Mechanism of Catalytic Hydration of Nitriles with Hydrotris(pyrazolyl)borato (Tp) Ruthenium Complexes

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The aquo-amido complexes TpRu(PPh_3)(H_2O)(NHC(O)R) (R = Me, Ph), which can be prepared by refluxing a THF solution of TpRu(PPh_3)(RCN)H containing excess water or more conveniently by reacting TpRu(PPh_3)(RCN)Cl with NaOH in THF in the presence of water, are found to be active for catalytic hydration of nitriles to amides. The catalysis proceeds via a mechanism that is distinctly different from the common ones involving intramolecular nucleophilic attack of a hydroxo (or aquo) ligand or external attack of a hydroxide ion (or water) at the carbon atom of the η^1-coordinated nitrile to form the metal amide intermediate and subsequent protonation of amido ligand by an adjacent aquo ligand or solvent water. The new mechanism involves the intermediacy of a relatively stable complex containing a chelating *N*-imidoylimidato ligand; ring-opening nucleophilic attack of this ligand by water is the product-generating step. Formation of the *N*-imidoylimidato complex from TpRu(PPh_3)(H_2O)(NHC(O)R) involves several steps. The initial one is displacement of the H_2O ligand by a nitrile molecule to yield the nitrile-amido species TpRu(PPh_3)(RCN)(NHC(O)R). This is followed by an unusual linkage isomerization of the N-bonded amido ligand to an O-bonded imido, which then undergoes nucleophilic attack at the carbon atom of the nitrile ligand in the complex; facile 1,3-proton shift between the nitrogen atoms on the resulting ring completes the reaction. The *N*-imidoylimidato complexes TpRu(PPh_3)(κ^2-*N*,*O*-NH═CMeN═CMeO), TpRu(PPh_3)(κ^2-*N*,*O*-NH═CPhN═CPhO), and TpRu(PPh_3)(κ^2-*N*,*O*-NH═CMeN═CPhO) were independently prepared, and the molecular structure of TpRu(PPh_3)(κ^2-*N*,*O*-NH═CPhN═CPhO) was determined by X-ray crystallography. To study the feasibility of the proposed mechanism for nitrile hydration with the aquo-amido complexes, theoretical calculations were performed at the Becke3LYP level of DFT theory to examine the whole catalytic cycle. It is learned that there is a substantially high barrier for the hydrolysis of the highly stable *N*-imidoylimidato complex, a step involving the ring-opening nucleophilic attack of this ligand by water, and this is probably the reason for the requirement of a relatively high reaction temperature.

Introduction

Catalytic hydration of nitriles to amides is an important transformation both in laboratory scale and in industry. In addition to higher chemoselectivity, i.e., the amides are not further hydrolyzed to the undesirable carboxylic acids, other advantages of the transition-metal-complex-catalyzed nitrile hydration reactions over the conventional acid- and base-catalyzed reactions include milder reaction conditions and higher tolerance to other functional groups.[1] A well-known mechanism for the transition-metal-catalyzed nitrile to amide conversion involves intramolecular nucleophilic attack of a hydroxo ligand or external attack of a hydroxide ion at the carbon atom of the η^1-coordinated nitrile molecule and subsequent protonation of the nitrogen atom.[2] In a palladium-catalyzed nitrile hydration reaction, on the basis of kinetic experiments, it was proposed that formation of amide resulted from both internal and external attack, which occur at similar rates, on the nitrile ligand by the neighboring aqua ligand and the solvent water, respectively.[3] Parkins's homogeneous platinum phosphinito complex [PtH(PMe_2OH)(PMe_2O)$_2$H] represents one of the most efficient catalysts for hydration of nitriles to amides. The cationic nitrile complex [Pt(RCN)(PMe_2OH)(PMe_2O)H]$^+$ is the active species responsible for the catalysis, which begins by intramolecular nucleophilic attack of the PMe_2OH hydroxyl at the carbon center of the nitrile ligand, forming an intermediate that contains a five-membered-ring iminol-type ligand; addition of a H_2O molecule across the C═N bond of the iminol-type ligand and subsequent proton transfer yields the amide. Coordination of a nitrile to the metal center regenerates the active species.[4] Intramolecular attack by the hydroxo ion, bound to one metal center, at the nitrile molecule bonded to the other metal center

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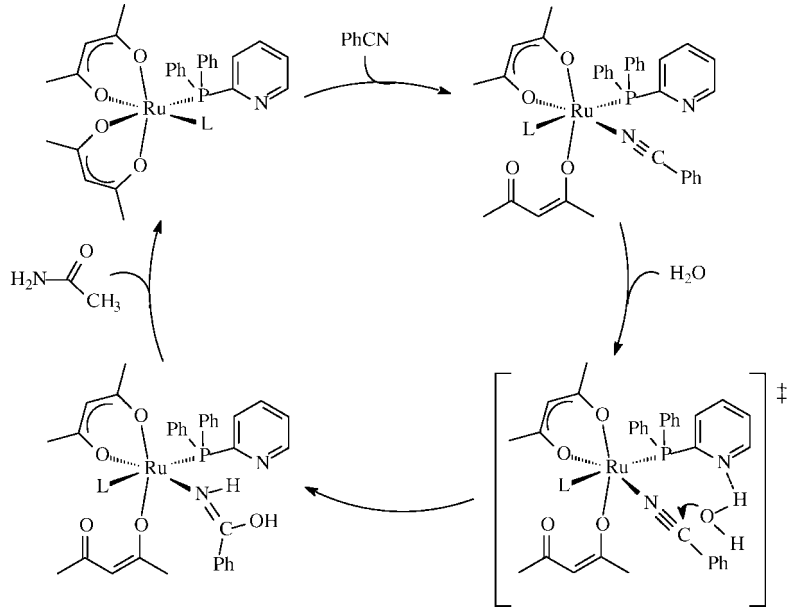
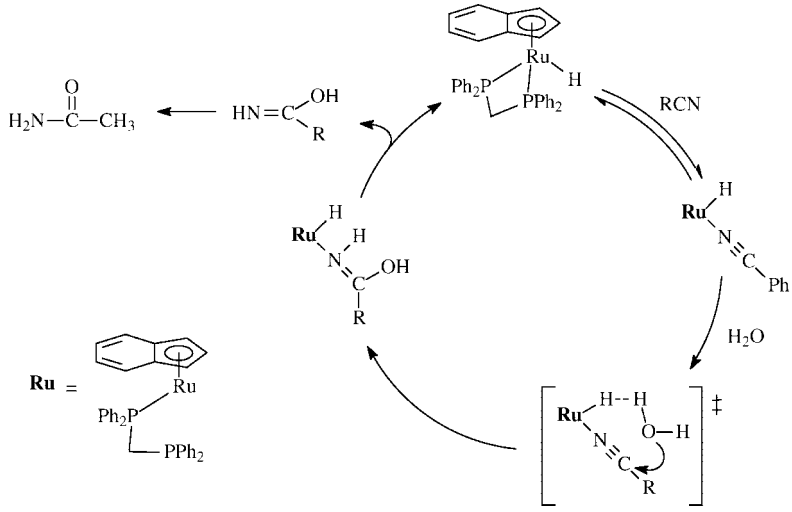
Scheme 1



Scheme 2



in dinuclear iron,[5] cobalt,[6] copper,[7] palladium,[8] rhenium,[9] and nickel[10] systems has also been reported.

It has recently been reported that the ruthenium complex *cis*-$Ru(acac)_2(PPh_2py)_2$ (acac = acetylacetonate; PPh_2py = 2-diphenylphosphinopyridine) is an excellent catalyst for the hydration of nitriles to amides under neutral conditions. The feature of the proposed mechanism is that nucleophilic addition of water to the nitrile ligand is promoted by hydrogen-bonding interaction of the former with the pendant pyridinyl moiety of the PPh_2py ligand (Scheme 1).[11]

We have also reported that the catalytic hydration of nitriles with an indenylruthenium hydride complex is promoted by Ru−H···H−OH dihydrogen-bonding interaction between the hydride ligand and the incoming water molecule (Scheme 2). It was shown by theoretical calculations that the presence of the dihydrogen-bonding interaction in the transition state lowers the barrier of the nucleophilic attack of H_2O at the carbon center of the bound nitrile.[12]

Very recently, it was reported that the cyano moiety of the ligand (6-cyano-2-pyridylmethyl)bis(2-pyridylmethyl)amine in a dichloroferrous complex was hydrated to the corresponding carboxamide; this is the first example of hydration of nitrile on a ferrous complex. It is proposed that the hydration proceeds via an "outer-sphere mechanism", which does not require the

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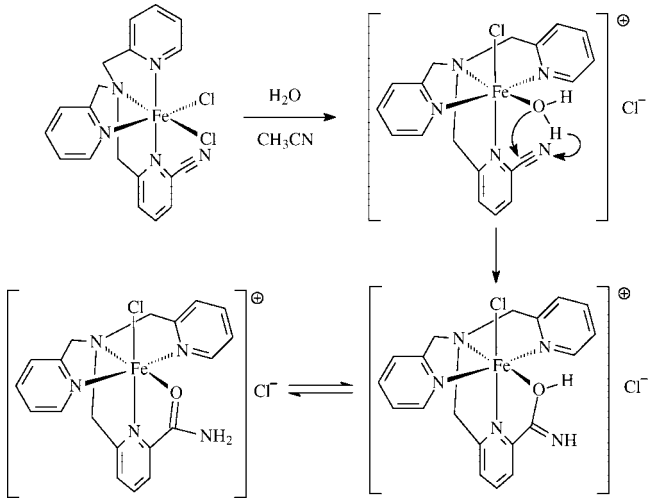
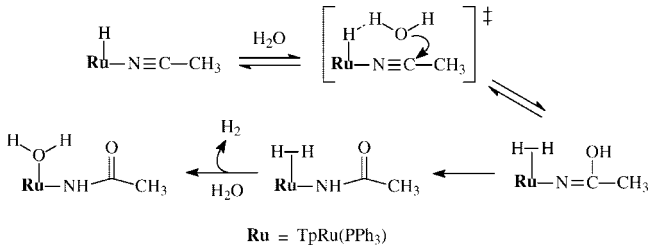
Scheme 3



Scheme 4



Ru = TpRu(PPh$_3$)

coordination of the nitrile moiety; it is activated in the vicinity of a metal-coordinated water molecule (Scheme 3).[13]

We have recently reported that while the ruthenium hydride complex TpRu(PPh$_3$)(CH$_3$CN)H (Tp = hydrotris(pyrazolyl)borate) (**1**) is readily attacked by water to yield the aquo-acetamido complex TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (**2a**), the chloro analogue TpRu(PPh$_3$)(CH$_3$CN)Cl fails to react with water. The proposed reaction sequence featuring dihydrogen bond-mediated nucleophilic attack of water at the bound nitrile is shown in Scheme 4.[14] We report here catalytic hydration of nitriles to amides with **2a** and its benzamido analogue TpRu(PPh$_3$)(H$_2$O)(NHC(O)Ph) (**2b**) and discuss the detailed mechanism of the catalytic reaction. The uniqueness of this mechanism, in comparison to those of the transition-metal-catalyzed nitrile hydration reactions reported in the literature, will be demonstrated.

