5.33 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.05 (dd, 1 H, J_{HH} = 17.5, 1.8 Hz, CHC*H*H), 4.96 (dd, 1 H, J_{HH} = 10.4, 1.8 Hz, CHCH*H*), 1.27 (s, 3 H, Me), 1.18 (s, 3 H, Me), 0.80 (d, 9 H, J_{HP} = 6.3 Hz, PMe_3). ^{13}C NMR (100.4 MHz, C_6D_6): δ 306.90 (J_{CP} = 26.6 Hz, J_{CH} = 111 Hz, C_α), 151.83 (J_{CP} = 4.5 Hz, *C*HCH_2), 106.55 (CH*C*H_2), 102.42 (Cp), 99.85 (Cp), 56.28 (quaternary), 31.41 (J_{CP} = 4.4 Hz, Me), 30.42 (J_{CP} = 6.0 Hz, Me), 20.44 (J_{CP} = 17.7 Hz, PMe_3). IR (C_6D_6): 3070 (w), 2940 (s), 2900 (s), 2850 (m), 1625 (w), 1420 (m), 1365 (w), 1298 (w), 1279 (m), 1020 (sh), 1010 (m), 942 (s), 933 (sh), 892 (m), 818 (w), 790 (vs), 780 (sh), 720 (w), 710 (s), 660 (w) cm^{-1}; ^{31}P NMR (36.27 MHz, C_6D_6: δ +11.91. Anal. Calcd for $C_{19}H_{29}TiP$: C, 67.86; H, 8.70. Found: C, 67.83; H, 8.18.

Preparation of PMe_2Ph Adduct 2b. The adduct **2b** was prepared by the same procedure described for **2a** using $PPhMe_2$ (60 μL, 0.42 mmol). Phosphine adduct **2b** was obtained as a tan powder (84 mg, 55%). ^1H NMR (400 MHz, C_6D_6): δ 13.23 (d, 1 H, J_{HP} = 6.8 Hz, H_α), 7.22–7.09 (m, 5 H, Ph), 6.22 (dd, 1 H, J_{HH} = 10.6, 17.6 Hz, C*H*CH_2), 5.46 (s, 5 H, Cp), 5.37 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.07 (d, 1 H, J_{HH} = 17.6, CHC*H*H), 4.96 (d, 1 H, J_{HH} = 10.6 Hz, CHCH*H*), 1.30 (s, 3 H, Me), 1.29 (d, 3 H, J_{HP} = 6.8 Hz, P*Me*MePh), 1.21 (s, 3 H, Me), 1.18 (d, 3 H, J_{HP} = 6.4 Hz, PMe*Me*Ph). ^{13}C NMR (100.4 MHz, C_6D_6): δ 309.38 (J_{CP} = 24.9 Hz, J_{CH} = 115 Hz, C_α), 151.80 (J_{CP} = 3.0 Hz, *C*HCH_2), 140.92 (J_{CP} = 13.2 Hz), 131.52 (J_{CP} = 10.3 Hz), 129.11, 128.34, 106.71 (CH*C*H_2), 102.96 (Cp), 100.17 (Cp), 56.67 (J_{CP} = 3.0 Hz, quaternary), 31.68 (J_{CP} = 4.4 Hz, Me), 30.40 (J_{CP} = 5.8 Hz, Me), 21.59 (J_{CP} = 22.1 Hz, P*Me*MePh), 20.01 (J_{CP} = 20.5 Hz, PMe*Me*Ph). ^{31}P NMR (36.27 MHz, C_6D_6): δ +25.10. IR (C_6D_6): 3015 (w), 2950 (s), 2900 (m), 2860 (w), 1625 (w), 1480 (w), 1465 (w), 1432 (s), 1365 (m), 1285 (w), 1275 (w) 1091 (w), 1065 (w), 1015 (s), 937 (m), 900 (s), 825 (w), 792 (vs), 740 (s), 722 (w), 692 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{31}TiP$: C, 72.35; H, 7.84. Found: C, 72.12; H, 7.59.

