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X-ray Structure and Reactivity of [Ru(bpy)₂(CO)H]PF₆·¹/₂C₃H₆O (bpy = 2,2'-Bipyridyl), a Possible Intermediate in the Water-Gas Shift Reaction Catalyzed by Ruthenium Polypyridyl Complexes

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The structure of [Ru($C_{10}H_8N_2$)₂(CO)H]PF₆·¹/₂C₃H₆O is reported. The compound crystallizes in the monoclinic $C2/c$ space group with unit cell parameters a = 26.680 (4) Å, b = 7.005 (3) Å, c = 25.936 (2) Å, and β = 93.96 (2)° (V = 4836.04 Å³, Z = 8). The cationic species has a cis geometry for CO and H. The ruthenium–hydride and ruthenium–carbon distances are 1.68 (4) and 1.804 (6) Å, respectively. The average ruthenium–nitrogen distance is 2.109 Å. In acidic solution the title compound acts as a hydride donor to produce dihydrogen gas in a pseudo-first-order reaction; the second-order rate constant for this reaction is 0.105 ∓ 0.01 dm³ mol⁻¹ s⁻¹ at 303 K with an activation energy 56 ∓ 2 kJ mol⁻¹. A value of −100 ∓ 8 J mol⁻¹ deg⁻¹ has been obtained for the entropy of activation. The consequences of these results for the possible reaction mechanism of the homogeneous water-gas shift reaction catalyzed by [Ru(bpy)₂(CO)Cl]⁺ are discussed.

Introduction

In the search for new catalysts in photochemical and electrochemical domains some interesting and unexpected ruthenium bis(2,2'-bipyridyl) complexes have been reported. Recently a series of Ru(bpy)₂–carbonyl (bpy = (2,2'-bipyridyl) complexes have been prepared with properties quite different from those normally expected for Ru(bpy)₂ complexes.[1–4] One of the most interesting carbonyl complexes obtained is [Ru(bpy)₂(CO)H]PF₆·¹/₂C₃H₆O (1). The lowest energy metal-to-ligand charge-transfer band of this complex is found at approximately the same wavelength as that of [Ru(bpy)₃]²⁺, but the complex is not luminescent.[1c,4b] For the corresponding osmium–hydrido complex, room-temperature emission has been reported.[4b] The photochemical behavior of the ruthenium hydride is in contrast with that of other carbonyl complexes. Photodecarbonylation of the hydride complex is not efficient (quantum yield at 365 nm is <0.001) while the quantum yield for [Ru(bpy)₂(CO)Cl]⁺ under the same conditions is 0.09.[1d] In earlier papers, some chemical reactions of [Ru(bpy)₂(CO)H]⁺ were reported and evidence presented[1c,e] for the acid-induced production of hydrogen gas and for the hydrogenation of acetone. In these reactions the carbonyl hydride acts as a stoichiometric reagent. Recently Ru(bpy)₂–hydrides have been proposed as intermediates in the water-gas shift reaction catalyzed by [Ru(bpy)₂(CO)Cl]⁺.[5,6] It was thought that a detailed investigation of Ru(bpy)₂–hydrides might lead to a better understanding of their reactivity and result in the development of efficient catalytic systems for the photochemical production of hydrogen gas or for homogeneous hydrogenation reactions. In this paper the structure of [Ru(bpy)₂(CO)H]PF₆·¹/₂C₃H₆O (1) and a kinetic investigation of the stoichiometric production of dihydrogen gas in acidic solution are reported.

Experimental Section

X-ray Crystallographic Procedures. [Ru(bpy)₂(CO)H]PF₆·¹/₂C₃H₆O was prepared as described elsewhere.[1c] Orange needles were obtained after recrystallization from acetone–water mixtures. A single crystal of dimensions 0.45 × 0.17 × 0.12 mm was mounted on a Enraf-Nonius CAD-4 four-circle diffractometer. A summary of the crystal data and details on the intensity data collection, obtained at room temperature, have been given in Table I. The ruthenium atom positions were obtained from a three-dimensional Patterson map, and subsequent difference Fourier maps were used for the other atoms. Non-hydrogen atoms were refined anisotropically. Hydrogen positions were locatable in difference Fourier maps, but coupled symmetrically to parent atoms (C–H = 0.96 Å), and were refined only for equal thermal parameters in each ring of the ligands. Acetone hydrogen atoms were not refined because of the disorder of the molecule (near ¹/₄, ¹/₄, 0). Scattering factors and anomalous dispersion corrections were taken from the literature.[7] No absorption corrections were carried out. The estimate of agreement

