J. Am. Chem. Soc. **1998,** *120,* 10553−10554 10553

Reversible Formation of Bis(2,2′-bipyridine)rhodium(III) Dihydride from Bis(2,2′-bipyridine)rhodium(I) and Dihydrogen. Direct Transfer of Dihydrogen from Rhodium(III) Dihydride to Rhodium(I)

Susan G. Yan, Bruce S. Brunschwig,* Carol Creutz,
Etsuko Fujita,* and Norman Sutin*

Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973-5000

Received June 25, 1998

Oxidative addition of H_2 to a transition metal complex is an important step in many catalytic hydrogenation and hydroformylation reactions.[1] The existence of molecular hydrogen complexes[2] shows that H_2 may act as a two-electron σ-bonding ligand without undergoing complete oxidative addition.[3−5] Thus, H_2 complexes may serve as intermediates in H_2 oxidative addition reactions (eq 1) and have been implicated in solar energy conversion schemes directed toward the photoreduction of water.[6]

$$M^{I}L_n + H_2 \rightleftharpoons L_nM^{I}(H_2) \rightleftharpoons L_nM^{III}(H^-)_2 \qquad (1)$$

We have investigated the oxidative addition of H_2 to bis(2,2′-bipyridine)rhodium(I) to form the corresponding Rh^{III} *cis*-dihydride. Herein we report the kinetics and thermodynamics of dihydride formation and present the first evidence for the net transfer of H_2 in a bimolecular self-exchange reaction.

Bis(2,2′-bipyridine)rhodium(I), $Rh(bpy)_2^+$ (bpy = 2,2′-bipyridine), can be prepared by chemical,[7] electrochemical,[8] photochemical[9,10] or radiation chemical[11] reduction of Rh^{III} complexes. The X-ray structure of $[Rh(bpy)_2]ClO_4{\cdot}CH_3CN$ shows the $Rh(bpy)_2^+$ to have a tetrahedrally distorted square-planar structure and to be stacked along a 2-fold screw axis.[12] The properties of $Rh(bpy)_2^+$ have previously been studied in connection with the photochemical reduction of water to H_2 and to explore its water−gas-shift activity.[8,13] It was in the context of the latter studies that the reaction of $Rh(bpy)_2^+$ with H_2 was first noted.

Solutions of $Rh(bpy)_2^+$ in acetone, prepared either by photochemical reduction of $Rh(bpy)_2(C_2O_4)^+$ at 313 nm[10,14] or by dissolution of $[Rh(bpy)_2]PF_6$, obtained by reducing the Rh^{III} complex with $NaBH_4$,[7] are reddish purple and air-sensitive. All manipulations were performed in an argon-filled glovebox or on a vacuum line. The $Rh(bpy)_2^+$ solutions feature an absorbance maximum at 552 nm ($\epsilon_{552} = 1.25 \times 10^4$ M^{-1} cm^{-1}),[10,14] slightly red-shifted from its position in aqueous alkali.[8] Upon addition of H_2, the visible absorption bands decrease, and a shoulder appears at ~350 nm. The result is an almost colorless solution, consistent with the conversion of the Rh^{I} to a Rh^{III} dihydride complex. Removal of H_2 by argon bubbling or freeze−thaw evacuation regenerates the initial $Rh(bpy)_2^+$ absorbance.

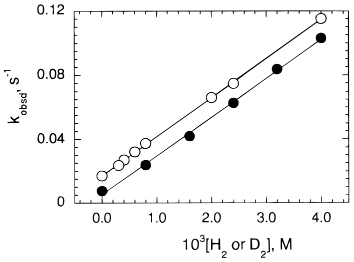


Figure 1. Plot of rate constants for formation of rhodium(III) dihydride as a function of H_2 concentration in acetone at 25 °C (○) H_2, (●) D_2. $[H_2] = [D_2] = 4.0 \times 10^{-3}$ M/atm at 25 °C.

