Dynamic Processes in *cis* Dihydrogen/Hydride Complexes of Ruthenium

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Since the isolation and characterization of the first transition metal dihydrogen complexes,[1] the possibility that a fluxional polyhydride complex might also contain a dihydrogen ligand has been actively investigated.[2] Of particular interest in this context is the dynamic behavior of complexes containing one dihydrogen and one hydride ligand, which are expected to be prototypical of the larger class of polyhydrides. Excluding the large group of known complexes with hydride and dihydrogen ligands *trans* to each other, which exhibit relatively high barriers to site exchange between hydride and dihydrogen ligands,[3] we focus on complexes with hydride and dihydrogen ligands in *cis* positions. Several complexes of this type have been reported. All show interesting dynamic properties, exhibiting exchange of hydrogen environments between the dihydrogen and the hydride ligands, as revealed by variable temperature NMR studies. Examples of this situation include the iridium complex $[IrH(H_2)(bq)(PPh_3)_2]^+$ (bq = benzoquinolate), which was reported by Crabtree and co-workers to undergo hydrogen site exchange between the dihydrogen and hydride ligands with $\Delta G^{\ddagger}_{240} = 10$ kcal/mol.[4] An iron complex $[FeP(CH_2CH_2CH_2PMe_2)_3(H_2)H]^+$, which has $\Delta G^{\ddagger}_{200} = 9.1$ kcal/mol for permutation of the hydrogen environments was reported by Field and Bampos.[5] In these and other reported examples[6] of *cis* dihydrogen/hydride complexes, interconversion of the hydride and dihydrogen environments also requires significant rearrangement on the part of the ancillary ligands, which might be expected to contribute substantially to the activation energy for the process.

To isolate the hydride/dihydrogen exchange process from other ligand rearrangements, a dihydride complex with *cis* hydride ligands related by a mirror plane is required. Such a species can then be protonated to give a cationic dihydrogen/hydride complex where a dynamic process could readily interconvert the hydrogen environments with very limited movement by the ancillary ligands.[7]

We now report our investigations of the synthesis, structure, and dynamic behavior of ruthenium dihydrogen/hydride complexes of the form $[(PCy_3)_2RuH(H_2)(L_2)]^+$. Using very low-temperature NMR spectroscopy, we have succeeded for the first time in measuring the rate of these very rapid dynamic processes.

Reaction of $(PCy_3)_2RuH(H_2)Cl$[8] with bidentate nitrogen ligands such as 2,2′-bipyridine and 1,10-phenanthroline affords the hydrido-chloride complexes $(PCy_3)_2Ru(bipy)HCl$ and $(PCy_3)_2Ru(phen)HCl$ in good yield.[9] Treatment of $(PCy_3)_2RuH(H_2)Cl$ with carbon monoxide gives immediate and quantitative conversion to $(PCy_3)_2Ru(CO)_2HCl$. The hydrido-chloride complexes react with $NaBH_4$ or $LiAlH_4$ in THF to give the corresponding dihydride complexes.[10] Protonation with $(CF_3SO_2)CH_2$ affords cationic complexes $[(PCy_3)_2Ru(bipy)(H_2)H]^+$ (**1**) and $[(PCy_3)_2Ru(phen)(H_2)H]^+$ (**2**). Protonation of the dicarbonyl dihydride complex with $[H(Et_2O)_2][B(Ar)_4]$ (Ar = 3,5-$(CF_3)_2C_6H_3$) affords $[(PCy_3)_2Ru(CO)_2(H_2)H]^+$ (**3**).[11]

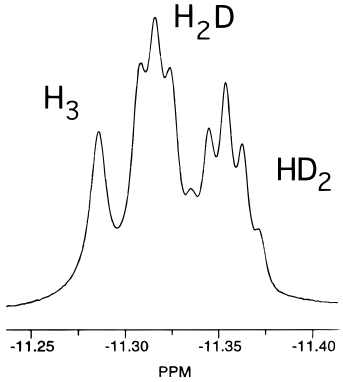
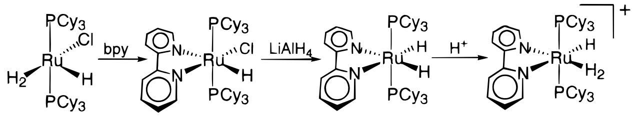


Figure 1. Partial 750 MHz $^1H\{^{31}P\}$ NMR spectrum of a mixture of **1**, **1**-d_1, and **1**-d_2 (298 K).