Table I. Crystallographic Data and Intensity Collection Parameters for [Ru(bpy)₂(CO)H]PF₆·¹/₂C₃H₆O

formula	[Ru($C_{10}H_8N_2$)₂(CO)H]PF₆·¹/₂C₃H₆O
fw	616.43
space group	$C2/c$
a, Å	26.680 (4)
b, Å	7.005 (3)
c, Å	25.936 (4)
β, deg	93.96 (2)
V, Å³	4836.0 (2)
Z	8
d_{calcd}, g/cm³	1.69
cryst size, mm	0.45 × 0.17 × 0.12
λ(Mo Kα), Å	0.710 73 (graphite monochromatized)
μ(Mo Kα), cm⁻¹	7.70
T, K	295
F(000), electrons	2430.2
orientation reflecns: no.; range (θ), deg	24; −11 < θ < +11
scan method	ω–θ
data colln range (θ), deg	2 < θ < 30
systematic extinctions	h + k = odd: $h0l$ = odd
region of reflecns	0 ≤ h ≤ 37; −9 ≤ k ≤ 9; 0 ≤ l ≤ 36
measd indep reflecns	7566
significant reflecns	3395
R^a	0.0417
$R_w{}^b$	0.0418

$^a R = \sum|\Delta F|/\sum|F_o|$. $^b R_w = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma_F^2$.

between equivalent reflections is 0.0315. Calculations were carried out on the Leiden University Computer (AMDAHL V7B). The programs used were SHELX 76 and the Leiden X-ray system written or modified by E. W. Rutten-Keulemans and R. A. G. de Graaff.

(1) (a) Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Vos, J. G.; Cardin, C. J.; Costa, S. R.; Edwards, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 750. (b) Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *Inorg. Chim. Acta* **1982**, *64*, L75. (c) Kelly, J. M.; Vos, J. G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 628. (d) Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1986**, 253. (e) Kelly, J. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans* **1986**, 1045.
(2) (a) Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1213. (b) Choudhury, D.; Jones, R. F.; Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1143.
(3) (a) Black, D. S.; Deacon, G. B.; Thomas, N. C. *Transition Met. Chem. (N.Y.)* **1980**, *5*, 317. (b) Black, D. S.; Deacon, G. B.; Thomas, N. C. *Aust. J. Chem.* **1982**, *35*, 2445. (c) Black, D. S.; Deacon, G. B.; Thomas, N. C. *Polyhedron* **1983**, *2*, 409.
(4) (a) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Organometallics* **1983**, *2*, 55. (b) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241.
(5) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885.
(6) Tanaka, K.; Morimoto, M.; Tanaka, T. *Chem. Lett.* **1983**, 901.
(7) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

†University of Leiden.
‡National Institute for Higher Education.

Table II. Fractional Atomic Coordinates Multiplied by 10^5 for Ru, 10^3 for the Hydrogen Atoms, and 10^4 for All Other Atoms[a]

