$ = 17 Hz, $^2J_{PH}$ = 6 Hz CH$_2$), 1.37 (3H, d, $^3J_{PH}$ = 13 Hz, PC(CH$_3$)$_2$), 1.19 (9H, d, $^3J_{PH}$ = 13 Hz, PC(CH$_3$)$_3$), 1.00 (9H, d, $^3J_{PH}$ = 13 Hz, PC(CH$_3$)$_3$), 0.90 (3H, d, $^3J_{PH}$ = 12 Hz, PC(CH$_3$)$_2$), 0.71 (9H, d, $^3J_{PH}$ = 12 Hz, PC(CH$_3$)$_3$), 0.49 (1H, d, $^2J_{HH}$ = 16 Hz, Ru−CH$_2$), 0.44 (1H, d, $^2J_{HH}$ = 16 Hz, Ru−CH$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 207.4 (t, $^2J_{PC}$ = 13 Hz, CO), 147.7 (t, $^2J_{PC}$ = 12 Hz, phenyl ipso), 128.4 (s, phenyl 3/5 position), 123.9 (s, phenyl 4 position), 122.5 (vt, N = 12 Hz, phenyl 2/6 position), 37.4, (vt, N = 14 Hz, PC), 36.8 (vt, N = 10 Hz, PC), 36.3 (vt, N = 20 Hz, CH$_2$), 31.7, 31.2 (vt, N = 4 Hz, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 82.7 (d, $^2J_{PP}$ = 245 Hz, PBu$_2$), 46.3 {d, $^2J_{PP}$ = 244 Hz, P(^{t}Bu)(CMe$_2$-CH$_2$)}. Note: Elemental analysis could not be obtained due to instability of the product. This complex reacts to form an unidentified product in approximately 48 h at room temperature.

(PCP)Ru(CO)(CH$_3$) (8). In a 100 mL round-bottom flask, (PCP)Ru(CO)Cl (0.0557 g, 0.0997 mmol) was dissolved in approximately 50 mL of THF. Methyllithium (1.6 M in the, 0.136 mmol) was added dropwise using a microsyringe. The volatiles were removed under reduced pressure, and the solids were dissolved in benzene. The solution was filtered through a fine porosity frit, and the volatiles were removed under reduced pressure to yield a brown solid (0.0471 g, 0.0877 mmol, 88%). Orange microcrystals were obtained upon recrystallization from pentane at −40 °C. IR (solution cell THF): ν_{CO} = 1893 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, δ): 7.29 (2H, d, $^3J_{HH}$ = 8 Hz, phenyl 3/5 position), 7.15 (1H, t, $^3J_{HH}$ = 8 Hz, phenyl 4 position), 3.43 (2H, dt, $^2J_{HH}$ = 17 Hz, J_{PH} = 7 Hz, P−CH$_2$), 3.32 (2H, dt, $^2J_{HH}$ = 17 Hz, J_{PH} = 9 Hz, P−CH$_2$), 1.20, 0.84 (each 18 H, each a vt, N = 12 Hz, CH$_3$), 0.24 (3H, t, $^3J_{PH}$ = 4 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 208.7 (t, $^2J_{PC}$ = 9 Hz, CO), 151.9 (t, $^2J_{PC}$ = 11 Hz, RuC), 124.2 (s, PCP 4 position), 123.9 (s, PCP 3 and 5 position), 120.9 (vt, N = 17 Hz, PCP 2 and 6 position), 38.0 (vt, N = 15 Hz, PC), 37.6 (vt, N = 18 Hz, CH$_2$), 36.3 (vt, N = 13 Hz, PC), 31.2, 30.1 (each a vt, N = 5 Hz, CH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 84.9. Note: Elemental analysis could not be obtained due to instability of the product. This complex undergoes intramolecular elimination to form the cyclometalated complex **7** in approximately 24 h.