Formulation of these species as dihydrogen hydride complexes is based primarily upon the observation of H−D coupling upon partial deuteration of the hydride ligands. Exposure of a THF-d_8 solution of complex **1** to D_2 leads to rapid incorporation of deuterium, as evidenced by the appearance of new resonances in the hydride region of the ^1H NMR spectrum (Figure 1).

By means of methodology previously employed in our studies of iridium dihydrogen/hydride complexes,[7] an analysis of the isotope effects on the chemical shifts and the H−D couplings for **1**-d_1 ($J_{H-D} = 5.5$ Hz) and **1**-d_2 ($J_{H-D} = 6.7$ Hz) leads to the conclusion that there is a nonstatistical distribution of deuterium between the dihydrogen and the hydride environments, with a slight preference for deuterium to occupy the hydride site. The H−D coupling in the dihydrogen ligand ($^1J_{H-D}$) is calculated to be ∼19 Hz. A similar analysis for complex **2** is consistent with $^1J_{H-D} = \sim 17$ Hz in the dihydrogen ligand. On the basis of the known inverse correlation of $^1J_{H-D}$ values with H−H distance,[12]

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(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−452.

(2) Compare Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783 and references therein.

(3) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−284

(4) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4023−4037.

(5) Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587−588.

(6) Other reported *cis* dihydrogen/hydride complexes: Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19−C22. Jia, G.; Drouin, S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906−916. Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279−287. See also ref 3, page 200.

(7) Two such compounds have been reported in the literature, $[TpIr(PR_3)(H_2)H]^+$ and $[(PR_3)_4Ru(H_2)H]^+$. In neither case was a barrier to exchange measured, but it was estimated to be 4.5 kcal/mol for the iridium case. Oldham, W. J., Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028−11036. Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716−3731.

(8) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *18*, 3867−3869.

(9) The hydridochloride $(PCy_3)_2Ru(CO)_2HCl$ has been previously reported: Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800−3804. Data for new hydrido-chloride complexes: $(PCy_3)_2Ru(bipy)HCl$: ^1H NMR (δ, THF-d_8, PCy_3 resonances omitted): 10.2, d, 1H.; 8.9, d, 1H.; 8.0, d, 1H.; 7.9, d, 1H.; 7.5, t, 1H.; 7.32, d, 1H.; 7.28, d, 1H.; 6.8, t, 1H.; −11.5, t, 1H, Ru−H, $J_{HP} = 28$ Hz. $(PCy_3)_2Ru(phen)HCl$: 10.6, d, 1H.; 9.3, d, 1H.; 8.2, d, 1H.; 7.9, d, 1H.; 7.8, dd, 1H.; 7.3, t, 1H.; 7.28, d, 1H.; 6.8, t, 1H.;-11.4, t, 1H, Ru−H, $J_{HP} = 27$ Hz.

(10) The dihydride $(PCy_3)_2Ru(CO)_2H_2$ has been previously reported.[9] Data for new dihydride complexes: $(PCy_3)_2Ru(bipy)H_2$: ^1H NMR: (δ, THF-d_8, PCy_3 signals omitted): 9.5, d, 2H.; 8.1, d, 2H.; 7.3, t, 2H.; 6.9 ppm, t, 2H.; −13.9, t, $J_{HP} = 29$ Hz, 2H, Ru−H. $(PCy_3)_2Ru(phen)H_2$: 9.8, d, 2H.; 7.9, d, 2H.; 7.7, s, 2H.; 7.4, dd, 2H: −13.4, t, 2H, Ru−H, $J_{HP} = 28.4$ Hz.

