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Theoretical Mechanistic Study of Rhodium(I) Phosphine-Catalyzed H/D Exchange Processes in Aqueous Solutions

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The mechanism of hydrogen isotope exchange between a catalytically active rhodium dihydride ($[RhH_2Cl(PR_3)_3]$) and acidic water has been investigated by means of density functional calculations carried out for model complexes interacting with protonated water clusters. The protonation of hydride ligands by hydrated H_3O^+ is shown to occur via dihydrogen-bonded adducts, which can easily transform to cationic hydrido-dihydrogen species ($[RhH(H_2)Cl(PR_3)_3]^+$). The structure and possible internal rearrangements of this intermediate are characterized, and a low barrier (~3 kcal/mol) for η^2-H_2 rotation is found. The energy gap for the protonation/deprotonation process is estimated to be in the same range. The structures and the relative stabilities of the involved species suggest that the leaving proton in the deprotonation step may either shift back to the original water molecule or alternatively transfer to another H_2O.

Introduction

Aqueous organometallic catalysis has attracted considerable attention in the last two decades,[1−3] since water is a cheap, readily available, and most environmentally friendly solvent. Although only a few industrial processes are based on water-soluble catalysts, aqueous or aqueous−organic biphasic systems are always worth consideration when no anhydrous conditions are required. Hydride complexes of transition metal phosphines have been of great interest in organometallic catalysis.[4,5] In many cases, the application of water-soluble analogues proved to be very efficient in the hydrogenation of different functionalities of organic compounds and also in the reduction of CO_2, which is a promising C_1 building block in organic synthesis.[6−9]

The H/D isotope exchange between hydrogen and the solvent has always been considered as an important mechanistic aspect of catalytic hydrogenation reactions. The incorporation of different amounts of H or D isotopes in the catalytically reduced products can indirectly inform us about the occurrence of such isotope exchange reactions during catalytic processes. Several ways of catalytic deuteration of olefinic substrates have been reported;[10−12] however, the direct investigation of isotope exchange between the catalytically active hydride species and water was not investigated in aqueous systems prior to our report that showed that certain water-soluble tertiary phosphine complexes of rhodium(I) and ruthenium(II) catalyze the H/D isotope exchange between H_2−D_2O and D_2−H_2O under mild conditions with unprecedented efficiency.[13,14] We found that the rate of this reaction was strongly influenced by the pH of the solutions: the catalytic activity dropped significantly in alkaline solutions and no isotopic exchange was observed at pH > 12. Thus we arrived at a conclusion that the H/D exchange likely involves the protonation of a hydride species by hydronium, resulting in a hydrido-dihydrogen complex (Scheme 1). These complexes, however, have not been identified as reaction intermediates, which is not surprising if we consider that only a very few complexes of this type have been detected in aqueous solutions (see for example ref 15).

Proton transfer reactions between transition metal hydrides and various proton donors have been the

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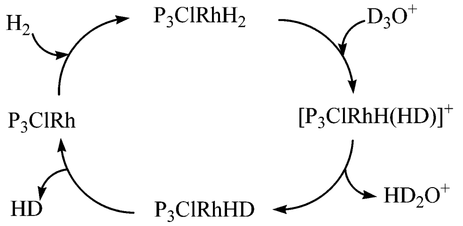
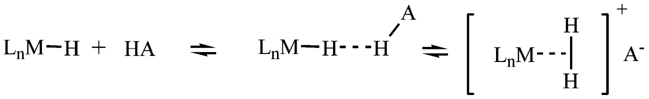
Scheme 1



Scheme 2



subject of several recent theoretical studies.[16–18] Most of these protonation reactions have been shown to occur via the formation of H···H hydrogen-bonded adducts (dihydrogen bond formation), followed by their conversion into cationic dihydrogen complexes (Scheme 2).

The strength of the H···H interaction has been correlated with the acidity of the HA species.[16–18] It has been shown that for poor or moderate proton donors, weakly bound dihydrogen intermediates are formed, whereas strong proton donors (such as H_3O^+, for instance) yield η^2-H_2 dihydrogen species directly without energy barrier. It has also been recognized that the solvent medium can greatly influence the energetics of the proton transfer, because the charged species involved in these processes are preferentially stabilized with polar solvents, so the gas phase energetics may vary significantly if solvent effects are taken into account.[16] Solvent effects are even more important in aqueous solutions as compared to those in organic solvents, since water is not merely a solvent, but it acts as a reactive medium by supplying the protons via a hydrogen-bonded network. This effect has been clearly demostrated in a recent work presented by Chu et al.,[19] who found that the degree of protonation of a monocationic ruthenium hydride complex is notably altered by the presence of water aggregates in organic solutions.