atom	x/a	y/b	z/c	B(iso), Å²
Ru	12411 (1)	2568 (4)	21211 (2)	3.335 (9)
H	171 (2)	178 (5)	230 (1)	4.2 (9)
C	880 (2)	1881 (8)	2488 (2)	5.3 (2)
O	676 (2)	2951 (6)	2738 (2)	8.7 (2)
N(11)	1448 (1)	−1550 (5)	2728 (1)	3.48 (10)
C(12)	1765 (2)	−2999 (6)	2624 (2)	3.43 (12)
C(13)	1882 (2)	−4394 (7)	2986 (2)	4.66 (15)
C(14)	1687 (2)	−4330 (8)	3460 (2)	5.4 (2)
C(15)	1382 (2)	−2841 (8)	3571 (2)	4.76 (15)
C(16)	1272 (2)	−1485 (7)	3199 (2)	4.20 (14)
N(21)	1760 (1)	−1583 (5)	1785 (1)	3.28 (10)
C(22)	1959 (2)	−2967 (6)	2106 (2)	3.23 (12)
C(23)	2326 (2)	−4187 (7)	1947 (2)	4.42 (15)
C(24)	2483 (2)	−4041 (8)	1463 (2)	4.9 (2)
C(25)	2277 (2)	−2674 (8)	1140 (2)	4.9 (2)
C(26)	1918 (2)	−1472 (7)	1311 (2)	4.18 (14)
N(31)	1031 (1)	1660 (5)	1436 (1)	3.48 (10)
C(32)	662 (2)	845 (6)	1130 (2)	3.44 (13)
C(33)	494 (2)	1691 (7)	665 (2)	4.8 (2)
C(34)	714 (2)	3368 (8)	513 (2)	5.7 (2)
C(35)	1088 (2)	4157 (7)	821 (2)	5.3 (2)
C(36)	1238 (2)	3282 (7)	1279 (2)	4.56 (15)
N(41)	645 (1)	−1546 (5)	1774 (2)	3.55 (11)
C(42)	455 (2)	−958 (6)	1314 (2)	3.46 (12)
C(43)	88 (2)	−2014 (7)	1037 (2)	4.64 (15)
C(44)	−74 (2)	−3676 (8)	1246 (3)	5.6 (2)
C(45)	124 (2)	−4267 (7)	1714 (3)	5.3 (2)
C(46)	483 (2)	−3184 (7)	1969 (2)	4.70 (15)
P	3886 (1)	6834 (2)	417 (1)	5.23 (5)
F(1)	3985 (2)	4647 (5)	391 (2)	10.4 (2)
F(2)	4222 (2)	6866 (6)	949 (2)	10.9 (2)
F(3)	3843 (2)	9049 (5)	458 (2)	9.8 (2)
F(4)	3425 (1)	6537 (6)	731 (2)	10.0 (2)
F(5)	3587 (2)	6840 (6)	−108 (2)	10.4 (2)
R(6)	4375 (1)	7177 (7)	114 (2)	10.1 (2)
O(5)	2361 (4)	2239 (16)	662 (5)	10.7 (3)
C(51)	244 (1)	237 (3)	22 (1)	8.3 (3)
C(52)	2218 (4)	3942 (15)	−30 (5)	15.3 (3)
H(13)	21062 (0)	−54457 (0)	29016 (0)	6.0 (6)
H(14)	17582 (0)	−53715 (0)	37121 (0)	6.0 (6)
H(15)	12540 (0)	−27142 (0)	39170 (0)	6.0 (6)
H(16)	10463 (0)	−3982 (0)	32776 (0)	6.0 (6)
H(23)	24646 (0)	−51745 (0)	21800 (0)	5.6 (5)
H(24)	27420 (0)	−48973 (0)	13483 (0)	5.6 (5)
H(25)	23862 (0)	−25275 (0)	7759 (0)	5.6 (5)
H(26)	17616 (0)	−4975 (0)	10762 (0)	5.6 (5)
H(33)	2112 (0)	11118 (0)	4512 (0)	5.5 (5)
H(34)	5983 (0)	39738 (0)	1844 (0)	5.5 (5)
H(35)	12551 (0)	53413 (0)	7174 (0)	5.5 (5)
H(36)	15147 (0)	38537 (0)	15035 (0)	5.5 (5)
H(43)	−575 (0)	−15566 (0)	6944 (0)	4.8 (5)
H(44)	−3405 (0)	−44541 (0)	10652 (0)	4.8 (5)
H(45)	162 (0)	−55084 (0)	18572 (0)	4.8 (5)
H(46)	6222 (0)	−36069 (0)	23245 (0)	4.8 (5)

[a] Estimated standard deviations are given in parentheses; (0) means that the coordinate was not refined.

