Protonation of [tpmRu(PPh$_3$)$_2$H]BF$_4$ [tpm = Tris(pyrazolyl)methane] – Formation of Unusual Hydrogen-Bonded Species

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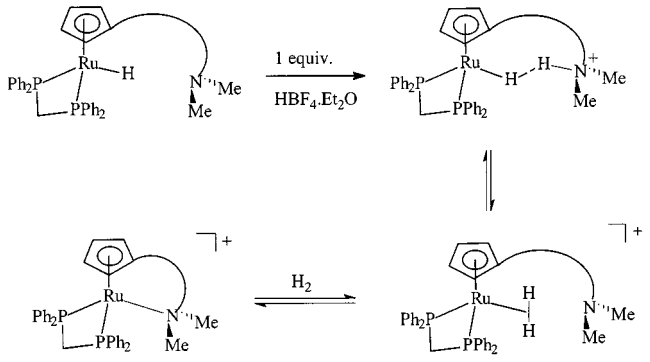
Protonation of [tpmRu(PPh$_3$)$_2$H](BF$_4$) with excess HBF$_4$Et$_2$O in CD$_2$Cl$_2$ yielded, in a straightforward manner, the dicationic η^2-dihydrogen complex [tpmRu(PPh$_3$)$_2$(H$_2$)](BF$_4$)$_2$, which, as expected, is more acidic than its monocationic Tp [Tp = hydrotris(pyrazolyl)borate] analog [TpRu(PPh$_3$)$_2$(H$_2$)]BF$_4$ (pK_a: 2.8 vs. 7.6). The complex [tpmRu(PPh$_3$)$_2$(H$_2$)](BF$_4$)$_2$ is unstable towards H$_2$ loss at ambient temperature. However, acidification of [tpmRu(PPh$_3$)$_2$H]BF$_4$ with excess aqueous HBF$_4$ or aqueous triflic acid in [D$_8$]THF gave very interesting results. Variable-temperature ^{1}H- and ^{31}P-NMR studies revealed that the aqueous acid did not fully protonate the metal hydride to form the dihydrogen complex, but a hydrogen-bonded species was obtained. The feature of this species is that the strength of its Ru–H···H–(H$_2$O)$_m$ interaction decreases with temperature; this phenomenon is unusual because other complexes containing dihydrogen bonds show enhanced M–H···H–X interaction as the temperature is lowered. Decrease of the dihydrogen-bond strength with temperature in the present case can be attributed to the decline of acidity that results from the formation of larger H$^+$(H$_2$O)$_n$ ($n > m$) clusters at lower temperatures; steric hindrance of these large clusters also contribute to the weakening of the dihydrogen bonding interactions. At higher temperatures, facile H/H exchange occurs in Ru–H···H–(H$_2$O)$_m$ via the intermediacy of a "hydrogen-bonded dihydrogen complex" Ru–(H$_2$)···(H$_2$O)$_m$. To investigate the effect of the H$^+$(H$_2$O)$_m$ cluster size on the strength of the dihydrogen bonding in [tpmRu(PPh$_3$)$_2$H]$^+$, molecular orbital calculations at the B3LYP level have been performed on model systems, [tpmRu(PH$_3$)$_2$H]$^+$ + H$^+$(H$_2$O) and [tpmRu(PH$_3$)$_2$H]$^+$ + H$^+$(H$_2$O)$_2$. The results provide further support to the notion that the formation of larger H$^+$(H$_2$O)$_n$ clusters weakens the Ru–H····H(H$_2$O)$_n$ dihydrogen bonding interaction.

Introduction

The recent discovery of intramolecular[1] and intermolecular[2] M–H···H–A dihydrogen bonding between a transition-metal hydride and a hydrogen-bond donor containing an O–H or an N–H group has attracted much attention. It has been shown that such hydride–proton interactions may significantly contribute to the stabilization of organometallic structures in mononuclear complexes[3] and cluster hydride derivatives.[1h,4] They may also be very important in the elucidation of reaction pathways occurring on the surface of transition-metal clusters bearing hydride ligands.[1h,4] Furthermore, complexes containing dihydrogen bonding have been proposed as intermediates for the formation of η^2-dihydrogen complexes or heterolytic cleavage of η^2-H$_2$ ligand.[5] This proposal has been vividly demonstrated by our recent work on intramolecularly hydrogen-bonded ruthenium complexes containing [2-(dimethylamino)ethyl]cyclopentadienyl and [3-(dimethylamino)propyl]cyclopentadienyl ligands (Scheme 1). The intramolecularly hydrogen-bonded complexes were unequivocally characterized by relaxation time T_1 measurements and spin saturation transfer study; the dihydrogen complexes in Scheme 1 were unstable toward H$_2$ loss.[6]



Scheme 1

Chaudret et al.[7] have recently reported the first direct observation of an intermolecular dynamic proton transfer equilibrium: *trans*-(dppm)$_2$HRuH···HOPh ⇌ *trans*-[(dppm)$_2$HRu(H$_2$)]$^+$(OPh)$^-$, when excess PhOH was added to a C$_6$D$_6$ or C$_7$D$_8$ solution of (dppm)$_2$RuH$_2$. The use of 10 equiv. of the more acidic alcohol, hexafluoroisopropyl alcohol (HFP) in place of PhOH resulted in complete proton transfer to give the η^2-dihydrogen complex *trans*-[(dppm)$_2$HRu(H$_2$)]$^+$[OCH(CF$_3$)$_2$]$^-$ immediately. Therefore, it seems that isolation of the hydrogen-bonded complex