The primary goal of our present work was to provide a theoretical background for the proposed reaction mechanism of the H/D exchange catalyzed by water-soluble rhodium(I) hydrides, namely, [RhH$_2$Cl(*m*TPPMS)$_3$][20] and [RhH$_2$Cl(PTA)$_3$][21,22] (*m*TPPMS = sodium salt of meta-sulfonatophenyl-diphenyl-phosphine, PTA = 1,3,5-triaza-7-phosphaadamantane). We applied density functional theory for model systems involving the simplified versions of these metal hydride complexes interacting with various sized $H_3O^+(H_2O)_n$ clusters, which are meant to represent the protonating agents in the aqueous medium.

Computational Details

[RhH$_2$Cl(PMe$_3$)$_3$] was adopted as a model for the catalytically active [RhH$_2$Cl(*m*TPPMS)$_3$] species, which means that we employed PMe$_3$ to represent the aromatic phosphine ligand. We are aware of the drawbacks of phosphine truncation in modeling reactions of metal-phosphine complexes;[23] however, on the basis of the similarity of the donor/acceptor properties of PMe$_3$ and PAr$_3$ type phosphines,[24] and also assuming that the bulky substituents on the phosphine ligands in [RhH$_2$Cl(*m*TPPMS)$_3$] are not involved directly in the investigated H/D exchange process (neither do they represent steric hindrance for this process), we do not expect to introduce significant errors in the obtained relative energies by the applied phosphine simplification.

We first carried out density functional theory calculations to identify the structures of [RhH$_2$Cl(PMe$_3$)$_3$] and its protonated form [RhH(H$_2$)Cl(PMe$_3$)$_3$]$^+$, and then we examined the interaction of water clusters with these model complexes. In some cases, we also located the transition states corresponding to the protonation/deprotonation step of the reaction. Normal coordinate analysis has been used to verify the nature of these stationary points, and for each transition structure we calculated the intrinsic reaction coordinate (IRC) routes toward the corresponding minima. If the IRC calculations failed to reach the energy minima on the potential energy surface, we performed geometry optimizations from the initial phase of the IRC path (pseudo-IRC calculations).

All calculations have been performed at the B3LYP/SDDP level of density functional theory using the Gaussian 98 program,[25] where B3LYP is the applied hybrid functional[26–28] and SDDP refers to a basis set including the Stuttgart-Dresden relativistic small core ECP basis set for rhodium and the Dunning/Huzinaga DZ + polarization all-electron basis set for the lighter atoms.[29–32] For selected structures, we estimated the effect of the bulk solvent medium by the application of the polarizable continuum model (PCM)[33] as implemented in Gaussian 98. Reaction field calculations (using $\epsilon = 78.4$ for water) were carried out for the structures optimized in the gas phase.

Results and Discussion

A. Gas Phase Structures of [RhH$_2$Cl(PMe$_3$)$_3$] and Its Protonated Forms. We first consider the struc-

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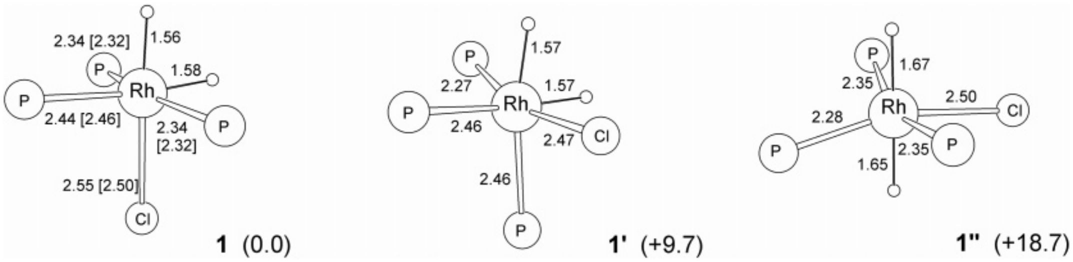

Figure 1. Optimized structures with selected bond lengths (in Å) and their relative stabilities (in kcal/mol) of possible isomers of [$RhH_2Cl(PMe_3)_3$]. X-ray structural data available for the analogous [$RhH_2Cl(PPh_3)_3$] complex are shown in brackets.

