

**Dihydrogen-Bond-Promoted Catalysis: Catalytic Hydration of Nitriles with the Indenylruthenium Hydride Complex ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(dppm)H (dppm = Bis(diphenylphosphino)methane)**

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**Abstract:** The indenylruthenium hydride complex ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(dppm)H was found to be active in catalyzing the hydration of nitriles to amides. The chloro analogue ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(dppm)Cl was, however, found to be inactive. Density functional theory calculations at the B3LYP level provide explanations for the effectiveness of the hydride complex and the ineffectiveness of the chloro complex in the catalysis. It is learned that the presence of a Ru–H···H–OH dihydrogen-bonding interaction in the transition state lowers the reaction barrier in the case of ( $\eta^5\text{-C}_9\text{H}_7$ )Ru(dppm)H, but in the chloro system, the corresponding transition state does not contain this type of interaction and the reaction barrier is much higher. A similar dihydrogen-bond-promoting effect is believed to be responsible for the catalytic activity of the hydrotris(pyrazolyl)borato (Tp) ruthenium complex TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)H in CH<sub>3</sub>CN hydration. The chloro analogue TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)Cl shows no catalytic activity.

## Introduction

The unconventional hydrogen bond (dihydrogen bond) M–H···H–X between the proton-accepting M–H (M = B, transition metal) and the proton donor X–H (X = O, N) has attracted much attention in the past 10 years.<sup>1</sup> It has been shown that such a hydride–proton interaction may significantly contribute to the stabilization of transition-metal complexes. Complexes containing dihydrogen bonds have been proposed to be intermediates for the formation of  $\eta^2$ -dihydrogen complexes or heterolytic cleavage of the  $\eta^2\text{-H}_2$  ligand.<sup>2</sup> More interestingly, the dihydrogen bond, with its substantial strength and directionality, might play important roles in controlling reactivity and regioselectivity of chemical reactions.<sup>3</sup> For example, it has been found that the ( $\eta^2\text{-2-pyridinecarboxaldehyde-N,O}$ )iridium complex [IrH<sub>2</sub>( $\eta^2\text{-2-C}_5\text{H}_4\text{NCHO-N,O}$ )(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> undergoes selective imination with an equimolar mixture of 2-amino-

phenol and 4-aminophenol, favoring the 2-aminophenol-derived product; the outcome appears to be the result of its stabilization by intramolecular Ir–H···H–O dihydrogen bonding and presumably the stabilization of the transition state leading to it.<sup>3c</sup> Aime et al. have suggested that the dihydrogen-bonding interaction may be even more important in transition-metal cluster chemistry in directing the stereochemistry of ligand attachment to the clusters and in determining the regioselectivity of reactions in these systems. Thus, reaction of the electronically unsaturated osmium cluster H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> with EtNH<sub>2</sub> and Et<sub>2</sub>NH yields exclusively the syn product, stabilized by an intramolecular N–H···H–Os interaction, which would not be possible in the anti isomer.<sup>3c,d</sup>

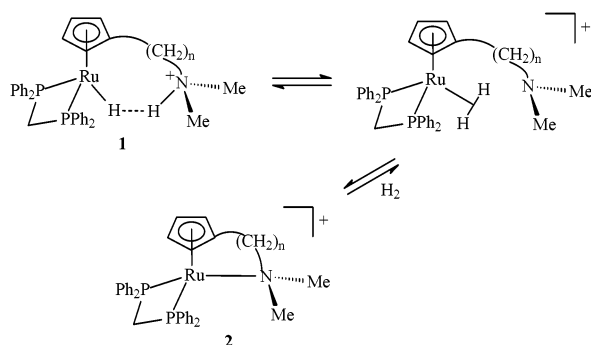
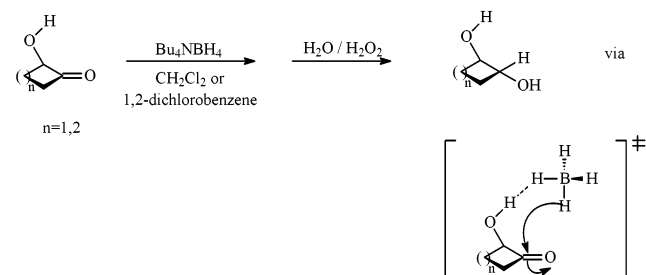
We have synthesized the (aminocyclopentadienyl)ruthenium hydride complex **1** and demonstrated that an intramolecular N–H···H–Ru dihydrogen bond plays an important role in mediating proton transfer and subsequent formation of Ru–N bonds (Scheme 1). It is suggested that **1** is in equilibrium with the  $\eta^2$ -dihydrogen intermediate, H<sub>2</sub> loss from which results in the formation of the Ru–N-bonded chelated structure, and the reverse Ru–N bond hydrogenolysis can be achieved at 60 °C under 60 atm. Complex **2** was found to catalyze CO<sub>2</sub> hydrogenation to formic acid, although in low yields. The crucial step

