Solution Chemistry of a Water-Soluble η^2-H$_2$ Ruthenium Complex: Evidence for Coordinated H$_2$ Acting as a Hydrogen Bond Donor

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Abstract: The ability of an η^2-H$_2$ ligand to participate in intermolecular hydrogen bonding in solution has long been an unresolved issue. Such species are proposed to be key intermediates in numerous important reactions such as the proton-transfer pathway of H$_2$ production by hydrogenase enzymes. We present the synthesis of several new water-soluble ruthenium coordination complexes including an η^2-H$_2$ complex that is surprisingly *inert* to substitution by water. The existence of dihydrogen hydrogen bonding (DHHB) was experimentally probed by monitoring the chemical shift of H-bonded Ru$-$(H$_2$) complexes using NMR spectroscopy, by UV$-$visible spectroscopy, and by monitoring the rotational dynamics of a hydrogen-bonding probe molecule. The results provide strong evidence that coordinated H$_2$ can indeed participate in intermolecular hydrogen bonding to bulk solvent and other H-bond acceptors.

Introduction

The ability of the dihydrogen ligand to participate in hydrogen bonding is relatively unexplored in spite of the fact that H-bonded adducts of H$_2$ may be key intermediates in numerous chemical and biochemical processes.[1-3] For example, proton-transfer reactions, including biological hydrogen production, feature intermediates in which a hydrogen-bonded L$_n$M$-$(H$_2$) intermediate is likely (Figure 1a). Unambiguous evidence for this bonding motif is scarce, but the results of several studies suggest that H-bonding to an H$_2$ ligand may be possible. Crabtree[4] and Morris,[5] for example, independently showed that certain metal hydrides can accept an H-bond from an appropriate H-donor (Figure 1b), a result that yields a deprotonated dihydrogen H-bond-type structure.

Most examples of coordinated H$_2$ participating in H-bonding are limited to the solid state,[7,8] typically in the structure of ion-pairs.[9,10] Although H-bonding may be responsible for the crystalline arrangement of these molecules, other factors such as steric and electronic repulsion and crystal packing forces are likely to give similar energetic stabilization. In solution, the
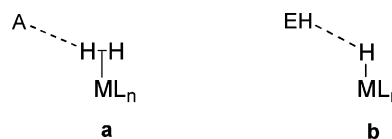

Figure 1. (a) Proposed dihydrogen H-bonding (DHHB) and (b) dihydrogen bonding (DHB), also known as hydridic/protonic hydrogen bonding.[6]

occurrence and importance of H-bonding to H$_2$ is even more nebulous. The few instances in which a hydrogen bond to H$_2$ is proposed in solution involve a counterion acting as the H-bond acceptor.[11-15] This feature suggests that the formation of a tight ion pair may be the driving force for the association rather than H-bonding. In fact, intermolecular H-bonding to H$_2$ in solution has been proposed to be improbable because it was thought that an η^2-H$_2$ ligand would be screened from the surroundings by the shell of co-ligands.[16] In contrast to this suggestion, however, several computational papers have shown the plausibility of intermolecular H-bonding to H$_2$.[17-21] In this paper, we report the synthesis of a new ruthenium η^2-H$_2$ complex that is

(1) Belkova, N. V.; Shubina, E. S.; Epstein, L. M. *Acc. Chem. Res.* **2005**, *38*, 624−631.
(2) Bakhmutov, V. I. *Eur. J. Inorg. Chem.* **2005**, 245−255.
(3) Epstein, L. M.; Shubina, E. S. *Coord. Chem. Rev.* **2002**, *231*, 165−181.
(4) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014−11019.
(5) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356−8357.
(6) Crabtree and Morris termed this interaction "dihydrogen bonding"[4] and "hydridic/protonic hydrogen bonding,"[5] respectively.
(7) Albinati, A. et al.; *J. Am. Chem. Soc.* **1993**, *115*, 7300−7312.
(8) Van der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831−4841.
(9) Webster, C. E.; Gross, C. L.; Young, D. M.; Girolami, G. S.; Schultz, A. J.; Hall, M. B.; Eckert, J. *J. Am. Chem. Soc.* **2005**, *127*, 15091−15101.
(10) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270−2278.
(11) Belkova, N. V.; Besora, M.; Epstein, L. M.; Lledos, A.; Maseras, F.; Shubina, E. S. *J. Am. Chem. Soc.* **2003**, *125*, 7715−7725.
(12) Basallote, M. G.; Besora, M.; Duran, J.; Fernandez-Trujillo, M. J.; Lledos, A.; Manez, M. A.; Maseras, F. *J. Am. Chem. Soc.* **2004**, *126*, 2320−2321.
(13) Belkova, N. V.; Ionidis, A. V.; Epstein, L. M.; Shubina, E. S.; Gruendemann, S.; Golubev, N. S.; Limbach, H.-H. *Eur. J. Inorg. Chem.* **2001**, 1753−1761.
(14) Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc. Dalton Trans.* **1999**, 4475−4486.
(15) Gutsul, E. I.; Belkova, N. V.; Babakhina, G. M.; Epstein, L. M.; Shubina, E. S.; Bianchini, C.; Peruzzini, M.; Zanobini, F. *Russ. Chem. Bull.* **2003**, *52*, 1204−1206.
(16) Braga, D.; De Leonardis, P.; Grepioni, F.; Tedesco, E. *Inorg. Chim. Acta* **1998**, *273*, 116−130.
(17) Orlova, G.; Scheiner, S. *J. Phys. Chem. A* **1998**, *102*, 260−269.
(18) Orlova, G.; Scheiner, S. *J. Phys. Chem. A* **1998**, *102*, 4813−4818.
(19) Kovacs, G.; Schubert, G.; Joo, F.; Papai, I. *Organometallics* **2005**, *24*, 3059−3065.
(20) Chu, H. S.; Xu, Z.; Ng, S. M.; Lau, C. P.; Lin, Z. *Eur. J. Inorg. Chem.* **2000**, 993−1000.
(21) Gusev, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 14249−14257.