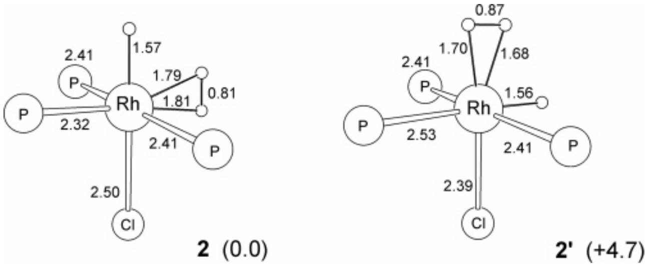

Figure 2. Optimized structural parameters (in Å) and relative energies (in kcal/mol) for the two forms of [$RhH(H_2)Cl(PMe_3)_3$]$^+$.

tures of relevant hydride complexes without the presence of water clusters. The optimized structures of the three isomers of [$RhH_2Cl(PMe_3)_3$] are shown in Figure 1. As expected from the *trans* influence order of the coordinated ligands in this complex ($H^- \geq PR_3 > Cl^-$), the *cis-mer* isomer (**1**) is the most favored structure among the possible forms. Here, the *cis-mer* notation refers to the *cis* arrangement of the hydrides and meridional phosphine ligands. The calculations predict that the other two structures, *cis-fac* (**1′**) and *trans-mer* (**1″**), are 9.7 and 18.7 kcal/mol less stable than **1**. The presence of **1** under the experimental conditions used for the rhodium(I) phosphine-catalyzed H/D exchange reactions was clearly established with multinuclear NMR spectroscopy;[34] therefore we assumed in our present study that this species is involved in the protonation process. We note that the molecular structure of the [$RhH_2Cl(PPh_3)_3$] complex is available from X-ray diffraction studies,[35,36] and it also reveals the *cis-mer* arrangement of the coordinated ligands.

In principle, three protonation sites exist in complex **1** corresponding to the protonation of two hydrides and the chloride ligands. Although the protonation of halide ligands has been observed experimentally for several hydrohalide complexes,[37] this scenario is quite unlikely in the present H/D exchange process that involves the cleavage/formation of the metal−hydride bond. The structures of the two possible cationic hydrido-dihydrogen isomers formed upon the protonation of complex **1** are depicted in Figure 2.

The gas phase calculations estimate that complex **2** is 4.7 kcal/mol more stable than **2′**, and this energy difference becomes slightly larger (5.9 kcal/mol) when solvation energies of the two forms (as obtained from PCM calculations) are taken into account. These results indicate that the protonation of the hydride being in *trans* position to the phosphine ligand in complex **1** is energetically more favored than the other hydride. The stability order between **2** and **2′** is also related to the *trans* influence of the metal−hydride bond on the coordination of the PMe_3 and Cl^- ligands. However, it is apparent from the structural data (i.e., the lengthening of the H−H bond) that the coordination of H_2 is stronger in **2′**, which follows from the difference in the σ-donor/π-acceptor properties of the ligands that are in *trans* position to H_2 in **2** and **2′**.[38] Since the PMe_3 ligand is a good σ-donor and a moderate π-acceptor,[24] both components of the metal−dihydrogen interaction are reduced in **2**.

On the basis of the electronic total energies of **1** and **2**, the gas phase proton affinity of the dihydride complex is estimated to be 245 kcal/mol, which is shifted to 268 kcal/mol if ZPE corrections (−6.0 kcal/mol) and solvent effects (+29 kcal/mol) are included. This value is very close to the proton affinity of bulk water (270.3 kcal/mol),[39] providing an indication that the assumed protonation/deprotonation process is thermodynamically feasible.

Due to the stabilizing electrostatic interactions between the positively charged H_2 moiety and the hydride ligand (referred to as *cis* effect, see ref 40), the coordinated H_2 molecule is coplanar with the Rh−H bond in both **2** and **2′**. The energy barriers corresponding to the rotation about the Rh−H_2 axis in these complexes are calculated to be 2.5 and 1.3 kcal/mol, respectively, indicating a reduced Rh(d)−H_2(σ*) back-bonding interaction in the transition state of H_2 rotation in **2**, where the H_2 ligand becomes coplanar with the three phosphines. These energy barriers are fairly low, and although they refer to gas phase calculations, they suggest that a rapid H_2 rotation might be considered as a possible process in establishing a more detailed mechanistic picture of the H/D exchange reaction.

