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

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The five-coordinate parent amido complex (PCP)Ru(CO)(NH2) (2) (PCP = 2,6-(CH3)2P-1′Bu2)2C6H3) 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 cyclometallated 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 cyclometallated complex. Determination of activation parameters for the intramolecular C–H activation transformations of 2 and 8 reveal identical ΔH‡ (18(1) kcal/mol) with ΔS‡ = −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)(NH2) to yield (PCP′)Ru(CO)(NH3)(X) (X = Me or H; PCP′ = 2,6-(CH2-Ph2)2C6H3). The results indicate that the activation of dihydrogen is both exoergic and endothermic. In contrast, the addition of a C–H bond of methane across the Ru–NH2 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 complexes that possess nondative ligands were rare compared with early and middle transition elements in complexes that possess nondative ligands were rare compared with early and middle transition elements in complexes that possess nondative ligands were rare. 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 dx2−y2 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.3,7,8,11,13

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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 prediction 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. For example, octahedral Ru(II) (d⁶) amido complexes possess sufficient basicity to deprotonate relatively weak acids, including some C–H bonds. 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 is possible to transiently bind nonpolar X–H (e.g., H–H or C–H) bonds to the metal center, thereby activating the substrate toward intramolecular deprotonation (Scheme 1). Similar transformations have been observed for early transition metal imido complexes.

A recent computational study of C–H activation of nonpolar bonds using TpRu(L)(L′)(NHPh) complexes has not been attained. One possible limitation for the activation of nonpolar bonds using TpRu(L)(L′)(NHR) (L = H or ¹Bu) complexes form ion pairs due to deprotonation of phenylacetylene. 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-(CH₂PtBu₂)₂C₆H₃) provides a precursor to a five-coordinate Ru(II) amido complex. The reaction of (PCP)Ru(CO)(Cl) with ammonia yields (PCP)Ru(CO)(Cl)(NH₃) (as indicated by IR and NMR spectroscopy) (eq 1); however, the lability of the ammonia ligand prevents the isolation of complex 1, and quantitative reversal 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)(NH₃) systems reported herein.

The in situ reaction of the ammonia complex 1 with [Na][N(SiMe₃)₂] yields (PCP)Ru(CO)(NH₂) (eq 2).

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Complex 2 is characterized by a resonance at 72.9 ppm (31P NMR) due to equivalent phosphine fragments and a triplet at 4.36 ppm (1H NMR) due to the amido protons ($^1$J_HP = 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 1H NMR spectrum of (PCP)Ru(CO)(ND$_2$) (2-d$_2$) that is synthesized by substituting ND$_3$ for NH$_3$. 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(NH$_2$)$_2$) system is more $\pi$-basic than the ((PCP)Ru(Cl)) and ((PCP)Ru(NH$_3$)$_2$)$^+$ 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 bisamine complex [(PCP)Ru(CO)(NH$_3$)$_2$][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 ND$_3$, 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(SiMe$_3$)$_2$] results in the formation of the amido complex 2 after workup (Scheme 2).