amenable to a detailed H-bonding study. Among the remarkable properties of this complex is the finding that in aqueous solution the η^2-H_2 ligand is not substituted by water. We hypothesized that DHHB might be responsible for this substitutional inertness because other ligands not capable of forming H-bonds easily substituted the η^2-H_2 ligand. Experiments showed that H-bonding between a neutral molecule and a coordinated H_2 ligand (DHHB) is in fact possible, and this may contribute to the inertness of the coordinated η^2-H_2 ligand.

Results and Discussion

Synthesis of the Water-Soluble *trans*-[Ru(DMeOPrPE)₂Cl₂] (I), *trans*-[Ru(DMeOPrPE)₂H(H₂)]⁺ (II), and *trans*-[Ru-(DMeOPrPE)₂H(CO)]⁺ Complexes. Hydrogen bonding to a metal−dihydrogen complex was studied using the water-soluble *trans*-[Ru(DMeOPrPE)₂H(H₂)]⁺ complex. This complex was prepared from *trans*-[Ru(DMeOPrPE)₂Cl₂] (**I**) using either polar (aqueous solvent) or nonpolar solvents (toluene or THF).

$$\text{(1)} \quad 70\%$$
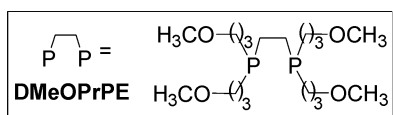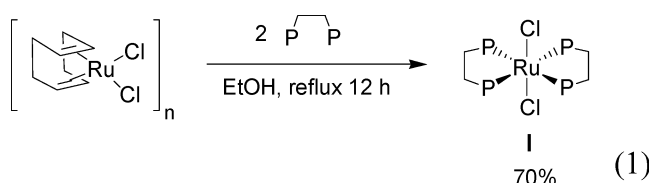
The *trans*-[Ru(DMeOPrPE)₂Cl₂] complex (**I**) was synthesized in good yields using [Ru(COD)Cl₂]$_n$ and 2 equiv of DMeOPrPE in refluxing ethanol (eq 1). The dark-yellow powder is soluble in most common laboratory solvents including water ($\sim$12 mM) and exhibits a singlet at 44.4 ppm in the ^{31}P{^{1}H} NMR spectrum, confirming a *trans* geometry. Slow cooling of a concentrated toluene solution of **I** resulted in the precipitation of yellow crystals suitable for X-ray crystallographic analysis. The structure (Figure 2) shows an octahedral coordination environment around ruthenium with *trans*-chloride ligands.

$$\text{(2)}$$
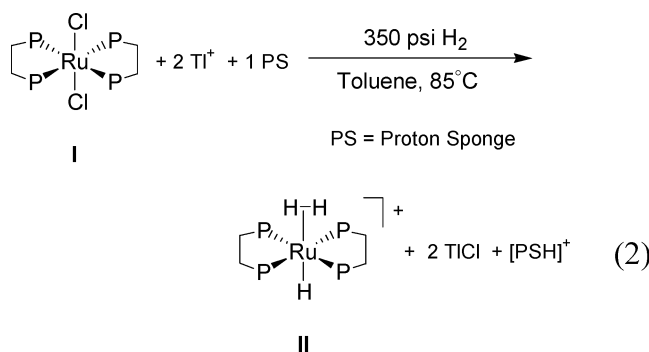
The synthesis of *trans*-[Ru(DMeOPrPE)₂H(H₂)]⁺ (**II** as the BAr′ or PF₆⁻ salts; BAr′ = tetrakis{3,5-bis(trifluoromethyl)-phenyl}borate proceeded smoothly using 350 psig of H₂ and *trans*-[Ru(DMeOPrPE)₂Cl₂], TlBAr′ or TlPF₆ as a chloride abstractor, and 1,8-bis(dimethylamino)naphthalene (Proton Sponge) as a proton scavenger in toluene or THF solvents (eq 2). Alternatively, complex **II−Cl** was also prepared in aqueous
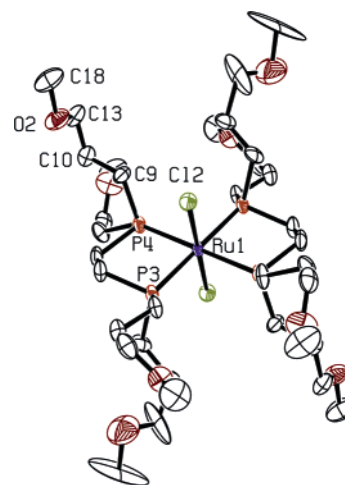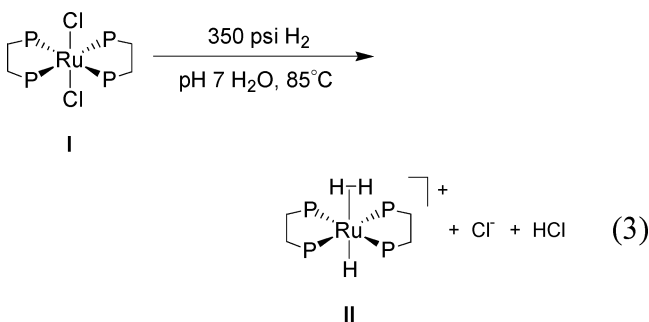