Another type of internal rearrangement typical of cationic *cis*-$MH(H_2)^+$ complexes, namely, the intramolecular H exchange between the hydride and dihydrogen,[40,41] might also be relevant to the title reaction; thus we located the transition state corresponding to the single-step H-transfer between **2** and **2′**. The esti-

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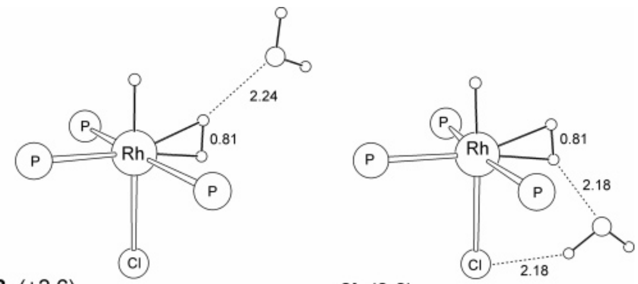


3 (+2.6) **3'** (0.0)

Figure 3. Optimized structures and relative energies (in kcal/mol) of complexes obtained via protonation of **1** with a single H_3O^+.

mated barrier for the **2** → **2′** transition is 9.7 kcal/mol (5.0 kcal/mol for the **2′** → **2** process), which indicates that a fast H/H_2 scrambling in the present cationic hydrido-dihydride complex is quite unlikely to occur at room temperature.

B. Interaction of [$RhH_2Cl(PMe_3)_3$] with a Single Hydronium Ion. The simplest molecular model one can consider to describe the protonation process in the present reaction corresponds to the interaction of the dihydride complex **1** with H_3O^+. In line with previous theoretical studies on related reactions,[16−18] we find a spontaneous proton transfer to the metal hydride if the Rh−H bonds in **1** are approached with a single hydronium cation. The protonation occurs without energy barrier because H_3O^+ is an extremely strong proton donor and the reaction leads to a cationic hydrido-dihydrogen species with a water molecule coordinated to the H_2 unit in a coplanar arrangement (see Figure 3).

Because of the difference found in the relative stabilities of **2** and **2′**, the protonation of the hydride *trans* to PMe_3 is more favored, and depending on the initial direction of the H_3O^+ attack, two different structures (**3** and **3′**) are found for the **2**···H_2O complex. In both structures, the water molecule is linked via the O atom to one of the hydrogens of the H_2 unit, but structure **3′** is further stabilized by Cl···HO hydrogen-bonding interaction between the chloride ligand and water. Consequently, complex **3′** is predicted to be 2.6 kcal/mol more stable than **3**.

To estimate the influence of the solvent water molecules on the internal H_2 rotation in the hydrido-dihydrogen complex, we performed geometry optimizations for the perpendicular arrangement of the dihydrogen ligand in **3** and **3′** and found a slight increase in the rotational barrier as compared to that in complex **2** (these barrier are 3.1 and 3.3 kcal/mol for **3** and **3′**, whereas it is 2.5 kcal/mol for complex **2**).

C. Interaction of [$RhH_2Cl(PMe_3)_3$] with (H_3O^+)(H_2O)$_2$. As a first step in extending our model, we added two water molecules to H_2O in **3** and examined the protonation process by identifying the structures of the **1**···(H_3O^+)(H_2O)$_2$ and **2**···(H_2O)$_3$ complexes as well as that of the corresponding transition state. In these calculations, the molecular models were restricted to have C_s symmetry by assuming that the water molecules adjacent to H_3O^+ are either coplanar with the hydronium and the two Rh−H bonds or lie perpendicular to this plane. One representative of the four possible arrangements (in which both water molecules lie in the plane defined above) is depicted in Figure 4. We found that the models corresponding to the other three arrangements of the water molecules (planar-perpendicular, perpendicular-planar, and perpendicular-perpendicular) gave very similar relative energies for the two forms of the rhodium hydride complexes; the variation was less than 1 kcal/mol. These symmetrical models allow us to increase the size of the model water clusters, which would otherwise be computationally prohibited. Although the located C_s minima may not correspond to