The reaction of TpRu(L')(NR) (R = H or ^1Bu) or trans-(DMPE)Ru(H)(NH$_2$)$_2$ systems with phenylacetylene results in alkyne deprotonation to form the ion pairs [TpRu(L')(NR)][PhC$_2$] and [trans-(DMPE)-Ru(H)(NH$_2$)$_2$][PhC$_2$], respectively. The combination of amido complex 2 with phenylacetylene rapidly produces (PCP)Ru(CO)(C=CPH) (5) and NH$_3$ (Scheme 3). Complex 5 has also been prepared by the reaction of (PCP)Ru(CO)(Cl) with [Li][PhC$_2$] (Scheme 3). The formation of 5 from the amido complex 2 and phenylacetylene could proceed through the initial formation of (PCP)Ru(CO)(NH$_3$)(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). 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 H$_2$ 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; coordination to transition metal centers has been demonstrated to increase the acidity of dihydrogen. For example, ruthenium-bound dihydrogen complexes exhibit pK$_a$ values as low as ~5. 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 conditions, the coordination of dihydrogen is more facile. This compares with the ease of metal–dihydrogen bond formation in other metal systems.
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 31P NMR spectrum (95.7 ppm, JPH = 21 Hz) and a new hydride resonance at −16.17 ppm (triplet, JPH = 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) (2) with dihydrogen at low temperature (−78 °C) in a sealed NMR tube allows the observation of complex 6 as a reaction intermediate by 1H and 31P 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) dihydro complex (PCP)Ru(H)2(CO)-(NH3) followed by reductive N−H bond formation yields (PCP)Ru(CO)(NH3) (6). Although examples are rare, eliminations of amine N−H bonds from d6 metal centers have been reported.32,53 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(III)-(PPh3)2[N(SiMe2CH2)2PPh2] deprotonates dihydrogen to yield Ru(Cl)(H)(PPh3)[NH(SiMe2CH2)2PPh2].55 Although 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 non-dative Pt−Cl bond is a key step in the mechanism of the Shilov reaction.57

In C6D6, (PCP)Ru(CO)(NH3) (2) undergoes intramolecular C−H activation of a methyl group of a tBu 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 1H NMR spectroscopy reveals that the transformation is first-order in complex 2 (kobs = 6.0(3) × 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 1H 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 spectroscopy.

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$_2$)(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 for 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$_3$/ND$_3$/H 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 3Bu 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 meridional (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)Ru(CO)(Cl) (M = Ru or Os) exhibit square pyramidal structures in the solid state. 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 ($\DeltaG^\ddagger$) 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](image-url)  
**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.

![Figure 3](image-url)  
**Figure 3.** B3LYP/SBK(d) optimized geometry of (PCP')Ru(CO)(NH$_2$) (2) model reactant showing pertinent bond lengths and bond angles.

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 \( \text{PCP} \)-Ru(CO)(NH2) (2), a variety of coordination isomers of the product (PCP’)-Ru(CO)(NH3)(X) were investigated at the B3LYP/6-31G(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 exothermic by 8.9 kcal/mol. The corresponding C–H activation of methane is strikingly different, being endothermic by 3.7 and endothermic by 13.6 kcal/mol. Hence, the calculations are in qualitative agreement with experimental observations; that is, (PCP)Ru(CO)(NH2) (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 should be more favorable.

Perhaps the most interesting aspect of the computational comparison of dihydrogen versus methane activation is that the methane activation is endothermic 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)(NH3)(H) yields a value of 71.6 kcal/mol.

\[
\Delta H \approx \text{BDE}_{\text{Ru}–\text{NH}_2} + \text{BDE}_{\text{X}–\text{H}} - \text{BDE}_{\text{Ru}–\text{NH}_3} - \text{BDE}_{\text{N}–\text{H}} - \text{BDE}_{\text{Ru}–\text{X}} \tag{7}
\]