Acetone solutions containing bis(2,2′-bipyridine)rhodium(III) dihydride, prepared by reaction of $(0.4{-}2.0) \times 10^{-4}$ M $Rh(bpy)_2^+$ with H_2, were irradiated for 60 s at 25 °C using a 150-W xenon lamp equipped with a 300-nm long-pass filter. Irradiation results in the dissociation of the dihydride and generation of H_2 and the purple $Rh(bpy)_2^+$. The photolyzed solutions were well-shaken, and the regeneration of the dihydride (disappearance of the photogenerated $Rh(bpy)_2^+$) was followed by UV/vis absorption spectroscopy.

$$Rh(bpy)_2^+ + H_2 \underset{k_{r(H)}}{\overset{k_{f(H)}}{\rightleftharpoons}} [Rh^{III}(bpy)_2(H^-)_2]^+ \qquad (2)$$

The pseudo-first-order rate constants for the return to equilibrium are given by $k_{obsd} = k_f[H_2] + k_r$ and the observed rate constants are plotted as a function of $[H_2]$ in Figure 1. The slope of the plot yields $k_{f(H)} = 24.4$ M^{-1} s^{-1}, and the intercept gives $k_{r(H)} = 1.70 \times 10^{-2}$ s^{-1} at 25 °C. From the ratio of rate constants, $K_H = k_f/k_r = 1.43 \times 10^3$ M^{-1}. The value of K_H determined from the equilibrium concentrations is 1.45×10^3 M^{-1}, in excellent agreement with the value calculated from the rate constants. The rate and equilibrium constants were not affected by the addition of a 10-fold excess (~10^{-3} M) of 2,2′-bipyridine. No kinetic evidence for the presence of a H_2 adduct was obtained, indicating that the dihydride is considerably more stable than the H_2 complex in the temperature range studied. This conclusion is supported by the NMR evidence presented below.

The rate constant $k_{f(D)}$ for dideuteride formation is virtually identical to the rate constant for dihydride formation, consistent with the transition state for the oxidative addition resembling the reactants.[15] By contrast, $k_{r(D)}$ is significantly smaller than $k_{r(H)}$. The absorbance data give $K_D = 3.36 \times 10^3$ M^{-1}, so that K_H/K_D is 0.43 at 25 °C. From K_D and $k_{f(D)}$, the value of $k_{r(D)}$ is 7.5×10^{-3} s^{-1}, corresponding to $k_{r(H)}/k_{r(D)} = 2.3$. The significantly larger isotope effect for reductive elimination correlates with the inverse equilibrium isotope effect. The isotope effects are similar to those seen in other systems.[15−19]

---

(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Tinke, R. G. *Principles of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−452. (b) Kubas, G. *Acc. Chem. Res.* **1988**, *21*, 120−128.

(3) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101.

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

(5) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913−926.

(6) Sutin, N.; Creutz, C.; Fujita, E. *Comments Inorg. Chem.* **1997**, *19*, 67−92.

(7) Martin, B.; McWhinnie, W. R.; Waind, G. M. *J. Inorg. Nucl. Chem.* **1961**, *23*, 207−233.

(8) Chou, M.; Creutz, C.; Mahajan, D.; Sutin, N.; Zipp, A. P. *Inorg. Chem.* **1982**, *21*, 3989−3997.

(9) Chan, S. F.; Chou, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369−379.

(10) Shinozaki, K.; Takahashi, N. *Inorg. Chem.* **1996**, *35*, 3917−3924.

(11) (a) Mulazzani, Q. G.; Emmi, S.; Hoffman, M. Z.; Venturi, M. *J. Am. Chem. Soc.* **1981**, *103*, 3362−3370. (b) Mulazanni, Q. G.; Venturi, M.; Hoffman, M. Z. *J. Phys. Chem.* **1982**, *86*, 242−247. (c) Schwarz, H. A.; Creutz, C. *Inorg. Chem.* **1983**, *22*, 707−713.

(12) Szalda, D. J., to be published.

(13) Mahajan, D.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1985**, *24*, 2063−2067.

(14) (a) The UV−visible spectrum of methanol solutions of $Rh(bpy)_2(C_2O_4)^+$ shows an intense absorption band at 306 nm, $\epsilon = 2.7 \times 10^4$ M^{-1} cm^{-1}, with a shoulder at ~313 nm, $\epsilon \approx 2.6 \times 10^4$ M^{-1} cm^{-1}. (b) The intense transition in the visible spectrum of $Rh(bpy)_2^+$ is metal-to-ligand charge transfer in character.