Reaction of 1 and PPh_2Me. To a 5-mm NMR tube containing **1** (10 mg, 0.04 mmol) in 0.5 mL of benzene-d_6 was added 20 μL of PPh_2Me (0.10 mmol). The tube was placed in the probe of the JEOL-GX400 NMR instrument, and the reaction was monitored by ^1H NMR spectroscopy. The reaction was observed to reach an equilibrium between **1** and its PPh_2Me adduct **2c**, with an approximate ratio of 1:1, within 1 h. ^1H NMR (400 MHz, C_6D_6) assignment based on exclusion of peaks attributable to **1**: δ 12.32 (d, 1 H, J_{HP} = 5.9 Hz, H_α), 7.22–7.02 (m, 10 H, Ph), 6.14 (dd, 1 H, J_{HH} = 17.6, 10.5 Hz, C*H*CH_2), 5.49 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.36 (d, 5 H, J_{HP} = 2.0 Hz, Cp), 5.12 (d, 1 H, J_{HH} = 17.6 Hz, CHC*H*H), 4.97 (d, 1 H, J_{HH} = 10.5 Hz, CHCH*H*), 1.65 (d, 3 H, J_{PH} = 6.0 Hz, PMe), 1.38 (s, 3 H, Me), 1.26 (s, 3H, Me). ^{13}C NMR (100.4 MHz, C_6D_6): δ 312.20 (J_{CP} = 23.5 Hz, J_{CH} = 110 Hz, C_α).

Equilibrium Measurements. To each of three 5-mm NMR tubes was added 400 μL of a 0.096 M solution of **1** in benzene-d_6 (10 mg of **1** to each). One, two, and four equivalents (7.2, 14.3, and 28.6 μL) of $PMePh_2$ were added to the tubes along with additional benzene-d_6 to bring the volume of the contents of each tube to 450 μL. The samples were stored at −20 °C until use. Each tube was placed in the probe of the JEOL-GX400. The reactions were monitored by ^1H NMR spectroscopy until no change was observed for 30 min. All samples required less than 1.5 h to reach equilibrium. The equilibrium ratio was measured by integration of the doublet at δ 4.90 (H_α of **1**) and the doublet at δ 4.97 (CHCH*H* of **2c**). The three derived equilibrium constants were averaged to obtain the reported constant.

Preparation of the $AlMe_2Cl$ Adduct 3. To a −40 °C solution of **1** (250 mg, 0.96 mmol) in 2.0 mL of toluene was added 400 μL of a 2.5 M $AlMe_2Cl$ solution (1.0 mmol of $AlMe_2Cl$). An immediate color change from red to purple was observed. After 30 min at −40 °C, the volatiles were removed in vacuo at −10 °C yielding a drak purple solid. The solid was redissolved in −10 °C pentane. A small amount of insoluble material was discarded. Slow cooling of the pentane solution to −50 °C afforded 95 mg (28%) of **3** as a purple powder. Solid **3** was stored at −40 °C. In solution, **3** is unstable at temperatures above 10 °C. ^1H NMR (90 MHz, C_6D_6, 10 °C): δ 9.78 (s, 1 H, H_α), 6.63 (dd, 1 H, J_{HH} = 16.6, 10.0, C*H*CH_2), 5.85 (s, 5 H, Cp), 5.61 (s, 5 H, Cp), 5.04 (d, 1 H, J_{HH} = 16.6, CHC*H*H), 5.01 (d, 1 H, J_{HH} = 10.0, CHCH*H*), 1.20 (s, 3 H, Me), 0.96 (s, 3 H, Me), −0.13 (s, 3 H, Al*Me*Me), −0.24 (s, 3 H, AlMe*Me*). ^{13}C NMR (22.5 MHz, C_6D_6, 10 °C): δ 225.83 (d, J_CH = 116 Hz, H_α), 150.51 (d, *C*HCH_2), 113.33 (d, Cp), 111.12 (d, Cp), 109.12 (t, CH*C*H_2), 59.13 (quaternary), 34.83 (q, Me), 30.99 (q, Me), −4.7 (br q, H_{CH} = 115 Hz, $AlMe_2$). Anal. Calcd for $C_{18}H_{26}TiAlCl$: C, 61.29; H, 7.43. Found: C, 60.96; H, 7.23. A more complete analysis was precluded by the thermal instability of **3**.