Results and Discussion

Catalytic Hydration of Nitriles to Amides with TpRu(PPh$_3$)(CH$_3$CN)H (1) and TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (2a) and NMR Monitoring of the 1- and 2a-Catalyzed Hydration of Acetonitrile. In view of the fact that **1** reacts readily with water to form the aquo-acetamido complex **2a**, we anticipated that **1** might be a catalyst for the hydration of nitriles to amides. In fact **1** was found to be active for the catalysis. The results of a few cases of **1**-catalyzed hydration of nitriles to amides are shown in Table 1. In the **1**-catalyzed hydration of acetonitrile (in 1,4-dioxane-d_8) carried out in a sealed NMR tube, after heating at 90 °C for 230 min, the ^{31}P{^{1}H} spectrum of the solution taken at room temperature showed signals at δ 61.6, 66.6, and 69.4 ppm. Another signal at δ 60.8 ppm started to emerge after heating for 470 min. This signal gained intensity at the expense of the other signals and finally became the only signal after 1700 min; we later verified that it corresponds to **4a**, which is the most stable species in the catalytic cycles of the **1**- and **2a**-catalyzed acetonitrile hydration reactions (vide infra). As can be seen from Table 1, the catalytic activity of the aquo-acetamido complex **2a** is very similar to that of **1**. A **2a**-catalyzed hydration reaction of acetonitrile was monitored by NMR spectroscopy (Figure 1). The room-temperature ^{31}P{^{1}H} NMR spectrum of a 1,4-dioxane-d_8 solution of **2a** in a needle-valved NMR tube immediately taken after the addition of 25 equiv of acetonitrile and 180 equiv of water and application of 10 atm of Ar gas (to prevent boiling of the solution at high temperatures) showed a singlet at δ 59.0 ppm corresponding to **2a** and another singlet of approximately equal intensity at δ 54.3 ppm; this signal is due to the nitrile-amido complex TpRu(PPh$_3$)(CH$_3$CN)(NHC(O)CH$_3$) (**3a**), which we later synthesized and characterized in situ. After heating the solution in the NMR tube in the probe at 50 °C for 30 min, the ^{31}P{^{1}H} NMR spectrum taken at this temperature showed, in addition to the signals of **2a** and **3a**, a new singlet at δ 60.8 ppm; this signal is due to complex **4a**, which contains a chelating *N*-imidoylimidato ligand, κ^2-*N,O*-NH=CMeN=CMeO$^-$. The ratio **2a**:**3a**:**4a** was ~2:2:1. After heating the tube for another 30 min at 75 °C, the ^{31}P{^{1}H} spectrum (at 75 °C) of the solution showed that the ratio **2a**:**3a**:**4a** was approximately 1:1:1. Heating the solution at a higher temperature (90 °C) for another 30 min led to total conversion of **2a** and **3a** to **4a**, as indicated by the presence of only one signal, which is due to **4a**, in the ^{31}P{^{1}H} NMR spectrum. The solution was further heated for 200 min at 120 °C; at the end of this period, complex **4a** remained the only detectable species by ^{31}P{^{1}H} NMR spectroscopy. It should be pointed out that the ^{1}H NMR spectra taken concurrently with the ^{31}P spectra showed that the hydration of acetonitrile began to occur and proceed to a very small extent at 90 °C; the catalysis occurred more readily at 120 °C, and approximately 30% of the acetonitrile was converted to acetamide after heating at this temperature for 200 min. The above-mentioned NMR monitoring experiments seem to indicate that the **2a**-catalyzed nitrile hydration is more amenable to a detailed mechanistic study, and in view of the fact that its catalytic activity might be similar to that of **1**, we therefore decided to carry out a detailed investigation of nitrile hydration with **2a** and its analogues with different amido ligands. Moreover, we have learned later that **2a** can be more conveniently synthesized by reacting TpRu(PPh$_3$)(CH$_3$CN)Cl with NaOH in THF in the presence of a small amount of water (eq 1).

Table 1. Comparison on 1- and 2a-Catalyzed Nitrile Hydration[a]

	conversion (%)[b]	
substrate	TpRu(PPh$_3$)(CH$_3$CN)(H) (**1**)	TpRu(PPh$_3$)(NHCOCH$_3$)(H$_2$O) (**2a**)
acetonitrile[c]	8.3	8.7
benzonitrile	7.3	8.8
benzyl cyanide	trace	trace
propionitrile	11.8	14.5
crotononitrile	37.5	39.8

[a] Reaction conditions: catalyst, 4.6 μmol; nitrile:water:catalyst = 500:600:1; solvent, 1,4-dioxane (0.5 mL); reaction condition: 72 h; 120 °C; temperature (oil bath) 120 °C. [b] Determined by ^{1}H NMR spectroscopy; based on nitrile used. [c] Nitrile:water: catalyst = 1000:1000:1; neat substrate.

The results of the **2a**-catalyzed hydration of nitriles are shown in Table 2; the reactions were carried out at 150 °C (oil bath temperature) instead of 120 °C since conversions at this temperature are much higher than those at the lower temperature.

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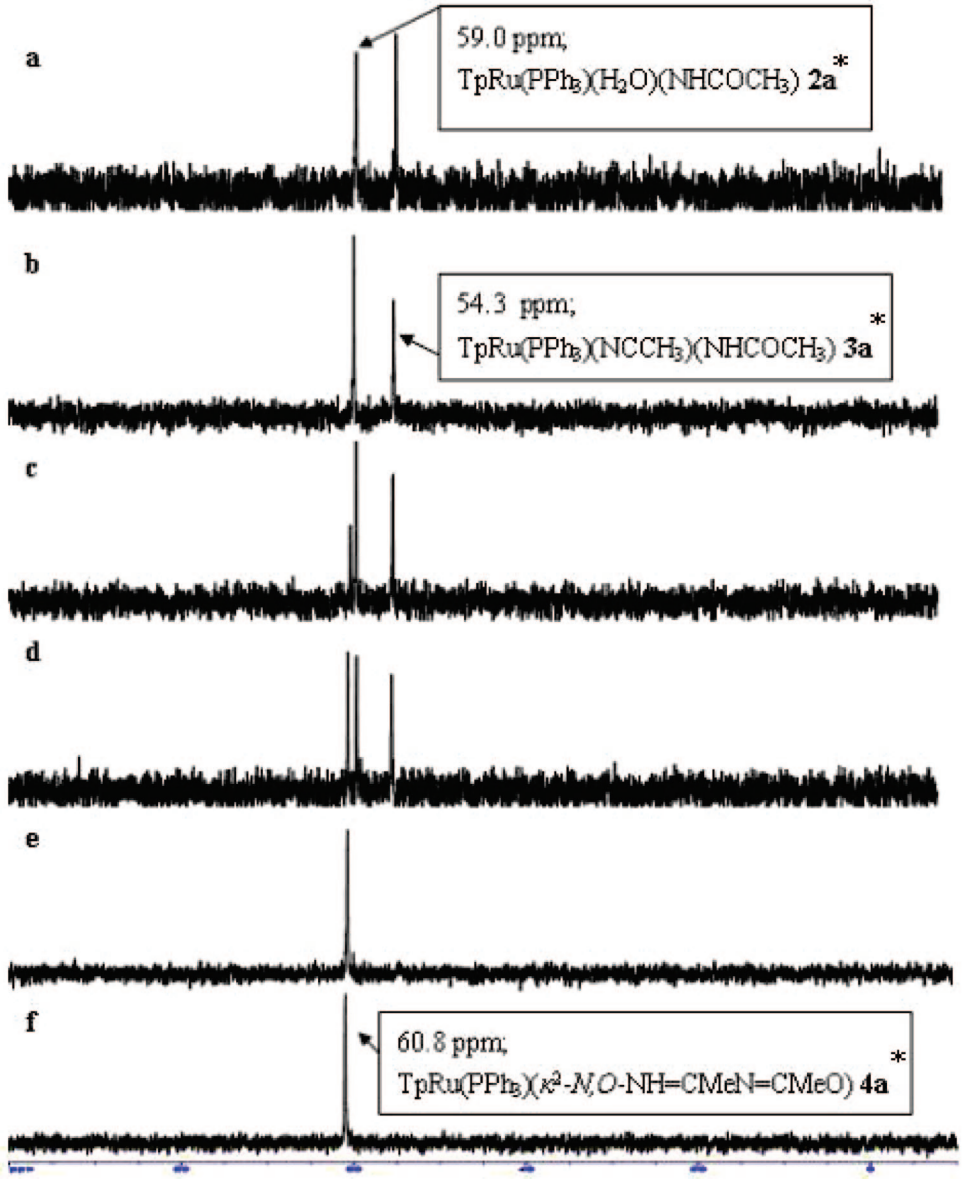


Figure 1. ^{31}P NMR study of **2a**-catalyzed hydration of acetonitrile: (a) immediately after addition of nitrile and water at room temperature; (b) 12 h at room temperature; (c) 50 °C for 30 min; (d) 75 °C for 30 min; (e) 90 °C for 30 min; (f) 105 °C for 30 min. ^{31}P{^{1}H} NMR spectra were taken at temperatures indicated. *The chemical shifts of **2a**, **3a**, and **4a** in the presence of water and nitrile are slightly different from those of the authentic samples taken in 1,4-dioxane-d_8.

$$\mathrm{TpRu(PPh_3)(CH_3CN)Cl} + \mathrm{NaOH} \xrightarrow{\mathrm{THF/H_2O}} \underset{\mathbf{2a}}{\mathrm{TpRu(PPh_3)(H_2O)(NH{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}CH_3)}} \quad (1)$$

The Ar pressure was applied to prevent the solution from boiling too vigorously in the tube. In general, aryl nitriles are hydrated more readily than the aliphatic analogues. The order of reactivity of the aryl nitriles, 4-chlorobenzonitrile > benzonitrile > 4-methoxybenzonitrile, seems to indicate that nucleophilic attack of H_2O at the nitrile is an important step of the catalytic reaction. Using the hydration of acetonitrile as an example, it can be seen that catalytic activity of **2a** (TOF = 5.3) is low compared to that of Parkin's highly efficient platinum complex [PtH(PMe_2-OH)(PMe_2O)$_2$H] (TOF = 380)[4a] and other platinum complexes [PtH(H_2O)(PMe_3)$_2$]OH (TOF = 178)[2b] and [PtH(H_2O)-(PEt_3)$_2$]OH (TOF = 70),[2b] but is comparable with those of the less effective catalysts such as [Cp*Ir(η^3-$CH_2CHCHPh$)-($NCCH_3$)]$^+$ (TOF = 8.3),[2d] [($MeCp$)$_2$Mo(OH)(H_2O)]$^+$ (TOF = 4.2),[2c] and η^5-C_9H_7)Ru(dppm)H (TOF = 12).[12] Complex **2a** is not a very active catalyst for nitrile hydration; however, as will be shown in later sections, catalysis with this complex proceeds by a mechanism very different from the conventional ones.