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- (1) (a) Crabtree, R. H.; Siebbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 248. (b) Crabtree, R. H. *Science* **1998**, *282*, 2000. (c) Custelcean, R.; Jackson, J. E. *Chem. Rev.* **2001**, *101*, 1963.
- (2) (a) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 2655. (b) Abdur-Rashid, K.; Gusev, D. G.; Laugh, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 834. (c) Gründemann, S.; Ulrich, S.; Limbach, H. H.-H.; Golubev, N. S.; Denisov, G. S.; Epstein, L. M.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1999**, *38*, 2550. (d) Caballero, A.; Jalón, F. A.; Manzano, B. R. *Chem. Commun.* **1998**, 1879. (e) Basallote, M. G.; Durán, J.; Fernández-Trujillo, J.; Mániz, M. A.; de la Torre, J. R. *J. Chem. Soc., Dalton Trans.* **1998**, 745. (f) Ayllón, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000. (g) Schlaf, M.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 625. (h) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014.

- (3) (a) Abad, M. M.; Atheaux, I.; Maisonnat, A.; Chaudret, B. *Chem. Commun.* **1999**, 381. (b) Guari, Y.; Ayllon, J. A.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1998**, *37*, 640. (c) Aime, S.; Férriz, M.; Gobetto, R.; Valls, E. *Organometallics* **1999**, *18*, 2030. (d) Aime, S.; Gobetto, R.; Valls, E. *Organometallics* **1997**, *16*, 5140. (e) Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007. (f) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021.

**Scheme 1.** Intramolecular N—H···H—Ru Dihydrogen Bond Mediating Proton Transfer**Scheme 2.** Dihydrogen-Bond-Controlled Diastereoselective Borohydride Reduction of  $\alpha$ -Hydrocycloalkanones

in the catalysis is proposed to be the heterolytic cleavage of  $H_2$  to generate **1**.<sup>4</sup> Theoretical investigation indicated that H-bonding of the amine-bound proton in **1** to the oxygen atom of an incoming  $CO_2$ , which is not coordinated to the metal center, enhances the electrophilicity at the carbon of the molecule, enabling it to abstract the hydride from the metal to form the transient metal–formate intermediate.<sup>5</sup>

Jackson et al. have unequivocally demonstrated control via dihydrogen bonding of the diastereoselective borohydride reduction of  $\alpha$ -hydrocycloalkanones to give the trans diols (Scheme 2); the reduction reactions with tetrabutylammonium borohydride in the non-hydrogen-bonding solvents  $CH_2Cl_2$ ,  $ClCH_2CH_2Cl$ , and *o*-dichlorobenzene are accelerated about 150 times relative to the reductions of the corresponding unsubstituted cycloalkanones. These effects are greatly reduced in the presence of competing hydrogen-bonding alcohols or anions such as  $F^-$ ,  $Cl^-$ , and  $Br^-$ . This is a well-recognized instance of a directing effect specifically mediated by dihydrogen bonding.<sup>6</sup>

Although it is now established that dihydrogen bonds can be utilized to control reactivity and selectivity of chemical reactions, well-recognized cases of dihydrogen bonds playing an essential role in promoting catalytic reactions are still rare. We are here to provide a novel example demonstrating that the catalytic hydration of nitriles to amides by an indenylruthenium hydride complex is in fact promoted by the Ru—H···H—OH dihydrogen bond.

## Results and Discussion

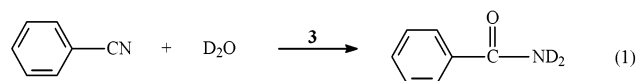
**Catalytic Hydration of Nitriles to Amides with  $(\eta^5-C_9H_7)-Ru(dppm)H$  (**3**).** We have recently been studying C—H bond activation by the indenylruthenium hydride complex  $(\eta^5-C_9H_7)-$

**Table 1.** Catalytic Hydration of Nitriles to Amides with  $(\eta^5-C_9H_7)Ru(dppm)H$  (**3**)<sup>a</sup>

| entry            | substrate           | turnover no. <sup>b</sup> |
|------------------|---------------------|---------------------------|
| 1 <sup>c</sup>   | $C_6H_5CN$          | 800                       |
| 2 <sup>d</sup>   | $C_6H_5CN$          | 300                       |
| 3 <sup>d</sup>   | 4- $NO_2-C_6H_4CN$  | 210                       |
| 4 <sup>d</sup>   | 4- $CH_3O-C_6H_4CN$ | 40                        |
| 5 <sup>c</sup>   | $CH_3CN$            | 865                       |
| 6 <sup>c,e</sup> | $CH_3CN$            | 200                       |

<sup>a</sup> Typical reaction conditions: catalyst, 0.0017 mmol; substrate: $H_2O$ :catalyst = 1000:1000:1; reaction time, 72 h; temperature for entries 1–4, 120 °C; temperature for entries 5 and 6, reflux temperature. <sup>b</sup> Turnover no. (TON) = mol of product/mol of catalyst. <sup>c</sup> In neat substrate. <sup>d</sup> Solvent 1-pentanol (2 mL). <sup>e</sup>  $TpRu(PPh_3)(CH_3CN)H$  used as catalyst.

