First NMR Observation of the Intermolecular Dynamic Proton Transfer Equilibrium between a Hydride and Coordinated Dihydrogen: $(dppm)_2HRuH\cdots H{-}OR = [(dppm)_2HRu(H_2)]^+(OR)^-$

José A. Ayllón, Corinne Gervaux, Sylviane Sabo-Etienne, and Bruno Chaudret*

Laboratoire de Chimie de Coordination CNRS, 205 Route de Narbonne, F-31077 Toulouse-Cedex, France

Received February 3, 1997⊗

*Summary: A dynamic equilibrium between the dihydride trans-$RuH_2(dppm)_2$ (**1**) and the hydrido dihydrogen complex $[(dppm)_2HRu(H_2)]^+(OR)^-$ in the presence of phenol or hexafluoroisopropyl alcohol has been established by ^1H NMR, and the thermodynamics of the reaction (namely $\Delta H = 17 \pm 3$ kcal·mol^{-1} and $\Delta S = 75.8$ eu in the case of phenol addition) could be determined.*

The presence of hydrogen bonds between a transition metal hydride and a hydrogen bond donor containing an O−H or an N−H group has recently been established intramolecularly by Crabtree[1] and Morris[2] and intermolecularly by Crabtree in the solid state[3] and Epstein and Berke in solution.[4] Complexes displaying such hydrogen bonding have been proposed to be important intermediates for the formation of dihydrogen complexes[5] or the reverse reaction, namely the base-promoted heterolytic splitting of dihydrogen. In this respect, a dihydrogen tautomer has been proposed to be involved in the deuteration reaction of a complex containing a hydride ligand hydrogen-bonded to the acidic proton of a thiolatopyridinium ligand;[2a] however, no direct evidence for such a process has been obtained.

We have recently shown that hydrogen bonding to $Cp^*(PCy_3)RuH_3$ leads, in solution, to an enhancement of the exchange couplings present in this complex[6] and have suggested that exchange couplings are good sensors for the establishment of hydrogen bonds. It was, however, interesting to find out whether not only the spectroscopic properties but also the reactivity of hydride complexes could be modified by hydrogen bonding. We, therefore, looked at the interaction between selected hydrogen bond donors and $RuH_2(dppm)_2$ (**1**),[7] a complex existing as a mixture of *cis*- and *trans*-isomers in dynamic equilibrium and in a *ca.* 1:4 relative ratio at room temperature. We were particularly interested in studying the influence of hydrogen bonding on this equilibrium and on the specific reactivity of each isomer. We describe in this communication the first direct NMR observation of a dynamic equilibrium between a hydride and a dihydrogen complex. The intermediacy of a dihydrogen-bonded species is suggested, Scheme 1.

Addition of excess phenol to a C_6D_6 or a C_7D_8 solution of **1** was monitored by ^1H NMR and ^{31}P NMR spectroscopy. At room temperature, only a slight upfield shift of the hydride signals of both isomers was observed (for *trans*-**1**·PhOH, $\Delta\delta \cong 25$ ppb and for *cis*-**1**·PhOH, $\Delta\delta \cong 10$ ppb). In addition, the signal of *trans*-**1**·PhOH displays a significant broadening. T_1 measurements recorded at room temperature (400 MHz) in C_7D_8 give values of 750 ms for *trans*-**1** and 100 ms for *trans*-**1**/3.3 equiv of PhOH (hereafter named *trans*-**1**·PhOH) and values of 447 ms for *cis*-**1** and 404 ms for *cis*-**1**/ 3.3 equiv. of PhOH. At 243 K (C_7D_8, 400 MHz), the signal for *trans*-**1**·PhOH broadens considerably and new peaks are observed near −6.3 and −2.4 ppm. When the temperature is lowered further (see Figure 1), no significant change was observed in the signal of *cis*-**1**·PhOH but the intensity of the signal for *trans*-**1**·PhOH decreased considerably as the resonances attributed to a new compound **2** increased, namely a quintet at −6.29 ppm (J_{P-H} = 18 Hz) and a very broad peak at −2.43 ppm (relative integration ratio, 1:2). The signals of *trans*-**1**·PhOH and **2** (but not *cis*-**1**·PhOH) disappear below 223 K, but all observations can be reversed when increasing the temperature again. A determination of the relaxation time T_1 of the different signals was carried out at 233 K (400 MHz) in the presence of two different phenol concentrations, namely 2.35 and 3.3 equiv of PhOH, compared to the initial concentration of $RuH_2(dppm)_2$. This led to values of, respectively, 78 and 35 ms (−2.43 ppm, **2**), 130 and 85 ms (−4.63 ppm, *trans*-**1**·PhOH), 144 and 104 ms (−6.29 ppm, **2**), and 505 and 430 ms (−7.22 ppm, *cis*-**1**·PhOH). In addition, the broad peaks attributed to the phenol proton hydrogen-bonded to or in exchange with *trans*-**1**·PhOH, respectively, at 6.1 (2.35 equiv) and 3.50 ppm (3.3 equiv) display short relaxation times, 105 and 85 ms, similar to those of the hydride signal at −4.63 ppm. In the same conditions (233 K, toluene-d_8, 400 MHz) but in