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Registry No. **1**, 99798-41-1; **2a**, 100228-64-6; **2b**, 100228-65-7; **2c**, 100228-66-8; **3**, 100228-67-9; $AlMe_2Cl$, 1184-58-3; 3,3–dimethylcyclopropene, 3907-06-0; Tebbe reagent, 67719-69-1; benzophenone, 119-61-9; 3,3-dimethyl-1,1-diphenyl-1,4-pentadiene, 67731-48-0; 1,1,2-trimethylcyclopropane, 4127-45-1.

Isolation of Intermediates in the Water Gas Shift Reactions Catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$

Hitoshi Ishida, Koji Tanaka, Masaru Morimoto, and Toshio Tanaka*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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The water gas shift (WGS) reaction catalyzed by bis(2,2′-bipyridine)carbonylruthenium(II) complexes under mild conditions (70–150 °C; 3–20 kg/cm^2 of CO) has been investigated. Turnover numbers for the H_2 formation of about 500 in 20 h have been obtained in an aqueous KOH solution containing $[Ru(bpy)_2(CO)Cl](PF_6)$ (bpy = 2,2′-bipyridine) as a catalyst precursor. The solvolysis of $[Ru(bpy)_2(CO)Cl]^+$ in an aqueous solution affords $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, which exists as an equilibrium mixture with $[Ru(bpy)_2(CO)(OH)]^+$ in a weak alkaline solution. Coordinated H_2O of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ is readily substituted by CO to produce $[Ru(bpy)_2(CO)_2]^{2+}$, which undergoes a nucleophilic attack of OH^- to afford $[Ru(bpy)_2(CO)C(O)OH]^+$. This hydroxycarbonyl complex not only exists as an equilibrium mixture with $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)(COO^-)]^+$ in alkaline media but also undergoes a decarboxylation reaction at elevated temperatures to give CO_2 and $[Ru(bpy)_2(CO)H]^+$, which further reacts with H_3O^+ to evolve H_2 and regenerate $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. All these species involved in the cycle of the WGS reaction catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ have been isolated or characterized by spectrophotometry.

Introduction

Since the homogeneous water gas shift (WGS) reaction (eq 1) catalyzed by transition-metal complexes was reported in 1977,[1] a large number of homogeneous WGS reactions under mild conditions have been studied by

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

employing mono- and polynuclear transition-metal carbonyl complexes,[2,3] of which ruthenium carbonyl clusters have attracted much attention as very active catalysts for the WGS reaction.[4] The WGS reaction catalyzed by transition-metal complexes in alkaline media at elevated temperature has been suggested to involve the following key steps: (i) a nucleophilic attack of OH^- or H_2O on the carbon atom of CO coordinated to transition metals, giving a hydroxycarbonyl complex (eq 2),[5] (ii) a thermal decarboxylation of the hydroxycarbonyl complex to afford CO_2 and a metal hydride (eq 3), and (iii) H_2 evolution by the

$$\text{M-CO} + OH^- \rightarrow \text{M-COOH} \qquad (2)$$

$$\text{M-COOH} \rightarrow \text{M-H} + CO_2 \qquad (3)$$

reaction of the metal hydride with protons or water. However, few hydroxycarbonyl, hydride, and aquo intermediates involved in each step have been isolated so far. This paper reports systematic isolation of all the possible intermediates in the WGS reaction catalyzed by $[Ru(bpy)_2(CO)Cl]^+$ (bpy = 2,2′-bipyridine) which is a catalyst precursor in aqueous alkaline solutions; part of this paper has appeared recently.[6]