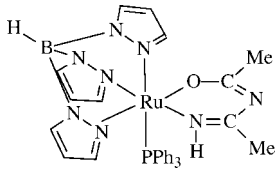
Synthesis of TpRu(PPh$_3$)(CH$_3$CN)(NHC(O)CH$_3$) (3a). Complex **2a** reacted with excess acetonitrile at room temperature in THF to form **3a**; however, during the workup when the acetonitrile was removed under reduced pressure, a small portion of **3a** was reconverted to **2a**, probably due to the fact that the small amount of water present in the solution was not as readily removed as the acetonitrile, and therefore its concentration in the solution increased. Complex **3a** prepared by this method is therefore always contaminated by a small amount of **2a**. Complex **3a** prepared in 1,4-dioxane-d_8 in an NMR tube can, however, be characterized in situ by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR spectrum of **3a** shows the typical nine-peak pattern of the Tp ligand in the downfield region (δ 7.19−7.31 ppm), indicative of the presence of three inequivalent ligands trans to the pyrazolyl moieties of the Tp

Table 2. Catalytic Hydration of Nitriles with $TpRu(PPh_3)(H_2O)(NHC(O)CH_3)$ (2a)[a]

entry	substrate	turnover number (TON)[b,c]	turnover frequency (TOF)[d]
1	anisonitrile	174	7.3
2	benzonitrile	182	7.6
3	4-chlorobenzonitrile	200	8.3
4	acetonitrile	128	5.3
5	benzyl cyanide	80	3.3
6	butyronitrile	112	4.7
7	crotononitrile	74	3.1
8	hexanenitrile	62	2.6
9	isobutyronitrile	100	4.2
10	propionitrile	96	4.0
11[e]	acetonitrile	118	4.9
12[e]	benzonitrile	178	7.4

[a] Reaction conditions: catalyst, 4.6 μmol; catalyst: nitrile:water = 1:200:2000; solvent, 1,4-dioxane (to fill up to a total volume of ~0.4 mL); pressure: Ar = 10 atm; temperature (oil bath) 150 °C; time: 24 h. [b] Determined by ^{1}H NMR spectroscopy; based on nitrile used. [c] Mole of product per mole of catalyst. [d] Mole of product per mole of catalyst per hour. [e] Catalyst: $TpRu(PPh_3)(\kappa^2$-*N,O*-NH=CMeN=CMeO) (**4a**).

Chart 1



ligand. The N−H is shown as a slightly broadened singlet at δ 3.22 ppm. The methyl protons of the acetamido ligand and the coordinated acetonitrile appear as two singlets at δ 1.73 and 2.05 ppm, respectively. A singlet that corresponds to the carbonyl carbon of the acetamido ligands is seen at δ 178.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 58.8 ppm.

Synthesis of $TpRu(PPh_3)(\kappa^2$-*N,O*-NH=CMeN=CMeO) (4a). Complex **4a**, the most stable species observed in the course of the **2a**-catalyzed hydration of acetonitrile, was independently prepared by reacting **2a** with excess CH_3CN in 1,4-dioxane in a sealed tube at an oil bath temperature of 130 °C. We initially took **4a** as the acetamide-acetamido complex $TpRu(PPh_3)(NH_2C(O)CH_3)(NHC(O)CH_3)$ since the NMR and IR spectroscopic data of the complex seem to be consistent with this structure; we thought that $TpRu(PPh_3)(NH_2C(O)CH_3)(NHC(O)CH_3)$ could have been readily formed by exchange of the water ligand of **2a** for a nitrile molecule and subsequent hydration of the latter. Several attempts to grow single crystals of **4a** for X-ray crystallographic study failed. However, a successful X-ray crystallographic study of **4b**, the phenyl analogue of **4a**, and density functional theory study (vide infra) later help to deduce that **4a** is not the acetamido-acetamide complex; it is instead a complex containing a chelating *N*-imidoylimidato ligand, $TpRu(PPh_3)(\kappa^2$-*N,O*-NH=CMeN=CMeO) (see Chart 1). The NMR and IR data can be accounted for with this structure. Thus, in the ^{1}H NMR spectrum, the two singlets at δ 2.06 and 2.47 are due to the two methyl groups of the ring; the three legs trans to the Tp ligand are inequivalent, therefore giving rise to the nine-peak pattern in the low-field region. The two peaks observed at δ 168.1 and 176.1 ppm in the $^{13}C\{^1H\}$ NMR spectrum are accountable by the two imino carbons (C=N) of the chelate ligand, and the presence of the imino groups in the ring is corroborated by the stretching frequencies of 1577 and 1654 cm^{-1} in the IR spectrum, which also shows the N−H stretch at 3382 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 60.0 ppm. Therefore, the reaction of **2a** with acetonitrile at room temperature is a simple ligand substitution reaction in which the water ligand exchanges for a CH_3CN molecule, forming **3a**; at elevated temperature, **3a** evolves into **4a**.

Synthesis of $TpRu(PPh_3)(H_2O)(NHC(O)Ph)$ (2b) and $TpRu(PPh_3)(PhCN)(NHC(O)Ph)$ (3b). The aquo-benzamido complex **2b** was readily prepared by reacting $TpRu(PPh_3)(PhCN)Cl$ with NaOH in THF/H_2O. The molecular structure of **2b**[15] is very similar to that of the previously reported **2a**.[14] The ^{1}H NMR spectrum of **2b** shows the N−H as a slightly broadened singlet at δ 5.92 ppm. The carbonyl carbon of the benzamido ligand appears as a singlet at δ 181.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ spectrum shows a singlet at δ 58.8 ppm, corresponding to the phosphine ligand of **2b**. The low carbonyl stretching frequency ($\nu_{(C=O)}$ = 1525 cm^{-1}) is consistent with the fact that the imido form makes a significant contribution to the structure. It was reported that a ruthenium-acetamido complex exhibits a low carbonyl amide stretching frequency ($\nu_{(C=O)}$ = 1545 cm^{-1}).[16] Complex **2a**, which we recently reported, also displays a low carbonyl stretching frequency ($\nu_{(C=O)}$ = 1540 cm^{-1}).[14] The N−H stretching frequency of **2b** can be observed at 3354 cm^{-1}; it is shifted to 2360 cm^{-1} (theoretical value is 2377 cm^{-1} for $TpRu(PPh_3)(D_2O)(NDC(O)Ph)$.

Unlike the acetonitrile-acetamido complex **3a**, which cannot be prepared in pure form due to contamination by a small amount of **2a**, the benzonitrile-benzamido complex $TpRu(PPh_3)(PhCN)(NHC(O)Ph)$ (**3b**) can be readily synthesized in pure form by reacting **2b** with excess benzonitrile at room temperature in THF. The ^{1}H NMR spectrum of **3b** shows the N−H as a slightly broadened singlet at δ 5.03 ppm. The carbonyl carbon appears at a singlet at δ 178.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum, while the triphenylphosphine shows up as a singlet at δ 57.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The IR spectrum (KBr) of this complex shows the C=O, C≡N, and N−H stretchings, respectively, at 1602, 2238, and 3359 cm^{-1}.

NMR Monitoring of $TpRu(PPh_3)(H_2O)(NHC(O)Ph)$ (2b)-Catalyzed Hydration of Benzonitrile. A **2b**-catalyzed hydration reaction of benzonitrile (in 1,4-dioxane-d_8) was monitored by NMR spectroscopy. Benzonitrile (25 equiv) and water (180 equiv) were added to a 1,4-dioxane-d_8 solution of **2b** in a pressure-valved NMR tube, which was then pressurized with Ar (10 atm); the $^{31}P\{^1H\}$ NMR spectrum of the solution immediately taken showed that **2b** was completely converted to a new species corresponding to a singlet at δ 54.3 ppm (Figure 2). The new species is the benzonitrile-benzamido complex $TpRu(PPh_3)(PhCN)(NHC(O)Ph)$ (**3b**). After heating the solution at 75 °C in the probe for 15 min, the $^{31}P\{^1H\}$ NMR spectrum taken at this temperature showed a new and small singlet at δ 59.5 ppm, and ^{1}H NMR spectroscopy indicated that a trace amount of hydration product benzamide was generated. The probe temperature was then raised to 105 °C, and after 35 min, 40% of product (based on the benzonitrile added) was formed. $^{31}P\{^1H\}$ NMR spectroscopy indicated that **3b** completely changed to a species corresponding to a singlet at δ 59.5 ppm. This signal was due to the *N*-imidoylimidato complex $TpRu(PPh_3)(\kappa^2$-*N,O*-NH=CPhN=CPhO) (**4b**), which was later synthesized independently and characterized by X-ray crystallography. The solution was then heated for a further 240 min at 120 °C, at the end of this period the conversion of benzonitrile to

(15) The X-ray molecular structure, crystal data, refinement details, and bond distances and angles of **2b** can be found in the Supporting Information.

(16) Yi, C. S.; He, Z.; Guzei, I. A. *Organometallics* **2001**, *20*, 3641.

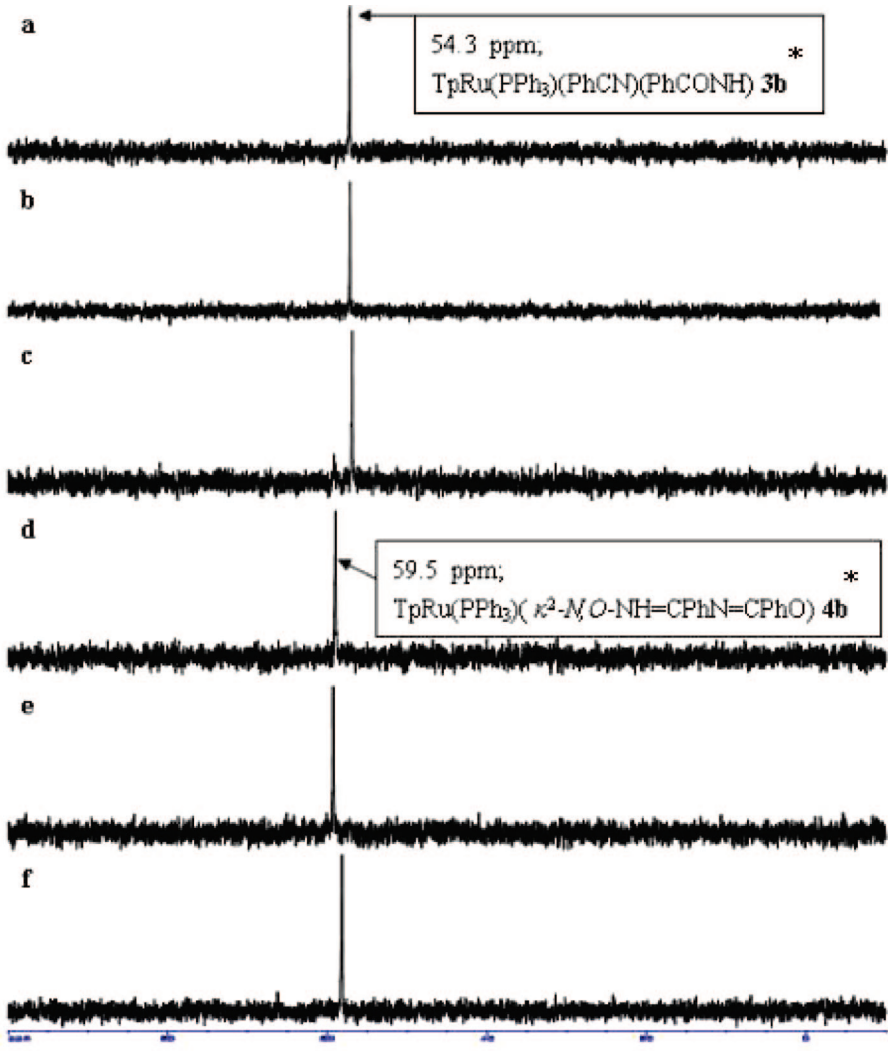


Figure 2. ^{31}P NMR study of **2b**-catalyzed hydration of benzonitrile: (a) immediately after addition of substrate and water at room temperature; (b) 50 °C for 15 min; (c) 75 °C for 15 min; (d) 105 °C for 35 min; (e) 120 °C for 30 min; (f) 120 °C for 210 min. ^{31}P{^{1}H} NMR spectra were taken at the temperature indicated. *The chemical shifts of **3b** and **4b** in the presence of water and nitrile are slightly different from those of the authentic samples taken in 1,4-dioxane-d_8.

benzamide was 44%, and **4b** remained the only detectable species by ^{31}P{^{1}H} NMR spectroscopy.