(15) Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders: W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049−8054.

(16) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353−354.

(17) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629−7636.

(18) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023.

(19) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179−9190.

S0002-7863(98)02208-2 CCC: $15.00

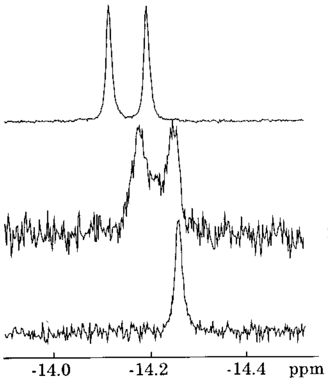


Figure 2. Temperature dependence of the hydride region of the NMR spectrum (acetone-d_6, 300 MHz) of $(bpy)_2Rh(H)_2^+/Rh(bpy)_2^+$ mixtures in the presence of excess H_2 (1 atm at 25 °C).

The room-temperature ^{1}H NMR spectrum of the dihydride in acetone-d_6 exhibits a single peak in the metal hydride region at −14.4 ppm. A doublet had been expected on the basis of the spin−spin interaction of the (equivalent) hydrides with ^{103}Rh (100% abundance) which has spin $^1/_2$. The observation of a single peak indicates that the lifetime of the dihydride is less than 0.01 s at room temperature. As the temperature is lowered, the dihydride peak splits into the anticipated doublet with $J_{Rh-H} = 26$ Hz (Figure 2). The Rh−H coupling of the dihydride may be compared with $J_{Rh-H} = 30$, 18.9 and 14.7 Hz in *cis*-$[Rh(trien)(H)_2]^+$ (trien = triethylenetetramine),[20] $TpRh(PPh_3)(H)_2$ (Tp = hydridotris(1-pyrazolyl)borate),[21] and $[Rh(PP_3)(H)_2]^+$ ($PP_3 = P(CH_2PPh_2)_3$),[22] respectively. The room-temperature ^{1}H NMR spectrum of the monohydride, prepared by reaction of $Rh(bpy)_2^+$ in acetone-d_6 with CF_3SO_3H, exhibits a doublet centered at −13.25 ppm with $J_{Rh-H} = 13$ Hz, identical to the Rh−H coupling reported for $[Rh(CN)_5H]^{3-}$.[23]

To further characterize the complex, the spin−lattice relaxation time T_1 of the coordinated hydride was determined as a function of temperature. The T_1(min) value of 345 ms at 186 K is consistent with a dihydride structure since H_2 complexes typically exhibit T_1(min) values <100 ms at 300 MHz.[24] The NMR spectrum of the HD complex provides additional evidence for the dihydride structure. The hydride doublet of the HD complex is shifted slightly upfield (0.02−0.04 ppm), but the Rh−H coupling constant is unchanged. No evidence for H−D coupling was observed, indicatiing a relatively long H−D distance (>1.4 Å)[25] and further supporting the description of the complex as a dihydride.

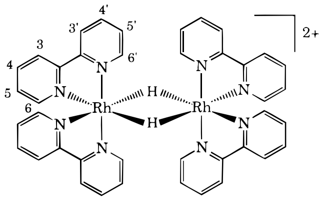
The aromatic H NMR spectrum of $Rh(bpy)_2^+$ in acetone-d_6 features two doublets at low fields due to H(6) and H(3) and two pseudotriplets at higher fields due to H(4) and H(5). This pattern is typical of bis- and tris-bipyridine complexes in which the pyridine rings have identical magnetic environments.[26−31] Although eight aromatic H resonances are expected for $[Rh^{III}(bpy)_2(H^-)_2]^+$, only three are observed in the room-temperature spectrum—two broad bands at high field due to H(4)/H(4′) and H(5)/H(5′) and a narrower band at lower field due to H(3)/H(3′). The resonances due to H(6) and H(6′) are not seen. As the temperature is lowered, an aromatic H spectrum very similar to that of $Rh(bpy)_2(C_2O_4)^+$ develops.