$Ru(dppm)H$  (**3**) and have learned that **3** is capable of promoting deuteration of some aromatic solvents such as benzene, toluene, xylene, and chlorobenzene with  $D_2O$  in the presence of  $H_2$ , which also undergoes H/D exchange with  $D_2O$ . It was, however, found that in the case of benzonitrile deuteration of the compound did not occur; instead, it was hydrated to give the deuterated benzamide (eq 1).



Catalytic hydration of nitriles to amides is an important reaction both in the laboratory and in industry. The advantages of transition-metal-complex-catalyzed reactions over the conventional acid- and base-catalyzed ones include milder reaction conditions, higher tolerance to other functional groups, and higher regioselectivity; i.e., the amides are not converted into carboxylic acids.<sup>7</sup> In light of the **3**-catalyzed hydration of benzonitrile to give benzamide, other nitriles are examined for the hydration reactions. The results of the **3**-catalyzed hydration reactions are shown in Table 1. Since 4-nitrobenzonitrile and 4-methoxybenzonitrile are water-insoluble solids, the hydration reactions of these substrates have to be performed in the organic solvent 1-pentanol (entries 3 and 4, Table 1).

In transition-metal-catalyzed nitrile hydration, the C—O bond formation step involves nucleophilic attack by water (or hydroxide) upon the coordinated nitrile. Coordination of both the aquo (or hydroxo) ligand and the nitrile to the metal center raises the probability of internal nucleophilic attack, but the free water (or hydroxide) involved in external attack is more nucleophilic than the coordinated aquo (or hydroxo) ligand.<sup>7</sup> Intramolecular attack by the hydroxo ion bound to one metal center at the nitrile molecule bonded to the other metal center in dinuclear iron,<sup>8</sup> cobalt,<sup>9</sup> copper,<sup>10</sup> palladium,<sup>11</sup> rhenium,<sup>12</sup> and nickel<sup>13</sup> systems have also been reported.

**Proposed Mechanism for **3**-Catalyzed Hydration of Nitriles to Amides.** For comparison purposes, we also examined the catalytic activity of the chloro analogue of **3**,  $(\eta^5-C_9H_7)-Ru(dppm)Cl$  (**4**), in nitrile hydration reactions. To our surprise, however, it was found that **4** was inactive for all the substrates tested. Complexes **3** and **4** can provide a vacant site for the nitrile by  $\eta^5 \rightarrow \eta^3$  ring slippage, which is a well-known

(4) Chu, H. S.; Lau, C. P.; Wong, K. Y.; Wong, W. T. *Organometallics* **1998**, *17*, 2768.

(5) (a) Matsubara, T. *Organometallics* **2001**, *20*, 19. (b) Matsubara, T.; Hirao, K. *Organometallics* **2001**, *20*, 5759.

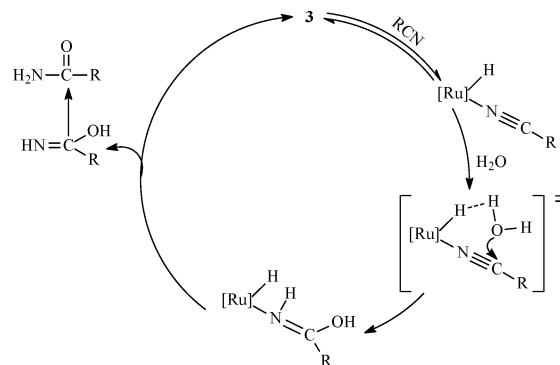
(6) Gatling, S. C.; Jackson, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 8655.

(7) (a) Ghaffar, T.; Parkins, A. W. *J. Mol. Catal. A: Chem.* **2000**, *160*, 249. (b) Kaminskaja, N. V.; Kostić, N. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3677. (c) Kim, J. H.; Britten, J.; Chin, J. *J. Am. Chem. Soc.* **1993**, *115*, 3618. (d) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *J. Org. Chem.* **1992**, *57*, 2521. (e) Jensen, C. M.; Troglor, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723.