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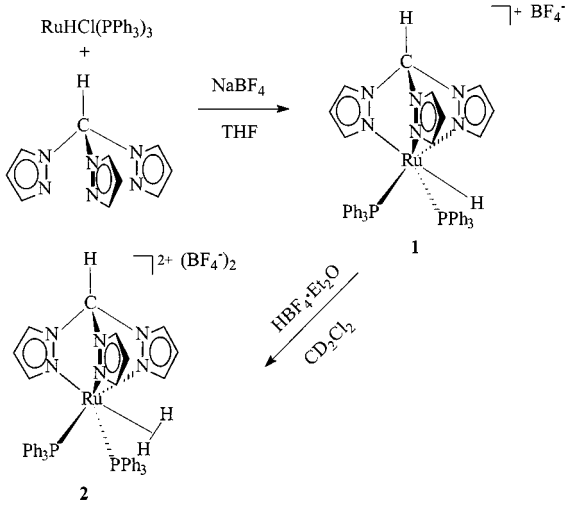
L_nM–H···HA is very dependent on the acid strength of HA. We report here that protonation of the monocationic ruthenium hydride complex $[tpmRu(PPh_3)_2H]^+$ [tpm = tris(pyrazolyl)methane] with $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 readily yields the dicationic η^2-dihydrogen complex $[tpmRu(PPh_3)_2(H_2)]^{2+}$, while on the other hand, acidification of the hydride precursor with aqueous HBF_4 or aqueous CF_3SO_3H in [D$_8$]THF generates a hydrogen-bonded species $[tpmRu(PPh_3)_2H{\cdots}H(H_2O)_m]^{2+}$, which displays some unusual and interesting behaviors in variable temperature ^{1}H- and ^{31}P-NMR spectroscopy.

Results and Discussion

Synthesis, Characterization, and Acidity Measurement of $[tpmRu(PPh_3)_2(H_2)](BF_4)_2$ (2)

The dihydrogen complex $[tpmRu(PPh_3)_2(H_2)](BF_4)_2$ (**2**) was synthesized according to the sequence shown in Scheme 2. Reaction of $RuHCl(PPh_3)_3$ with tpm and $NaBF_4$ in THF gave $[tpmRu(PPh_3)_2H]BF_4$ (**1**); adoption of the synthetic route of the analogous Tp complex $TpRu(PPh_3)_2H$ [Tp = hydrotris(pyrazolyl)borate][8] to **1** was not successful. The Tp hydride complex was prepared by sodium borohydride reduction of the chloro precursor $TpRu(PPh_3)_2Cl$, which in turn was synthesized by reaction of $RuCl_2(PPh_3)_3$ with KTp.[9] An analogous reaction of $RuCl_2(PPh_3)_3$ with tpm in the presence of $NaBF_4$ did not, however, yield $[tpmRu(PPh_3)_2Cl]BF_4$ in a pure form, instead it was contaminated with some reddish brown solids. We have learned that the reaction of the neutral facial ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (^{Me}Cn) with $RuCl_2(PPh_3)_3$ and $NaBF_4$ is always plagued by impurities too.[10]



Scheme 2

The ^{1}H-NMR spectrum of **1** shows the hydride signal as a triplet at $\delta = -13.98$ ($J_{HP} = 27.6$ Hz). The coupling constant is similar to those reported for analogous complexes with three-legged piano-stool structures. For example, J = 34.0 Hz for $CpRu(PPh_3)_2H$,[11] and 26.4 Hz for $TpRu(PPh_3)_2H$.[8] The presence of the hydride ligand is also confirmed by IR spectroscopy, which shows the ν(Ru–H) at 2054 cm^{-1} (KBr). That the net positive charge in **1** improves the Ru–H binding is evidenced by comparison of its ν(Ru–H) with that of $TpRu(PPh_3)_2H$ [ν(Ru–H) = 2008 cm^{-1}, KBr].[8] The ^{31}P{^{1}H}-NMR spectrum of **1** shows one resonance at $\delta = 68.3$, indicative of the chemical equivalence of the phosphorous atoms. The molecular dihydrogen complex **2** was prepared in situ by protonation of **1** with $HBF_4{\cdot}Et_2O$ in [D$_2$]dichloromethane at –50 °C.

The presence of the η^2-H_2 moiety in **2** was confirmed by variable-temperature relaxation time T_1 measurements and the observation of a large $^1J_{HD}$ value for the corresponding isotopomer $[tpmRu(PPh_3)_2(HD)](BF_4)_2$. The ^{1}H-NMR spectrum of **2** showed a broad signal at $\delta = -8.04$, integrating for two hydrogen atoms. A minimum T_1 value of 24 ms was recorded at 241 K and 400 MHz. Acidification of **1** with excess DBF_4 gave the η^2-HD isotopomer, which showed a 1:1:1 triplet ($^1J_{HD}$ = 31.1 Hz) of a 1:2:1 triplet ($^2J_{HP}$ = 5.7 Hz) centered at $\delta = -8.06$ in the ^{1}H-NMR spectrum.

The pseudo aqueous pK_a of **2** was estimated by studying the equilibrium shown in Equation 1 with ^{1}H NMR in CD_2Cl_2, using the hydride complex $[^{Me}CnRu(dppe)H]^+$ (^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) as the base.

$$[tpmRu(PPh_3)_2(H_2)]^{2+} + [^{Me}CnRu(dppe)H]^+ \rightleftharpoons [tpmRu(PPh_3)_2H]^+ + [^{Me}CnRu(dppe)(H_2)]^{2+} \quad (1)$$

The pseudo aqueous pK_a value of $[^{Me}CnRu(dppe)(H_2)]^{2+}$ has been determined previously in CD_2Cl_2 using a similar method.[12a] The equilibrium mixture could be conveniently obtained by protonating a mixture of $[tpmRu(PPh_3)_2H]^+$ and $[^{Me}CnRu(dppe)H]^+$ with a limited amount of $HBF_4{\cdot}Et_2O$. The equilibrium was obtained at –60 °C because the η^2-dihydrogen complex **2** is unstable towards H_2 loss at higher temperatures. The relative concentrations of the dihydrogen complexes and metal hydrides in the equilibrium were estimated from integration of the upfield hydride signals in the ^{1}H-NMR spectrum. The pK_a of **2** was estimated to be 3 according to Equation 2. K_{eq} in Equation 2 is the equilibrium constant of Equation 1.