Synthesis and X-ray Crystallographic Study of TpRu(PPh$_3$)(κ^2-*N*,*O*-NH=CPhN=CPhO) (4b). Analogous to **4a**, complex **4b** was synthesized by reacting TpRu(PPh$_3$)(H$_2$O)(NHC(O)Ph) (**2b**) with benzonitrile in 1,4-dioxane at elevated temperature. Crystals of **4b** suitable for X-ray diffraction study were obtained by layering hexane on a CH_2Cl_2 solution of the complex. Figure 3 shows the molecular structure of **4b**. The crystal data and refinement details are given in Table 3. Selected bond distances and angles are listed in Table 4.

The determination of the structure of **4b** deserves some comments. Similar to **4a**, **4b** was first thought to be the benzamide-benzamido complex TpRu(PPh$_3$)(NH$_2$C(O)Ph)(NHC(O)Ph), but initial X-ray structural refinement gave a reasonably good structure **A** (Chart 2) containing a κ^2-*N,N* chelate ligand instead of the benzamide-benzamido structure. It seems that the κ^2-*N,N* chelate ligand might have been formed in a straightforward manner via nucleophilic attack of the benzamido ligand at the carbon center of the bound benzonitrile (Scheme 5).

However, when we later carried out density functional theory calculations to elucidate the mechanism of the **2a**-catalyzed hydration of nitriles, it was learned that **A′**, the methyl analogue of **A** (Chart 2), is a highly unstable species; it lies 21.6 kcal/mol higher in electronic energy than **2a** + MeCN. This finding is in sharp contrast to the NMR study described above, which clearly indicated that **4a** or **4b** is the most stable species observed in the course of the **2a**- or **2b**-catalyzed hydration of nitrile. Such a serious disagreement between the DFT calculations and the experimental NMR results is quite unexpected. We therefore suspected that we might have taken a nitrogen atom for an oxygen atom and vice versa in the initial X-ray crystallography analysis and therefore interchanged the iminato nitrogen with the oxygen atom. With this N/O exchange, X-ray structure refinement gave a good structure for **4b**, shown in Figure 3. DFT calculations also show that **4a**, the methyl analogue of **4b**, is a very stable structure, being 5.6 kcal/mol (electronic energy) more stable than **2a** + MeCN. Taking a nitrogen atom for an oxygen atom and vice versa is not uncommon in X-ray crystallography analysis. This part of our work represents a very good example demonstrating that computational chemists might be of great help to their experimental counterparts in structure elucidation. Apparently, at elevated temperature, the N-bound benzamido ligand changes its bonding mode to become an O-bonded imido ligand; nucleophilic attack at the carbon atom

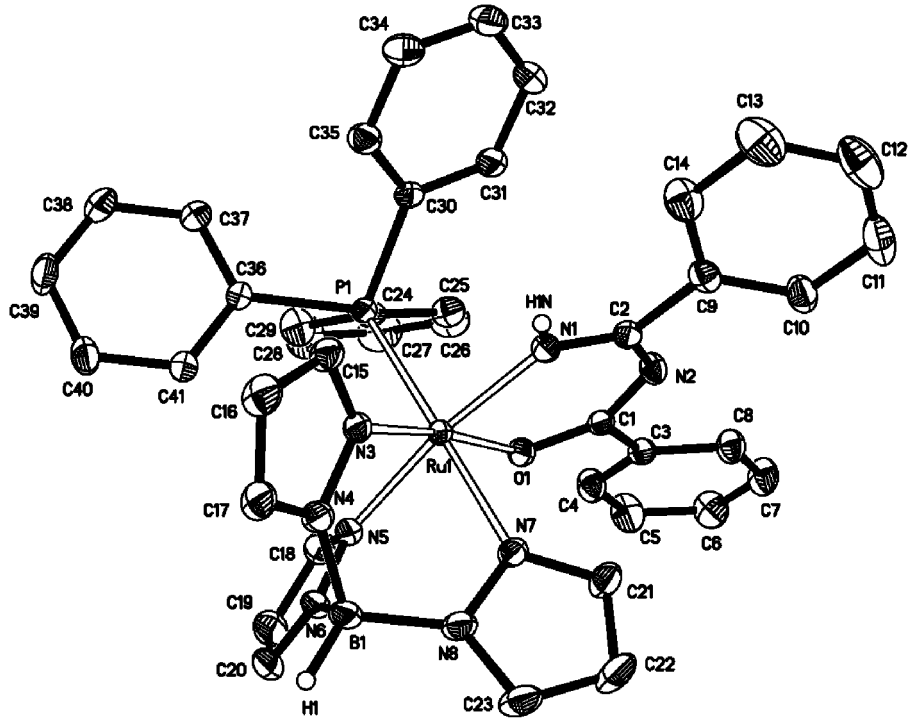


Figure 3. Molecular structure of TpRu(PPh$_3$)(κ^2-*N,O*-NH═CPhN═CPhO) (**4b**).

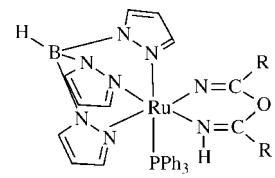
Table 3. Crystal Data and Structure Refinement for 4b

empirical formula	$Ru(C_2ON_2Ph_2)(PPh_3)(C_9H_9N_6BH).C_6H_{14}$
fw	885.8
temperature	296(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 9.7128(3) Å, α = 90°
	b = 22.7762(8) Å, β = 94.3970(10)°
	c = 19.9220(7) Å, γ = 90°
volume	4394.2(3) Å^3
Z	4
density (calcd)	1.339 g/cm^3
absorp coeff	0.439 mm^{-1}
F(000)	1840
cryst size	0.40 × 0.32 × 0.18 mm^3
θ range for data collection	2.05 to 27.66°
index ranges	$-12 \le h \le 12$, $-29 \le k \le 29$, $-26 \le l \le 25$
no. of reflns collected	101 213
no. of indep reflns	10 224 [R(int) = 0.0596]
completeness to θ = 27.55°	99.8%
absorp corr	none
max. and min. transmn	1.000 and 0.770
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	10 224/0/536
goodness-of-fit on F^2	1.002
final R indices [$I > 2\sigma(I)$]	R1 = 0.0453, wR2 = 0.1044
R indices (all data)	R1 = 0.0625, wR2 = 0.1183
largest diff peak and hole	0.484 and −0.555 e Å^{-3}

Table 4. Selected Bond Distances and Bond Angles for 4b

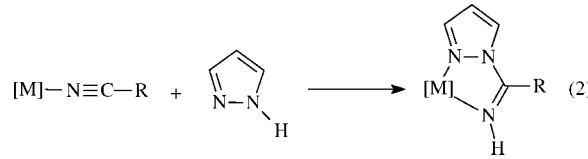
Bond Distances (Å)			
Ru(1)−N(1)	2.0178(19)	Ru(1)−N(3)	2.0654(19)
Ru(1)−N(5)	2.081(2)	Ru(1)−N(7)	2.127(2)
Ru(1)−O(1)	2.0461(16)	C(1)−O(1)	1.276(3)
C(1)−N(2)	1.330(3)	C(2)−N(2)	1.359(3)
N(1)−C(2)	1.291(3)	N(1)−H(1N)	0.6226
Bond Angles (deg)			
N(1)−Ru(1)−O(1)	87.59(7)	N(1)−Ru(1)−N(3)	92.92(8)
O(1)−Ru(1)−N(5)	89.35(7)	N(3)−Ru(1)−N(5)	89.10(8)
N(1)−Ru(1)−N(7)	86.71(8)	O(1)−Ru(1)−N(7)	87.26(7)
N(3)−Ru(1)−N(7)	85.20(8)	N(5)−Ru(1)−N(7)	85.43(8)
N(1)−Ru(1)−P(1)	93.58(6)	O(1)−Ru(1)−P(1)	93.36(5)
N(3)−Ru(1)- P(1)	94.18(6)	N(5)−Ru(1)−P(1)	94.31(6)
C(2)−N(1)−Ru(1)	127.16(17)	C(1)−O(1)−Ru(1)	125.22(16)
C(2)−N(1)−H(1N)	110.9	Ru(1)−N(1)−H(1N)	121.9
O(1)−C(1)−N(2)	129.4(2)	N(1)−C(2)−N(2)	126.6(2)
C(1)−N(2)−C(2)	123.7(2)		

Chart 2



A (R = Ph) **A'** (R = Me)

of the benzonitrile ligand followed by 1,3-proton shift results in the formation of **4b** (Scheme 6). The reaction of the O-bonded imido ligand with the coordinated benzonitrile to form the *N*-imidolylimidato chelate ligand in **4b** is similar to the addition of the N−H bond of a pyrazole across the coordinated nitrile C≡N bond to form a metal-ligated pyrazolylamidino group (eq 2).[17] The *N*-imidolylimidato ligands in **4a** and **4b** are isoelectronic with acetylacetonate and 3-azapentane-2,4-diiminate anions[18] (Chart 3). Aromaticity of the chelate rings in **4a** and **4b** imparts high stability to the complexes.

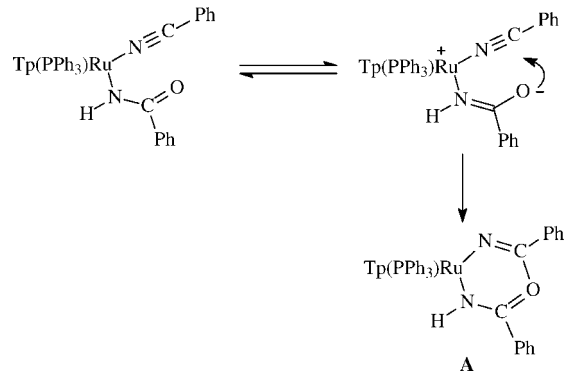


(2)

The *N*-imidolylimidato chelate ring in **4b** (Figure 3) is basically planar. The six atoms of the ring deviate within 0.012

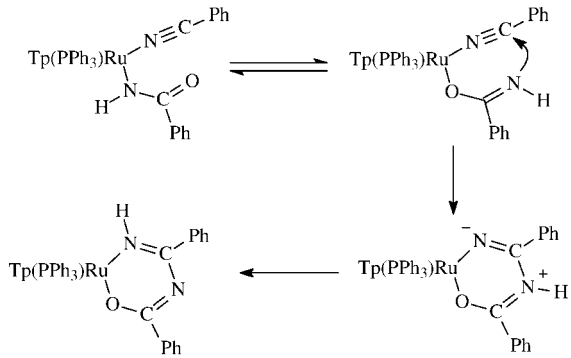
(17) Arroyo, M.; Miguel, D.; Villafañe, F.; Nieto, S.; Pérez, J.; Riera, L. *Inorg. Chem.* **2006**, *45*, 7018.