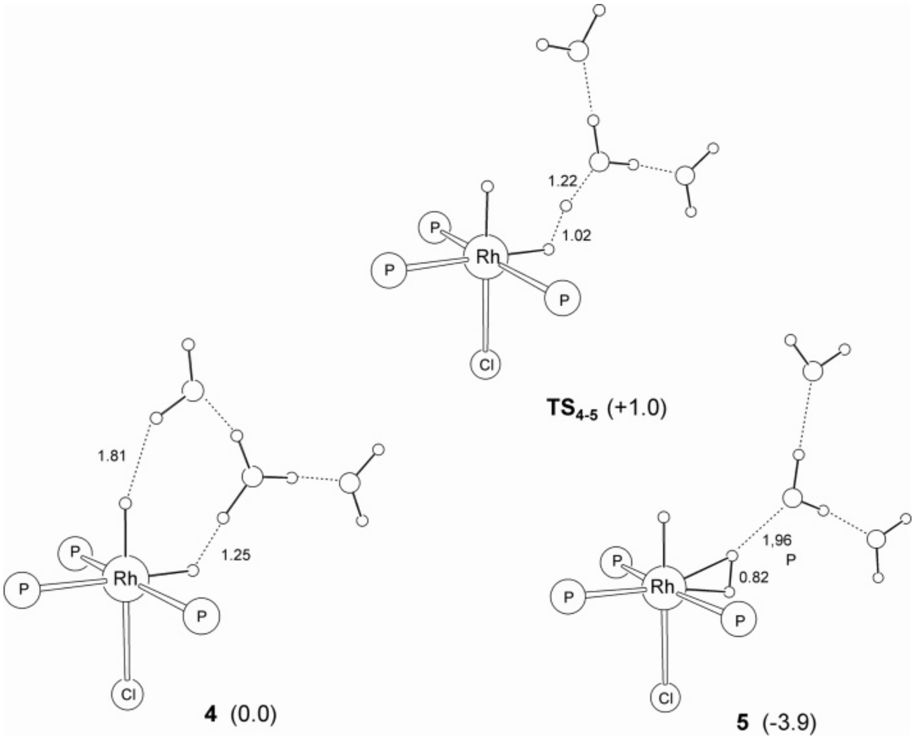


Figure 4. Optimized structures and relative energies of stationary points identified for the trimeric models.

the energetically most favored structures, we assume that the symmetry constraint does not alter significantly the relative energetics of the proton transfer process.

As a result of hydration, the acidity of H_3O^+ is notably reduced,[39] and as opposed to the previous model, the proton transfer from hydronium does not occur spontaneously, but it proceeds via the formation of a dihydrogen-bonded intermediate (**4**). The short distance between the H atoms of Rh−H and H_3O^+ reveals a strong H···H interaction, and complex **4** represents a well-defined energy minimum along the reaction coordinate. Another type of dihydrogen bond formed between the other hydride and a water molecule is apparent in complex **4**; however, this attractive H···H interaction is much weaker than the $Rh{-}H\cdots H{-}OH_2^+$ bond. Calculations carried out for a model involving the dihydride species **1** and a single water molecule indicate that the strength of the Rh−H···H−OH dihydrogen bond is about 7.5 kcal/mol, which is less than those predicted for Mo and Re hydride complexes by Orlova et al. (11−13 kcal/mol[17]), but notably larger than the average strength of hydrogen bonds between water molecules.

The transition state ($\mathbf{TS}_{4-5}$) located en route toward the protonated form of the rhodium complex lies only 1 kcal/mol above complex **4**. The energy balance of the protonation process in this model reaction is 3.9 kcal/mol in favor of the hydrido-dihydrogen species. In complex **5**, the H···O distance in the $H_2\cdots OH_2$ linkage is predicted to be about 0.3 Å shorter than in **3**, pointing to an increased strength of dihydrogen−$(H_2O)_n$ interaction in the extended model, which is another manifestation for the variation of proton affinity of water clusters as a function of increasing size.

We note that geometry optimizations carried out for complexes **4** and **5** without symmetry constraints leads to structures with nonplanar $(H_3O^+)(H_2O)_2$ and $(H_2O)_3$ units. The distortion of the H-bonded water clusters is due to weak $C{-}H\cdots OH_2$ type hydrogen bonds formed between the methyl groups of the PMe_3 ligands and the O atoms of the water clusters. These interactions are more enhanced in complex **4**, in which the water cluster carries a positive charge; therefore the energy difference between structures **4** and **5** decreases to 1.8 kcal/mol, still fairly close to that obtained with the C_s models (3.9 kcal/mol).

We followed two directions to further improve the present model. First the solvation energies for the optimized structures of **4**, $\mathbf{TS}_{4-5}$, and **5** were estimated in terms of single-point PCM calculations, and we found that as a result of solvent effects the stability order of the two minima has interchanged and complex **5** became 2.9 kcal/mol less stable than **4**. The energy barrier for the protonation in this model is 3.1 kcal/mol. In another approach, we involved two more water molecules in the model clusters and examined the effect of explicit model extension.