$$pK_a(\mathbf{2}) = pK_{eq} + pK_a([^{Me}CnRu(dppe)(H_2)]^{2+}) \quad (2)$$

The dihydrogen complex **2** is a new entry into the relatively small family of dicationic η^2-dihydrogen complexes.[12] In contrast to the abundance of monocationic dihydrogen complexes, the number of well-characterized dicationic dihydrogen complexes is still limited. The double positive charge of the metal center in these complexes lowers the effectiveness of $d\sigma(M)\rightarrow\sigma^*(H_2)$ back bonding, and increases the $\sigma(H_2)\rightarrow d\sigma(M)$ interaction. It is therefore expected that depletion of electron density in the η^2-H_2 ligand renders the dicationic dihydrogen complexes very

acidic. Dicationic dihydrogen complexes, which demonstrate high reactivity toward heterolysis of η^2-H_2 ($pK_a < -2$) and high room-temperature stability with respect to loss of H_2, both in solid state and in solution, have recently been reported, including $[Os(bpy)(PR_3)_2(CO)(H_2)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$; bpy = 2,2′-bipyridine),[12b][12c] $[Os(phen)(PPh_3)_2(CO)(H_2)]^{2+}$ (phen = 1,10-phenanthroline),[12c] $[Os(dppp)_2(CO)(H_2)]^{2+}$,[12d] *trans*-$[Os(dppe)_2(CH_3CN)(H_2)]^{2+}$,[12e] and *trans*-$[Fe(dppe)_2(L)(H_2)]^{2+}$ (L = CO, CNH).[12f] A strong $\sigma(H_2)\rightarrow d\sigma(M)$ interaction is believed to be dominant in these complexes.

Less stable (H_2 loss at room temperature), but acidic dicationic dihydrogen complexes are exemplified by $[Os(P\mathit{i}Pr_3)_2(CH_3CN)_3(H_2)]^{2+}$,[12g] $[Ru(bpy)(PPh_3)_2(CO)(H_2)]^{2+}$,[12c] and $[Ru(dppp)_2(CO)(H_2)]^{2+}$.[12d] We have recently reported the synthesis and acidity of some dicationic dihydrogen complexes containing the facial triazacyclononane ligands $[^{R}CnRu(L)(L')(H_2)]^{2+}$ [^{H}Cn = 1,4,7-triazacyclononane, ^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane; L,L′ = $(PPh_3)_2$, dppe, and CO, PPh_3]; the acidity of the complexes $[^{H}CnRu(PPh_3)_2(H_2)]^{2+}$ (pK_a = 4.5) and $[^{Me}CnRu(dppe)(H_2)]^{2+}$ (pK_a = 3.8), although low in comparison to those of the aforementioned dicationic dihydrogen complexes, are nevertheless significantly higher than those of their monocationic hydrotris(pyrazolyl)borato (Tp) and Cp analogoues (by 3–4 pK_a units). The carbonyl-containing complexes $[^{H}CnRu(PPh_3)(CO)(H_2)]^{2+}$ (pK_a = –1.3) and $[^{Me}CnRu(PPh_3)(CO)(H_2)]^{2+}$ (pK_a = –2.6) are also more acidic than their monocationic Tp counterpart $[TpRu(PPh_3)(CO)(H_2)]^{+}$ (pK_a = –0.6), but to a smaller extent. The non-carbonyl-containing ^{R}Cn dihydrogen complexes are stable in the solid state at room temperature, but in solution the η^2-H_2 ligand is displaced by strongly coordinating solvent such as acetonitrile.[12a] It should be mentioned that dicationic dihydrogen complexes are not necessarily acidic, for example, $[Os(NH_3)_4(L)(H_2)]^{2+}$ [12h,12i] and $[Os(en)_2(L)(H_2)]^{2+}$,[12j] reported by Taube and co-workers, which tightly bind H_2, are not acidic, probably due to the strong electron-donating effect of the NH_3 and en ligands.

The fact that complex **2** is more acidic than the analogous dicationic ^{R}Cn dihydrogen complexes $[^{H}CnRu(PPh_3)_2(H_2)]^{2+}$ [12a] and $[^{Me}CnRu(PPh_3)_2(H_2)]^{2+}$ [12a] seems to indicate that the tpm ligand is less electron donating than ^{R}Cn. As expected, **2** is significantly more acidic than the analogous monocationic Tp and Cp complexes. On the other hand, the stability of **2** is lower than that of the ^{R}Cn, Tp, and Cp counterparts. The η^2-H_2 of **2** is labile at –15 °C. In fact, addition of $HBF_4{\cdot}Et_2O$ to **1** in CD_2Cl_2 at room temperature resulted in immediate evolution of H_2, which gave a signal at δ = 4.62 in the ^{1}H-NMR spectrum. The major product of the reaction was the aquo complex $[tpmRu(PPh_3)_2(H_2O)](BF_4)_2$ (**3**),[13] which was formed by displacement of η^2-H_2 by residual H_2O in the solvent, only a trace amount of **2** was detected (vide infra). It is noteworthy that the T_1(min) of **2** is larger than that of the monocationic analog $[TpRu(PPh_3)_2(H_2)]BF_4$,[8] and its $^1J_{HD}$ value is smaller than that of the latter. The weaker H–H interaction of the η^2-H_2 ligand in **2** relative to that of the η^2-H_2 in $[TpRu(PPh_3)_2(H_2)]BF_4$ may be due the fact that the tpm ruthenium fragment $[tpmRu(PPh_3)_2]^{2+}$ is a stronger σ-acceptor than the Tp counterpart. Morris has pointed out that the lower H–H bond strength of the η^2-H_2 in $[Os(pys)(PPh_3)_2(CO)(H_2)]BF_4$ (pys = 2-pyridinethiolate) is a result of the strong $\sigma(H_2)\rightarrow d\sigma(M)$ interaction.[14]

Acidification of [tpmRu(PPh$_3$)$_2$H](BF$_4$) (1) with Aqueous HBF$_4$ or Aqueous CF$_3$SO$_3$H

While protonation of **1** with excess $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 generated **2** in a straightforward manner, acidification of **1** in [D$_8$]THF with excess aqueous HBF_4 or aqueous CF_3SO_3H gave quite different results. No dihydrogen gas evolution was detected, even when the acidification was carried out at room temperature; and no signal seemed to be observable in the upfield region of the ^{1}H-NMR spectrum (Figure 1, left). However, a very broad signal became detectable at –15°C; and it gradually evolved into a broad triplet as the temperature was lowered to –45°C; the broad triplet sharpened when the temperature was further decreased to –60°C . The spectral change with temperature was found to be reversible, i.e. the triplet gradually broadened into the baseline again with increasing temperature. Concurrent off-resonance decoupled ^{31}P-NMR spectra are also shown in Figure 1 (right). It can be seen that as the triplet hydride peak starts broadening out at –45 °C, H–P coupling in the ^{31}P-NMR spectrum disappears. The phosphorus peak also sharpens as the hydride signal broadens into the baseline. Like the VT ^{1}H-NMR study, the spectral changes with temperature in the ^{31}P-NMR measurements are also reversible. In fact, if the protonation reaction was carried out at –60°C, and the temperature gradually raised to 20°C, the sets of ^{1}H- and ^{31}P-NMR spectra collected at various temperatures were identical to those depicted in Figure 1. It is interesting to note that throughout the whole variable-temperature NMR study, signals pertaining to η^2-H_2 ligand and free H_2 were not observed.