Figure 2. ORTEP representation of **I**. Ellipsoids shown at 50% probability.

solutions by treating solutions of **I** dissolved in water buffered to pH 7 (phosphate or MOPS buffer) with 350 psig H₂ at 85 °C for 1−2 h (eq 3). Solutions containing the light-yellow complex

$$\text{(3)}$$

II gave rise to a single resonance in the ^{31}P{^{1}H} NMR spectrum at δ 63.4 and had ^{1}H resonances for the η^2-H_2 and hydride ligands as a broad singlet and quintet, respectively, at δ −6.6 (s) and δ −11.4 (quint). The quintet has a $^2J_{HP}$ of 20 Hz and is consistent with *cis* P−H coupling.[22,23] The ^{1}H T_1(−20 °C) value of the H₂ resonance was experimentally determined to be 21.1 ms at 500 MHz and corresponds to an H−H distance of 0.86 Å and 1.06 Å for fast and slow rotation, respectively.[24] H/D exchange was noted for the η^2-H_2 ligand in the presence of methanol-d_4 to form the HD isotopolog. From the isotopolog (Figure 3b), the $^1J_{HD}$ was found to be 32.1 Hz and corresponds to an H−H distance of 0.88 Å using Morris' relationship[25] and 0.90 Å using Heinekey's relationship.[26] This distance (as measured by the $^1J_{HD}$ method) is slightly shorter than the analogous iron species by $\sim$0.04 Å and correlates well with the trend in the H−H bond distance in going from Fe to Ru shown by Morris.[22]

Complex **II** was readily substituted by CO. Thus, the reaction of **II−PF₆** with 20 psig CO in toluene cleanly formed *trans*-[Ru(DMeOPrPE)₂H(CO)]PF₆ within 5 min (Figure 4). The

(22) 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*, 4876−4887.
(23) Mathew, N.; Jagirdar, B. R.; Gopalan, R. S.; Kulkarni, G. U. *Organometallics* **2000**, *19*, 4506−4517.
(24) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.
(25) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407.
(26) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127−132.
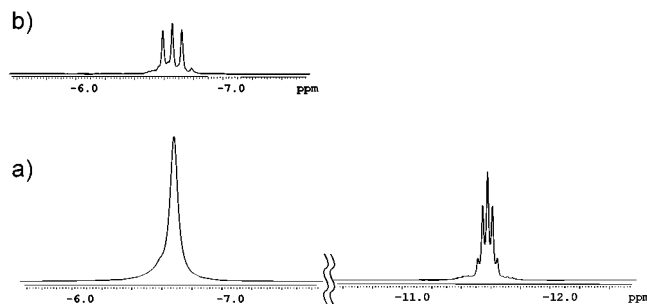
Figure 3. ^{1}H NMR spectra (298 K) of the hydride region of **II**−PF$_6$ (a) in toluene-d_8 and the HD isotopolog (b) in toluene-d_8 with added methanol-d_4.
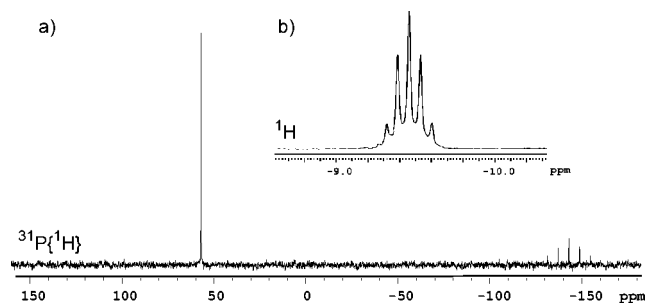

Figure 4. (a) ^{31}P{^{1}H} NMR spectrum in toluene-d_8 (298 K) of *trans*-[Ru-(DMeOPrPE)$_2$H(CO)]PF$_6$ and (b) ^{1}H NMR spectrum (hydride region) of *trans*-[Ru(DMeOPrPE)$_2$H(CO)]PF$_6$.

complex is characterized by a singlet in the ^{31}P{^{1}H} NMR spectrum at δ 57.0 and a quintet in the ^{1}H NMR spectrum ($^2J_{HP}$ of 21 Hz) and it exhibits a ν_{CO} stretch at 1965 cm^{-1}, suggesting moderate d$_\pi$ basicity of the Ru center.