Kinetic Measurements. $[Ru(bpy)_2(CO)H]PF_6 \cdot {}^1/_2C_3H_6O$ was dissolved in water with use of standard grade Amberlite resin IRA-400 (Cl). So in a typical experiment 70 mg of **1** and 2 g of the resin were stirred for 6 h in 30 cm³ of Milli-Q water. The solution was then filtered and used as obtained. Solutions prepared in this way are stable for several days if kept at 5 °C. The concentration of the ruthenium hydride complex was determined from its exctincfion coefficient.[1c] For experiments at pHs between 2 and 3, Britten–Robinson buffers were used (ionic strength 0.12 M); below pH 2 measurements were carried out in HCl solution (ionic strength 0.03 M). The reaction mixtures for the kinetic experiments were obtained by mixing 2.5 cm³ of buffer solution and 0.5 cm³ of the ruthenium hydride solution. The reactions were followed with a Shimadzu UV-240 spectrophotometer linked to a Commodore 8032-SK minicomputer, a CMM 8050 disk drive, and a 4028 printer. Rate constants were calculated manually by using the Guggenheim method[8] or

(8) Swinbourne, E. S. *Analysis of Kinetic Data*; Nelson and Sons: London, 1971.

Table III. Selected Bond Distances (Å) of $[Ru(bpy)_2(CO)H]PF_6 \cdot {}^1/_2C_3H_6O$ with Standard Deviations

About Ruthenium			
Ru–H	1.68 (4)	Ru–N(21)	2.123 (4)
Ru–C	1.804 (6)	Ru–N(31)	2.073 (4)
Ru–N(11)	2.065 (3)	Ru–N(41)	2.176 (3)

About the Hydride Ion			
H–C	2.29 (4)	H–N(21)	2.72 (4)
H–O	3.16 (4)	H–C(22)	3.44 (4)
H–N(11)	2.69 (4)	H–N(31)	2.79 (4)
H–C(12)	3.45 (4)	H–C(36)	3.04 (4)

In the Carbonyl Group	
C–O	1.152 (6)

In PF_6^-			
P–F(1)	1.557 (4)	P–F(4)	1.534 (4)
P–F(2)	1.593 (4)	P–F(5)	1.529 (4)
P–F(3)	1.559 (4)	P–F(6)	1.589 (4)

In Acetone			
C(51)–C(52)	1.40 (2)	O(5)–C(51)	1.17 (1)

Table IV. Selected Bond Angles (deg) of $[Ru(bpy)_2(CO)H]PF_6 \cdot {}^1/_2C_3H_6O$ with Standard Deviations

About Ruthenium			
N(11)–Ru–N(21)	78.1 (1)	N(31)–Ru–N(41)	76.9 (1)
N(11)–Ru–N(31)	170.3 (1)	N(31)–Ru–H	95.3 (13)
N(11)–Ru–N(41)	96.2 (1)	N(31)–Ru–C	91.8 (2)
N(11)–Ru–H	91.1 (12)	N(41)–Ru–H	171.8 (2)
N(11)–Ru–C	86.2 (2)	N(41)–Ru–C	100.5 (2)
N(21)–Ru–N(31)	94.6 (1)	H–Ru–C	82.2 (14)
N(21)–Ru–N(41)	87.5 (1)	Ru–C–O	175.8 (5)
N(21)–Ru–H	90.5 (13)		
N(21)–Ru–C	170.7 (2)		

In the PF_6^- Anion			
F(3)–P–F(6)	87.2 (2)	F(5)–P–F(6)	87.3 (2)
F(1)–P–F(6)	88.8 (2)	F(3)–P–F(5)	91.3 (2)
F(2)–P–F(3)	88.0 (2)	F(1)–P–F(5)	92.5 (2)
F(1)–P–F(2)	87.9 (2)	F(1)–P–F(4)	92.0 (2)
F(3)–P–F(4)	91.9 (2)	F(4)–P–F(6)	177.6 (3)
F(1)–P–F(3)	174.3 (3)	F(4)–P–F(5)	94.9 (3)
F(2)–P–F(6)	89.7 (3)	F(2)–P–F(4)	88.0 (2)
F(2)–P–F(5)	176.9 (2)		