D. Interaction with $(H_3O^+)(H_2O)_4$. The pentameric model clusters have been constructed by appending two water molecules to complexes **4′** and **5′** as indicated in Figure 5. Here, **4′** and **5′** refer to trimeric models, in which one of the water molecules in the first hydration shell is coplanar with the hydronium, while the other is perpendicular to this plane. We have chosen this arrangement because it enables to extend the trimeric model by two different types of hydrogen bonds in the second hydration shell, since one of the additional H_2O molecules acts as a proton donor and the other as a proton acceptor. The structures of these model complexes (**6** and **7** in Figure 5) have been allowed to relax in geometry optimizations carried out with C_s symmetry constraint.

Our calculations indicate that the inclusion of two water molecules from the second hydration shell has only a small effect on the relative stability of the two forms of the rhodium hydride complex. The pentameric model predicts the protonated form (complex **7**) to be 5.8 kcal/mol more stable than the dihydride complex (**6**), whereas this energy difference is 4.0 kcal/mol if the corresponding trimeric models (**4′** and **5′**) are considered for comparison. It should be emphasized here that the relative energies of the two forms of the rhodium hydride complex might be sensitive to the nature of hydrogen bonds defined between the first and the second hydration shell, but we think that the present choice (that involves both types of H-bond) is consistent with a dynamic picture where the number of proton donor and acceptor type H-bonds are statistically averaged for a given solvent molecule.

An interesting finding emerging from the optimized structure of **7** is that in addition to the proton-donating water molecule, another H_2O is found in the close vicinity of the dihydride unit of the protonated rhodium complex, which suggests that the H/D exchange process in bulk water may involve two different water molecules, one acting as a proton donor and the other as a proton acceptor.

On the basis of these results we constructed other type of pentameric model involving the first neighbors of the two water molecules that interact directly with the η^2-H_2 ligand (see Figure 6) and attempted to locate the stationary points characteristic for this mechanistic picture.

We indeed identified complex **8** as a minimum on the C_s potential energy surface, and we were also able to show that the hydrido-dihydride species in **8** can be easily deprotonated by H^+ transfer from the dihydride ligand to any of the two adjacent water molecules. However, the structure of the protonated water cluster has completely rearranged in the optimization procedure. For instance, the H_2O molecule linked to the two proton acceptor water molecules in **8** migrated to the terminal waters. Nevertheless, these calculations showed that the energies of the $\mathbf{1}\cdots(H_3O^+)(H_2O)_4$ complexes prior to the structural rearrangement are close to that of complex **8** within a few kcal/mol, again underlining the feasibility of the protonation/deprotonation step in this reaction.

E. Mechanism of H/D Exchange. All the results presented in the previous sections are in line with the mechanism of the H/D exchange proposed from experimental findings.[13,14] According to the calculations, the assumed intermediate, the $[RhH(H_2)Cl(PR_3)_3]^+$ complex, is identified as a well-defined energy minimum not only on the gas phase potential energy surface but also in the presence of water clusters. Of the two possible hydrido-dihydrogen isomers, the one derived by the protonation of the Rh−H *trans* to the phosphine ligand