Scheme 5



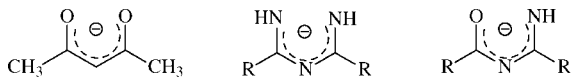
A

Scheme 6



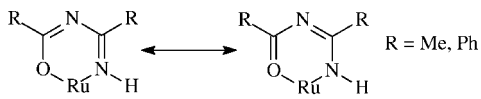
4b

Chart 3



Acetylacetonate 3-azapentane-2,4-diiminate *N*-imidolylimidate

Chart 4



N-imidoylimidate *N*-acylamidinate

Å from the best plane. The three C−N bonds in the chelate ring are longer than the normal C=N double bond and shorter than the normal C−N single bond, while the C−O bond distance falls between normal C−O single and C=O double bonds.[19] Hence π-bond delocalization is present in the ring. In other words, the two limiting structures, *N*-imidoylimidate and *N*-acylamidinate (Chart 4), contribute to the bond lengths in the chelate ring. The N(1)−C(2) bond distance (1.291(3) Å) is shorter than that of N(2)−C(1) (1.330(3) Å) and significantly shorter than the N(2)−C(2) bond length (1.359(3) Å).

Reports on molecular structures of *N*-imidoylimidato complexes are rare; in fact, there is only one report in the literature describing the X-ray structures of two *N*-imidoylimidato complexes RuCl(κ^2-*N*,*O*-NH=CMeN=CMeO)(CO)(PPh_3)$_2$ and RuCl(κ^2-*N*,*O*-NH=CMeN=CMeO)(CO)(PPh_3)$_2$.[20] The C−N bond distances in the chelate ring of **4b** are comparable to the corresponding C−N bond distances in the chelate rings of the two reported *N*-imidoylimidatoruthenium complexes. The O(1)−C(1) bond distance (1.276(3) Å) in the ring of **4b** is slightly shorter than that (1.284(8) Å) in the chelate ligand of RuCl(κ^2-*N*,*O*-NH=CMeN=CMeO)(CO)(PPh_3)$_2$, but slightly longer than the corresponding bond length in RuCl(κ^2-*N*,*O*-NH=CMeN=CMeO)(CO)(PPh_3)$_2$.

Synthesis of TpRu(PPh_3)(κ^2-*N*,*O*-NH=CMeN=CPhO) (4c). The unsymmetrical *N*-imidoylimidato complex **4c** was prepared by reacting TpRu(PPh_3)(H_2O)(NHC(O)Ph) (**2b**) with acetonitrile in 1,4-dioxane at elevated temperature and was characterized by NMR and IR spectroscopies. The proton NMR signal of N−H is difficult to identify, it is probably masked by the peaks of the Tp ligand and the aromatic signals of the phosphine ligand; the methyl signal appears as a singlet at 2.13 ppm in the ^{1}H NMR spectrum. The ^{31}P{^{1}H} spectrum shows a singlet at δ 59.1 ppm, corresponding to the phosphine ligand of **4c**. The two imino carbons (C=N) of the *N*-imidoylimidato ligand appear as two singlets at δ 168.72 and 170.37 ppm in the ^{13}C{^{1}H} NMR spectrum. The IR spectrum (KBr) of this complex shows the stretching frequencies of the two C=N bonds at 1671 and 1973 cm^{-1}. The N−H stretching can be observed at 3305 cm^{-1}. Mass spectroscopy shows the parent peak at *m*/*z* 738.09. Unfortunately, we have not been able to grow single crystals of **4c** for X-ray crystallographic study.

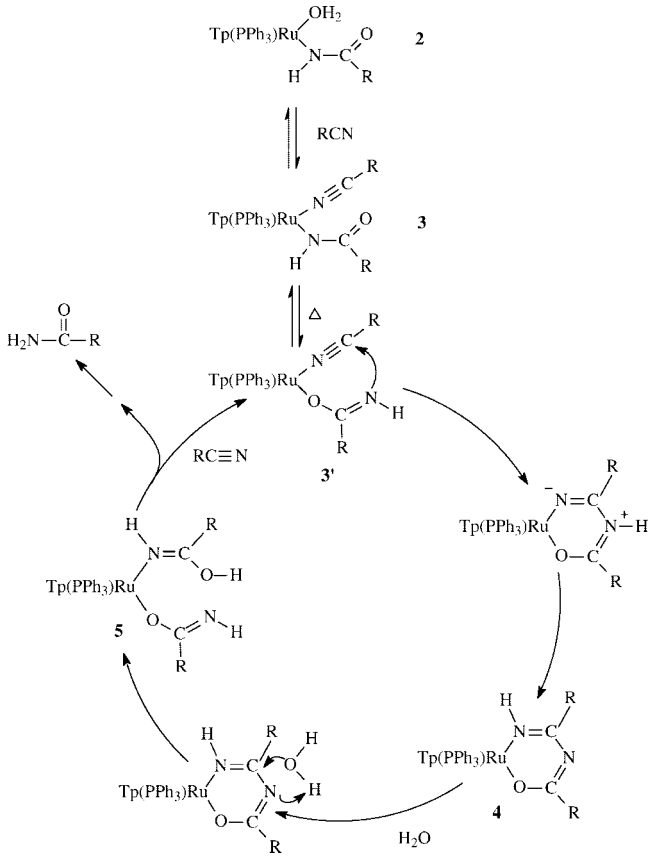
Proposed Mechanism for the Catalytic Hydration of Nitriles to Amides. Taking into account the results of the NMR-monitored catalytic reactions shown in Figures 1 and 2, we propose a mechanism for the catalytic hydration of nitriles to amides with the aquo-amido complex (Scheme 7). It is interesting to note that unlike many known catalytic systems for hydration of nitriles to amides in which the product-generating step is internal protonation of the amido ligand by an adjacent aquo ligand,[2] the aquo-amido complexes **2a** and **2b** are very stable species; the coordinated water in **2a** or **2b** does not protonate the amido ligand but is involved in intra- and intermolecular hydrogen-bonding interactions with it. The reaction begins with displacement of the aquo ligand in the aquo-amido complex **2** by the nitrile to form the nitrile-amido complex **3**. At elevated temperatures, the N-bonded amido ligand of **3** isomerizes to the O-bonded imido ligand, forming **3**. It is quite surprising that this linkage-isomerization would occur since the N-bonded imido ligand should be a better match with the metal center than the O-bonded imido from the HSAB point of view. Nucleophilic attack of the imido nitrogen at the carbon center of the coordinated nitrile and subsequent proton shift leads to the formation of the *N*-imidoylimido complex **4**, which is the most stable species in the catalytic cycle. Attack of water at the carbon center between the two nitrogen atoms in the *N*-imidoylimido ligand breaks the C−N bond and opens the ring, and subsequent protonation of the nitrogen atom results in the generation of the amido-iminol intermediate **5**. The cycle is completed by ligand exchange of the iminol molecule with a substrate nitrile molecule and subsequent tautormerization of the iminol to the product amide or tautormerization of the iminol ligand (in **5**) to an amide ligand and subsequent ligand exchange

(18) (a) Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1994**, *3615*. (b) Robinson, V.; Taylor, G. E.; Woodward, P.; Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Dalton Trans.* **1981**, *1169*. (c) Green, M.; Taylor, S. H.; Daly, J. J.; Sanz, F. *J. Chem. Soc., Chem. Commun.* **1974**, *361*.

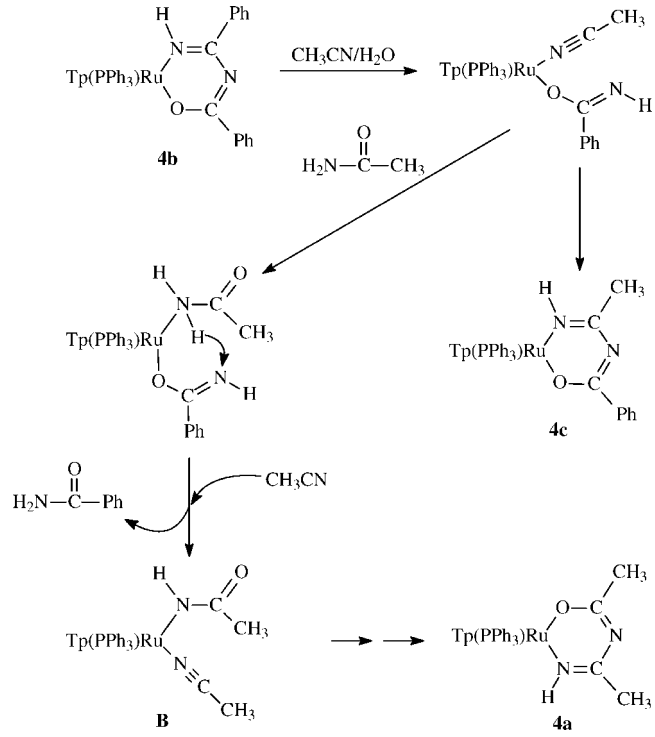
(19) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, *S1*.

(20) Hiraki, K.; Kinoshita, Y.; Kinoshita-Kawashima, J.; Kawano, H. *J. Chem. Soc., Dalton Trans.* **1996**, *291*.

Scheme 7



Scheme 8



of the latter with a substrate nitrile molecule.[21] Independently prepared *N*-imidoylimido complex **4a** has been found to exhibit catalytic activity in nitrile hydration basically identical to that of $TpRu(PPh_3)(H_2O)(NHC(O)CH_3)$ (**2a**) (Table 2, entries 11 and 12). It is worth pointing out $RuCl(\kappa^2\text{-}N,O\text{-}NH{=}CRN{=}CR'O)(CO)(PPh_3)_2$ (R, R′ = aromatic groups), the only *N*-imidoylimido complexes reported to date, do not catalyze the hydration of nitrile.[20]

Side reactions might also occur outside the catalytic cycle, as demonstrated by an experiment using $TpRu(PPh_3)(\kappa^2\text{-}N,O\text{-}NH{=}CPhN{=}CPhO)$ (**4b**) as catalyst for the hydration of acetonitrile. The reaction was carried out in a NMR tube in 1,4-dioxane at 100 °C with 25 and 100 equiv of acetonitrile and water, respectively, to give product conversion of 44% after 24 h; at the end of the reaction, it was found by $^{31}P\{^1H\}$ NMR spectroscopy that **4b** was partially converted to $TpRu(PPh_3)(\kappa^2\text{-}N,O\text{-}NH{=}CMeN{=}CPhO)$ (**4c**) and $TpRu(PPh_3)(\kappa^2\text{-}N,O\text{-}NH{=}CMeN{=}CMeO)$ (**4a**). The three *N*-imidoylimido complexes **4b**, **4c**, and **4a** were present in a 1:2:1 ratio. The conversion of **4b** to **4c** and **4a** can probably be accounted for by the reaction sequence depicted in Scheme 8. The hydration product acetamide can attach to the metal center. Transfer of one of its NH_2 protons to the O-bonded imido ligand and subsequent ligand displacement would generate the acetonitrile-acetamide species **B**, which would form **4a** via N-bond amido/O-bonded imido isomerization and subsequent cyclization.