phenomenon for  $\eta^5$ -indenyl transition-metal complexes,<sup>14</sup> or by unarming of the dpmm ligand. If the crucial step of the hydration reaction is nucleophilic attack at the carbon atom of the bound nitrile to form the C–O bond, complex **4**, which contains a more electronegative chloro group, would render the carbon of the bound nitrile more susceptible to nucleophilic attack, and therefore it is expected that **4** would be more active than **3** for the catalytic processes. However, our work shows that the reverse is true. One may argue that **3** but not **4** could react with water to form the hydroxo complex ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru(dpmm)(OH), which is the real active species. Previous theoretical calculations and experimental work have indicated that the  $\sigma$ -bond metathesis reaction of water with a metal hydride to give a metal hydroxo species should be feasible.<sup>15</sup> This hypothesis, however, seems unlikely in our case, since in each of the catalytic reactions with **3** in Table 1, the complex was recovered unchanged after the catalysis. We also monitored the reaction of **3** with 10 equiv each of acetonitrile and water in THF-*d*<sub>8</sub> at 80 °C by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy at 4 and 8 h intervals for a period of 48 h; it was observed that while the nitrile was gradually converted to amide, complex **3** remained unchanged throughout the experiment. Furthermore, it was learned that after heating at 80 °C a THF-*d*<sub>8</sub> solution of **3** containing 20 equiv of H<sub>2</sub>O for 4 days, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} spectroscopy showed no sign of any new complex; **3** remained intact.

Despite the fact that the hydride complex **3** is active while the chloro analogue **4** is inactive in the catalytic nitrile hydration reactions, we still believe that during the catalysis with the former, nucleophilic attack at the carbon atom of the bound nitrile by H<sub>2</sub>O is a crucial step of the process. A proposed reaction mechanism to account for the effectiveness and ineffectiveness of **3** and **4**, respectively, is depicted in Scheme 3. We suggest that the **3**-catalyzed nitrile hydration reaction is a dihydrogen-bond-promoted reaction; the dihydrogen-bonding interaction between the hydride ligand and the incoming water molecule might be crucial in lowering the activation energy of the C–O formation step of the hydration reaction. That the chloro complex **4** is not active is probably attributable to the fact that the chloro ligand is not as capable as the hydride ligand of **3** in playing an active role. The decrease of turnover number in carrying out the hydration of benzonitrile in 1-pentanol (entry 2, Table 1) results from the ability of the solvent to compete with Ru–H for H bonding with H<sub>2</sub>O. A further decrease of turnover number in the case of 4-nitrobenzonitrile (entry 3, Table 1) is probably due to the fact the nitro group of the substrate

**Scheme 3.** Proposed Mechanism of **3**-Catalyzed Hydration of Nitrile



can compete even more keenly with Ru–H for H bonding with H<sub>2</sub>O. The electron-donating methoxyl group of 4-methoxybenzonitrile renders the nitrile carbon less electrophilic to nucleophilic attack by H<sub>2</sub>O; therefore, this substrate gives a low turnover number of 40 only. We have also compared the catalytic activity of the hydrotris(pyrazolyl)borato (Tp) ruthenium hydride complex TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)H and its chloro analogue TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)Cl and have learned that the hydride complex is active in catalyzing the hydration of acetonitrile, while the chloro complex is totally inactive. Therefore, it seems that the promoting effect of dihydrogen bonding in the catalysis of nitrile hydration is not a feature unique to the indenyl ruthenium hydride complex **3**; it is also present in TpRu(PPh<sub>3</sub>)(CH<sub>3</sub>CN)H, and it might be common to other metal hydride complexes as well.

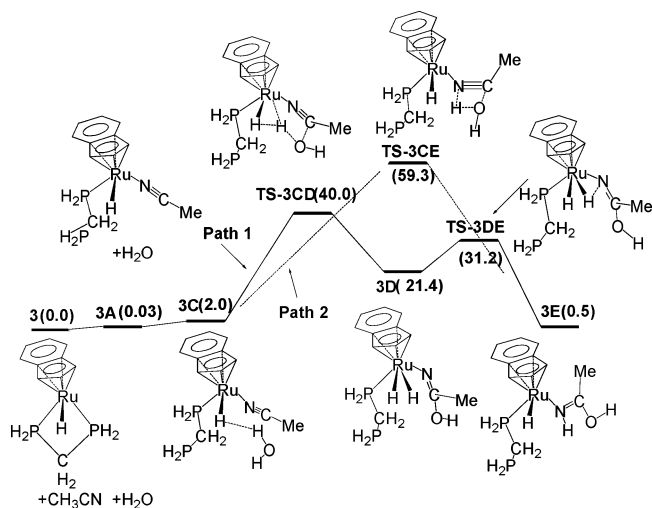
**Theoretical Study.** To study the feasibility of the proposed reaction mechanism (Scheme 3) for the **3**-catalyzed nitrile hydration reactions, theoretical calculations at the B3LYP level of density function theory to study a more detailed catalytic pathway (with acetonitrile as the substrate) were carried out. To reduce the computer cost, the model catalyst ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)Ru(H<sub>2</sub>-PCH<sub>2</sub>PH<sub>2</sub>)H, in which the phenyl groups of the dpmm ligand were replaced by H atoms, was used.