In Acetone	
O(5)–C(51)–C(52)	114.0 (18)
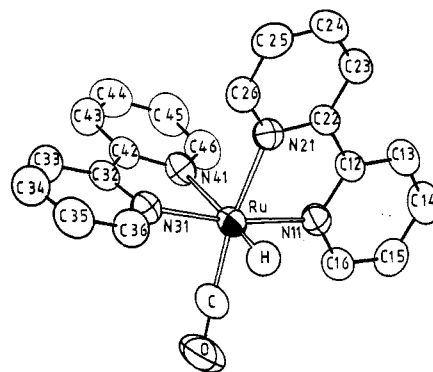
Figure 1. ORTEP[16] projection and atomic numbering for the cationic complex $[Ru(bpy)_2(CO)H]^+$.

by using least-squares methods with a plot of log $[(OD_0 - OD_\infty)/(OD_t - OD_\infty)]$ vs. time t, where OD_0 is the optical density at time 0. OD_t the optical density at time t, and OD_∞ the optical density at infinite time. Rate constants reported are averages obtained from at least three experiments. The slopes of plots of ln k_{obsd} vs. $1/T$ and k_{obsd} vs. $[H^+]$ were obtained by using least-squares methods.

Results and Discussion

Description and Discussion of the Structure. Selected bond distances and angles have been given in Tables II–V. Table V
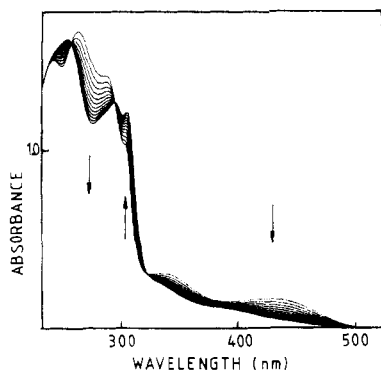
Figure 2. UV/vis spectra taken during the acid-induced decomposition of the ruthenium hydride complex (5×10^{-5} mol/dm^3), pH 2.06, temperature 303 K, time between scans 2 min).

Table VI. Pseudo-First-Order and Second-Order Rate Constants for the Formation of Dihydrogen

pH	temp, K	$10^4 k_{obsd}$, s^{-1}	$10^2 k$, dm^3 mol^{-1} s^{-1}
1.27	297	42.0 ∓ 4.0	7.8 ∓ 0.8
	303	56.0 ∓ 5.0	10.5 ∓ 1.0
	313	102 ∓ 10	19.0 ∓ 2.0
1.47	297	28.5 ∓ 2.0	8.4 ∓ 0.8
	303	36.0 ∓ 3.0	10.6 ∓ 1.0
	313	58.0 ∓ 5.0	17.1 ∓ 1.5
2.06	298	7.5 ∓ 0.7	8.6 ∓ 0.8
	303	10.3 ∓ 1.0	11.8 ∓ 1.2
	309	16.3 ∓ 1.5	18.7 ∓ 1.8
	313	22.3 ∓ 2.0	25.5 ∓ 2.5
	323	42.6 ∓ 4.0	50.0 ∓ 5.0
2.64	303	2.1 ∓ 0.2	9.2 ∓ 0.9
2.90	303	1.4 ∓ 0.1	11.0 ∓ 1.0

Figure 3. Plot of k_{obsd} [H$^+$] (temperature 303 K).