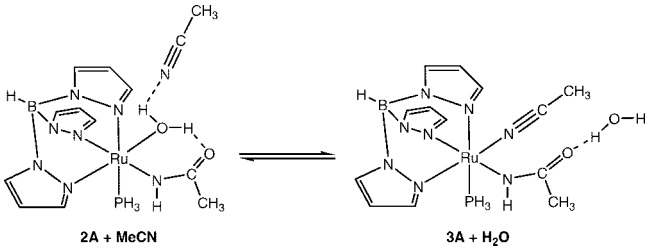
Computational Study. To study the feasibility of the proposed reaction mechanism shown in Scheme 7 for the catalytic hydration of nitriles to amides, theoretical calculations were performed at the Becke3LYP level of DFT theory to examine the whole catalytic cycle for R = CH_3. To reduce the computer cost, PH_3 was used to model PPh_3 in our calculations. The errors incurred from the simplification in the phosphine ligand are expected to be small because the phosphine ligand is present in every species calculated and only the relative energies among the different species calculated are important in our discussion. This is indeed supported by our additional calculations using PPh_3 as the ligand. When PH_3 was used as the model ligand, the electronic energy difference between $TpRu(PH_3)(CH_3CN)(NHC(O)CH_3)$ (a model complex of **3a**) and $TpRu(PH_3)(\kappa^2\text{-}N,O\text{-}NH{=}CMeN{=}CMeO)$ (a model complex of **4a**) was calculated to be 16.5 kcal/mol. When PPh_3 was used as the ligand and Ph instead of Me as the substitutents, the energy difference between $TpRu(PPh_3)(PhCN)(NHC(O)Ph)$ and $TpRu(PPh_3)(\kappa^2\text{-}N,O\text{-}NH{=}CPhN{=}CPhO)$ was calculated to be 17.4 kcal/mol.

Experiments described above show that the addition of acetonitrile and water to the 1,4-dioxane solution of **2a** led to an equilibrium between **2a** and **3a** at room temperature in the experiments. We first investigated the relative stability of complexes **2a** and **3a**. Considering the coexistence of acetonitrile, water, and complexes in the solution, it is necessary to add acetonitrile to **2a** and water to **3a** for addressing the important hydrogen bonding in the calculations. The calculation results reveal that the electronic energy difference between **2A**, a model complex of **2a**, with acetonitrile and **3A**, a model complex of **3a**, with water is only 0.1 kcal/mol (Scheme 9), consistent with the experimental observation that the ratio **2a**:**3a** is ~1:1.

The energetics related to the proposed reaction sequence shown in Scheme 7 is illustrated in Figure 4. Selected optimized

(21) A reviewer suggests that **3′** might be hydrolyzed directly by water to form **5**, an equilibrium is established between **5** and **4**, and the latter lies outside the catalytic cycle. We think this mechanism is unlikely. Our calculations show that conversion of **3′** to **4** has a very low barrier (6.4 kcal/mol, see Figure 4). On the other hand, direct hydrolysis of the coordinated nitrile in **3′** is expected to have a much higher energy barrier. Our previous study (see Scheme 4 and ref 14) shows that even with the assistance of strong Ru-H···H-OH dihydrogen bonding interaction in the transition state and the formation of a relatively stable η^2-dihydrogen intermediate, the barrier of direct hydrolysis of the nitrile ligand in the TpRu complex is quite high (31.95 kcal/mol).

Scheme 9



structural parameters of the species involved in the reaction sequence are shown in Figure 5. As expected, the energy barrier of 28.9 kcal/mol for isomerization of N-bonded amido-coordinated **3A** to O-bonded imido-coordinated **3A′** is relatively high, consistent with an elevated temperature being needed in the experiments. **3A′**, which corresponds to the active species in the catalytic cycle (Scheme 7), is energetically located at 8.0 kcal/mol above **3A**. Nucleophilic attack of the imido nitrogen at the carbon center of the coordinated nitrile in **3A′** to form a cyclic complex **4A′** needs to overcome an energy barrier of only 6.4 kcal/mol. Although **4A′** is energetically more stable than **3A′**, it is a zwitterionic species. A subsequent 1,3-proton shift could occur easily with the aid of water molecules,[22] leading to the formation of the complex **4A** (a model complex for **4a**). Along with the isomerization of **4A′** to **4A**, a good π-conjugated system is formed in the *N*-imidoylimido ligand, making **4A** the most stable species in the catalytic cycle. Comparison of the structural parameters obtained from calculations for **4A** and experiments for **4b** (the X-ray structure of **4a** is not available) (Figure 5) reveals that the calculated structure reproduces well the experimental one.

The hydrolysis of **4A** starts from attack of water at the carbon center between the two nitrogen atoms in the *N*-imidoylimido ligand and finishes with the breaking of C−N bond, resulting in the generation of the amido-iminol intermediate **5A**, which is slightly more unstable than **4A′**. **5A** can then undergo an enol-to-keto tautomerization to give energetically more stable amido-amide intermediate **5A′**. We did not calculate the barriers for the hydrolysis and enol-to-keto tautomerization processes involved. Enol-to-keto tautomerization processes are commonly found in organic chemistry and are believed to have very small barriers in solution.[23] Calculations of the hydrolysis and tautomerization processes are difficult computationally because solvation, which influences significantly the proton transfer processes, needs to be considered.

In **5A′**, the hydration product molecule, acetamide (NH_2-$C(O)CH_3$), acts as a ligand. It can easily dissociate from **5A′** to form a 16e metal fragment that takes an acetonitrile (CH_3CN) to regenerate **3A′**, completing the catalytic circle. We calculated the dissociation barrier roughly by fixing the distances between the Ru atom and the O and N atoms of acetamide both to 5.0 Å in the calculations. The barrier is evaluated to be 10.9 kcal/mol. Moreover, the free energy increases by only 4.8 kcal/mol for the ligand exchange process, indicating that the ligand exchange can occur.

The computational results indicate that the formation of the highly stable intermediate **4A** and a substantially high barrier for the hydrolysis step to regenerate the active species **3A′** hinder the catalytic reactions.

Conclusions

Previous works on kinetic and mechanistic studies on transition-metal-catalyzed hydration of nitriles in the literature illustrate that intramolecular or external nucleophilic hydroxo attack at the carbon atom of the η^1-coordinated nitrile molecule gives the metal amide intermediate, and subsequent protonation of the amido ligand by an adjacent aquo ligand generates the product.[2] We have, however, in this work, shown that the aquo-amido complexes **2a** and **2b** that we employ for study of nitrile hydration are stable toward intramolecular protonation of the amido ligand by the aquo ligand; instead, displacement of the aquo ligand in **2a** or **2b** by a nitrile molecule and N-amido/O-imido linkage isomerization starts the catalytic cycle of nitrile hydration. Our work demonstrates that catalytic hydration of nitriles with **2a** or **2b** proceeds via a unique mechanism involving the intermediacy of a relatively stable complex containing a chelating *N*-imidoylimidato ligand, and ring-opening nucleophilic attack of this ligand by water generates the product. Moreover, our work also represents one of the few examples of detailed theoretical investigation of the mechanism of nitrile hydration with homogeneous organometallic systems.[24]

Experimental Section

Ruthenium trichloride, $RuCl_3 \cdot 3H_2O$, pyrazole, sodium borohydride, triphenylphosphine, and organic substrates were obtained from Aldrich, International Laboratory, and Acros. Triphenylphosphine was recrystallized from ethanol before use. Solvents were distilled under a dry nitrogen atmosphere with appropriate drying agents: hexane, diethyl ether, tetrahydrofuran, and 1,4-dioxane with sodium benzophenone; dichloromethane, acetonitrile, and chloroform with calcium hydride. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The complexes $TpRu(PPh_3)(CH_3CN)H$,[25] $TpRu(PPh_3)(CH_3CN)Cl$,[25] and $TpRu(PPh_3)_2Cl$[26] were prepared according to literature methods. Deuterated NMR solvents, purchased from Armar and Cambrigde Isotope Laboratories, were dried with P_2O_5. High-purity argon gas was supplied by Hong Kong Oxygen.

Proton NMR spectra were obtained from a Bruker DPX 400 spectrometer. Chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 MHz, and chemical shifts were externally referenced to 85% H_3PO_4 in D_2O. $^{13}C\{^1H\}$ NMR spectra were taken on a Bruker DPX 400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to C_6D_6 (δ = 128.1 ppm) and 1,4-dioxane-d_8 (δ = 67.16 ppm). High-pressure NMR studies were carried out in commercial 5 mm Wilmad pressure-valved NMR tubes. Infrared spectra were obtained from a Bruker Vector 22 FT-IR spectrophotometer. Electrospray ionization mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer with the samples dissolved in dichloromethane. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

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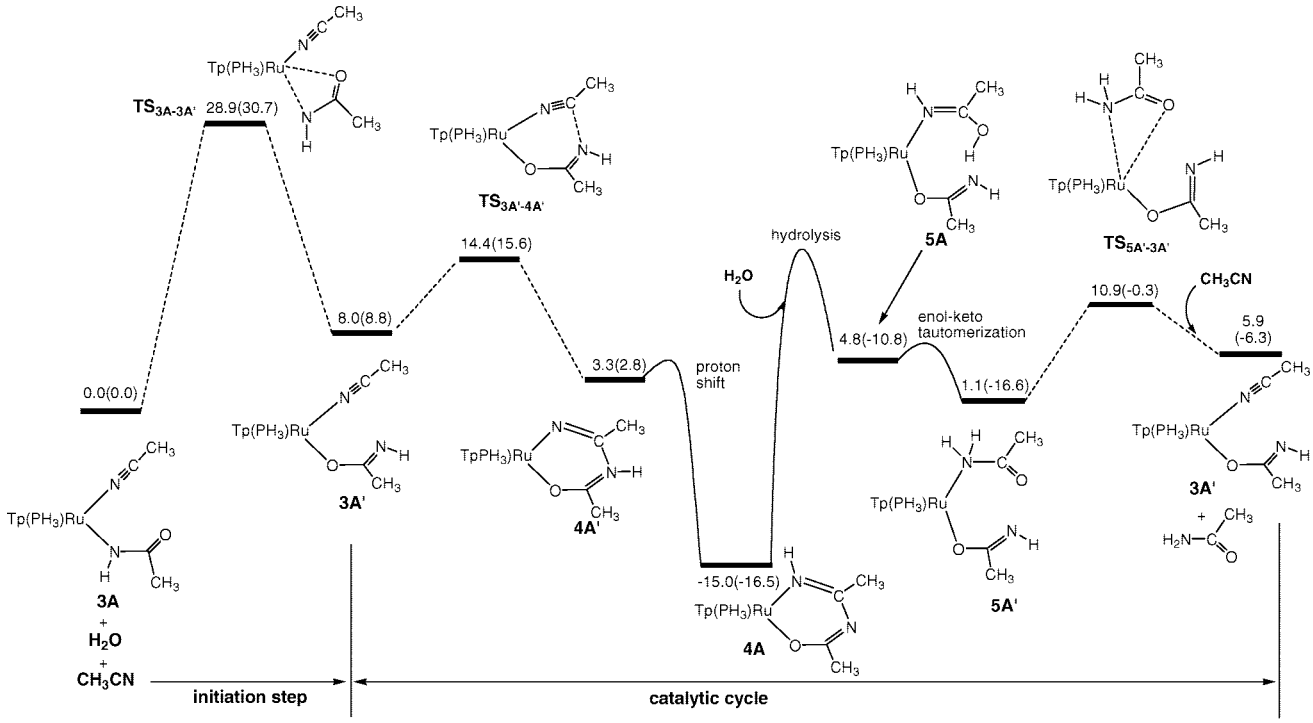