Reaction of (PCP)Ru(CO)(NH$_2$) (2) with H$_2$ at −78 °C. A screw cap NMR tube was charged with approximately 0.025 g of (PCP)Ru(CO)(NH$_2$) (**2**) in 1 mL of toluene-d_8. The solution was cooled to −78 °C in a dry ice/acetone bath. Dihydrogen was bubbled through the solution until the solution changed from orange to light yellow (approximately 5 min). The tube was kept at −78 °C until transferred to the NMR probe which

was precooled to −50 °C. ^{1}H and ^{31}P NMR spectra were acquired at regular time intervals, allowing the observation of the formation of (PCP)Ru(CO)(H)(NH$_3$) as a reaction intermediate.

Reaction of (PCP)Ru(CO)(NH$_2$) (2) with PhC≡CH at −78 °C. A screw cap NMR tube was charged with (PCP)Ru-(CO)(NH$_2$) (0.0311 g, 0.0577 mmol) in 1 mL of toluene-d_8. The solution was cooled to −78 °C in a dry ice/acetone bath. Phenylacetylene (7 μL, 0.0637 mmol) was added via microsyringe. The tube was kept at −78 °C until transferred to the NMR probe which was precooled to −80 °C. Conversion to (PCP)Ru(CO)(C≡CPh) (**5**) and NH$_3$ was observed in ^{1}H and ^{31}P NMR without observation of reaction intermediates.

Reaction of TpRu(PMe$_3$)$_2$(NH$_2$) with H$_2$. In a 50 mL round-bottom flask, TpRu(PMe$_3$)$_2$(NH$_2$) was dissolved in approximately 20 mL of THF. Dihydrogen was bubbled through the solution for 2 h. The volatiles were removed under reduced pressure, and the resulting solids were dissolved in C$_6$D$_6$ to give a homogeneous solution. ^{1}H NMR spectroscopy revealed the presence of only TpRu(PMe$_3$)$_2$(NH$_2$).

Kinetic Studies for the Cyclometalation of (PCP)Ru-(CO)(NH$_2$) (2) or (PCP)Ru(CO)(Me) (8). The general procedures for all kinetic analyses of cyclometalation reactions for (PCP)Ru(CO)(Me) (**8**) and (PCP)Ru(CO)(NH$_2$) (**2**) were similar. A representative procedure is provided: In a reaction vial, (PCP)Ru(CO)(Me) (**8**) (0.1251 g, 0.2320 mmol) was dissolved in 2.96 g of C$_6$D$_6$. A small amount of Cp$_2$Fe was added as an internal standard. The solution was transferred into three screw cap NMR tubes, and ^{1}H NMR spectra were acquired with the delay time set to 10 s. The solutions were then heated in an oil bath. The disappearance of complex **8** was monitored at regular time intervals using ^{1}H NMR spectroscopy. The formation of complex **7** and methane was observed. In addition, the formation of methane and ammonia (for reactions with complex **2**) was confirmed by GC/MS analysis.

Computational Methods. Quantum calculations were carried out using the Gaussian 98 package.[64] The B3LYP hybrid functional was employed for all calculations.[65] Heavy atoms were described with the Stevens relativistic effective core potentials (ECPs) and valence basis sets (VBSs).[66,67] The valence basis sets of main group elements were augmented with a d polarization function. This ECP/VBS combination, termed SBK(d), has been validated for the calculation of a wide variety of transition metal properties in previous studies.[43,68–70]

All stationary points were fully optimized without symmetry constraint. All species investigated are closed-shell singlets. Several conformations of the different ligands were investigated by torsion about the appropriate metal−ligand bonds;

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the lowest energy conformers found were used in the analyses given below. The energy Hessian was calculated at all stationary points to characterize them as minima (no imaginary frequencies). The quoted energies include zero-point, enthalpy, and entropic corrections determined from unscaled vibrational frequencies calculated at the B3LYP/SBK(d) level of theory. All energetic determinations were done at 298.15 K and 1 atm.

Supporting Information Available: Cartesian coordinates for all optimized minima are given. ^{1}H and ^{31}P NMR spectra of complexes **1**, **2**, **4**, and **6**–**8** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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