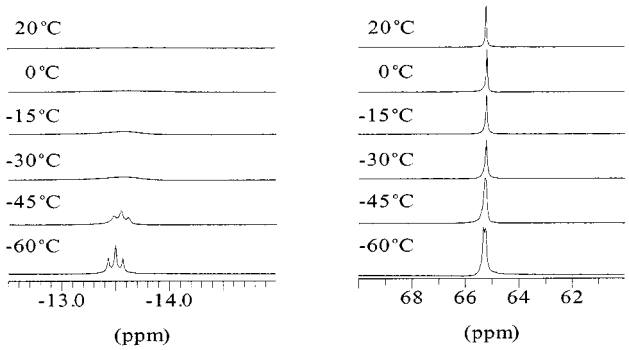
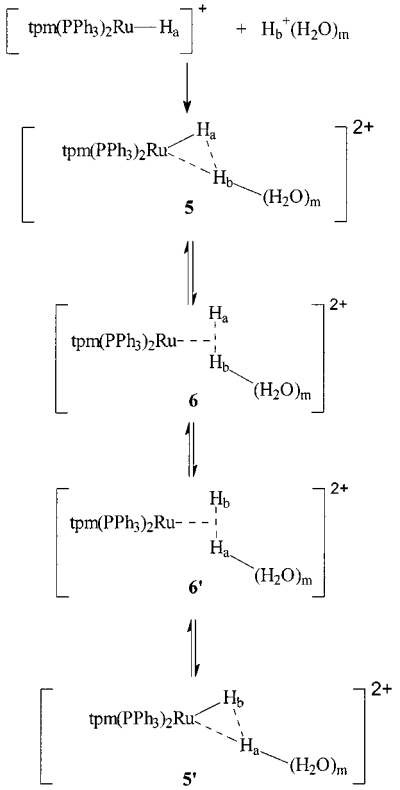


Figure 1. Variable-temperature (left) ^{1}H-NMR spectra (upfield region) and (right) ^{31}P-NMR spectra of $[tpmRu(PPh_3)_2H]^+$ + aq HBF_4 in [D$_8$]THF

The fact that acidification of **1** with aqueous HBF_4 or aqueous CF_3SO_3H in [D$_8$]THF gave identical result, as revealed by VT ^{1}H- and ^{31}P-NMR studies, seemed to indicate that the two acids were leveled to the same species in the

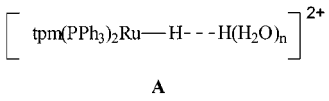
two systems. We assume that the acids were both leveled to $H^+(H_2O)_m$, and have to admit that the precise state of solvation of H^+ was unknown.[15] It seems, however, that the pK_a value (–1.74)[16] commonly assigned to H_3O^+ does not reflect the actual acidity of the aqueous HBF_4 or aqueous CF_3SO_3H in our case. Failure to generate the dihydrogen complex **2** with aqueous HBF_4 or aqueous CF_3SO_3H implies that acidity of either acid might only be close to or even lower than that of $[tpmRu(PPh_3)_2(H_2)]^{2+}$, and therefore is not able to effect complete proton transfer to **1**. In our recent work, we have attributed deprotonation of the η^2-H_2 ligands in $[TpRu(L_2)(H_2)]^+$ [L_2 = $(PPh_3)_2$, dppe][8][12a] and $[^RCnRu(L_2)(H_2)]^{2+}$ [^RCn = 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane; L_2 = $(PPh_3)_2$, dppe][12a] by H_2O in THF/H_2O or organic/aqueous mixed solvents to strong solvation of H^+ by H_2O; all these complexes have pK_a values higher than 3.



Scheme 3

Spectral changes of the hydride signal in the VT ^{1}H-NMR study of the acidification reaction of **1** with aqueous acid are contrary to the behaviors of the hydride signals of complexes containing dihydrogen bonding. The hydride signals of these complexes usually broaden as the temperature goes down, due to strengthening of the M–H···H–X interaction, and they sharpen as the temperature is increased because of weakening of the dihydrogen bonding. The unusual spectral behavior displayed by the hydride ligand of **1** in the acidification process can be reconciled by the sequence depicted in Scheme 3. Acidification of **1** with aqueous acid generates the hydrogen-bonded species **5**; at higher temperature, rapid H/H exchange between Ru–H and $H^+(H_2O)_m$ (**5** ⇌ **5′**) via the intermediacies of a pair of transient η^2-dihydrogen complexes (**6** and **6′**) leads to broadening-out of the hydride signal. The feature of this pair (**6** and **6′**) is that the η^2-H_2 ligand, which is hydrogen-bonded to the $(H_2O)_m$, does not dissociate readily from the metal center, and that might be the reason for not observing free H_2 in the course of the VT ^{1}H-NMR study. Analogously, Crabtree et al. have very recently reported that hydrogen-bonding provided by a pendant amine group is the key factor that allows stabilization of an Ir–(HF) complex.[17] Species similar to **5** (or **5′**) and **6** (or **6′**) have been proposed as intermediates in the protonation of *cis*-$[FeH_2\{PCH_2CH_2PPh_2)_3\}]$ to form the η^2-dihydrogen complex.[18]

At low temperature (–60° C), acidity decreases due to higher degree of solvation of H^+, i.e. formation of larger cluster $H^+(H_2O)_n$; Ru–H···$H(H_2O)_n$, dihydrogen bonding in **A** weakens and therefore results in sharpening of the hydride signal.



