Three-centre dihydrogen bond with fast interchange between proton and hydride: a very active catalyst for D^+–H_2 exchange†

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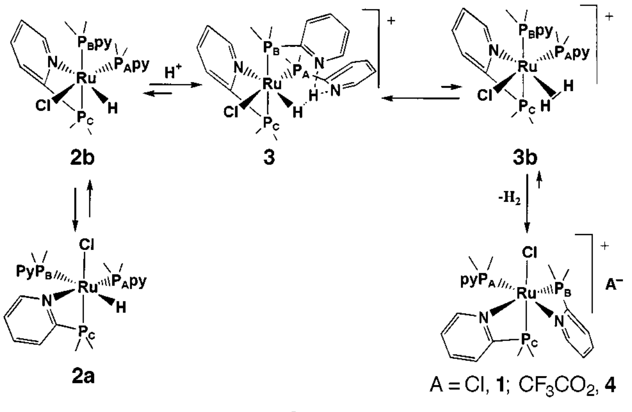
Protonation of a ruthenium hydride containing the hemilabile ligand PPh_2py gave a complex with a three-centre dihydrogen bond (Ru–H···H–Py_2), and this system exhibits a fast proton/hydride interchange and is a very active catalyst for D^+–H_2 exchange.

The term dihydrogen bond[1] was introduced by Crabtree to designate hydrogen bonds in which the proton acceptor is the σ-electron pair of a transition metal hydride. This type of hydrogen bond has now largely been enlightened by intramolecular examples from Crabtree *et al.*[2] and Morris and coworkers,[3] or by intermolecular cases described by Crabtree and coworkers[4] in the solid state and Epstein and coworkers[5] in solution. The study of such chemical bonds is not only of academic importance, but these types of interaction may also be present in intermediates related to hydrogenation, hydrogen transfer and H–D exchange.[3] We envisaged the synthesis of Ru^{II} complexes possessing several PPh_2py ligands. The affinity of the Ru^{II} centre for phosphorus, and the predicted strain of the resulting four-membered cycles when this phosphine is chelated, anticipates its hemilabile behaviour, the easy accessibility of unsaturated species and the presence of basic pyridine groups near the Ru centre, which could operate as efficient proton abstractors from weak acids such as alcohols or hydrogen, could give rise to interesting catalytic properties. We describe the preparation of PPh_2py–ruthenium complexes including an unprecedented three-centre dihydrogen bond that has special properties.

The reaction of $RuCl_2$(bpzm)(cod) or RuClH(bpzm)(cod)[6] [bpzm = bis(pyrazol-1-yl)methane, cod = cycloocta-1,5-diene] with 3 mol equiv. of PPh_2py gives, after the appropriate work up procedure, the new complexes $[RuCl(\eta^1\text{-}PPh_2py)(\eta^2\text{-}PPh_2py)_2]Cl$ **1** and $RuClH(\eta^1\text{-}PPh_2py)_2(\eta^2\text{-}PPh_2py)$ **2**, respectively. Two isomers of **2** are present in solution, **2a** and **2b** (Scheme 1), and their ratio depends on the solvent and temperature. This supports the existence of an equilibrium in solution between the two species. The facial structure of **1** and **2a** and the mer for **2b** (Scheme 1) are deduced by considering characteristic J_{PP} couplings for the three observed resonances for each compound.[7] The chelating η^2 coordination of some PPh_2py groups, as proposed in Scheme 1, is supported by the characteristic upfield shift of the corresponding ^{31}P NMR signals with respect to the free phosphine ligand.[8] The hydride resonance in the ^1H NMR spectrum of **2a** appears at δ −7.46 and shows a distinctly higher H–P coupling constant with one phosphorus, while that of the *mer* isomer **2b** (δ −11.58) exhibits typical *cis* coupling constants to the three phosphorus centres.[7] This chemical shift is characteristic of a hydride in a *trans* disposition to an N-donor ligand,[9a] as has been found in polyphospine derivatives of Ru, and is in contrast with the values expected for analogous compounds with a Cl^- in a *trans* disposition.[9b] The cationic nature of **1** has been confirmed by conductivity measurements in acetone solution.