(11) Data for complex **1**: ^1H NMR (δ, THF-d_8, PCy_3 resonances omitted): 9.5, d, 2H.; 9.0, d 2H.; 8.3, t, 2H.; 7.7, t, 2H.; Ru−H_3 −11.1, t, 3H, J_{HP} = 11.4 Hz. ^{31}P NMR: 38.5 br s. Complex **2**: ^1H NMR (δ, THF-d_8, PCy_3 resonances omitted): 9.58 d, 2H.; 8.7 d 2H.; 8.2, s, 2H.; 8.0, dd, 2H.; Ru−H_3 −10.9, t, 3H, $J_{HP} = 14$ Hz. Complex **3**: ^1H NMR (240 K, δ, CD_2Cl_2, PCy_3 resonances omitted): Ru−H_3 −16.8 br t, 3H, J_{HP} not resolved.

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the H−H distance in the dihydrogen ligand in complexes **1** and **2** is found to be ~1.1−1.2 Å.

The observation of a single hydride resonance for the two distinct proton envrinonments in **1** and **2** at ambient temperature is consistent with a rearrangement process which is rapid on the NMR time scale. In an attempt to obtain the limiting chemical shifts for the dihydrogen and hydride resonances and the rate of exchange, the low temperature ^{1}H NMR spectra of **1** and **2** and partially deuterated samples were examined down to 170 K in THF-d_8. While substantial broadening of the hydride resonance was observed, no low-temperature limiting spectra could be obtained. The broadening of the resonances at low temperature is attributed to efficient dipole−dipole relaxation, leading to short T_1[13] and T_2 values.[14] This rapid relaxation problem persists to a lesser extent even with heavily deuterated samples, in which the only proton resonances in the hydride region are due to **1**-d_2 or **2**-d_2. These results exemplify a fundamental limitation to using ^{1}H NMR spectroscopy to probe very rapid dynamic processes in cases where short H−H distances lead to efficient dipole−dipole relaxation.

We next examined complex **3**, motivated by the recent report of Kubas and co-workers that binding dihydrogen *trans* to CO ligands limits the degree of H−H bond lengthening.[15] We reasoned that a shorter, stronger H−H bond in the bound dihydrogen might lead to a higher barrier for the site exchange process. Samples of **3** were prepared as above by protonation of the corresponding neutral dihydride. While **1** and **2** are stable in solution at room temperature, complex **3** is only stable under hydrogen below 240 K. At 240 K, a single broad hydride resonance was observed for **3**. Mixtures of **3**/**3**-d_1/**3**-d_2 were prepared by exposure of solutions of **3** to D_2. The observed J_{H-D} value is 10.5 Hz for both **3**-d_1 and **3**-d_2, consistent with a statistical distribution of deuterium and $J_{H-D} = 31.5$ Hz in the dihydrogen ligand. This corresponds to an H−H distance of ~0.9 Å.[12] Examination of the hydride resonances of **3**/**3**-d_1/**3**-d_2 by very low temperature ^{1}H NMR spectroscopy showed line broadening attributable to relaxation processes as noted above for **1** and **2**.

The dynamic process in complex **3** also is amenable to examination by ^{13}C NMR spectroscopy. Samples of **3** enriched in ^{13}C were prepared by treatment of $(PCy_3)_2RuH(H_2)Cl$ with ^{13}CO, followed by reduction and protonation as above. The ^{13}C NMR spectrum of enriched **3** at 168 K exhibits a single sharp triplet resonance in the carbonyl region at 196.3 ppm, consistent with coupling to two ^{31}P nuclei ($J_{C-P} = 6.5$ Hz). Upon lowering the temperature to 130 K in $CDFCl_2/CDF_2Cl$ (2:1), broadening of the signal and ultimately decoalescence was observed to give two broad resonances centered at 195 and 197 ppm (Figure 2).