Probing the Occurrence of DHHB. In the absence of exogenous ligands, aqueous solutions containing **II**−Cl are stable for several months *without* an atmosphere of H$_2$. We hypothesized that this inertness to substitution by water may be attributed to other than purely electronic reasons, such as H-bonding to the η^2-H$_2$ ligand. More specifically, one possible explanation lies in the ability of water to form H-bonded networks. It is plausible that the network may be localized around the coordinated H$_2$ and inhibit ligand substitution by physically protecting the coordinated H$_2$. Because little is known about the capacity of coordinated H$_2$ to form H-bonded adducts with an appropriate H-bond acceptor, we sought to examine this possibility. Although myriad methods are available to probe the occurrence of hydrogen bonding, many of them were not compatible with the Ru−H$_2$ system, and consequently the detection of an H-bonding interaction required carefully designed experiments. For example, an obvious choice to evaluate an H-bonding interaction with an η^2-H$_2$ ligand is to measure the change in the H−H bond distance by either the $^1J_{(HD)}$ or T_1(min) methods in the presence or absence of an H-bond acceptor.[24−26] However, the $^1J_{(HD)}$ value showed no significant change outside of experimental error when comparing H-bond accepting solvents to H-bond neutral solvents. This result is not unexpected and can be rationalized by considering the potential energy surface (PES) of a coordinated H$_2$ ligand. It has been shown that if the H−H distance for an H$_2$ ligand is in the short regime (<1.2 Å) the PES is rather steep, and small energetic changes (typical of H-bonding) are not expected to cause a measurable change in the H−H distance.[21,27]
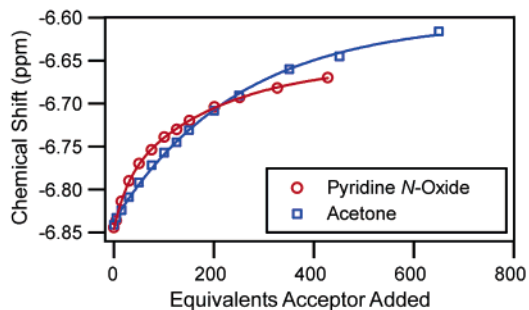
Figure 5. The titration of hydrogen-bond acceptors, pyridine *N*-oxide (red ○) and acetone (blue □), into solutions of **II**−BAr′ (298 K) yields a downfield shift of the (H$_2$) resonance in the ^{1}H NMR spectrum.

Another logical detection method is to examine the H-bond donor stretching vibration in the IR spectrum and look for a bathochromic shift in the presence an acceptor.[28] However, the M−H$_2$ stretch is typically very weak and often not observable.[29,30] Accordingly, examination of the vibrational spectra of **II** both by IR and Raman spectroscopy did not reveal any peaks attributable to an M−H$_2$ bonding mode. Therefore, an analysis of the shift in the vibrational mode could not be applied to the solutions containing **II**.

Three Tests Demonstrating DHHB. Because many of the typical methods for determining the presence of H-bonding were not applicable to the *trans*-[Ru(DMeOPrPE)$_2$H(H$_2$)]$^+$ system, one direct method and two indirect methods were used to test for the presence of DHHB. For the first test, it is noted that if H-bonding to bulk solvent is possible then the H$_2$ resonance in the ^{1}H NMR spectrum should undergo a downfield shift when increasing amounts of a hydrogen bond acceptor are added.[31] To eliminate a potentially competing effect of ion-pairing, a large, non-coordinating anion (BAr′) was used.[32,33] Accordingly, when compounds of different H-bond accepting strength (pyridine *N*-oxide >acetone) were titrated into toluene-d_8/methylene chloride-d_2 (1:1) solutions containing **II**−BAr′, (Figure 5), a small (170 and 225 ppb) downfield shift of the H$_2$ resonance was found and the shape of the binding isotherm changed with the type of H-bond acceptor added.[34] These results are consistent with a structural arrangement in which the η^2-H$_2$ ligand on **II** interacts with the H-bonding solvent. From the binding isotherm in Figure 5, values of the association constant were extracted (using an iterative fitting program[35]) that correlated with a weak

(27) Heinekey, D. M.; Lledos, A.; Lluch, J. M. *Chem. Soc. Rev.* **2004**, *33*, 175−182.
(28) Hadzi, D.; Bratos, S. In *The Hydrogen Bond: Recent Developments in Theory and Experiments*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: New York, 1976; pp 565−611.
(29) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity*; Kluwer Academic/Plenum: New York, 2001.
(30) Sweany, R. L. In *Transition Metal Hydrides*; Dedieu, A. Ed.; VCH: New York, 1992; pp 65−101.
(31) Tucker, E. E.; Lippert, E. In *The Hydrogen Bond: Recent Developments in Theory and Experiments*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: New York, 1976; pp 791−830.
(32) Organic fluorine has been purported to almost never accept a hydrogen bond (see ref. 33).
(33) Dunitz, J. D.; Taylor, R. *Chem.−Eur. J.* **1997**, *3*, 89−98.
(34) Each spectrum was internally referenced to TMS and the shift in the H$_2$ resonance was significantly larger than for any other resonance in the spectrum. Note that non-specific changes in the chemical shift can occur because the nature of the solvent can change over the course of the titration. However, the small shifts in the non-H$_2$ resonances (ca. 0.06 ppm) indicate that these non-specific changes in the solvent are small compared to the shift in the H$_2$ resonance (ca. 0.2 ppm). The non-specific shifts are expected to be the major contributors to error in the K_a determinations.
(35) Bisson, A. P.; Hunter, C. A.; Morales, J. C.; Young, K. *Chem.−Eur. J.* **1998**, *4*, 845−851.