Experimental Section

Materials. Bis(2,2′-bipyridine)dichlororuthenium(II), $Ru(bpy)_2Cl_2$,[7] tris(2,2′-bipyridine)ruthenium(II) dichloride, $[Ru(bpy)_3]Cl_2$,[8] and bis(2,2′-bipyridine)carbonylhydridoruthenium(II) hexafluorophosphate, $[Ru(bpy)_2(CO)H](PF_6)$[9] were prepared according to the literature. A C_2H_5OH/H_2O (1:1 v/v, 50 cm^3) solution contaiing $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (420 mg, 0.81 mmol) and $Na_2MoO_4{\cdot}2H_2O$ (200 mg, 0.82 mmol) was stirred in a sealed tube at 120 °C for 18 h. The reaction mixture was cooled to room temperature to give a black precipitate of $(bpy)_2\overline{Ru\text{-}O\text{-}Mo\text{-}O}(O)_2$ which was collected by filtration, washed with water, ethanol, and then diethyl ether, and dried in vacuo: 51% yield; mp 150 °C dec. Anal. Calcd for $C_{20}H_{16}N_4MoO_4Ru$: C, 41.90; H, 2.81; N, 9.77. Found: C, 41.42; H, 2.89; N, 9.83.

Preparation of $[Ru(bpy)_2(CO)Cl](PF_6)$. An ethylene glycol solution (100 cm^3) containing $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (137 mg, 0.26 mmol) and a catalytic amount of $Ru(bpy)_2O_2MoO_2$ (12 mg, 0.02 mmol) was refluxed for 6 h, during which time the color of the solution changed from purple to reddish brown. After being cooled to room temperature, the solution was evaporated to about a quarter volume in vacuo, and water (50 cm^3) was added. The resulting solution was filtered, and the filtrate was mixed with an aqueous (5 cm^3) solution of NH_4PF_6 (200 mg, 1.2 mmol) to afford an orange precipitate, which was collected by filtration, chromatographed on alkaline alumina using CH_3CN/C_6H_6 (1:1 v/v) as an eluent, and then recrystallized from CH_3CN/C_6H_6: 80% yield; mp 290 °C dec; $\nu(C{\equiv}O)$ 1960 cm^{-1}. Anal. Calcd for $C_{21}H_{16}ClF_6N_4OPRu$: C, 40.56; H, 2.59; N, 9.01. Found: C, 40.27; H, 2.64; N, 9.16.

Preparation of $[Ru(bpy)_2(CO)_2](PF_6)_2$. An aqueous (15 cm^3) suspension of $[Ru(bpy)_2(CO)Cl](PF_6)$ (354 mg, 0.57 mmol) under 10 kg/cm^2 of CO in a stainless-steel bomb was stirred magnetically at 150 °C for 20 h. After the bomb was cooled to room temperature, the CO pressure was released. The resulting colorless solution was filtered. To the filtrate was added NH_4PF_6 (810 mg, 5.0 mmol) dissolved in a small amount of water (5 cm^3) to yield a white precipitate, which was collected by filtration and crystallized from CH_3CN/C_6H_6 (1:1 v/v): 70% yield; mp 280 °C; $\nu(C{\equiv}O)$ 2040, 2085 cm^{-1}. Anal. Calcd for $C_{22}H_{16}F_{12}N_4O_2P_2Ru$: C, 34.80; H, 2.12; N, 7.38. Found: C, 34.98; H, 2.29; N, 7.65.

Preparation of $[Ru(bpy)_2(CO)(H_2O)][B(C_6H_5)_4]_2{\cdot}H_2O$. An aqueous acidic solution (400 cm^3) of $[Ru(bpy)_2(CO)H](PF_6)$ (50 mg, 0.085 mmol) at pH 4.0 (adjusted with 1.0 N HCl) was stirred for 1 h at room temperature and then concentrated to about a half volume under reduced pressure. To the resulting solution was added $NaB(C_6H_5)_4$ (120 mg, 0.35 mmol) dissolved in a small amount of water (5 cm^3) at pH 4.0 to afford a yellow precipitate, which was collected by filtration and recrystallized from $MeOH/H_2O$ (pH 4.0): 50% yield; mp 120 °C dec; the amount of H_2O solvated was determined by ^1H NMR in CD_3CN; $\nu(C{\equiv}O)$ 1990 cm^{-1}, $\nu(O{-}H)$ 3040 cm^{-1}. Anal. Calcd for $C_{69}H_{60}B_2N_4O_3Ru$: C, 73.05; H, 5.51; N, 4.94. Found: C, 72.76; H, 5.34; N, 5.30.