Scheme 1

In order to investigate the ability of complexes **2b** and **2a** to transfer a proton to the hydride with the formation of a dihydrogen bond, 3 equiv. of CF_3CO_2H were added to a **2b** : **2a** (7 : 2 ratio) CD_3CN solution at −40 °C. Under these conditions both isomers were transformed into a unique cationic compound: $[RuClH(\eta^2\text{-}PPh_2py)\{(\eta^1\text{-}PPh_2py)_2H\}]CF_3CO_2$ **3** (Scheme 1). The identical integration of the hydride and proton resonances of **3** indicates that only one proton has been transferred from CF_3CO_2H. The signal of the newly introduced proton was strongly shifted downfield and appeared at δ *ca.* 20. Such a strongly deshielded resonance has been ascribed to acidic protons in very fast exchange between two basic centres.[9a,10] Consequently, this proton must be in fast exchange between the pyridine fragments of the two monodentate phosphines. The resonance of the surplus acid proton appeared separately at δ *ca.* 5. The chemical shifts of the hydride and phosphorus atoms of **3** were only slightly modified with respect to **2b**[7] and therefore the relative disposition of the ligands must be similar in these two complexes. On raising the temperature, both the pyridinium proton and hydride resonances of **3** broadened. The enormous chemical shift difference between the exchanging resonances (> 9000 Hz) prevented the observation of the coalescence. However, kinetic parameters can be calculated by lineshape analysis in the temperature range below the coalescence. This study was undertaken in $(CD_3)_2CO$ (−90 to −10 °C), which allows lower temperatures than CD_3CN. An E_a value of 13.6 ± 2.7 kcal mol^{-1} was obtained ($A = 3.8 \times 10^{14}$). The exchange between the hydride and the pyridinium proton was also confirmed by spin saturation transfer. The irradiation of the hydride resonance of **3** reduced the pyridinium proton integral by *ca.* 50% at −40 °C. Above room temperature, both in $(CD_3)_2CO$ or CD_3CN solution, H_2 was lost and a new product, $[RuCl(\eta^1\text{-}PPh_2py)(\eta^2\text{-}PPh_2py)_2]CF_3CO_2$ **4** (Scheme 1) was formed with an identical structure to **1**, as deduced from its ^{31}P NMR spectrum.[7]

In order to show the existence of a dihydrogen bond in **3**, the T_1(min) of the hydride group both for **2b** and **3** was determined (300 MHz). CD_2Cl_2 was used as the solvent in order to prevent the possible participation of basic or protic solvents in the relaxation rate of the pyridinium proton and, indirectly, over the exchanging hydride. An addition of exactly 1 equiv. of CF_3CO_2H was performed in order to avoid the relaxation rate average with free protons. Under these conditions, the hydride of **2b** shows a T_1(min) of 217 ms at −35 °C, whereas the T_1(min) for both the hydride and pyridinium proton of **3** is 85 ms at −20 °C. In the latter complex the T_1 values determined are identical for the pyridinium proton and the hydride over the temperature range studied (−90 to −10 °C). This must be a consequence of the observed exchange between these two protons. We have considered that the excess of the hydride relaxation in **3**, as compared to **2b**, is due to the Ru–H···H–py$_2$ dipole–dipole interaction. In this relaxation the two ^{14}N pyridinium atoms must also participate because the proton, which is bonded to these two groups, is exchanging with the hydride with a half-life of 0.5, according to the aforementioned magnetization transfer experience. The contribution for each ^{14}N has been estimated to be 1.85 s^{-1}.[11] Hence, the relaxation rate due exclusively to the dipole–dipole interaction with the pyridinium proton is deduced to be 5.30 s^{-1}. Using Morris' approximation,[12] a d_{HH} = 1.70 Å has been calculated, a value that is in the range for a dihydrogen bond and demonstrates its existence in **3**.

Although the phenomenon has been previously described,[2b] the proton–hydride exchange already discussed for a dihydrogen bond is very rare, and Crabtree has postulated the participation of non-classical species as intermediates. Neither Crabtree nor our group have detected this intermediate in solution (**3b** in Scheme 1). However, Chaudret and coworkers[13] have recently reported some examples where an intermolecular exchange between coordinated molecular dihydrogen and weak acid protons has been observed.

The loss of H_2 near room temperature shows the lability of the proposed non-classical species **3b** and this opens up the possibility of interchange with free H_2. Besides, the heterolytic cleavage of an H_2 molecule coordinated in this hypothetical complex would be possible considering the observed higher basicity of the pyridine centres with respect to the hydride in **2**. These two characteristics point to a possible activity of **2** toward D^+–H_2 exchange in protic deuterated solvents.