Consistent with known differences in metal–alkyl versus metal–hydride bond dissociation energies, the corresponding Ru–CH3 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 is the root cause of the surprising endothermicity of methane activation by (PCP’)-Ru(CO)(NH3) (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)(NH3) product. This gain is estimated to be 31.8 kcal/mol from the relevant B3LYP/6-31G(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 \( \Delta \Delta H \)'s 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–NH3 and Ru–NH2 indicates that the difference is significant: BDE_{Ru–NH2} = 52.5 kcal/mol; BDE_{Ru–NH3} = 12.6 kcal/mol; \( \Delta \text{BDE} = 39.9 \) kcal/mol (Scheme 6). The calculations of a small BDE for the Ru–NH3 linkage is consistent with the general experimental observation that ammonia is weakly coordinated to the (PCP’)-Ru(H)(CO)(X)(NH3) 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–CH3 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)(NH3)(Me) should convert to (PCP’)-Ru(CO)(NH2) and methane. Experimentally, the addition of ammonia to (PCP’)-Ru(CO)(Me) (8) forms an equilibrium between (PCP’)-Ru(CO)(Me)(NH3) and (PCP’)-Ru(CO)(Me)(NH3), 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)(NH3) cannot be definitively determined.
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\textsubscript{3} to the methyl complex 8 (1.5 equiv based NMR spectroscopy) is more rapid (\(k_{\text{obs}} = 1.2 \times 10^{-4} \text{ s}^{-1}\) at 30 °C) than in the absence of ammonia (\(k_{\text{obs}} = 5.5 \times 10^{-5} \text{ s}^{-1}\) at 30 °C; Figure 4) suggests the possibility of a direct conversion of (PCP)Ru(CO)(Me)\textsubscript{2}(NH\textsubscript{3}) to complex 7 and methane. Such a pathway would require the initial formation of (PCP)Ru(CO)(NH\textsubscript{2})\textsubscript{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.). 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–amine 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 intramolecular 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. The observation of intramolecular 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 exergonic and endothermic, while the addition of a C–H bond of methane across the Ru–NH\textsubscript{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-amine 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\textsubscript{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\textsubscript{2}O\textsubscript{5}. Benzene-d\textsubscript{6} was purified by distillation from CaH\textsubscript{2}, degassed, and stored over 4 Å sieves. CDC\textsubscript{13}, toluene-d\textsubscript{8} and CD\textsubscript{2}Cl\textsubscript{2} were degassed via three freeze–pump–thaw cycles and stored over 4 Å sieves. Room-temperature \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were obtained on a Varian Mercury 400 or 300 MHz spectrometer. All \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were referenced against tetramethylsilane using residual proton signals (\(^1\text{H}\) NMR) or the \(^{13}\text{C}\) resonances of the deuterated solvent (\(^{13}\text{C}\) NMR). \(^{31}\text{P}\) NMR spectra were obtained on a Varian 300 MHz (observed frequency 161 MHz) spectrometer and referenced against external 85% H\textsubscript{3}PO\textsubscript{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 synthesis of TpRu(PMe\textsubscript{3})(NH\textsubscript{3})\textsubscript{2}, (PCP)Ru(CO)\textsubscript{2}, and (PCP)Ru(CO)(H) have been previously reported. All reagents were used as purchased from commercial sources.

(1) A screw cap NMR tube was charged with approximately 0.025 g of (PCP)Ru(CO)Cl\textsubscript{3} in 1 mL of CDCl\textsubscript{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\textsubscript{2})\textsubscript{2}Cl\textsubscript{2} (1) was observed by \(^1\text{H}\), \(^{13}\text{C}\), and \(^{31}\text{P}\) NMR and IR; however, removal of excess NH\textsubscript{3} by purging or placing the solution under reduced pressure results in rapid and quantitative formation of the starting material (PCP)Ru(CO)Cl\textsubscript{3}. IR (solution cell CDCl\textsubscript{3}): \(\nu_{\text{CO}} = 1900 \text{ cm}^{-1}\); \(^1\text{H}\) NMR (CDCl\textsubscript{3}, \(\delta\)):
6.76 (2H, d, 3J HH = 7 Hz, phenyl 3/5 position), 6.60 (1H, t, 3J HH = 6 Hz, phenyl 4 position), 3.14 (4H, m, CH2), 2.85 (3H, bs, NH3), 1.17, 1.14 (each 18H, each v, N = 12 Hz, CH3). 

13C(C1) NMR (CDCl3, δ): 207.4 (t, 3J PC = 12 Hz, CO), 147.7 (t, 3J PC = 12 Hz, PCP phenyl), 128.4, 123.9 (each a s, PCP phenyl), 122.5 (v, N = 13 Hz, PCP phenyl), 37.4 (v, N = 14 Hz, PC), 36.8 (v, N = 10 Hz, PC), 36.3 (v, N = 20 Hz, CH2), 31.7, 31.2 (each a v, N = 4 Hz, CH3). 31p (1H) NMR (CDCl3, δ): 78.3.