---

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

[1] (a) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348. (b) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R.H. *J. Am. Chem. Soc.* **1995**, *117*, 3845. (d) Peris, E.; Wessel, J.; Patel, B. P.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2175. (e) Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007.

[2] (a) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (b) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (c) Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001.

[3] (a) Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (b) Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1996**, 991.

[4] Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

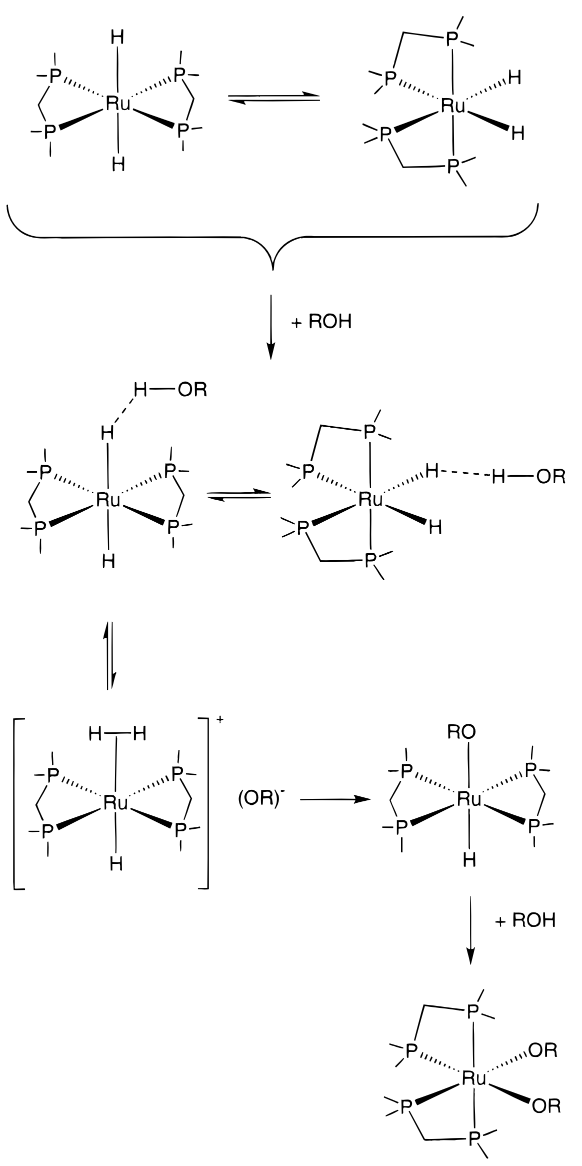
[5] (a) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (c) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913.

[6] Ayllon, J. A.; Sabo-Etienne, S.; Chaudret, B.; Ulrich, S.; Limbach, H.-H. *Inorg. Chim. Acta*, in press.