A

Weakening of the dihydrogen bonding in **A** at low temperature can also be rationalized in terms of steric effect of the large cluster $H^+(H_2O)_n$.

Another possible scenario for the protonation of **1** with aqueous acid is the occurrence of a rapid proton transfer between **1** and H_2O (Equation 3); lowering the temperature would slow down this proton exchange and the low temperature spectrum closely resembles that of complex **1**. But the equilibrium depicted in Equation 3 does not seem to be in congruence with the VT NMR spectra shown Figure 1.

$$\underset{\mathbf{1}}{[tpmRu(PPh_3)_2H]^+} + H_3O^+ \rightleftharpoons \underset{\mathbf{2}}{[tpmRu(PPh_3)_2(H_2)]^{2+}} + H_2O \quad (3)$$

If such a rapid proton transfer occurs, it is most likely that a weighted average of hydride signals of **1** and **2** is observed, and the phosphorus signal is also an average of those of **1** and **2**. However, careful examination of the VT ^{1}H- and ^{31}P-NMR spectra does not reveal the existence of these average signals. It is also noteworthy that no H_2 loss was observed when the system was allowed to stand at room temperature. Had the equilibrium depicted in Equation 3 existed, the equilibrating **2** should have evolved H_2 while standing at room temperature. We have learned that **2** is unstable with respect to H_2 loss at –15 °C.

Dihydrogen bonding between the protonated water cluster $H(H_2O)_m^+$ and the hydride in **5** (or **5′**) was characterized by IR spectroscopy in THF at room temperature. A THF solution of **2** showed the ν(RuH) band at 2040 cm^{-1}, upon addition of 10 equiv. of aqueous HBF_4, this band was shifted to a lower wavenumber at 1967 cm^{-1}. Berke, Epstein, and co-workers have characterized intermolecular hydrogen bonding of acidic alcohols to the hydride ligand of $WH(CO)_2(NO)L_2$ by IR spectroscopy in hexane at 200 K. The IR spectrum of the tungsten hydride complex showed

a low-wavenumber shoulder in the ν(WH) band, in the presence of 3 equiv. of hexafluoro-2-propanol (HFIP).[2e] Unfortunately, it is not possible to characterize the dihydrogen bonding between **2** and protonated water cluster by measurement of T_1(min) because the strength of the Ru–H···H(H$_2$O)$_{m\ or\ n}$ dihydrogen bond in the system varies with temperature. Furthermore, it is not possible to measure T_1 at –30 °C or above since the hydride signal broadens into the baseline at these temperatures. Acidification of **1** with HBF$_4$·Et$_2$O in CD$_3$OD/[D$_8$]THF gave practically identical results as the protonation of **1** with aqueous HBF$_4$ in [D$_8$]THF. This is not surprising since it is expected that methanol behaves very similarly to H$_2$O in this process. Quantum chemical calculations described in the following section also seem to support our proposal of Scheme 3.

At this point, we would like to comment on the formation of aquo complex [tpmRu(PPh$_3$)$_2$(H$_2$O)](BF$_4$)$_2$ (**3**) in the room-temperature protonation reaction of **1** with HBF$_4$·Et$_2$O in CD$_2$Cl$_2$. The predominant form of acid in this system is Et$_2$OH$^+$, which is strong enough to fully protonate **1** to form **2**. The trace amount of water present in the system does not form the hydrogen-bonded species **5** (or **5′**) with **2** because it is protonated by Et$_2$OH$^+$ (Equation 4), which is a stronger acid than **2**. At –15°C or above, the η^2-H$_2$ ligand in **2** becomes labile, and the coordinatively unsaturated species generated upon dissociation of H$_2$ from **2** abstracts H$_2$O from the equilibrium (Equation 4) to form the thermodynamically stable aquo complex **3**.

$$Et_2OH^+ + H_2O \rightleftharpoons Et_2O + H_3O^+ \quad (4)$$

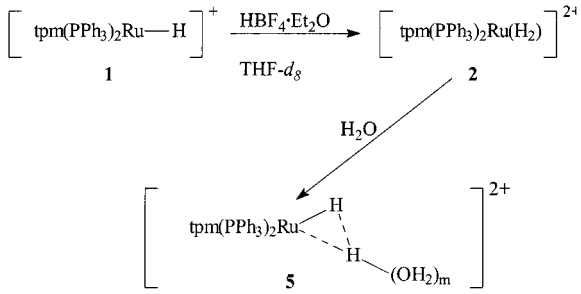
The H/H exchange proposed in Scheme 3 was further supported by H/D exchange, which occurred in the acidification of a [D$_8$]THF solution of **1** with CF$_3$SO$_3$D/D$_2$O. It was found that addition of CF$_3$SO$_3$D/D$_2$O (v/v, 1:1) to a [D$_8$]THF solution of **1** at room temperature led to immediate broadening of the hydride signal into the baseline. The upfield triplet signal, which re-appeared as the temperature was lowered to –60 °C, diminished considerably due to H/D exchange.

Structure **5** (or **5′**) can be viewed as an intermediate on the reaction path that leads to transient **6** (or **6′**), and then to the product of complete proton transfer from an acid to the metal hydride precursor. Gusev and Reinhart have very recently proposed that reactions of anionic ruthenium and rhenium hydrides with phenylacetylene first generate the hydrogen-bonded species [L$_n$M–H···H–C≡CPh]$^-$, which equilibrates with the transient [L$_n$M(μ-H$_2$)(CCPh)]$^-$ (Equation 5). The latter, which is analogous to **6** (or **6′**), then undergoes hydride transfer to the C$_\alpha$ atom of phenylacetylene to form the [L$_n$M–C(Ph)=CH$_2$]$^-$ vinyl intermediate.[19]

(5)

Generation of the Hydrogen-Bonded Complex from 2

We have been able to generate the hydrogen-bonded complex **5** from the η^2-dihydrogen complex **2**, and have monitored this transformation by using ^{1}H-NMR spectroscopy. Complex **2** was first formed in a 5-mm NMR tube by acidification of a [D$_8$]THF solution of **1** (0.4 mL) with 1 equiv. of HBF$_4$·Et$_2$O at –30 °C, subsequent addition of 50 μL of H$_2$O to the solution led to the disappearance of the η^2-H$_2$ signal of **2** and concomitant appearance of the very broad peak of the hydrogen-bonded hydride of **5** (Scheme 4).