Figure 4. Energy profile for the reaction sequence shown in Scheme 6. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

Alternative Method for Synthesis of TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (2a). The complex TpRu(PPh$_3$)(CH$_3$CN)Cl (0.20 g, 0.31 mmol) and NaOH (0.018 g, 1.5 equiv) were loaded into a two-necked round-bottom flask, which was then evacuated and flushed with nitrogen for four cycles. Freshly distilled THF (20 mL) and water (0.1 mL) were added to the flask, and the resulting solution was refluxed with stirring for 24 h. The solution was cooled to room temperature, the volume of which was reduced to 6 mL in vacuo, and 5 mL of hexane was added. The mixture was filtered to remove some insoluble solids; the filtrate was brought to dryness in vacuo to afford a yellow solid. The solid was recrystallized with dichloromethane and diethyl ether; it was collected and dried under vacuum for several hours at room temperature. Yield: 0.13 g (66%). Anal. Calcd (%) for C$_{29}$H$_{31}$BN$_7$O$_2$PRu: C 53.39, H 4.79, N 15.03. Found: C 53.31, H 4.81, N 15.09. IR (KBr): ν(C=O) = 1540 (m), ν(N−H) = 3337 (m), ν(B−H) = 2461 (m). ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 25 °C): δ 2.05 (s, 3H; C*H*$_3$C(O)NH), 4.67 (s, 1H; CH$_3$C(O)N*H*), 5.93 (t, 1H of Tp), 5.97 (t, 1H of Tp), 6.28 (t, 1H of Tp), 6.87 (d, 1H of Tp), 7.29 (d, 1H of Tp), 7.78 (d, 1H of Tp), 7.85 (d, 2H of Tp), 8.24 (d, 1H of Tp) (all coupling constants for Tp proton resonances are about 2 Hz), 7.24−7.68 ppm (2 multiplets, 15H of PPh$_3$). ^{31}P{^{1}H} NMR (161.7 MHz, 1,4-dioxane-d_8 25 °C): δ 59.3 (s). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 25 °C): δ 181.2 (s, CH$_3$*C*(O)NH), 25.7 (s, *C*H$_3$C(O)NH). ESI-MS (CH$_2$Cl$_2$): *m*/*z*: 635 [M − H$_2$O]$^+$.

In Situ Preparation of TpRu(PPh$_3$)(NCCH$_3$)(NHC(O)CH$_3$) (3a). Acetronitrile (45 μL, 86 mmol) was added to a solution of TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (**2a**) (5.0 mg, 7.7 μmol) in 0.4 mL of 1,4-dioxane-d_8 in a 5 mm NMR tube. The NMR tube was allowed to stand at room temperature for 3 h. An ^{1}H NMR spectrum of the solution was taken. Two sets of Tp signals (signal intensity ratio is over 9:1) in the low-field region are visible in the spectrum; the set with higher signal intensity is due to **3a** and the set with smaller signal intensity is due to **2a**. Complex **3a** was characterized in situ by NMR spectroscopy: ^{1}H NMR (400.13 MHz, 1,4-dioxane-d_8, 25 °C): δ 1.73 (s, 3H; C*H*$_3$C(O)NH), 2.05 (s, 1H; C*H*$_3$CN), 3.22 (s, 1H; CH$_3$C(O)N*H*), 5.92 (t, 1H of Tp), 5.93 (t, 1H of Tp), 6.22 (t, 1H of Tp), 6.71 (d, 1H of Tp), 6.83 (d, 1H of Tp), 7.68 (d, 1H of Tp), 7.78 (d, 1H of Tp), 7.82 (d, 1H of Tp), 7.95 (d, 1H of Tp) (all coupling constants for Tp proton resonances are about 2 Hz), 7.19−7.31 (m, 15H of PPh$_3$). ^{31}P{^{1}H} NMR (161.7 MHz, 1,4-dioxane-d_8, 25 °C): δ 58.8 (s). ^{13}C{^{1}H} NMR (100.61 MHz, 1,4-dioxane-d_8, 25 °C): δ 178.85 (s, CH$_3$*C*(O)NH).

Synthesis of TpRu(PPh$_3$)(κ^2-*N*,*O*-NH=CMeN=CMeO) (4a). A sample of TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (**2a**) (70 mg, 0.11 mmol) was loaded into a 11 mm tube with a Teflon screw cap, which was then evacuated and flushed with nitrogen for four cycles. Acetonitrile (0.56 mL, 100 equiv) and 1,4-dioxane (3 mL) were then added to the tube via syringes. The tube was heated in a 150 °C oil bath overnight. The solution was cooled and transferred to a 25 mL two-neck flask; the solvent of the solution was removed by vacuum. Hexane (3 mL) was added to the residual paste with vigorous stirring to produce a pale yellow complex. It was collected and dried under vacuum for several hours at room temperature. Yield: 25 mg (34%). Anal. Calcd (%) for C$_{31}$H$_{32}$BN$_8$OPRu: C 55.12, H 4.77, N 16.59. Found: C 55.08, H 4.71, N 16.51. IR (KBr): ν(C=N) = 1578, 1654 (m), ν(N−H) = 3382 (m), ν(B−H) = 2478 (m). ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 25 °C): δ 2.06 (s, 3H; NH=CC*H*$_3$N=CCH$_3$O), 2.47 (s, 1H; NH=CCH$_3$N=CC*H*$_3$O), 5.98 (t, 1H of Tp), 6.03 (t, 1H of Tp), 6.23 (t, 1H of Tp), 6.92 (d, 1H of Tp), 7.00 (s, 1H, N *H*), 7.75 (d, 1H of Tp), 7.81 (d, 1H of Tp), 7.86 (d, 1H of Tp), 7.88 (d, 1H of Tp), 7.89 (d, 1H of Tp) (all coupling constants for Tp proton resonances are about 2 Hz), 7.22 (m, 10H of PPh$_3$), 7.58 (m, 5H of PPh$_3$). ^{31}P{^{1}H} NMR (161.7 MHz, C$_6$D$_6$, 25 °C): δ 60.0 (s). ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 25-C): δ 176.1, 168.1 (s, NH=*C*MeN=*C*MeO). ESI-MS [M$^+$] = 676.35.

Synthesis of TpRu(PPh$_3$)(PhCN)(Cl). A sample of TpRu(PPh$_3$)$_2$Cl (0.55 g, 0.63 mmol) was loaded into a two-necked round-bottom flask, which was then evacuated and flushed with nitrogen for four cycles. Freshly distilled THF (15 mL) and benzonitrile (0.15 mL) were added into the flask. The mixture was refluxed for 3 h. The solvent was then removed in vacuo to afford an orange paste. Hexane (5 mL) was added to the residue, with stirring, to produce a yellow solid. The solid was collected and washed with hexane (3 × 5 mL); it was dried under vacuum for several hours at room temperature. Yield: 0.29 g (65%). Anal. Calcd (%) for

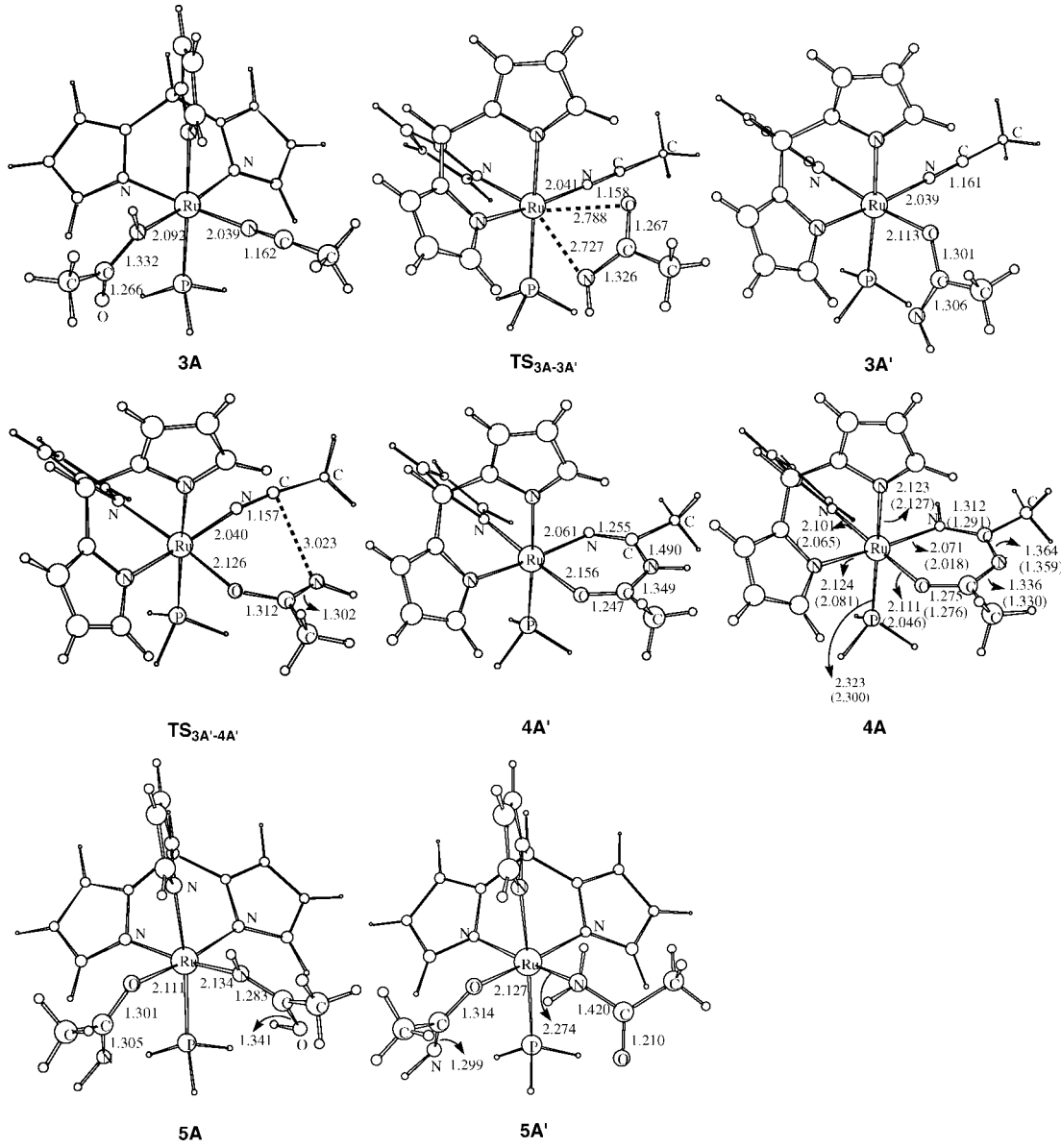

Figure 5. Selected optimized structural parameters calculated for the species involved in the reaction sequence shown in Figure 4 and Scheme 6. Bond lengths are given in Å. Experimental data of **4b** are shown in parentheses.

$C_{34}H_{30}BClN_7PRu$: C 57.12, H 4.23, N 13.71. Found: C 57.05, H 4.21, N 13.09. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25 °C): δ 5.75 (t, 1H of Tp), 5.85 (t, 1H of Tp), 6.23 (t, 1H of Tp), 6.61 (d, 1H of Tp), 7.20 (d, 1H of Tp), 7.64 (d, 2H of Tp), 7.68 (d, 1H of Tp), 8.11 (d, 1H of Tp) (all coupling constants for Tp proton resonances are about 2 Hz), 6.96−7.37 (m, 15H of PPh_3 and m, 5H of PhCN). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, 25 °C): δ 49.3 (s). ESI-MS [M^+] = 715.24.