The temperature dependence of the dihydride NMR spectrum requires that the complex undergoes another reaction in addition to the H_2 elimination, eq 2. First-order rate constants were derived by modeling the NMR line shapes using the peak separations and line widths in the absence of exchange and their midpoint.[32] The derived rate constants *increased* with the total Rh concentration and *decreased* with increasing H concentration. The observed kinetics are consistent with a rapid self-exchange reaction between

$$[\mathrm{Rh^{III}(bpy)_2(H^-)_2}]^+ + \mathrm{Rh^{I}(bpy)_2}^+ \overset{k_{ex}}{\rightleftharpoons} \mathrm{Rh^{I}(bpy)_2}^+ + [\mathrm{Rh^{III}(bpy)_2(H^-)_2}]^+ \quad (3)$$

the Rh^{III} dihydride and Rh^I. The rate constants for the self-exchange and the derived first-order rate constants are related by $k_{obsd} = k_{ex}[Rh_T]/(1 + K_H[H_2])$. Preliminary analysis of the NMR data yields $k_{ex} \approx 10^6\ M^{-1}\ s^{-1}$ at 25 °C.

The self-exchange formally involves the transfer of two electrons from Rh^I to Rh^{III} and two hydride ligands in the opposite direction and could proceed through a symmetrical bis(hydrido)-bridged intermediate. Many stable bis(hydrido)-bridged complexes are known,[33,34] and evidence for a H_2-bridged Ru^{II}_2 system[35] and for dihydride transfer in binuclear systems[36−38] has been presented. An Ir^I-catalyzed isomerization of its Ir^{III} dihydride[38] resembles the system studied here. Although that isomerization proceeds 10^8 times more slowly than the present exchange reaction, it is also believed to proceed via a bis(hydrido)-bridged intermediate. Moreover, in each case the coupled electron/hydride transfer may be effected through the transfer of two H atoms or a H_2 molecule. Regardless of their detailed mechanisms, the net reaction occurring in the exchange/isomerization systems is the transfer of H_2 from one complex to another. Additional studies are underway to determine the generality of the transfer reaction and to elucidate the factors responsible for the extraordinary variations in exchange/isomerization rates.



Acknowledgment. The authors thank Morris Bullock, Marcel Schlaf, Stanley Seltzer, Faisal Shafiq, and Charles Springer for very helpful discussions. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

JA982208E

---

(20) Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1963**, 3594−3599.

(21) Oldham, W. J., Jr.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028−11036.

(22) Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134−12140.

(23) Griffith, W. P.; Wilkinson, R. *J. Chem. Soc.* **1959**, 2757−2762.

(24) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

(25) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399.

(26) DeSimone, R. E.; Drago, R. S. *Inorg. Chem.* **1969**, *8*, 2517−2519.

(27) Lytle, F. E.; Petrovsky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239−247.

(28) Constable, E. C.; Seddon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 34−36.

(29) Ohsawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383−5386.

(30) Wehman, P.; Dol, G. C.; Moorman, E. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Fraanje, J.; Goubitz, K. *Organometallics* **1994**, *13*, 4856−4869.

(31) Orellana, G.; Ibarra, C. A.; Santoro, J. *Inorg. Chem.* **1988**, *27*, 1025−1030.

(32) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 14−20.

(33) Albinati, A.; Emge, T. J.; Koetzle, T. F.; Meillee, S. V.; Musco, A.; Venanzi, L. M. *Inorg. Chem.* **1986**, *25*, 4821−4827.

(34) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2661−2663.

(35) (a) Collman, J. P.; Wagenknecht, P. S.; Lewis, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 5654−5664. (b) The authors conclude that the H_2 ligand is symmetrically bound to both Ru^{II} centers with the H−H axis perpendicular to the Ru−Ru axis.

(36) Jones, W. D.; Maquire, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4544−4546.

(37) Deutsch, P. P.; Maquire, J. A.; Jones, W. D.; Eisenberg, R. *Inorg. Chem.* **1990**, *29*, 686−690.

(38) Kunin, A. J.; Johnson, C. E.; Maquire, J. A.; Jones, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1987**, *109*, 2963−2968.