and lists of structure factors and anisotropic thermal parameters are available as supplementary material. The structure of **1** consists of discrete [Ru(bpy)$_2$(CO)H]$^+$ and PF$_6^-$ units with acetone present in the lattice and not bound to the central metal ion. The ruthenium ions are coordinated in a distorted octahedron, with the bpy ligands in a cis geometry (see Figure 1). We assume that the units are held together by van der Waals forces, as no intermolecular hydrogen bonding is observed. One of the shortest intramolecular distances involving the hydride ion is between the hydride and the carbon atom of the carbonyl group (2.29 (4) Å). This distance is significantly shorter than the sum of the van der Waals distances for these atoms (2.9 Å). Judging from the bond angles, it appears that it is the carbonyl carbon that is distorted toward the hydride and not the reverse. This observation may be significant for the development of the mechanism for the formation of this compound during the catalytic cycle of the water-gas shift reaction. The close approach of the coordinated hydride ligand and the carbonyl carbon could mean that an interaction between these atoms exists; however, the H–Ru–C angle is rather large (82.2 (14)°) and therefore we cannot verify such an interaction. Ru–N distances vary from 2.176 (3) to 2.065 (4) Å, and the Ru–N distances trans to the carbonyl ligand and the hydride ligand are 2.123 (4) and 2.176 (3) Å, respectively. For the corresponding [Ru(bpy)$_2$(CO)Cl]$^+$ complex the Ru–N distance trans to the carbonyl group was found to be 2.17 (2) Å, while the Ru–N distance trans to the chloride ion was 2.06 (1) Å.[1a] The other two Ru–N distances in **1** are 2.065 (3) and 2.073 (4) Å while for the chloro carbonyl complex two values of 2.10 (1) Å were found. The variation of the Ru–N distances agrees with the trans influence expected for the ligands involved.[9] The Ru–H distance of 1.68 (4) Å is in the region expected for ruthenium hydride complexes and is normal for covalent metal–hydrogen bonds.[10] The Ru–C distance of 1.804 (6) Å is slightly shorter than the one reported for the chloro carbonyl complex (1.86 (3) Å). The shorter metal–carbon bond is most likely due to the increased σ-donation from the hydrido ligand to the metal. Consequently the C–O bond in the hydride complex of 1.152 (6) Å is longer than in the chloro complex (1.12 (3) Å). These changes are reflected in the infrared spectra of the compounds. The carbonyl stretching frequency of the chloro complex is found at 1965 cm^{-1} while for the microcrystalline ruthenium hydride a band at 1930 cm^{-1} has been reported.[1d] Infrared spectra from the samples that did yield single crystals showed two bands in the carbonyl region: one strong band at 1910 cm^{-1} and a band of medium intensity at 1890 cm^{-1}. These bands can possibly be assigned as the CO and Ru–H stretching vibrations, respectively. It is, however, not clear why these spectra are different from the ones obtained from microcrystalline samples, especially when X-ray data show no evidence for intermolecular
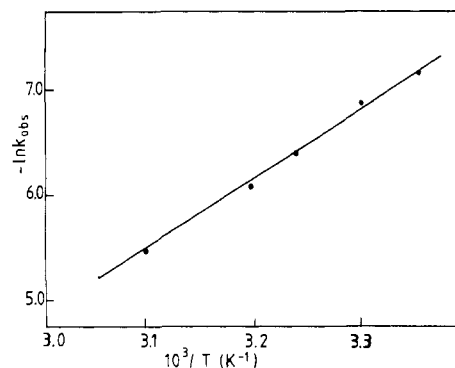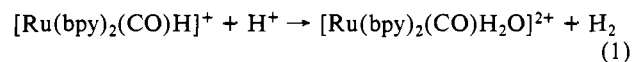

Figure 4. Plot of ln k_{obsd} vs. $1/T$ (pH 2.06).

interactions or for a disordered carbonyl group.

Kinetic Results. Earlier experiments have shown that **1** reacts as a hydride donor in acidic solution as in reaction 1.[1c,e] The

$$[\text{Ru(bpy)}_2(\text{CO})\text{H}]^+ + \text{H}^+ \rightarrow [\text{Ru(bpy)}_2(\text{CO})\text{H}_2\text{O}]^{2+} + \text{H}_2 \quad (1)$$

formation of hydrogen was confirmed by mass spectrometry, while the ruthenium compound formed was shown to be identical with an authentic sample[1d,11] of [Ru(bpy)$_2$(CO)H$_2$O]$^{2+}$ by UV/vis spectroscopy. Figure 2 shows a series of UV/vis spectra taken during the reaction of **1** at pH 2.06. Isosbestic points at 325, 298, and 262 nm indicate a clean reaction. Experiments at different pHs and temperatures were carried out, and the results have been given in Table VI. A plot of k_{obsd} vs. [H$^+$] has been given in Figure 3. Figure 4 shows the temperature dependence of the rate constant k_{obsd} at pH 2.06. The results obtained suggest a pseudo-first-order reaction, the rate for which can be written as

$$\text{rate} = -d(\text{RuH})/dt = k[\text{H}^+][\text{RuH}] = k_{obsd}[\text{RuH}] \quad (2)$$

From Figure 3 a value of 0.105 ∓ 0.01 dm^3 mol^{-1} s^{-1} was obtained for the second-order rate constant (at 303 K). The temperature

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(10) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

(11) O'Connell, C. M. Thesis, Trinity College, Dublin, Ireland, 1984.