Synthesis of TpRu(PPh$_3$)(H$_2$O)(NHC(O)Ph) (2b). Complex **2b** was prepared by using the same procedure as for the preparation of **2a** except that TpRu(PPh_3)(PhCN)Cl was used in place of TpRu(PPh_3)(CH_3CN)Cl. Yield: 86 mg (43%). Anal. Calcd (%) for $C_{34}H_{33}BN_7O_2PRu$: C 57.15, H 4.66, N 13.72. Found: C 56.98, H 4.72, N 13.73. IR (KBr): ν(C═O) = 1525 (m), ν(N−H) = 3354 (m), ν(B−H) = 2463 (m). ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 5.92 (s, 1H of N *H*), 5.96 (t, 1H of Tp), 5.99 (t, 1H of Tp), 6.16 (t, 1H of Tp), 6.91 (d, 1H of Tp), 7.31 (d, 1H of Tp), 7.75 (d, 1H of Tp), 8.01 (d, 2H of Tp), 8.21 (d, 1H of Tp), 7.32(d, 1H of phenyl ring of benzamido), 7.87 (m, 2H of phenyl ring of benzamido), 7.18, (m, 10H of PPh_3), 7.65 (m, 5H of PPh_3 and 2H of phenyl ring of benzamido). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, 25 °C): δ 58.8 (s). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 25 °C): δ 181.5 (s, Ph *C*(O)NH). ESI-MS [$M^+ - H_2O$] = 697.04.

Synthesis of TpRu(PPh$_3$)(NCPh)(NHC(O)Ph) (3b). A sample of TpRu(PPh_3)(H_2O)(NHC(O)Ph) (**2b**) (0.30 g, 0.42 mmol) was loaded into a 50 mL round-bottom flask, which was then evacuated and flushed with nitrogen for four cycles. Benzonitrile (81 μL; 2 equiv) and THF (3 mL) were added to the flask. The mixture was stirred overnight at room temperature. The solvent was then removed under vacuum to afford a yellow paste. Hexane (5 mL) was added to the residue, with stirring, to produce a yellow solid. The solid was collected and dried in vacuo. Yield: 0.22 g (65%). Anal. Calcd (%) for $C_{41}H_{36}BN_8OPRu$: C 61.58, H 4.54, N 14.01. Found: C 61.50, H 4.58, N 14.16. IR (KBr): ν(C═O) = 1602 (s), ν(C−N) = 2238 (m), ν(N−H) = 3359 (w), ν(B−H) = 2482 (m). ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ 5.03 (s, 1H of N *H*), 5.99 (t, 1H of Tp), 6.13 (t, 1H of Tp), 6.16 (t, 1H of Tp), 7.45 (d, 1H of Tp), 7.53 (d, 1H of Tp), 7.87 (d, 1H of Tp), 8.19 (d, 1H of Tp), 8.21 (d, 1H of Tp), 8.33 (d, 1H of Tp), 7.03 (m, 3H of phenyl ring of benznitrile), 7.75 (m, 2H of phenyl ring of benzamido), 7.21, (m, 10H of PPh_3), 7.91 (m, 5H of PPh_3 and 2H of phenyl ring of benzamido). ^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, 25 °C): δ 57.1 (s).

$^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ 178.4 (s, Ph *C*(O)NH). ESI-MS $[M^+] = 800.14$.

Synthesis of TpRu(PPh$_3$)(κ^2-*N*,*O*-NH=CPhN=CPhO) (4b). Complex **4b** was prepared by using the same procedure as for the preparation of **4a** except that TpRu(PPh$_3$)(H$_2$O)(NHC(O)Ph) (**2b**) and benzonitrile (3 equiv) were used instead of TpRu(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$) (**2a**) and acetonitrile (100 equiv). Yield: 44 mg (56%). Anal. Calcd (%) for $C_{41}H_{36}BN_8OPRu$: C 61.58, H 4.54, N 14.01. Found: C 61.42, H 4.51, N 13.92. IR (KBr): ν(C=N) = 1586, 1975 (m), ν(N−H) = 3320 (m), ν(B−H) = 2481 (m). ^1H NMR (400.13 MHz, C_6D_6, 25 °C): δ 5.96 (t, 1H of Tp), 6.06 (t, 1H of Tp), 6.09 (t, 1H of Tp), 7.03 (d, 1H of Tp), 7.07 (m, 10H of PPh$_3$), 7.49 (m, 5H of PPh$_3$ and 6H of phenyl rings of NH=CPhN=CPhO), 7.66 (d, 1H of Tp), 7.81 (dd, 2H of phenyl ring of NH=CPhN=CPhO), 7.92 (dd, 2H of phenyl ring of NH=CPhN=CPhO), 8.19 (d, 1H of Tp), 8.21 (d, 1H of Tp), 8.46 (s, 1H of N*H*), 8.89 (d, 1H of Tp), 8.91 (d, 1H of Tp). $^{31}P\{^1H\}$ NMR (161.7 MHz, C_6D_6, 25 °C): δ 57.6 (s). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ 165.7, 170.9 (s, NH=*C*PhN=*C*PhO). ESI-MS $[M^+] = 800.09$.

Synthesis of TpRu(PPh$_3$)(κ^2-*N*,*O*-NH=CMeN=CPhO) (4c). Complex **4c** was prepared by using the same procedure as for the preparation of **4b** except that acetonitrile (50 equiv) was used instead of benzonitrile (3 equiv). Yield: 29 mg (40%). Anal. Calcd (%) for $C_{36}H_{34}BN_8OPRu$: C 58.62, H 4.65, N 15.19. Found: C 58.14, H 4.80, N 15.12. IR (KBr): ν(C=N) = 1671, 1973 (m), ν(N−H) = 3305 (m), ν(B−H) = 2468 (m). ^1H NMR (400.13 MHz, C_6D_6, 25 °C): δ 2.13 (s, 3H of NH=CC*H*$_3$N=CPhO), 6.03 (t, 1H of Tp), 6.07 (t, 2H of Tp), 7.01 (d, 1H of Tp), 7.13 (m, 10H of PPh$_3$), 7.44 (m, 3H of phenyl ring of NH=CMeN=CPhO), 7.53 (m, 5H of PPh$_3$), 7.68 (d, 1H of Tp), 7.74 (d, 1H of Tp), 7.81 (d, 2H of Tp), 7.92 (m, 2H of phenyl ring of NH=CMeN=CPhO), 8.84 (d, 1H of Tp), 8.86 (d, 1H of Tp). $^{31}P\{^1H\}$ NMR (161.7 MHz, C_6D_6, 25 °C): δ 59.1 (s). $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 25 °C): δ 168.7, 170.4 (s, NH=*C*MeN=*C*PhO). ESI-MS $[M^+] = 738.09$.

General Procedure for Catalytic Hydration of Nitriles. The reactions were carried out in 5 mm pressure-valved NMR tubes. In a typical run, the catalyst (2.5 mg) was dissolved in a mixture of H$_2$O (0.14 mL, 2000 equiv), nitrile (0.04 mL, 200 equiv), and 1,4-dioxane (~0.2 mL). The tube was pressurized with 10 bar of argon and heated in a 150 °C silicon oil bath for 24 h. At the end of the reaction time, the tube was cooled to room temperature; a 0.1 mL aliquot of the solution was removed and analyzed by ^1H NMR spectroscopy (in $CDCl_3$). Comparison of the integrations of the characteristic peaks of the amide and the remaining nitrile gave the percent conversion of the reaction.

Monitoring of 1-Catalyzed Hydration of Acetonitrile with NMR Spectroscopy. A sample of **1** (2.7 mg) was loaded into a 5 mm pressure-valved NMR tube. The tube was evacuated and filled with nitrogen for three cycles. Acetonitrile (6 μL, 25 equiv), water (3 μL, 30 equiv), and 1,4-dioxane-d_8 (0.2 mL) were added via syringes. The resulting solution was heated at 90 °C under 10 bar of Ar. At different time intervals, the tube was cooled to room temperature and ^1H and ^{31}P NMR spectra of the solution were taken.

Monitoring of 2a- or 2b-Catalyzed Hydration of Acetonitrile and Benzonitrile with NMR Spectroscopy. Acetonitrile or benzonitrile (6 μL, 25 equiv) was added to a 5 mm pressure-valved NMR tube loaded with **2a** (2.5 mg) or **2b** (2.5 mg), respectively. Water (12 μL, 180 equiv) and 1,4-dioxane-d_8 (0.2 mL) were then added into the tube via syringes. The tube was heated inside the probe of the NMR spectrometer; ^1H and ^{31}P NMR spectra were collected at different temperatures (see Figures 1 and 2).

Crystallographic Structure Analysis of TpRu(PPh$_3$)(H$_2$O)(NHC(O)Ph) (2b) and TpRu(PPh$_3$)(κ^2-*N*,*O*-NH=CPhN=CPhO) (4b). Yellow crystals of **2b** and **4b** suitable for X-ray diffraction study were obtained by layering *n*-hexane on a dichloromethane solution of the complex. A suitable crystal **2b** with dimensions 0.28 × 0.14 × 0.10 mm or **4b** with dimensions 0.40 × 0.32 × 0.18 mm was mounted on a Bruker CCD area detector diffractomer and subjected to Mo Kα radiation (λ = 0.71073 Å) from a generator operating at 50 kV and 30 mA. The intensity data of **2b** and **4b** were collected in the range θ = 1.92−27.57° and 2.05−27.66°, respectively, with oscillation frames of Ψ and ω in the range 0−180°. A total of 1464 frames in **2b** and 1840 frames in **4b** were taken in four shells. An empirical absorption correction of the SADABS (Sheldrick, 1996) program based on Fourier coefficient fitting was applied. The crystal structures were solved by Patterson function methods and expanded by difference Fourier synthesis, and refined by full-matrix least-squares on F^2 using the Bruker Smart and Bruker SHELXTL program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms, except for the two on the aqua ligand in **2b** and the proton on *N*-imidoylimidato moiety in **4b**; they were located by difference electron density map. The R and R_w values of **2b** are 0.086 and 0.2099, respectively, and those of **4b** are 0.0453 and 0.1044, respectively.

Computational Details. Molecular geometries of all the model complexes were optimized at the Becke3LYP level of density functional theory.[27] Frequency calculations at the same level of theory have also been performed to confirm that all the stationary points are minima (no imaginary frequency) or transition states (one imaginary frequency). The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that such structures are indeed connecting two minima. Gibbs free energy at 298 K was obtained on the basis of the frequency calculations. The Ru and P atoms were described using the LANL2DZ basis set including a double-ζ valence basis set with the Hay and Wadt effective core potential (ECP).[28] In the case of P, a d polarization shell was added, with exponents of 0.387.[29] The 6-31G basis set was used for other atoms and polarization functions were added for atoms in the water molecule, O and N atoms of the acetamido ligand, and the CN group of the acetonitrile ligand. All calculations were performed with the Gaussian03 packages.[30]

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Supporting Information Available: Tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles, for complexes **2b** and **4b**. This material is available free of charge via the Internet http://pubs.acs.org.

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