The calculations have indicated that in the catalytic process the dissociation of one arm of the bidentate ligand from the metal center followed by the coordination of CH<sub>3</sub>CN is the initial event. The dpmm unarming requires only 15.2 kcal/mol. Figure 1 shows the possible reaction pathways together with calculated free energies (kcal/mol, in parentheses) for species involved in the reactions. Figure 2 gives the optimized structures for species involved in the reaction paths shown in Figure 1.

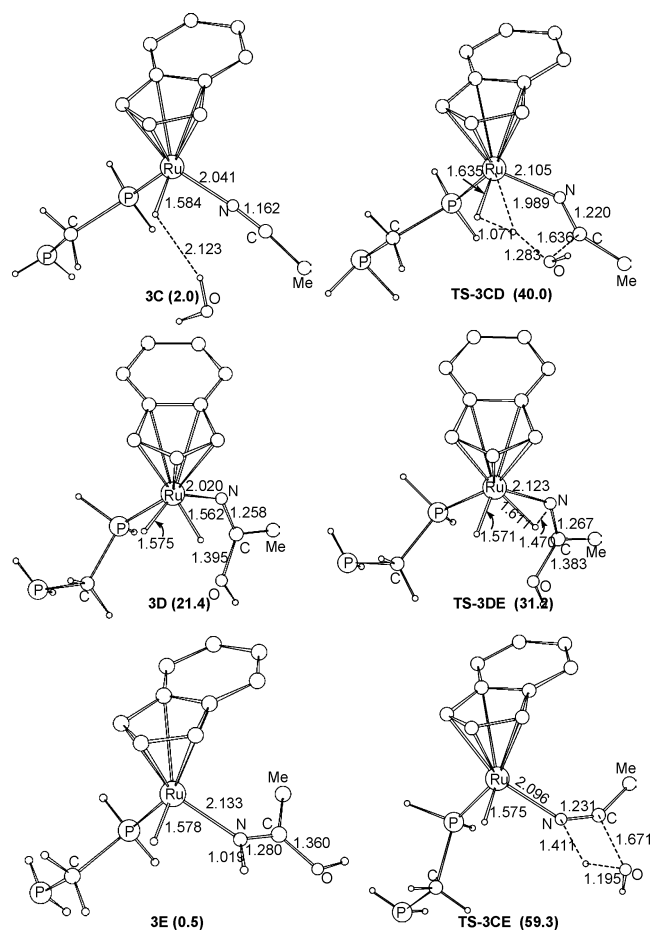
The acetonitrile-coordinated species **3C** is weakly dihydrogen bonded to a water molecule, having an H...H distance of 2.123 Å, and is in equilibrium with the hydride complex **3**. From **3C**, the concerted process (path 2 of Figure 1) has a substantially higher barrier than the stepwise pathway (path 1). For the stepwise pathway (path 1), the reaction overcomes a barrier of 38.0 kcal/mol through **TS-3CD**, which is the rate-determining step, forming a four-legged piano-stool cis dihydride intermediate **3D** (Figure 2). After the rate-determining barrier is surmounted, the reaction proceeds easily by having a proton transfer to form complex **3E**. The dissociation of the hydrated nitrile (HN=C(OH)Me) requires only 11.6 kcal/mol, making the catalytic circle feasible.

Supporting the hypothesis discussed above, the calculations show that a dihydrogen-bonding interaction exists from **3C** to

- (8) (a) Hazell, A.; Jensen, K. B.; McKenzie, C. J.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 3127. (b) Wilkinson, E. C.; Dong, Y.; Que, L., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8394.
- (9) (a) Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1571. (b) Meyer, F.; Heinze, K.; Nuber, B.; Zsolnai, L. *J. Chem. Soc., Dalton Trans.* **1998**, 207.
- (10) Frey, S. T.; Murthy, N. N.; Weintraub, S. T.; Thompson, L. K.; Karlin, K. D. *Inorg. Chem.* **1997**, *36*, 956.
- (11) McKenzie, C. J.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1988**, 112.
- (12) Bauer, C. B.; Concolino, T. E.; Eglin, J. L.; Roger, R. D.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2813.
- (13) (a) Meyer, F.; Kaifer, E.; Kircher, P.; Heinze, K.; Pritzkow, H. *Chem. Eur. J.* **1999**, *5*, 1617. (b) Meyer, F.; Hyla-Kryspin, I.; Kaifer, E.; Kircher, P. *Eur. J. Inorg. Chem.* **2000**, 771.
- (14) (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinann, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *200*, 219. (c) Calhorda, M. J.; Romão, C. C.; Veiros, L. F. *Chem. Eur. J.* **2002**, *8*, 868 and references therein.
- (15) (a) Milet, A.; Dedieu, A.; Kapteijn, G.; van Koten, G. *Inorg. Chem.* **1997**, *36*, 3223. (b) Yin, C.; Xu, Z.; Yan, S.-Y.; Ng, S. M.; Wong, K. Y.; Lin, Z.; Lau, C. P. *Organometallics* **2001**, *20*, 1216. (c) Crabtree, R. H.; Lavin, M.; Bonnevot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