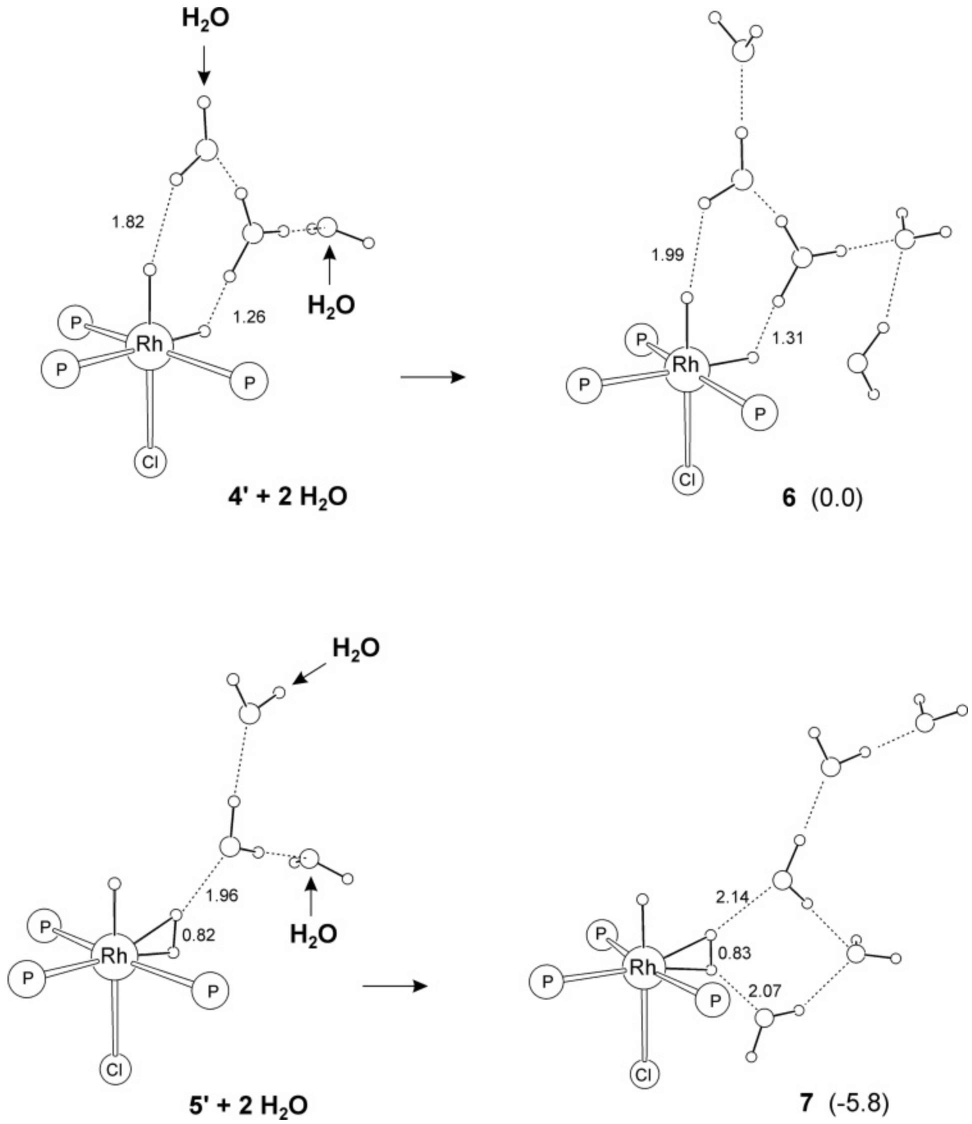


Figure 5. Construction and optimized structures of the dihydride and hydrido-dihydrogen complexes interacting with pentameric water clusters.

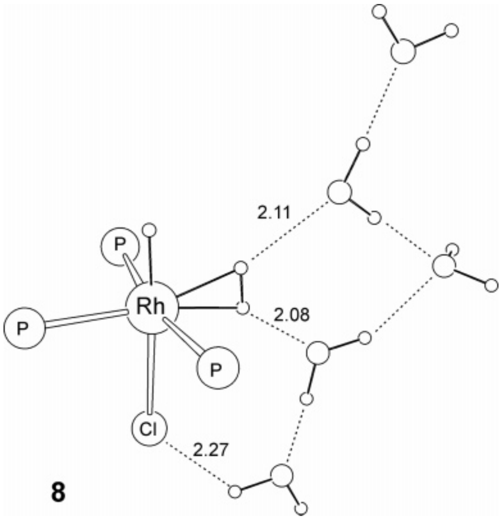


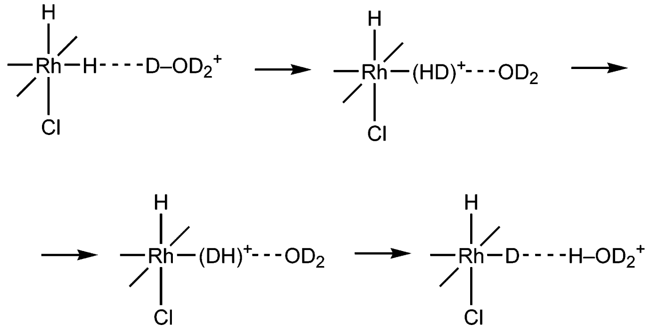
Figure 6. Optimized structure of the hydrido-dihydrogen complex interacting with a pentameric water cluster.

in complex **1** is found to be clearly favored energetically. The intermediacy of the $[RhH(H_2)Cl(PR_3)_3]^+$ complex is supported by the predicted energetics in that the relative stability of this species is calculated to be very similar to the dihydride complex. Furthermore, the protonated and deprotonated forms of the rhodium hydride complex seem to be separated only by a small energy barrier, suggesting a fast protonation/deprotonation process, which may explain that the hydrido-dihydrogen species could not be detected experimentally on the NMR time scale.[13,14] It should also be mentioned that in the present mechanistic model, the rate of formation for the protonated complex is proportional to the concentration of the hydronium ions (which is rather low even at acidic pH conditions), whereas the rate of deprotonation is proportional to $[H_2O]$, suggesting again that the intermediate complex is a short-lived species.