(PCP)Ru(Cl)(NH3)2 (2). (PCP)Ru(Cl)(Cl) (0.0969 g, 0.1736 mmol) was dissolved in approximately 30 mL of THF. Approximately 10 mL of a saturated solution of NH3 in THF was added. Upon combination of the two solutions, a color change from dark orange to yellow was observed. The reaction was stirred for 1 h. After removal of volatiles (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): νCO = 1890 cm−1, νNH = 3396, 3306 cm−1. 1H NMR (CDCl3, δ): 4.93 (2H, br, t, 3J HH = 9 Hz, NH2), 3.05 (2H, s, 2J HH = 11 Hz, 1J HH = 1 Hz, phenyl para/4 position), 2.50 (3H, bs, N), 1.26, 1.14 (each 18H, CH3). 13C(C6D6, δ): 78.6. Found: C 46.28, H 6.58.

IR (solution cell THF): νCO = 1936 cm−1. 1H NMR (CDCl3, δ): 7.09 (2H, d, 3J HH = 7 Hz, phenyl 3/5 position), 6.93 (1H, t, 3J HH = 7 Hz, phenyl 4 position), 3.47 (4H, v, N = 8 Hz, CH2), 1.50 (18H, v, N = 14 Hz, CH3), 1.17 (18 H, v, N = 13 Hz, CH3). 13C(C6D6, δ): 204.9 (t, 3J PC = 12 Hz, CO), 157.2 (s, phenyl 4 position), 157.2 (t, 3J PC = 7 Hz, phenyl ipso), 125.4 (s, phenyl 3/5 positions), 123.3 (v, N = 16 Hz, phenyl 2/6 positions), 38.0 (v, N = 14 Hz, PC), 36.7 (v, N = 16 Hz, PC), 33.7 (v, N = 22 Hz, CH2), 30.1 (v, N = 4 Hz, CH3), 29.4 (v, N = 4 Hz, CH3). 31p (1H) NMR (CDCl3, δ): 70.9. Anal. Calcld for C64H94RuN2O4P2: C 64.8, H 6.54. Found: C 64.8, H 6.58.

L(O)(PCP)Ru(Cl)(NH3)2(O)(OTf) (4). In a 50 mL round-bottom flask, 0.0816 g (0.121 mmol) of (PCP)Ru(Cl)(O)(OTf) (3) was dissolved in approximately 15 mL of THF. The 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 30 mL of THF, and the products were precipitated with approximately 30 mL of cyclopentane. Pale yellow crystals were isolated by filtration through a medium porosity froth (0.0690 g, 0.1027 mmol, 85%). IR (solution cell THF): νCO = 1905 cm−1. 1H NMR (CDCl3, δ): 7.29 (2H, d, 3J HH = 8 Hz, acetyldehyde meta position), 7.23–7.17 (4H, m, overlapping PCP and acetyldehyde 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), 3.67 (3H, s, N), 2.29 (3H, s, N), 1.35 (18H, each v, N = 14 Hz, CH3). 13C(C6D6, δ): 209.0 (t, 3J PC = 13 Hz, CO), 179.4 (t, 3J PC = 3 Hz, ipso phenyl), 152.5 (v, N = 15 Hz, PCP 3.5 or 2.6 position), 131.7 (t, 3J PC = 11 Hz CCPH), 130.3 (t, N = 14 Hz, PCP 4 or Ph o, m, p), 129.8 (t, 3J 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 (v, N = 15 Hz, PCP 3.5 or 2.6-position), 37.9 (v, N = 23 Hz, CH3), 37.8 (v, N = 15 Hz, PC), 37.0 (v, N = 17 Hz, PC), 30.0, 29.8 (each a v, N = 5 Hz, CH3). 31p (1H) NMR (CDCl3, δ): 80.0. Anal. Calcld for C51H38F4O4P2Ru: C 63.54, H 7.76. Found: C 63.52, H 7.74.