association to the coordinated H_2 ligand ($K_{\text{acetone}} = 0.07$ L mol^{-1}, $K_{\text{pyridine } N-\text{oxide}} = 0.27$ L mol^{-1}).[36]

For the second test, it was recognized that the NMR shift in the first test could be attributable to some factor other than DHHB, perhaps a polarity-induced conformational change or a solvent dielectric effect. To clarify the nature of the interaction, 4-nitropyridine N-oxide was employed as a solvatochromic probe because it has an absorbance maximum sensitive to H-bond donation.[37] The compound has a λ_{max} of 352 nm in toluene, but upon addition of **II**−**PF$_6$**, the λ_{max} undergoes a hypsochromic shift to 338 nm. The 14 nm (1180 cm^{-1}) shift is within the expected regime for moderate to weak H-bond donation.[37] To demonstrate that the observed shift was not caused by the hydride ligand or by a salt effect, the carbonyl analogue, [*trans*-Ru(DMeOPrPE)$_2$(CO)H][PF$_6$], was prepared. No shift in λ_{max} was observed when this complex was added to a solution of the 4-nitropyridine N-oxide. To examine the possibility of an anion effect, the BAr′ analogue was prepared, and again, a hypsochromic shift to 343 nm (745 cm^{-1}) was noted while the carbonyl analogue, [*trans*-Ru(DMeOPrPE)$_2$-(CO)H][BAr′], had no shift in λ_{max}. This result provides credible evidence that the H-bonding shift in solutions of 4-nitropyridine N-oxide containing **II** is directly related to the H_2 ligand and not the complex itself.

The third test is based on investigating the rotational dynamics of the H-bonded complex in solution and relies on the principle that an associated H-bonded complex will have a longer rotational correlation time (τ_c) than a non-H-bonded complex.[38] This method utilizes a hydrodynamic probe molecule capable of accepting H-bonds, pyridine N-oxide-d_5, chosen for its small size and low basicity.[39,40] The principle of the method and the procedure for using it have been described previously in a publication from our laboratory[38] and is based on the fact the rotational correlation time of an H-bond-accepting probe will increase in response to H-bonding. Deuterium NMR studies are particularly well-suited for the determination of rotational correlation times (τ_c) because the predominant relaxation mechanism is through quadrupolar interactions.[41,42] The expression governing the spin−lattice relaxation value (T_1) for quadrupolar nuclei is given in eq 4. Given prior knowledge of the asymmetry parameter, η_a, and the deuterium quadrupole coupling constant, DQCC, the rotational correlation time, τ_c, can be calculated by inserting the measured T_1 into eq 4, where ω_D is the Larmor frequency of ^{2}H.[38,42]

$$\frac{1}{T_1} = \frac{3}{10} \pi^2 (\text{DQCC})^2 \left(1 + \frac{\eta_a^3}{3}\right)\left(\frac{\tau_c}{1 + \omega_D^2 \tau_c^2} + \frac{4\tau_c}{1 + \omega_D^2 \tau_c^2}\right) \tag{4}$$

Equation 4 can be simplified by applying the extreme narrowing limit ($1 \gg \omega_D^2 \tau_c^2$), i.e., the rate of molecular tumbling is faster

(36) When the titration experiment was repeated with **II**-PF$_6$ in toluene-d_8, an opposite but much smaller ($\sim$40−80 ppb) trend was observed that is likely due to breaking up an ion-pair by a more polar titrant or to a dielectric effect.
(37) Lagalante, A. F.; Jacobson, R. J.; Bruno, T. J. *J. Org. Chem.* **1996**, *61*, 6404−6406.
(38) Szymczak, N. K.; Oelkers, A. B.; Tyler, D. R. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4002−4008.
(39) The pK_a value for pyridine N-oxide is 9.92 (in acetonitrile at 298 K; see ref. 40).
(40) Kaczmarczyk, E.; Wrobel, R.; Liwo, A.; Chmurzynski, L. *J. Mol. Struct.* **1999**, *477*, 113−118.

than the rate of the precession of the nuclei in the magnetic field.

$$\frac{1}{T_1} = \frac{3}{2} \pi^2 (\text{DQCC})^2 \left(1 + \frac{\eta_a^3}{3}\right)\tau_c \tag{5}$$

The asymmetry parameter and DQCC values of pyridine N-oxide are known,[43] and thus, calculation of the rotational correlation times is straightforward.