[7] Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

S0276-7333(97)00079-4 CCC: $14.00

Scheme 1. Reaction of *cis*/*trans*-$RuH_2(dppm)_2$ with Hydrogen Bond Donors



the absence of hydrogen-bond donors, the relaxation time of *trans*-**1** and *cis*-**1** were measured to be, respectively, 721 and 525 ms. This strongly suggests that the equilibrium between the *cis*- and the *trans*-forms of **1** is frozen but that a new equilibrium is present between *trans*-**1**·PhOH which may be associated to phenol through hydrogen bonding, and a hydrido dihydrogen complex, *trans*-$[(dppm)_2HRu(H_2)]^+ (OPh)^-$ (**2**). Integration ratios between the hydride signals of *trans*-**1**·PhOH and **2** were measured every 5 K between 243 and 223 K for a solution containing initially 3.3 equiv of PhOH, compared to the initial concentration of $RuH_2(dppm)_2$. This temperature range is very limited, but only *cis*-**1**·PhOH and *trans*-**1**·PhOH can be observed at 253 K or higher whereas below 223 K, the strong depletion of the signals of *trans*-**1**·PhOH and **2** against those of *cis*-**1**·PhOH is attributed to the precipitation of the cationic dihydrogen complex. The experiment could not be performed in a polar solvent in which **2** would be soluble (THF, acetone) since hydrogen bonding between phenol and the ruthenium hydrides does not take place in such media, as demonstrated by NMR, whereas in CD_2Cl_2, the equilibrium is observed near room temperature but **1** reacts slowly to give *trans*-$RuHCl(dppm)_2$, which prevented equilibrium measurements.[7] Nevertheless, these data allowed us to calculate an equilibrium constant at each temperature and, through an Arrhenius plot, to estimate the energy difference between the two species ($\Delta H = 17 \pm 3$ kcal·mol^{-1} and $\Delta S = 75.8$ eu). The reaction could also be followed by ^{31}P NMR (C_7D_8), where the singlet signal of *trans*-**1**·PhOH at 15.6 ppm (293 K) disappears when lowering the temperature with concomittant appearance of a new signal at 6.6 ppm (233 K) attributed to **2**. No modification in the signal of *cis*-**1**·PhOH (20.7 and 7.4 ppm) can be observed at all temperatures.