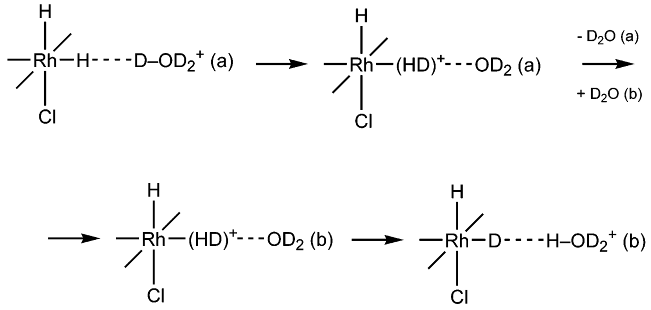
In addition to the structure and the relative stability of the assumed reaction intermediate, our results may also provide some information about the details of the H/D exchange reaction. Two possible mechanisms emerging from the present work are depicted in Schemes 3 and 4.

The mechanism summarized in Scheme 3 involves protonation of the dihydride by D_3O^+ via a dihydrogen-bonded complex resulting in the $RhH(HD)^+$ intermedi-

Scheme 3



Scheme 4



ate. The η^2-HD ligand may then undergo fast internal rearrangement so as the H atom of Rh−H becomes the leaving proton and it is transferred back to the D$^+$-donating D_2O molecule. A number of dynamic hydrogen exchange processes are known for transition metal hydrides,[40] of which the dihydrogen rotation appears to be a likely process in the present system since our calculations predict a rather low energy barrier (∼3 kcal/mol) even in the presence of solvent molecules.

An alternative mechanism can be suggested from our results (Scheme 4), in which the leaving proton of the intermediate is not transferred back to the same water molecule (D_2O(a)) but shifts to another adjacent water molecule (D_2O(b)). This process does not necessarily involve an internal η^2-HD rearrangement. Since the energy gap of the protonation/deprotonation step is estimated to be in the same range as the above rotational barrier, we cannot draw any conclusion about the preference of these mechanisms. Moreover, due to the complexity of the present solvent-mediated proton transfer reaction, it is anticipated that a dynamic study is required to provide further insight into the details of the reaction mechanism. It is also expected that the incorporation of nuclear quantum effects (tunneling and zero-point energy vibrations) for the exchanging hydrogens should also be taken into account, since both aqueous proton transfer[42] and internal hydrogen exchange process[40,43,44] are known to exhibit quantum behavior.

Finally, we mention that a recent kinetic study on H/D exchange reactions between water-soluble hydride $[RuH(PTA)_2Cp]$ and D_2O[45] deduced an activation barrier of $E_a = 17.0$ kcal/mol for the protonation/deprotonation process. The obtained barrier is significantly larger than those predicted by our theoretical models, but it has to be pointed out that the proton donor in the above reaction is assumed to be a neutral water molecule rather than H_3O^+ as it is in our system. In an attempt to estimate the energy barrier for an analogous reaction with the present rhodium complex ($[RhH_2Cl(PR_3)_3] + H_2O \rightarrow [RhH(H_2)Cl(PR_3)_3]^+ + OH^-$), we investigated the interaction of complex **1** with neutral $(H_2O)_3$ clusters. However, we were unable to locate the minimum corresponding to the **2**$\cdots(OH^-)(H_2O)_2$ species, because the hydrated OH^- ion spontaneously deprotonated the η^2-H_2 ligand in geometry optimizations. These results indicate that the direct water-induced H/D exchange mechanism is quite unlikely in the present reaction and the catalytic effect is indeed due to acidic medium.

Concluding Remarks

We have recently proposed that H/D isotope exchange reactions between H_2 and D_2O (or D_2 and H_2O) observed in the presence of water-soluble transition metal phosphine complexes occur via a cationic hydrido-dihydrogen intermediate formed by the protonation of catalytically active dihydrides.[13,14] We employed density functional theory in the present work to explore the structures and relative stability of model complexes relevant to these reactions. The proton donor in these models was represented by $(H_3O^+)(H_2O)_n$ clusters. The protonation of the dihydride complex (**1**) was found to be thermodynamically feasible with the present models, especially for the hydride ligand in *trans* position to a phosphine. Furthermore, the calculations suggest that the protonation/deprotonation step is kinetically allowed as well, since the estimated barriers are rather small. Consequently and in accord with the experimental findings, reactions (such as hydrogenation) involving Rh(I) hydrides in *aqueous media* are accompanied by extensive H/D exchange. Our theoretical study provides some hints for a detailed mechanistic picture; however, a dynamic approach is needed to obtain a refined mechanism for the present H/D exchange reaction.

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