Because solutions containing **II** can be easily converted to the *trans*-Ru(DMeOPrPE)$_2$(CO)H$^+$ complex, the τ_c value of an H-bond acceptor molecule in the presence of **II** can be compared to the τ_c value in the presence of *trans*-Ru(DMeOPrPE)$_2$(CO)-H$^+$, under the assumption that solutions containing equimolar **II** and *trans*-Ru(DMeOPrPE)$_2$(CO)H$^+$ are isoviscous. Although the correlation time is dependent on the solution viscosity according to the Stokes-Einstein-Debye theory, the effect of viscosity can be normalized by taking the ratio of the correlation times of the probe to an internal viscosity standard (cyclohexane) whose asymmetry parameter and DQCC are also known.[44] Because the effect of viscosity is maximized at high viscosity, measurements were taken in diphenyl methane ($\eta = 3.56$ cP). The T_1 values of the pyridine N-oxide-d_5 and cyclohexane-d_{12} were measured simultaneously by ^{2}H NMR spectroscopy.

Scheme 1
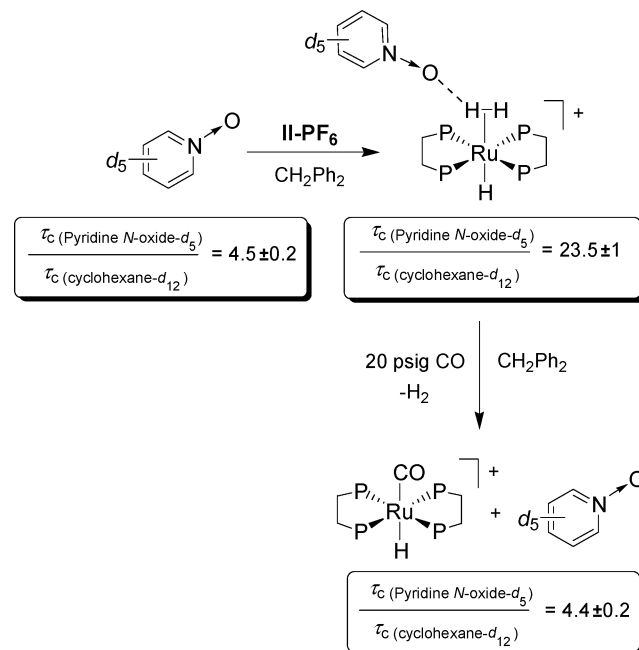
Using this procedure, it was determined that the ratio of τ_c-(pyridine N-oxide-d_5) to τ_c(cyclohexane-d_{12}) was 4.5 ± 0.2 in the absence of **II**−**PF$_6$**. In the presence of **II**−**PF$_6$**, the ratio of τ_c(pyridine N-oxide-d_5) to τ_c(cyclohexane-d_{12}) was 23.5 ± 1. Charging the NMR tube with 20 psig CO immediately converted **II** to *trans*-Ru(DMeOPrPE)$_2$(CO)H$^+$, as monitored by ^{31}P NMR spectroscopy, and the correlation time ratio was again deter-

(41) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961.
(42) Bakhmutov, V. I. *Practical NMR Relaxation for Chemists*; John Wiley & Sons, Ltd: West Sussex, 2004.
(43) Wamsler, T.; Nielsen, J. T.; Pedersen, E. J.; Schaumburg, K. *J. Magn. Res.* **1978**, *31*, 177−186.
(44) Barnes, R. G.; Bloom, J. W. *J. Chem. Phys.* **1972**, *57*, 3082−3086.

mined. The ratio was found to be 4.4 ± 0.2, which is essentially the same value determined for the probe molecule (Scheme 1). This result clearly demonstrates an interaction between pyridine *N*-oxide and **II** that is consistent with an associated complex and is likely a result of H-bonding.

Conclusions

Taken together, the results above provide strong evidence that the η^2-H_2 ligand can act as an H-bond donor and participate in DHHB. We suggest that the consequences of DHHB should be considered whenever M–H_2 complexes are reacted in H-bonding solvents. For example, a general class of proton-transfer reactions involves H_2 heterolysis,[45] and DHHB M–H_2 species have been proposed to exist as intermediates in these pathways.[13,46,47] Another example involves hydrogenation reactions that proceed by the sequential addition of H^+ and H^- across a polar double bond by an *ionic* mechanism. These are attractive candidate reactions for aqueous M–H_2 complexes and DHHB participation.[47,48] Finally, a particularly interesting point is that M–H_2 complexes may H-bond to solvent water. This finding has implications for the reactivity of coordinated H_2 in hydrogenase enzymes and other biological systems where H_2 is typically activated by a heterolytic mechanism and in which DHHB might be important.

Work is continuing to elucidate the electronic factors governing the stabilizing effect of hydrogen bonding to H_2 as well as to examine the effect that DHHB has on the lability and activation of the coordinated hydrogen molecule.

Experimental

Materials and Reagents. Unless otherwise noted, all manipulations were carried out in either a Vacuum Atmospheres Co. glove box (argon filled) or on a Schlenk line under argon or hydrogen using standard Schlenk techniques. The thallium hexafluorophosphate (*caution: thallium compounds are toxic!*), Proton Sponge, 4-nitropyridine *N*-oxide, pyridine *N*-oxide, and pyridine *N*-oxide-d_5 were obtained from commercial vendors and used as received. 1,2-Bis(bis(methoxypropyl)-phosphino)ethane,[49] TlBAr′,[50] and [RuCl$_2$(COD)]$_n$[51] were prepared by published literature procedures. Reagent grade solvents were dried according to published procedures and deoxygenated with either an argon purge or three freeze-pump thaw cycles prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories in 1 g Ampoules and dried over 3 Å molecular sieves prior to use.