Scheme 4

Quantum Chemical Study

The broadening/sharpening changes of the hydride signal for the dihydrogen-bonded species **5** observed in the variable-temperature NMR experiments show unusual behavior when compared to other dihydrogen bonded systems.[2e,7] In order to provide an insight into the understanding of the unusual behavior, quantum mechanical calculations at the density-functional B3LYP level of theory have been undertaken to investigate the structural details for the following model systems: [tpmRu(PH$_3$)$_2$H]$^+$, [tpmRu(PH$_3$)$_2$(H$_2$)]$^{2+}$, [tpmRu(PH$_3$)$_2$H]$^+$ + H$^+$(H$_2$O), and [tpmRu(PH$_3$)$_2$H]$^+$ + H$^+$(H$_2$O)$_2$. The [tpmRu(PH$_3$)$_2$(H$_2$)]$^{2+}$ system represents the complete proton transfer product in organic solvent. The latter two model systems represent the corresponding situation in aqueous/THF solution, and the relevant calculations allow us to study the effect of water aggregation on the dihydrogen bonding. They can also provide information on the structural details of protonated products under different acidity because one can consider that HBF$_4$·Et$_2$O is more acidic than H$^+$(H$_2$O), which in turn, is more acidic than H$^+$(H$_2$O)$_2$. It should be noted that the model systems cannot be directly related to the experimental systems because the actual degree of water aggregation in each experimental system cannot be well-defined. Therefore, the calculated H···H distances for different numbers of water molecules in the model systems are only useful in considering the trend, which qualitatively accounts for the effect of water aggregation on the dihydrogen bonding.

The optimized structures for the four model systems are shown in Figure 2. Consistent with the experimental finding that the direct protonation of [tmpRu(PPh$_3$)$_2$H]$^+$ with HBF$_4$·Et$_2$O in an organic solvent gives a non-classical dihydrogen complex, [tpmRu(PH$_3$)$_2$(H$_2$)]$^{2+}$. The H–H distance in this dihydrogen complex is calculated to be 0.81 Å with a symmetrical coordination of the η^2-H$_2$ unit (Ru–H: 1.82 Å).[20]

The calculations for the [tpmRu(PH$_3$)$_2$H]$^+$ + H$^+$(H$_2$O) system give a similar result. The system can be described as [tpmRu(PH$_3$)$_2$(H$_2$)···OH$_2$]$^{2+}$, again a non-classical dihydro-

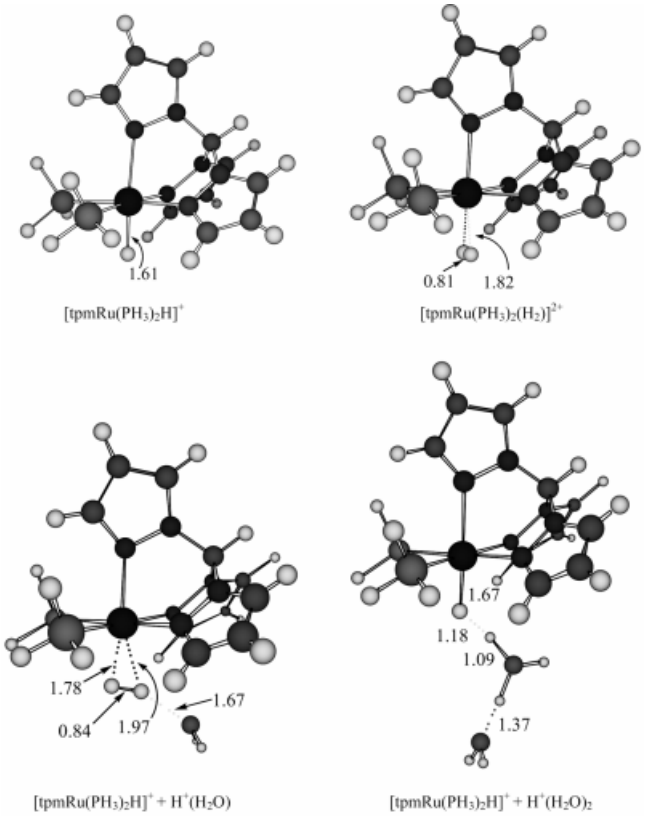


Figure 2. Optimized structures for model systems: $[tpmRu(PH_3)_2H]^+$, $[tpmRu(PH_3)_2(\eta^2\text{-}H_2)]^{2+}$, $[tpmRu(PH_3)_2H]^+ + H^+(H_2O)$, and $[tpmRu(PH_3)_2H]^+ + H^+(H_2O)_2$

gen complex, a weak hydrogen bond exists between one of the two hydrogen atoms and the oxygen atom of H_2O (H···O: 1.67 Å). The H–H distance (0.84 Å) in the η^2-H_2 unit lengthens only slightly, although the coordination of the η^2-H_2 ligand becomes unsymmetrical. The Ru–H distance on the side of the O···H hydrogen bonding is lengthened (1.97 Å) while the other is shortened (1.78 Å). The results of these calculations for the mono-water system suggest that $H^+(H_2O)$ is still very acidic, resulting in the formation of non-classical structure upon protonation.

Surprisingly, further association with one more water molecule, which gives the $[tpmRu(PH_3)_2H]^+ + H^+(H_2O)_2$ system, leads to a species that is close to a classical hydride. The metal-hydride distance, calculated to be 1.67 Å, is within the range of classical M–H distance[20g,21] {1.61 Å in $[tpmRu(PH_3)_2H]^+$}. In this system, the hydride ligand was also found to have a significant interaction with the proton from the $H^+(H_2O)_2$ unit. The H···H distance was calculated to be 1.18 Å. The typical H···H distance in other M–H···H–X systems is around 1.8 Å.[5] Apparently, in the current system, the hydride acceptor [H^+ in $H^+(H_2O)_2$] is very protonic when compared to other systems studied previously.[2e,7] In the structure of $[tpmRu(PH_3)_2H]^+ \cdots H^+(H_2O)_2$, one can clearly see the aggregate of $H^+(H_2O)_2$, which can be formulated as $H^+(H_2O)\cdots OH_2$. The additional H_2O is only weakly bounded through normal hydrogen bonding.