As a consequence of this possibility, H_2 (1 atm) was introduced at room temperature in a sealed NMR tube in contact with a solution of **2** in CD_3OD as a deuteron source. The evolution of the mixture was monitored by ^{1}H NMR spectroscopy during several hours. The change with time of the relative concentration of H_2 and HD observed in this way is depicted in Fig. 1. The relative concentration of D_2 was calculated accepting the constant concentration of the total dihydrogen isotopomers in solution. According to these results, a very efficient catalyst for D^+–H_2 exchange was present in solution. After 33 min, > 90% of H_2 was transformed. In 18 min the HD concentration reached its maximum and afterwards decreased as a consequence of D_2 formation. An increase in the residual CD_3OD OH signal, and not that of the CHD_2 group, was concomitantly observed. **2a** was the major isomer observed in solution and, surprisingly, during the experience the intensity of the hydride signal due to **2a** was scarcely reduced. Only after 7 days did this signal disappear and [$^2H_1$] **2a** was formed. However, very small signals for **2b** were detected at room temperature (**2a** : **2b** = 30 : 1, 20 °C) before the addition of H_2, and these disappeared instantaneously when the gas was present. Therefore, we propose that, although only small amounts of **2b** are present, this is the efficient catalyst for the process. This example shows a dramatic relationship between structure and reactivity.

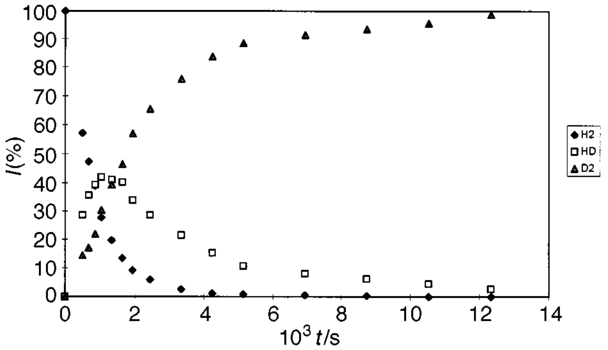


Fig. 1 Relative intensities of the NMR signals of the dihydrogen isotopomers *vs.* time in the D^+–H_2 exchange experiment with **2** CD_3OH; (◆) H_2, (□) HD, (▲) D_2

In conclusion, we present an example where the addition of a proton to the ruthenium monohydrides **2b** and **2a** forms a dihydrogen bond of three centres, and this system shows a fast exchange between the proton and hydride moieties. **2b**, and not **2a**, is extremely active in D^+–H_2 interchange processes. Experiments to assess the catalytic properties of these types of compounds in hydrogen transfer processes are in progress.

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Notes and References

† Dedicated to Professor Pascual Royo on his 60th birthday.

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7 NMR data (δ, J Hz, ^{1}H NMR, ref. TMS; $^{31}P\{^1H\}$ NMR, ref. 85% H_3PO_4, room temp. unless specified). **1**: $\delta_H(CDCl_3)$, 7–8 (m, 42H, PPh_2py). $\delta_P(CDCl_3)$, 47.10 (dd, $^2J_{PP}$ 33.6, 27.4, P_A), −7.9 (t, $^2J_{PP}$ 27.5, P_B or P_C), −6.35 (dd, $^2J_{PP}$ 33.6, 26.9, P_C or P_B). **2b**: $\delta_H(CD_3CN)$, 7–8 (m, 42H, PPh_2Py), −11.58 (dt, 1H, J_{HP} 26.2, 21.6, Ru–H). **2a**: $\delta_H(CD_3CN)$, 7–8 (m, 42H, PPh_2py), −7.46 (ddd, J_{HP} 115.2, 27.8, 21.8, Ru–H). **2b**: $\delta_P(CD_3CN)$, 69.38 (br, s), 55.53 (dd, J_{PP} 277, 24.4, P_B), −15.05 (br, d J_{PP} 277, P_C). **2a** $\delta_P(CD_3CN)$ 69.28 (br, s P_A), 8.74 (dd, J_{PP} 36.6, 12.8, P_B), −15.13 (br, s P_C). **3**: δ_H(CD$_3$CN, −40 °C), 20 (br, s 1H, pyH), 7–8 (m, 42H, PPh_2Py), −11.85 (dt, 1H, Ru–H). δ_P(CD$_3$CN, −40 °C), 77.55 (qnt, J_{PP} 30.5, P_A), 52.22 (dd, J_{PP} 278.3, 29.9, P_B), −24.33 (dd, J_{PP} 278.3, 32.4, P_C). **4**: δ_H (CD$_3$CN, 60 °C): 7–8 (m, 42H, PPh_2Py). δ_P(CD$_3$CN, 60 °C), 48.09 (t, J_{PP} 32.4, P_A), −3.96 (t, J_{PP} 27.5, P_B or P_C), −8.96 (t, J_{PP} 32.9, P_C or P_B).

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