Instrumentation and Procedures. $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at an operating frequency of 500.62 (^1H) and 202.45 (^{31}P) MHz. The ^1H chemical shifts were referenced to an internal TMS standard and ^{31}P chemical shifts were referenced to an external standard of 1% H_3PO_4 in D_2O. Note that the ^1H NMR data for the methyl and methylene regions in complexes containing the DMeOPrPE ligand were generally broad and uninformative and therefore are not reported in the synthetic descriptions

below. Solution concentrations of **II** were determined by an inverse-gated $^{31}P\{^1H\}$ experiment using an internal PPh$_3$ standard. For inverse-gated $^{31}P\{^1H\}$ spectra, the decoupler was turned on only during the acquisition. The pulse widths were calibrated to $\pi/2$ and the delay time was set to $5 \times T_1$ to ensure full relaxation. ^2H T_1 measurements were run proton-coupled on a Varian Unity/Inova 600 spectrometer operating at 92.10 MHz at 25 °C using the standard inversion–recovery technique $(\pi - \tau - \pi/2)$. Prior to data collection, a 10 min temperature equilibration period was used. T_1 values were determined by plotting the intensity as a function of delay time and fitting the resultant curve to a 3-parameter single-exponential function. Spectra were acquired unlocked and the recycle delay time was always >5 T_1. Spectrometer frequency drift was found to be negligible over the course of the experiments. Each ^2H NMR spectrum was acquired as 6852 points over a range of 1142 Hz and then zero-filled to 32 768 points. Unweighted Fourier transforms of each FID were phased carefully and subjected to baseline correction. When required, the samples were sealed under argon in 7 mm tubes fitted with Teflon valves. Electronic absorption spectra were recorded with a Hewlett-Packard 8453 UV–vis spectrophotometer, and the peak maximum was determined both by a peak detection algorithm of the spectrophotometer software package and by visual confirmation by the operator using an unsmoothed spectrum.

X-ray Crystallography. X-ray diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer at $T = 153(2)$ K with MoKα radiation ($\lambda = 0.71073$ Å). The crystallographic data and summary of the data collection and structure refinement are given in Table S1, see Supporting Information. Absorption correction was applied by SADABS.[52] The structure was solved using direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on reflection intensities (F^2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. Terminal $-CH_2OCH_3$ groups in the structure are flexible and there are elongations for thermal ellipsoids of some atoms. These groups were refined with restrictions; the average value of $C-O$ distances was used as a target for corresponding $C-O$ bond lengths. The H atoms were placed at calculated positions and were refined as riding atoms. All software and sources scattering factors are contained in the SHELXTL (5.10) program package (G.Sheldrick, Bruker XRD, Madison, WI).

Synthesis of *trans*-[Ru(DMeOPrPE)$_2$Cl$_2$] (I). To a flask containing [RuCl$_2$(COD)]$_n$ (2.10 g, 0.0075 mol) was added 80 mL of an ethanol solution of DMeOPrPE (5.80 g, 0.015 mol) and refluxed for 16 h yielding an orange-brown solution. The solvent was removed *in vacuo* and the resulting oil was taken up in boiling hexanes and hot-filtered (3 × 20 mL). The filtrate was cooled on ice to precipitate a yellow solid that was filtered and washed with cold hexanes. Yield: 4.9 g (70%), $^{31}P\{^1H\}$ δ 44.4 (s), MP: 61–63 °C Calc: C, 46.15; H, 8.61. Found: C, 46.24; H, 8.83.

Generation of *trans*-[Ru(DMeOPrPE)$_2$(H$_2$)H]PF$_6$ (II–PF$_6$). To a vessel containing *trans*-Ru(DMeOPrPE)$_2$Cl$_2$ (0.2843 g, 0.3037 mmol), TlPF$_6$ (0.2120 g, 0.6074 mmol), and Proton Sponge (0.0650 g, 0.3073 mmol) was added toluene (10 mL) and charged with H_2 (350 psig) and heated to 85 °C. After 16 h, the solution was cooled to room temperature and filtered through celite in an argon-filled glovebox to yield a pale-yellow solution. $^{31}P\{^1H\}$ NMR: δ 63.4 (s) and δ –143 (sept). ^1H NMR of the hydride region showed resonances at δ –6.6 (s) and δ –11.4 (quint., $^2J_{HP} = 20$ Hz). Following H/D exchange with CD$_3$OD, the HD isotopolog was visualized as a 1:1:1 triplet ($^1J_{HD} = 32.1$ Hz). $T_1(-20$ °C) = 21.1 ms.

Generation of *trans*-[Ru(DMeOPrPE)$_2$(H$_2$)H]BAr′ (II–BAr′). An identical procedure was used as stated above, but TlBAr′ was used in place of TlPF$_6$. Upon standing, the solution separated into two phases (colorless on top of a yellow liquid). Addition of an equal amount of CH$_2$Cl$_2$ mixed the two layers into a homogeneous light-yellow liquid.