These calculations indicate that the mono-water system prefers a dihydrogen non-classical structure, while the di-water system adopts a structure close to a classical hydride. Though weakly bound, the presence of an additional water molecule surprisingly switches the non-classical structure to a classical one with M–H···H–X dihydrogen bonding. This result suggests that a fast exchange can occur between classical and non-classical structures, as proposed in Scheme 3, when temperature increases. The association and dissociation of the weakly bound water molecule can be strongly influenced by temperature.

The current work deals with the effect of water aggregation on the H···H dihydrogen bonding. The stability of these dicationic hydrogen-bonded systems is another important topic that requires further attention. Theoretically, the evaluation of the H···H bonding strengths in the studied systems involves the charge-separation processes. Therefore, much higher levels of theory are necessary in order to produce some meaningful results. Clearly, the stability of these systems should be further studied both theoretically and experimentally.

Conclusion

We have shown in this study, the species that are proposed as intermediates along the reaction pathway of protonation of metal hydrides to form η^2-dihydrogen complexes. One of these species is a hydrogen-bonded metal hydride, $[tpmRu(PPh_3)_2H\cdots H(H_2O)_n]^{2+}$ (**A**), which is formed by acidification of $[tpmRu(PPh_3)_2H]^+$ with aqueous HBF_4 in [D_8]THF at –60 °C. The comparatively weak Ru–H···$H(H_2O)_n$ dihydrogen interaction is attributable to lower acidity and larger steric hindrance of the bulky $H^+(H_2O)_n$ clusters, which are the major forms of acid at low temperature. At higher temperatures, the degree of aquation of H^+ decreases and the smaller clusters $H^+(H_2O)_m$ ($m < n$) exhibit relatively higher acidity, therefore the species **5** (or **5′**) with stronger dihydrogen bonding become the major species in solution. Finally, a full-fledged η^2-dihydrogen complex $[tpmRu(PPh_3)_2(H_2)]^{2+}$ is generated when $tpmRu(PPh_3)_2H$ is protonated with $HBF_4{\cdot}Et_2O$ in CD_2Cl_2. The results of our quantum chemical calculations at B3LYP level on model systems, $[tpmRu(PH_3)_2H]^+ + H^+(H_2O)$ and $[tpmRu(PH_3)_2H]^+ + H^+(H_2O)_2$, indeed suggest that the Ru–H···$H(H_2O)_m$ dihydrogen bonding interaction greatly depends on the size of the water cluster. For the mono-water model system, a non-classical dihydrogen complex is preferred. The di-water system, however, gives a Ru–H···$H(H_2O)_2$ dihydrogen bonded species.

The acidification of metal hydrides normally leads to either non-classical η^2-H_2 dihydrogen complexes or formation of species with the M–H···H–X interaction (dihydrogen bonding). Strongly acidic conditions give non-classical complexes, while weakly acidic conditions result in dihydrogen bonding. Here, we demonstrate that the strength of hydride-proton interaction can be tuned through the association of water molecules to H^+.

Experimental Section

All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents[22] (solvent/drying agent): methanol/Mg/I$_2$, ethanol/Mg/I$_2$, acetonitrile/CaH$_2$, dichloromethane/CaH$_2$, tetrahydrofuran/Na/benzophenone, diethyl ether/Na, *n*-hexane/Na. Ruthenium trichloride, RuCl$_3$·3H$_2$O, pyrazole, sodium tetrafluoroborate, and [D$_1$]trifluoromethanesulfonic acid were purchased from Aldrich. Tetrafluoroboric acid in ethereal solution and aqueous solution were obtained from Fluka. Triphenylphosphane was obtained from Merck and was recrystallized from ethanol before use. The complexes RuHCl(PPh$_3$)$_3$ [23] and [^{Me}CnRu(dppe)H]BF$_4$ (^{Me}Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane)[12a] were synthesized according to literature methods. – Infrared spectra were obtained from a Nicolet Magna 750 Ft-IR spectrophotometer. ^{1}H-NMR spectra were recorded with a Bruker DPX-400 spectrometer; chemical shifts were reported relative to residual protons of the deuterated solvents. ^{31}P-NMR spectrum were measured at 161.7 MHz with a Bruker DPX-400 spectrometer; chemical shifts of these spectra were externally referenced to 85% H$_3$PO$_4$ in D$_2$O (δ = 0). Relaxation-time T_1 measurements were carried out at 400 MHz by the inversion-recovery method using the standard 180°–τ–90° pulse sequences. Elemental analyses were performed by M–H–W laboratories, Phoenix, AZ.

Trispyrazolylmethane (tpm): The ligand tpm was prepared by following a literature method,[24] with some modifications. A solution of pyrazole (10.00 g, 0.15 mmol) in 30 mL of THF was added to a vigorously stirred suspension of potassium (1.9 g, 50 mmol) in 200 mL of THF. After the potassium had completely reacted, chloroform (6.0 mL, 6.5 mmol) was slowly added over a period of 2 h, and the colloidal mixture was stirred under reflux for 36 h. The mixture was filtered at room temperature to remove the KCl, and the solvent of the filtrate was removed by using a rotary evaporator to yield a dark brown sludge. Pure trispyrazolylmethane was obtained by sublimation of the dark brown sludge. Yield: 3.1 g (9.5% based on pyrazole used).