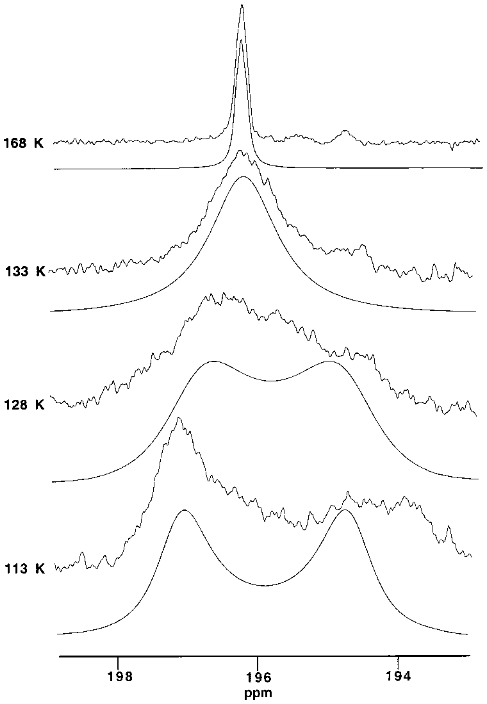
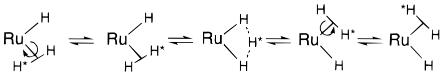


Figure 2. Partial 125 MHz ^{13}C NMR spectra at various temperatures for complex **3** enriched with ^{13}C at the carbonyl positions. Calculated line shapes are shown below the experimental data.

Data quality at these low temperatures is poor, in part due to the low solubility of complex **3**. Comparison of the observed spectra to computer simulated spectra reveals that most of the line broadening is due to slowing of the exchange process, but there is additional line broadening at the lowest temperatures which may arise from viscosity and relaxation effects. An approximate free energy of activation, $\Delta G^{\ddagger}_{120} = 5.5$ kcal/mol can be derived from these data. This is the lowest rearrangement barrier measured to date for a dynamic polyhydride and is actually comparable to reported barriers for rotation around slightly hindered C−C and C−N single bonds.[16]

If we assume that the slightly stretched H−H bond in the bound dihydrogen has retained most of its substantial bond energy,[17] it is quite remarkable that this fairly strong interaction is being disrupted at ~10^3 sec^{-1} at 130 K. We speculate that the reaction must be highly concerted, with a substantial degree of bond formation and bond breaking in a transition state which has approximate 2-fold symmetry. Complete scrambling of all three H atoms also requires rapid rotation of the bound dihydrogen ligand.[18] In the representation below, the fate of a labeled atom indicated with an asterisk is depicted.



The factors which determine the structure and dynamic behavior of complexes of this type are subtle and not well understood. It has been reported that a *neutral* complex very closely related to the species reported here, that is, $(PCy_3)_2Ru(Ph\text{-}py)(H_2)H$ (Ph-py = o-$C_6H_4C_5H_4N$), is also a dihydrogen/hydride complex. In this case, H−D coupling was not detected, and the hydride and dihydrogen ligands exhibit a large exchange coupling.[19] We are continuing to investigate complexes related to **1**−**3** to gain a better understanding of their structures and dynamic behavior.

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[12] An inverse correlation between H−H distance and $^1J_{H-D}$ has been reported by Morris and co-workers: 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. A very similar analysis has been reported by Heinekey and Luther: Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1996**, *35*, 4396−4399. Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127−132. An extension of this correlation to include dihydride complexes has been recently reported: Gründemann, S.; Limbach, H. H.; Buntkowsky, G.; Sabo-Etienne, S.; Chaudret, B. *J. Phys. Chem. A* **1999**, *103*, 4752−4754.

[13] Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

[14] Low-temperature line broadening in dynamic dihydrogen/hydride complexes has been investigated: Yao, W.; Faller, J. W.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *259*, 71−76.

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[18] With the exception of d^2 metal complexes, barriers to the rotation of bound dihydrogen are generally very low. Compare Jalon, F. A.; Otero, A.; Manzano, B. R.; Villasenor, E.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 10123−10124 and references therein.

[19] Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1998**, *120*, 4228−4229.