

Preliminary communication

Effects of dihydrogen bonding on fluxionality in  $\text{ReH}_5(\text{PPh}_3)_2\text{L}^1$

Ben P. Patel, Konstantinos Kavallieratos, Robert H. Crabtree \*

Yale University, Department of Chemistry, 225 Prospect St., New Haven, CT 06511-8107, USA

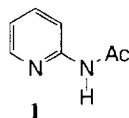
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Abstract

Hydride fluxionality in  $\text{ReH}_5(\text{PPh}_3)_2\text{L}$  (**2**, L = *N*-acetyl-2-aminopyridine) is affected by intramolecular  $\text{Re}-\text{H} \cdots \text{H}-\text{N}$  dihydrogen bonding.

Keywords: Rhenium; Hydride; Hydrogen bonding

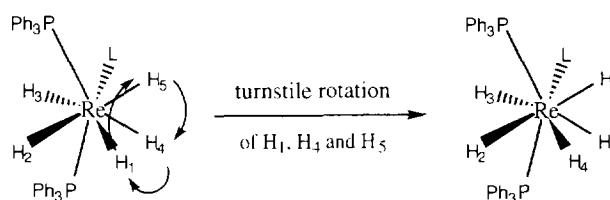
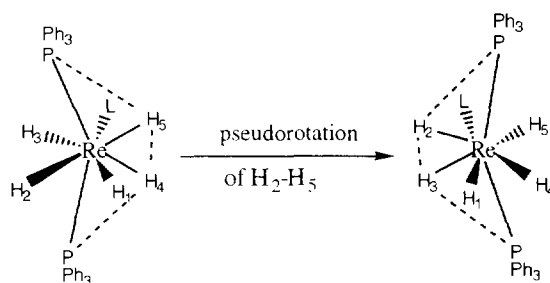
Recently we [1] and others [2–4] have reported a new type of hydrogen–hydrogen interaction, i.e. dihydrogen bonding, in which the M–H bonds of transition metal polyhydrides act as unconventional hydrogen bond acceptors for weakly acidic X–H (X = N,O) protons. Both intramolecular and intermolecular examples of dihydrogen bonding have been characterized with bond strengths of 15–25  $\text{kJ mol}^{-1}$  and H  $\cdots$  H distances of 1.75–2.2 Å, and we have now moved on to look at possible applications. We report here our initial results on perturbing the fluxionality rate of  $\text{ReH}_5(\text{PPh}_3)_2\text{L}$ , by incorporating a potential H-bond donor group in the ligand L, which we hoped would engage in intramolecular dihydrogen bonding with the hydride ligands. We have chosen to modify the common ligand pyridine to give **1**, L = *N*-acetyl-2-aminopyridine.



The new complex  $\text{ReH}_5(\text{PPh}_3)_2\text{L}$  (**2**, L = **1**), has been synthesized by reaction of **1** with  $\text{ReH}_7(\text{PPh}_3)_2$  in benzene over 12 h at 300 K, and has been characterized by microanalysis,  $^1\text{H}$  NMR and IR spectroscopy. Spectroscopic and analytical data for (**2**):  $^1\text{H}$  NMR (hydride

region) in ppm ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $-5.05$  (5H, br s); ( $\text{CD}_2\text{Cl}_2$ , 188 K)  $-0.674$  (1H, t,  $J_{\text{HP}}$  18 Hz),  $-3.45$  (2H, br s),  $-8.62$  (1H, t,  $J_{\text{HP}}$  18 Hz),  $-9.95$  (1H, br s).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K) 41.77 ppm. IR ( $\text{CH}_2\text{Cl}_2$ )  $\text{cm}^{-1}$ :  $\nu_{\text{N}-\text{H}}$  3278 (br), 3181 (br);  $\nu_{\text{Re}-\text{H}}$  2022 (m), 1900 (m), 1861 (m);  $\nu_{\text{C}=\text{O}}$  1700 (s). Elemental Anal. Found: C, 60.08; H, 5.12; N, 3.21.  $\text{C}_{43}\text{H}_{43}\text{N}_2\text{ORe}$ . Calc.: C, 60.62; H, 5.05; N, 3.29%.

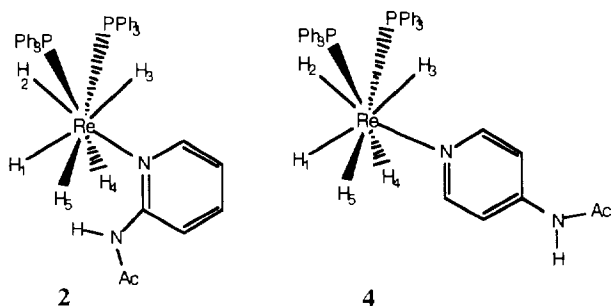
We previously found that the fluxional molecule  $\text{ReH}_5(\text{PPh}_3)_2\text{L}$  (**3**, L = py) undergoes two successive decoalescence events at 253 K and 233 K in the hydride region of the  $^1\text{H}$  NMR, which were ascribed to pseudorotation (253 K) and turnstile (233 K) mechanisms [5].