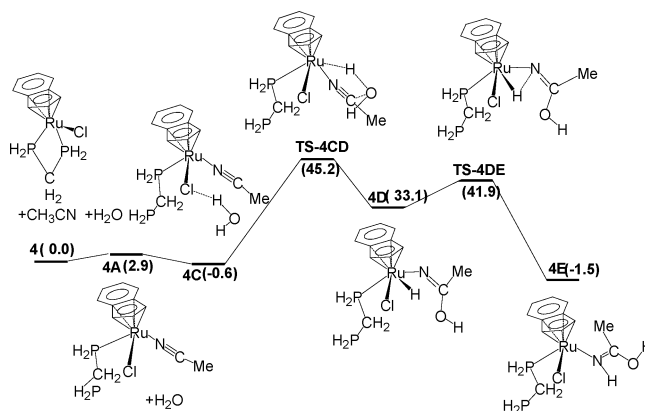


**Figure 1.** Schematic illustration of the mechanism for complex **3** together with calculated free energies (kcal/mol) for species involved in the reactions.

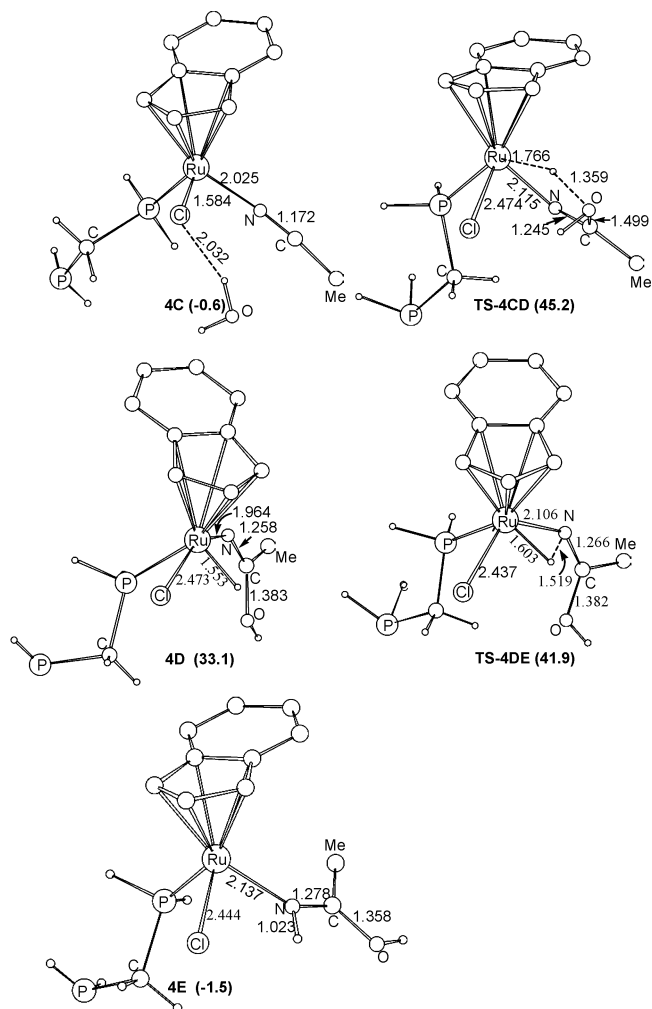


**Figure 2.** B3LYP optimized structures for those species shown in Figure 1. The free relative energies (kcal/mol) shown in parentheses take **3** + MeCN + H<sub>2</sub>O as the reference. For the purpose of clarity, hydrogen atoms on the indenyl ligand and the methyl group of MeCN are omitted.

the transition state **TS-3CD** in the rate-determining step. The selected structural parameters shown in Figure 2 indicate the strong H(water)- $\cdots$ -H(hydride) (1.071 Å) interaction in the transition state. The dihydrogen-bonding interaction makes **TS-3CD** an early transition state and lowers the reaction barrier. In contrast, the corresponding transition state **TS-4CD** for the chloro system (Figures 3 and 4) does not contain that type of