Scheme I. Mechanism for the Water-Gas Shift Reaction Catalyzed by [Ru(bpy)$_2$(CO)Cl]$^+$ As Proposed by Tanaka et al.[6]
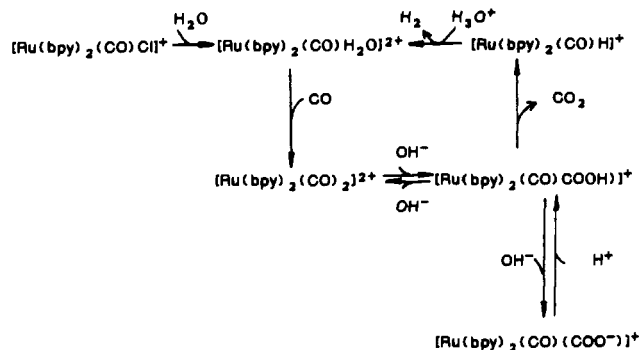
dependence of the second-order rate constant of the reaction suggests an activation energy of 53 ∓ 2 kJ/mol. The preexponential factor obtained from a plot of ln k against $1/T$ yields a value of -100 ∓ 8 J mol^{-1} deg^{-1} for ΔS of activation. These energy values are not unusual and agree well with those obtained for similar reactions.[12] The data indicate that **1** is a hydride donor. The hydride character of the metal–hydrogen bond can be explained by the presence of hard ligands such as 2,2′-bipyridyl.[13]

In a recent paper Tanaka et al.[6] reported that in basic solution the water-gas shift reaction is catalysed by [Ru(bpy)$_2$(CO)Cl]$^+$ at temperatures of about 150 °C. The reaction scheme (Scheme I) involves attack of hydroxy ions on coordinated CO producing CO$_2$ and attack of H$^+$ on [Ru(bpy)$_2$(CO)H]$^+$ to produce hydrogen. The results reported in this work support this mechanism. In view of the pH dependence of our results the formation of hydrogen is possibly the rate-determining step in strongly basic solutions. In the mechanism proposed for the water-gas shift

reaction, both OH$^-$ and H$^+$ ions are involved; one would therefore expect the efficiency of such a reaction to be pH-dependent. In a similar system Cole-Hamilton et al.[5] found such a pH dependency. In their photoassisted water-gas shift reaction catalyzed by the ruthenium carbonyl chloride complex, a maximum efficiency for hydrogen formation was observed at pH 9. These workers reported an activation energy of about 35 kJ mol^{-1} at pH 12.0 and at pH 8.9 while at pH 5.5 an activation energy of about 53 kJ mol^{-1} was obtained. This is in the same order of magnitude as the energy we determined for hydrogen elimination from the hydride complex. In their reaction mechanism complexes such as [Ru(bpy)$_2$ClH] and [Ru(bpy)$_2$ClH$_2$]$^+$ are proposed as intermediates. In view of the expected instability of hydride complexes which do not have strong π-acceptor ligands and the purple-red color expected for ruthenium bis(2,2′-bypyridyl) chloro hydrides,[14] the presence of appreciable amounts of such complexes seems unlikely. This is especially true in the case of the stoichiometric reaction as reported by Cole-Hamilton.[5] From our experiments it seems unlikely that [Ru(bpy)$_2$ClH$_2$]$^+$ is a stable complex which would only produce hydrogen on irradiation.

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(14) λ_{max} for Ru(bpy)$_2$Cl$_2$ is about 540 nm in DMF or dichloromethane.[15]
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