\* Corresponding author.

<sup>1</sup> Dedicated to Professor Malcolm Green on his 60th birthday.

The new pyridine complex, **2**, undergoes the same types of decoalescence at 238 K and 208 K in the  $^1\text{H}$  NMR, suggesting that the mechanism of fluxionality is unchanged but that the rate has been accelerated. Stronger dihydrogen bonding in the transition states for the fluxionality pathways could account for this result, but the acceleration in **2** could merely have been due to the electronic effect of the substituent on the pyridine ring. We therefore moved to **4** as our control <sup>2</sup>, where the electronic effect of the substituent is expected to be unchanged on moving from the ortho to the para position on the pyridine ring (the presence of similar  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}=\text{N}}$  bands in the IR spectra of **2** and **4** confirm this expectation), but where intramolecular dihydrogen bonds should not be able to form.



Our results show that although the electron donating effect of the substituent does increase the rate of hydride fluxionality, it does not completely account for the observed acceleration in the low temperature turnstile rotation of  $\text{H}_1$ ,  $\text{H}_4$  and  $\text{H}_5$  in **2**. We find that the pseudorotation process in both the ortho complex **2**, and the para complex **4**, occur with the same rate, but the turnstile rotation process in **2** is accelerated relative to **4**. Table 1 lists the barriers estimated by lineshape analysis for the two fluxional processes in **2–4**. We therefore suggest that this acceleration of fluxionality in the turnstile process of **2** is a result of stronger dihydrogen bonding in the transition state relative to the ground state. To rule out intermolecular  $\text{N}-\text{H} \cdots \text{H}-\text{Re}$  interactions, control experiments with various ratios of **2:1** and **3:1** were performed. No effects on hydride fluxionality were detectable by  $^1\text{H}$  NMR, as was expected, since intermolecular dihydrogen bonding is entropically disfavored in solution.

<sup>2</sup> We attempted to prepare the *N*-methyl derivative of **2** as the control, but were unable to isolate this complex.

Table 1

Estimated <sup>a</sup> free energies of activation for turnstile <sup>b</sup> and pseudorotation processes in **2–4**

	$W_{1/2}$ (Hz, 293 K)	$\Delta G^\ddagger$ turnstile ( $\pm 1.0 \text{ kJ mol}^{-1}$ )	$\Delta G^\ddagger$ pseudorotation ( $\pm 1.0 \text{ kJ mol}^{-1}$ )
<b>2</b>	102	35.9	41.7
<b>4</b>	144	38.9	41.6
<b>3</b>	184	40.3	43.5

<sup>a</sup> Natural linewidths were estimated from  $^1\text{H}\{^{31}\text{P}\}$  spectra at 183 K assuming 5 Hz line broadening from unresolved  $J_{\text{HH}}$  couplings. <sup>b</sup> Free energies for the turnstile process were calculated by standard methods using the initial line broadening technique to calculate the rate for the hydride ligand  $\text{H}_1$  leaving its coordination site [6].

The presence of dihydrogen bonding in the ortho complex, **2**, is supported by the characteristic [1] broadening and low energy shift ( $\Delta\nu = 228 \text{ cm}^{-1}$ ) of the  $\nu_{\text{N}-\text{H}}$  band in the IR spectrum of a dilute  $\text{CH}_2\text{Cl}_2$  solution of **2**, relative to the  $\nu_{\text{N}-\text{H}}$  band of a similarly prepared sample of **1**. However, in a similar comparison made with **4**, no broadening or shift to lower energy was observed for the  $\nu_{\text{N}-\text{H}}$  in the IR spectrum. Similar effects have previously been seen in the case of intermolecular  $\text{Re}-\text{H} \cdots \text{H}-\text{N}$  dihydrogen bonding [7]. Furthermore, we find that the  $\text{N}-\text{H}$  resonance in the  $^1\text{H}$  NMR spectrum of **2** is shifted downfield by 1.9 ppm relative to that of the  $\text{N}-\text{H}$  resonance of **1**. These observations are characteristic of hydrogen atoms involved in conventional hydrogen bonds [8].

These results show that the rate of fluxionality in the title complex can be modulated by intramolecular  $\text{Re}-\text{H} \cdots \text{H}-\text{N}$  interactions. This strategy of incorporating hydrogen bond donor groups in the ligand sphere may prove useful in future applications.

## Acknowledgements

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