[tpmRu(PPh$_3$)$_2$H]BF$_4$ (1): Samples of RuHCl(PPh$_3$)$_3$ (0.60 g, 0.60 mmol), tpm (0.15 g, 0.70 mmol), and NaBF$_4$ (0.072 g 0.66 mmol) were dissolved is 20 mL of THF and the solution was stirred at room temperature for 1 h. The solution was then concentrated to dryness under vacuum, and the residue was washed with methanol. Pure product was obtained by recrystallization of the residue with dichloromethane/hexane. Yield: 0.48 g (87%). – C$_{46}$H$_{41}$BF$_4$N$_6$P$_2$Ru: calcd. C 59.55, H 4.45, N 9.06; found C 59.48, H 4.48, N 8.94. – IR (KBr, cm^{-1}): ν(Ru–H) = 2054 (m). – ^{1}H NMR ([D$_6$]acetone, 400 MHz, 25 °C): δ = –13.82 (t, 1 H, $^3J_{HP}$ = 27.8 Hz), 5.99 (t, 2 H, pz, $^3J_{HH}$ = 2.36 Hz), 6.31 (t, 1 H, pz, $^3J_{HH}$ = 2.35 Hz), 6.83 (d, 1 H, pz, $^3J_{HH}$ = 1.70 Hz), 6.88 (d, 2 H, pz, $^3J_{HH}$ = 1.82 Hz), 7.13–7.37 (m, 30 H of PPh$_3$), 8.21 (d, 2 H, pz, $^3J_{HH}$ = 2.59 Hz), 8.48 (d, 1 H, pz, $^3J_{HH}$ = 2.57 Hz), 9.33 (s, 1 H, pz$_3$C*H*). – ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 161.70 MHz, 25 °C): δ = 70.6 (s).

In Situ Preparation of [tpmRu(PPh$_3$)$_2$(H$_2$)](BF$_4$)$_2$ (2): A sample of **1** (10 mg, 11 μmol) was dissolved in 0.4 mL of [D$_2$]dichloromethane, the solution was cooled to –50 °C inside the NMR probe, 1.3 μL of HBF$_4$ (13 μmol, 54% solution in diethyl ether) was then added. A period of 15 min was allowed for completion of the reaction before NMR spectra were recorded. – ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, –50 °C): δ = –8.04 [br. s, 2 H, Ru–(H$_2$)], 5.34 (s, 1 H, pz), 5.76 (s, 1 H, pz), 5.93 (s, 2 H, pz), 6.32 (s, 2 H, pz), 6.98–7.50 (m, 30 H of PPh$_3$), 7.98 (s, 2 H, pz), 8.41 (s, 1 H, pz), 9.33 (s, 1 H, pz$_3$C*H*). – ^{31}P{^{1}H} NMR (CD$_2$CL$_2$, 161.70 MHz, –50 °C): δ = 48.2 (s). Variable- temperature T_1 measurements on the H$_2$ signal were carried out by the inversion-recovery method using standard 180°–τ–90° pulse sequence. – T_1 (400 MHz, ms): 41.3 (203 K), 32.9 (213 K), 28.2 (223 K), 25.2 (233 K), 23.9 (243 K), 28.7 (253 K). T_1(min) (400 MHz, 241 K): 24.0 ms.

In Situ Preparation of [tpmRu(PPh$_3$)$_2$(HD)](BF$_4$)$_2$ ([D$_1$]-2): A sample of **1** (18 mg, 20 μmol) was dissolved in 0.4 mL of [D$_2$]dichloromethane. After cooling the solution to –50 °C, 2.1 μL of DBF$_4$ solution was added. – ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, –50 °C): δ = –8.06 (tt, J_{HD} = 31.1 Hz, J_{HP} = 5.8 Hz).

[tpmRu(PPh$_3$)$_2$(H$_2$O)](BF$_4$)$_2$ (3): A sample of **1** (300 mg, 0.3 mmol) was dissolved in 20 mL of CH$_2$Cl$_2$, excess HBF$_4$·Et$_2$O (100 μL, 54% solution in diethyl ether) was added, followed by addition of 5 μL of H$_2$O. The solution was stirred at room temperature for 30 min, and was then concentrated to dryness under vacuum to yield a pale yellow solid, which was washed with 20 mL of diethyl ether. Yield: 270 mg (88%). – C$_{46}$H$_{42}$B$_2$F$_8$N$_6$OP$_2$Ru: calcd. C 53.55, H 4.10, N 8.15; found C 53.36, H 3.93, N 8.07. – ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 20 °C): δ = 9.91 (s, 1 H, pz$_3$C*H*), 8.79 (d, 1 H, pz, $^3J_{HH}$ = 2.90 Hz), 8.55 (d, 2 H, pz, $^3J_{HH}$ = 2.78 Hz), 7.60–7.34 (m, 30H of PPh$_3$), 6.90 (d, 1 H, pz, $^3J_{HH}$ = 1.98 Hz), 6.43 (t, 2 H, pz, $^3J_{HH}$ = 2.48 Hz), 5.86 (t, 1 H, pz, $^3J_{HH}$ = 2.68 Hz), 5.52 (d, 1 H, pz, $^3J_{HH}$ = 2.31 Hz), 3.71 (s, 2 H, *H*$_2$O). – ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162 MHz, 20 °C): δ = 44.1 (s).

Acidity Measurement: The pK_a value of [tpmRu(PPh$_3$)$_2$(H$_2$)](BF$_4$)$_2$ was estimated by studying the equilibrium shown in Equation 1. In the experiment, appropriate amounts of [tpmRu(PPh$_3$)$_2$H]BF$_4$ and [^{Me}CnRu(dppe)H]BF$_4$ were dissolved in CD$_2$Cl$_2$ in an NMR tube, and a limited amount of HBF$_4$·Et$_2$O was then added. The ^{1}H-NMR spectrum was immediately taken at –60 °C. Relative molar concentrations of the equilibrated species were derived from the ^{1}H-NMR integrations of the hydride signals.

Protonation of [tpmRu(PPh$_3$)$_2$H]BF$_4$ (1) with Aqueous HBF$_4$: A sample of [tpmRu(PPh$_3$)$_2$H]BF$_4$ (**1**) (10 mg, 0.011 mmol) was dissolved in 0.4 mL of [D$_8$]THF in a 5-mm NMR tube, and 10 μL of aqueous HBF$_4$ (8 M) was added. The VT ^{1}H-NMR spectra were immediately taken.

Computational Details: The quantum mechanical calculations at the density-functional B3LYP level of theory used the effective core potentials of Wadt and Hay with double-ζ valence functions[25] for the Ru and P atoms. The standard 3–21G basis sets were applied to the first-row elements H, C, and N, with those hydrogens directly involved in hydrogen bonding (and dihydrogen bonding) augmented by single-ζ polarization functions (i.e. 3–21 g**).[26] The use of the 3–21G basis set in the calculations allows us to keep the computational expense reasonable due to the large size of the tmp ligand. All structures were fully optimized with the Gaussian98 package.[27]

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