(PCP)Ru(Cl)(NH3)2(H) (6). A screw cap NMR tube was charged with approximately 0.025 g of (PCP)Ru(Cl)(H) and 1 mL of CDCl3. 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(Cl)(NH3)(H) (6) was observed by 1H, 13C, and 31p 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(Cl)(H). IR (solution cell THF): νCO = 1905 cm−1. 1H NMR (CDCl3, 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, d, 3J HH = 16 Hz, J Ph = 8 Hz, CH3), 3.19 (2H, d, 3J HH = 17 Hz, J Ph = 6 Hz, CH3), 1.18, 1.06.
(each 18 H, each a vt, N = 12 Hz, CH₂), -16.17 (1H, t, J₇PH₂ = 21 Hz). The resonance due to bound NH₃ is not observed possibly due to overlap with a ¹Bu resonance. ¹³C(CH₃) NMR (Cd₆, δ): 208.1 (t, J₇PC = 13 Hz, CO), 149.9 (t, J₇PC = 11 Hz, PCC phenyl), 123.4 (s, PCC phenyl), 122.5 (vt, N = 16 Hz, PCC phenyl), 39.4 (vt, N = 14 Hz, PC), 36.8 (vt, N = 9 Hz, PC), 36.5 (vt, N = 21 Hz, CH₂), 30.0–29.7 (m, overlapping CH₃); note: missing one PCC phenyl resonance possibly due to coincidental overlap. ³¹P NMR (hydrogen coupled; Cd₆, δ): 95.7 (d, J₇PH₂ = 21 Hz).

Ru(CO)₆CH₂·CH₂P=BU₃·6·CH₃P(Bu)(C₆H₅)(CH₃CH₂)(7). In a 100 mL round-bottom flask, (PCC)Ru(CO)(Cl) (0.3837 g, 0.6867 mmol) was dissolved in approximately 50 mL of THF. Methylthionium (1.6 M in THF, 0.307 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 hours. Filtration of the solution through a fine porosity frit, and the volatiles were removed under reduced pressure, and the solids were dissolved in benzene. The solution was kept at 78 °C in a dry ice/acetone bath. Dihydrogen (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 ~50 °C. ¹H and ³¹P NMR spectra were acquired at regular time intervals, allowing the observation of the formation of (PCC)Ru(CO)(H)(NH₃) as a reaction intermediate.

Reaction of (PCC)Ru(CO)(NH₃)(2) with PhC=CH at ~78 °C. A screw cap NMR tube was charged with (PCC)Ru(CO)(NH₃)(2) (0.0311 g, 0.0577 mmol) in 1 mL of toluene-d₈. 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 ~50 °C. ¹H and ³¹P NMR spectra were acquired at regular time intervals, allowing the observation of the formation of (PCC)Ru(CO)(H)(NH₃) as a reaction intermediate.

Kinetic Studies for the Cyclometalation of (PCC)Ru(CO)(NH₃)(2) or (PCC)Ru(CO)(Me)(8). The general procedures for all kinetic analyses of cyclometalation reactions for (PCC)Ru(CO)(Me)(8) and (PCC)Ru(CO)(NH₃)(2) were similar. A representative procedure is provided: In a reaction vial, (PCC)Ru(CO)(Me)(8) (0.1251 g, 0.2320 mmol) was dissolved in 2.96 g of Cd₆. A small amount of CpFe was added as an internal standard. The solution was transferred into three screw cap NMR tubes, and ¹H 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 ¹H 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. The B3LYP hybrid functional was employed for all calculations. Heavy atoms were described with the Stevens relativistic effective core potentials (ECPs) and valence basis sets (VBs). 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. All stationary points were fully optimized without any 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;
the lowest energy conformers found were used in the analyses
given below. The energy Hessian was calculated at all station-
ary 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.

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Supporting Information Available: Cartesian coordi-
nates 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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