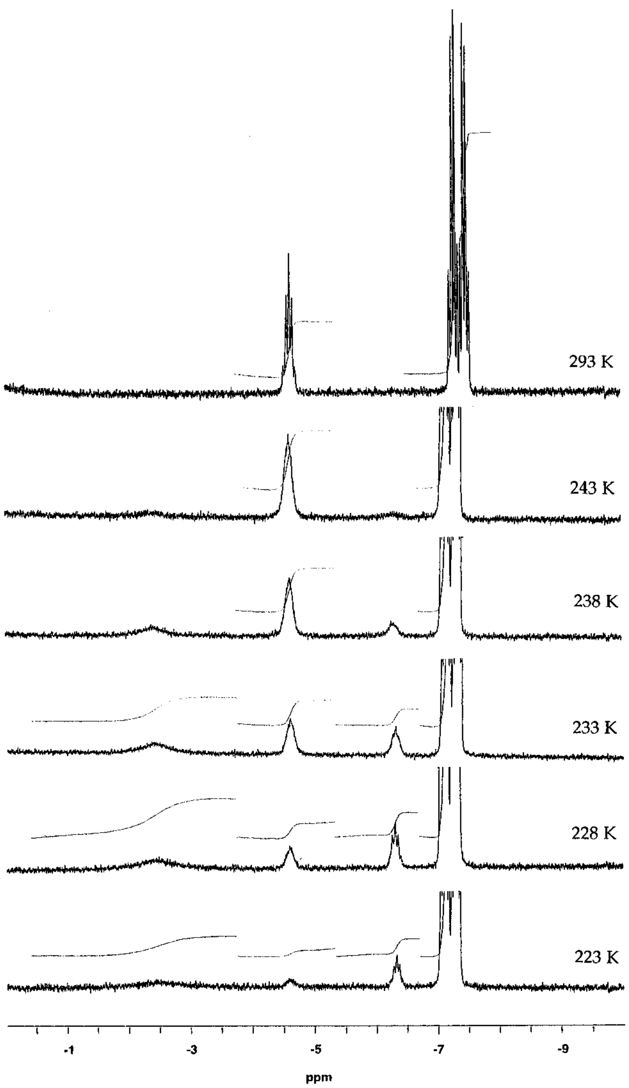


Figure 1. High-field ^1H NMR spectrum (C_7D_8, 400 MHz) of a solution of $RuH_2(dppm)_2$ and 3.3 equiv of phenol at variable temperature.

These observations demonstrate the presence of an equilibrium between two species, the system *trans*-$(dppm)_2HRuH$ associated with HOPh (**1**·PhOH) and a dihydrogen complex *trans*-$[(dppm)_2HRu(H_2)]^+(OPh)^-$ (**2**). **2** is a new example of ruthenium bis(diphosphine) hydrido dihydrogen complex, numerous examples of which have been prepared by Morris et al.[5,8] **2** is the ground state complex, the hydrogen-bonded dihydride being higher in energy. The energy difference is significantly larger than that reported by Field et al. for the protonation of $RuH_2(dmpe)_2$ in ethanol.[9] The T_1

value found for the dihydrogen signal of **2** is relatively long compared to the minimum values usually obtained by Morris[8] and is dependent upon the phenol concentration, in agreement with T_1 averaging due to exchange processes. Similarly, the T_1 values found for the hydride and phenol proton signals of *trans*-**1**·PhOH are very short compared to those found for *cis*-**1**·PhOH, which is itself shortened compared to the value recorded in the absence of phenol.

Field et al. have recently demonstrated the intermediacy of dihydrogen species during the reaction of $RuH_2(dmpe)_2$ with thiols,[9] and such a possibility was also reported by Yamamoto for the reaction of $RuH_2(PMe_3)_4$ with phenol.[10] The originality of our system is the presence of a dynamic equilibrium between **1**·PhOH and **2**, which is fully reversible according to the temperature. A likely explanation for this equilibrium is the presence of a strong hydrogen bond between *trans*-**1** and PhOH. This is suggested by the variations of the chemical shifts of the hydride signals in the presence of hydrogen bond donors and by T_1 measurements but needs to be further confirmed. In this respect, an infrared experiment and spin-saturation transfer experiments were carried out. The decrease in intensity and disappearance of the phenol ν O−H stretch was monitored by infrared upon increasing the concentration of **1**.[11] However, only a very broad band appeared near 3200 cm^{-1}. The second experiment was to record the ^1H NMR spectrum of a solution of **1** in the presence of excess phenol at 233 K in C_7D_8 and irradiate selectively the different peaks.[12] The main result is that upon irradiation of the phenol proton at 6.1 ppm, the intensity of the high-field peaks was reduced by 43% (−2.4 ppm, **2**, Ru−H_2), 43% (−4.7 ppm, *trans*-**1**·PhOH), 33% (−6.3 ppm, **2**, Ru−H), and 6% (−7.2 ppm, *cis*-**1**) whereas irradiation at −4.7 ppm leads to a 50% decrease of the peak at −2.4 ppm and a 84% decrease of that at −6.3 ppm. These observations can be interpretated as resulting from a rapid exchange process between *trans*-**1** and phenol on one side and **2** on the other. However, the exchange process between the hydride and the dihydrogen ligands of **2** is slow (see also the results of irradiation at −2.4 and −6.3 ppm[12]), and the decrease in intensity of the hydride signals of *trans*-**1** is significantly larger than that found for the hydride signal of **2**, in agreement with the presence of a NOE effect. This again suggests that phenol remains in the vicinity of one of the hydrides of *trans*-**1**, most probably through hydrogen bonding.