(45) Henry, R. M.; Shoemaker, R. K.; Dubois, D. L.; Dubois, M. R. *J. Am. Chem. Soc.* **2006**, *129*, 3002−3010.
(46) Ayllon, J. A.; Gervaux, C.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1997**, *16*, 2000−2002.
(47) Morris, R. H. In *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001; pp 1−38.
(48) Papish, E. T.; Magee, M. P.; Norton, J. R. In *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier: Amsterdam, 2001; pp 39−74.
(49) Miller, W. K.; Gilbertson, J. D.; Leiva-Paredes, C.; Bernatis, P. R.; Weakley, T. J. R.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem.* **2002**, *41*, 5453−5465.
(50) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Inorg. Chem.* **1997**, *36*, 1726−1727.
(51) Albers, M. O.; Ashworth, T. V.; Oosthuizen, H. E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 68−77.

(52) Sheldrick, G. M. *SADABS* (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, U.S.A.

Generation of *trans*-[Ru(DMeOPrPE)₂(H₂)H]Cl (II−Cl). To a vessel containing buffered water (10 mL, pH 7) was added Ru-(DMeOPrPE)₂Cl₂ (0.500 g), charged with H₂ (350 psig) and heated to 85 °C. After 6 h, the solution was pale yellow. ³¹P{¹H} NMR showed one resonance at δ 63.4 (s)

Generation of *trans*-[Ru(DMeOPrPE)₂H(CO)]⁺. A solution of **II** was prepared as described above and was charged with 2 atm of CO and briefly agitated. Within 5 min, only one resonance was noted in the ³¹P NMR spectrum. ³¹P{¹H} NMR: δ 57.0 (s) and δ −143.0 (sept). ¹H NMR of the hydride region showed a single resonance at δ −9.2 (quint., ²J_{HP} = 21 Hz). IR(toluene): (ν_{CO}) 1965 cm⁻¹.

Electronic Absorption Spectra of 4-Nitropyridine *N*-oxide with II and *trans*-[Ru(DMeOPrPE)₂H(CO)]⁺. The method given by Lagalante and co-workers was employed. An aliquot (∼0.5 mL) of a stock solution of 4-nitropyridine *N*-oxide in toluene was diluted with toluene and the absorption spectrum was recorded in a 3.5 cm³ quartz cuvette (1 cm path length). A solution of **II** was used to dilute an aliquot of 4-nitropyridine *N*-oxide to the previous concentration and the concentration of **II** was at least 10 times greater than the *N*-oxide. The same procedure was repeated for *trans*-[Ru(DMeOPrPE)₂H(CO)]⁺.

Titration of II with Various Hydrogen-Bond Acceptors. In a typical experiment, 0.6 mL of a solution of **II** (1.36 × 10⁻⁵ moles) in toluene-*d₈* or a 1:1 toluene-*d₈*/CD₂Cl₂ mixture for **II**-BAr′ was added to a screw-cap NMR tube equipped with a septum and inserted into the NMR probe and equilibrated at 298 K for 10 min. Varying aliquots of the acceptor were added via a gastight microsyringe and the tube was vigorously agitated for 15 s, then after another 10 min temperature equilibrium, a ¹H NMR spectrum was obtained and the procedure was repeated until the measured chemical shift showed little variance with added acceptor or saturation of the titrant was reached.

Determination of the τ_c of Pyridine *N*-oxide-*d₅* with II−PF₆. To a flask containing 3.14 × 10⁻⁴ moles of **II−PF₆** was added 0.6 mL of a solution of pyridine *N*-oxide-*d₅* in diphenyl methane (0.0854 mol L⁻¹, 5.124 × 10⁻⁵ mol). The mixture was agitated and added to an NMR tube followed by 2 μL cyclohexane-*d₁₂*. The ratio of τ_c pyridine *N*-oxide-*d₅*:τ_c cyclohexane-*d₁₂* was determined after obtaining the ²H T_1 values of each species. τ_c pyridine *N*-oxide-*d₅*:τ_c cyclohexane-*d₁₂* = 23.5 ± 1.

Determination of the τ_c of Pyridine *N*-oxide-*d₅* with *trans*-[Ru-(DMeOPrPE)₂H(CO)]PF₆. The J-Young tube containing **II**, pyridine *N*-oxide-*d₅* and cyclohexane-*d₁₂* in diphenyl methane was charged with 20 psig CO and the conversion to *trans*-[Ru(DMeOPrPE)₂H(CO)]PF₆ was monitored by ³¹P NMR spectroscopy and was complete within 10 min. The ratio of τ_c pyridine *N*-oxide-*d₅*:τ_c cyclohexane-*d₁₂* was determined after obtaining the ²H T_1 values of each species. τ_c pyridine *N*-oxide-*d₅*:τ_c cyclohexane-*d₁₂* = 4.4 ± 0.2.

Supporting Information Available: ³¹P NMR spectra of **I** and **II**, the crystallographic information including the cif file of **I** and tables of bond lengths and angles, and complete ref 7. This material is available free of charge via the Internet at http://pubs.acs.org

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