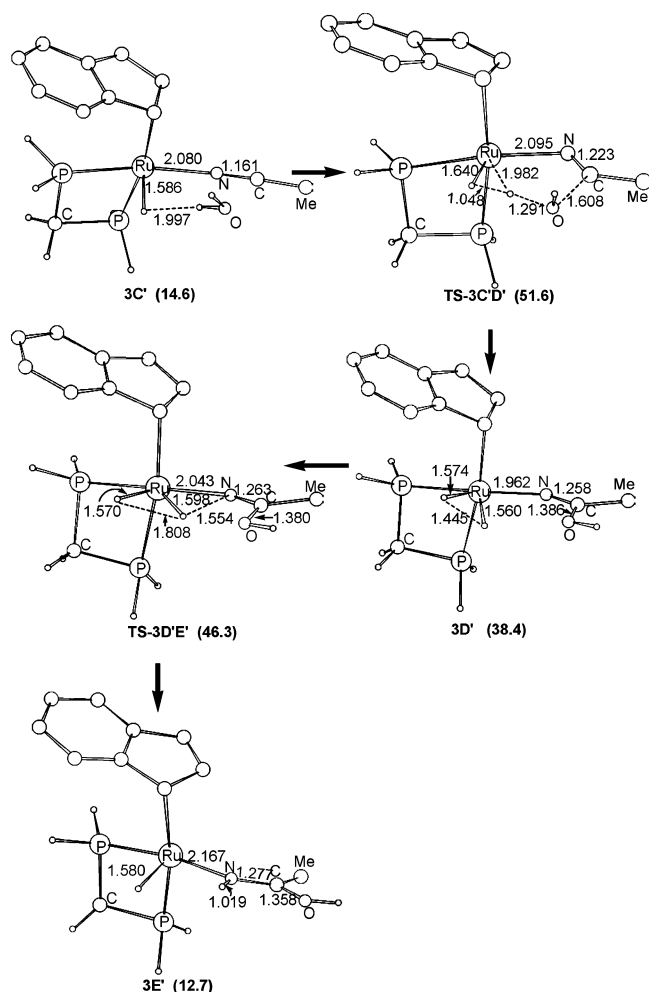
**Figure 3.** Schematic illustration of the mechanism for complex **4** together with calculated free energies (kcal/mol) for species involved in the reactions.



**Figure 4.** B3LYP optimized structures for those species shown in Figure 3. The free relative energies (kcal/mol) shown in parentheses take **4** + MeCN + H<sub>2</sub>O as the reference. For the purpose of clarity, hydrogen atoms on the indenyl ligand and the methyl group of MeCN are omitted.

interaction (H(water)- $\cdots$ -Cl = 2.582 Å) and is a late transition state having a structure closer to the four-legged piano-stool hydride intermediate **4D**. Therefore, for the chloro system the rate-determining step leading to the formation of a chloro-hydride intermediate has a much higher reaction barrier of 45.8 kcal/mol (Figure 3).

The possibility of having a hydration process that involves the ring slippage of the indenyl ligand was also investigated.



**Figure 5.** B3LYP optimized structures of intermediates and transition states for a hydration process that involves the ring slippage of the indenyl ligand. The free relative energies (kcal/mol) shown in parentheses take  $\mathbf{3} + \text{MeCN} + \text{H}_2\text{O}$  as the reference. For the purpose of clarity, hydrogen atoms on the indenyl ligand and the methyl group of MeCN are omitted.

Figure 5 gives the structural details for intermediates and transition states together with their relative free energies in the corresponding hydration process involving the ring slippage of the indenyl ligand. The results of calculations show that the energies of all the intermediates/transition states based on the ring-slipped structures are higher than the corresponding species shown in Figure 1 by more than 10 kcal/mol. Clearly, the ring slippage is much less favorable in comparison to the dppm unarming in the hydration process. Interestingly, all the ring-slipped structures calculated are of the  $\eta^1$  type instead of the  $\eta^3$  type. This result is understandable, in view of the fact that many 16-electron, five-coordinate Ru complexes are stable, particularly when there is a strong trans-influencing ligand present.<sup>16</sup> The dihydrogen-bonded species  $\mathbf{3C}'$  and the hydrated nitrile complex  $\mathbf{3E}'$  (Figure 5) can be described as having square-pyramidal structures with a hydride ligand occupying the axial position. The dihydride intermediate  $\mathbf{3D}'$  (Figure 5) is a capped square-pyramidal structure. First-order Jahn–Teller distortion is always expected for 16-electron, six-coordinate complexes

that are diamagnetic.<sup>17</sup> Therefore,  $\mathbf{3D}'$  does not adopt an octahedral structure.

Instead of the ring slippage commonly observed in chemical reactions involving  $\eta^5$ -indenyl systems,<sup>14</sup> the Ru indenyl hydride complex catalyzes the hydration reaction by the dppm unarming. This is not very unexpected, because ligand dissociation in other indenyl complexes has also been found as the initial event for chemical reactions.<sup>18</sup>

## Conclusion

It is now clear that dihydrogen bonding might play an important role in controlling reactivity and/or regioselectivity of chemical transformations; however, well-recognized instances of catalytic reactions promoted or mediated by dihydrogen bonds are still rare, although many might have gone unnoticed in the literature. We have here provided a clear example demonstrating the principle of promoting a catalytic reaction by the use of a  $\text{M}-\text{H}\cdots\text{H}-\text{X}$  dihydrogen-bonding interaction in an indenylruthenium hydride system; we believe that such a promoting effect might be common to other transition-metal hydride species also.

## Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Ruthenium trichloride,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , indene, bis(diphenylphosphino)methane (dppm), sodium borohydride, 4-nitrobenzotrile, 4-methoxybenzotrile, and pyrazole were purchased from Aldrich and were used as received. The complexes  $\text{InRu}(\text{dppm})\text{H}$ ,<sup>19</sup>  $\text{InRu}(\text{dppm})\text{Cl}$ ,<sup>19</sup>  $\text{TpRu}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{H}$ ,<sup>20</sup> and  $\text{TpRu}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{Cl}$ <sup>20</sup> were synthesized according to literature methods. Solvents were distilled under a dry nitrogen atmosphere with appropriate drying agents (solvent/drying agent): methanol/Mg– $\text{I}_2$ , ethanol/Mg– $\text{I}_2$ , acetonitrile/ $\text{CaH}_2$ , tetrahydrofuran/Na–benzophenone, diethyl ether/Na, *n*-hexane/Na, 1-pentanol/ $\text{K}_2\text{CO}_3$ , benzotrile/ $\text{K}_2\text{CO}_3$ . THF-*d*<sub>8</sub> and  $\text{CDCl}_3$  were dried over  $\text{P}_2\text{O}_5$  and  $\text{CaH}_2$ , respectively.

Proton NMR spectra were obtained from a Bruker DPX 400 spectrometer. Chemical shifts were reported relative to residual protons of the deuterated solvents. <sup>31</sup>P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 161.70 MHz; chemical shifts were externally referenced to 85%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$ .

**Catalytic Hydration of Neat Nitriles with  $\text{InRu}(\text{dppm})\text{H}$  ( $\mathbf{3}$ ).** In a typical run, a sample of  $\mathbf{3}$  (0.01 g, 0.017 mmol) was dissolved in a 1:1 mixture of nitrile and water (0.017 mol each). The solution was heated at 120 °C or at reflux for 72 h, after which the solution was cooled to room temperature, and the amide that formed was dissolved by addition of 1 mL of acetone. A 0.1 mL aliquot of the solution was removed and analyzed by <sup>1</sup>H NMR spectroscopy (in  $\text{CDCl}_3$ ). Comparison of the integrations of the characteristic peaks of the amide and the unreacted nitrile gave the turnover number of the reaction.

**Catalytic Hydration of Nitriles with  $\text{InRu}(\text{dppm})\text{H}$  ( $\mathbf{3}$ ) in 1-Pentanol.** To a sample of  $\mathbf{3}$  (0.01 g, 0.017 mmol) in 2 mL of 1-pentanol were added the nitrile and water (0.017 mol each). The resulting solution was heated at 120 °C for 72 h. At the end of the reaction time, the solution was cooled to room temperature, and a 0.1 mL aliquot of it was removed and analyzed by <sup>1</sup>H NMR spectroscopy (in  $\text{CDCl}_3$ ).

(16) (a) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671. (b) Huang, D.; Heyn, R. H.; Bollinger, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 292.

(17) (a) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320. (b) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772. (c) Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. *J. Am. Chem. Soc.* **1995**, *117*, 281. (d) Yang, S.-Y.; Leung, W.-H.; Lin, Z. *Organometallics* **2001**, *20*, 3198. (18) Gamasa, M. P.; Gimeno, J.; Gonzalez-Bernardo, C.; Marthin-Vaca, B. M. *Organometallics* **1996**, *15*, 302. (19) Oro, L. A.; Ciriano, M. A.; Campo, M.; Ffoces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117. (20) Lau, C. P.; Chan, W. C.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S. M.; Jia, G. *Organometallics* **1997**, *16*, 34.

Comparison of the integrations of the characteristic peaks of the amide product and the unreacted nitrile yielded the turnover number of the reaction.

**Computational Details.** Molecular geometries of the model complexes, in which the phenyl groups of the dppm ligand were modeled by hydrogen atoms, were optimized at the Becke3LYP (B3LYP) level of density functional theory.<sup>21</sup> Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The LANL2DZ effective core potentials and basis sets<sup>22</sup> were used to describe Ru, Cl, and P, while the standard 6-31G basis set was used for C, H, N, and O atoms. Polarization functions<sup>23</sup> were added for atoms in the water molecule ( $\zeta_d(\text{O}) = 1.154$ ,  $\zeta_p(\text{H}) = 1.1$ ), the CN group of the nitrile ligand ( $\zeta_d(\text{C}) = 0.6$ ,  $\zeta_d(\text{N}) = 0.864$ ), and

the hydride and chloride ligands ( $\zeta_d(\text{Cl}) = 0.514$ ). All of the calculations were performed with the Gaussian 98 software package.<sup>24</sup>

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- (21) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.

- (22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

- (23) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier Science: Amsterdam, 1984.
- (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.