When the experiment is carried out using 1 equiv of a more acidic hydrogen-bond donor, hexafluoroisopropyl alcohol (HFP) and the reaction was allowed to proceed for 30 min, a very broad peak is observed for *trans*-**1** at room temperature. When 10 equiv of HFP are added, NMR monitoring (C_6D_6) demonstrates the immediate disappearance of all peaks of **1** and the appearance of new peaks at −2.41, −6.51 (^1H NMR, relative integration ratio, 2:1), and 0 ppm (^{31}P NMR) which were attributed to *trans*-$[(dppm)_2HRu(H_2)]^+$ $[OCH(CF_3)_2]^-$ (**2′**). A new signal at *ca.* −19 ppm was attributed to *trans*-$(dppm)_2HRu[OCH(CF_3)_2]$ (**4**). **4** reacts further with excess HFP and transforms into the *cis*-dialkoxo complex $Ru[OCH(CF_3)_2]_2(dppm)_2$ (**3**), which could be isolated and is characterized by two triplets in the ^{31}P NMR spectrum at 21.13 and −13.96 ppm (J_{P-P} = 37.4 Hz). In this case, during the protonation process, we can observe the disappearance of both the peak of *cis*-**1** and that of *trans*-**1**.

In conclusion, we present in this communication the first direct observation of a dynamic equilibrium involving proton transfer between a hydride and a dihydrogen complex. Infrared and NMR evidence suggest the presence of dihydrogen bonding between the *trans*-isomer of **1** and phenol as the origin of this reversible proton transfer. However, it is difficult to dissociate observations resulting from proton transfer from those resulting from dihydrogen bonding. Only the *trans*-dihydride complex can be protonated in these mild conditions. This observation can be related to the demonstration by Crabtree and Eisenstein[3a] that hydrides *trans* to hydrides give preferentially hydrogen bonds when several possibilities are present and indicates a higher basicity of these hydrides. This study finally evidences all individual steps leading to the addition of weak acids to transition metal polyhydrides and demonstrates the necessary intermediacy of *trans*-complexes for the formation of a *cis*-dialkoxo derivative from a *cis*-dihydride.

Acknowledgment. The authors thank CNRS and the European Union, Brussels, via the Human Capital & Mobility Network Localization and Transfer of Hydrogen for support. We thank Pr. Hans-Heinrich Limbach and Dr. Odile Eisenstein for helpful discussions.

Supporting Information Available: Text giving experimental and spectroscopic data for complexes **3** and **4** (1 page). Ordering information is given on any current masthead page.

OM970079P

---

(8) See, for example: (a) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (b) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375.

(9) Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009.

(10) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404.

(11) Infrared spectra of a dichloromethane solution of phenol were recorded in the presence of increasing concentrations of **1**. We observed a significant reduction of the ν O−H band of phenol at 3580 cm^{-1}, together with the appearance of a weak very broad band near 3200 cm^{-1}. In a control experiment, we checked by ^1H NMR that in the same conditions, but in CD_2Cl_2, **1** remained unreacted.

(12) Irradiations at 233 K in C_7D_8: Irradiation of the signal at −2.4 ppm leads to a reduction of *ca.* 60% of the intensity of the signal at −4.7 ppm (*trans*-**1**·PhOH), 50% of the signal at −6.3 ppm (**2**, Ru−H), and *ca.* 20% of the signal at −7.2 ppm (*cis*-**1**·PhOH). When irradiating the signal at −6.3 ppm, *ca.* 32, 55, and 3% reductions were respectively observed for the signals at −2.4, −4.7, and −7.2 ppm. Irradiations at room temperature in CD_2Cl_2: In this solvent, the equilibrium between **1** and **2** is apparent at room temperature, and some transformation of **1** into $RuHCl(dppm)_2$ (**3**) occurs slowly. Irradiation of the phenol protons at 8.5 ppm leads, as expected, to a reduction of the hydride signal of *trans*-**1**·PhOH at −5.6 ppm by *ca.* 30% but interestingly to a more consequent reduction (*ca.* 60%) of the signal of *cis*-**1**·PhOH at −8.3 ppm. In addition, we also observe a reduction of the peaks of **2**.