Preparation of $[Ru(bpy)_2(CO)(OH)](PF_6){\cdot}H_2O$. An aqueous acidic solution (100 cm^3) of $[Ru(bpy)_2(CO)H](PF_6)$ (51 mg, 0.087 mmol) at pH 4.0 (adjusted with 1.0 N HCl) was stirred for 1 h at room temperature, and 1.0 N aqueous NaOH was then added to adjust the pH of the solution to 9.5. The resulting solution was filtrated, and the filtrate was concentrated to about a quarter volume under reduced pressure. When the pH value of the filtrate was adjusted to 11, an orange precipitate formed which was collected by filtration and dried in vacuo: 30% yield; mp 200 °C dec; the amount of H_2O solvated was determined by ^1H NMR in CD_3CN; $\nu(C{\equiv}O)$ 1980 cm^{-1}, $\nu(O{-}H)$ 3050 cm^{-1}. Anal. Calcd for $C_{21}H_{19}F_6N_4O_3PRu$: C, 40.59; H, 3.08; N, 9.01. Found: C, 40.32; H, 2.84; N, 8.87.

Preparation of $[Ru(bpy)_2(CO)C(O)OH](PF_6){\cdot}{}^1/_2H_2O$. An aqueous solution (300 cm^3) of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (144 mg, 0.19 mmol) at pH 9.5 (adjusted with 0.2 N NaOH) was concentrated to ca. 20 cm^3 under reduced pressures. When the pH value was adjusted to 10, a yellow precipitate formed which was collected by filtration, washed with ether, and dried in vacuo: 20% yield, mp 155 °C dec; the amount of H_2O solvated was determined by ^1H NMR in CD_3CN; $\nu(O{-}H)$ 3070 cm^{-1}, $\nu(C{\equiv}O)$ 1960 cm^{-1}, $\nu(C{=}O)$ 1587 cm^{-1}, $\nu(C{-}O)$ 1140 cm^{-1}. Anal. Calcd for $C_{22}H_{18}F_6N_4O_{3.5}PRu$: C, 41.26; H, 2.83; N, 8.75. Found: C, 41.08; H, 2.82; N, 8.87.

Preparation of $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6){\cdot}{}^1/_2CH_2Cl_2$. An anhydrous CH_3OH (50 cm^3) solution containing $[Ru(bpy)_2(CO)_2](PF_6)_2$ (77 mg, 0.10 mmol) and CH_3ONa (0.29 mmol) was stirred for 1 h under N_2 atmosphere at room temperature. The resulting solution was evaporated to dryness under reduced pressures. The crude product so obtained was dissolved in CH_2Cl_2 (90 cm^3), and the solution was dried with Na_2SO_4. The resulting solution was filtered, and the filtrate was evaporated to ca. 5 cm^3, giving a yellow solid, 80% yield; mp 110 °C dec; the amount of CH_2Cl_2 solvated was determined by ^1H NMR in CD_3CN; $\nu(C{\equiv}O)$ 1960 cm^{-1}, $\nu(C{=}O)$ 1605 cm^{-1}, $\nu(C{-}O)$ 1045 cm^{-1}. Anal. Calcd for $C_{23.5}H_{20}ClF_6N_4O_3PRu$: C, 41.03; H, 2.93; N, 8.14. Found: C, 41.02; H, 3.28; N, 7.86.

General Procedure for the WGS Reaction Studies. The WGS reaction was carried out in a stainless-steel bomb (65 cm^3) containing a glass tube in which a ruthenium catalyst (0.05 mmol)

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Table I. The Water Gas Shift Reaction

entry	cat.[a]	temp/°C	CO/kg/cm^2	KOH[b]/mmol	gaseous product[c] H$_2$	gaseous product[c] CO$_2$
1	$[Ru(bpy)_2(CO)Cl]^+$	100	3	3.2	3.8	
2	$[Ru(bpy)_2(CO)Cl]^+$	100	10	3.2	165	95
3	$[Ru(bpy)_2(CO)Cl]^+$	150	5	3.2	112	46
4	$[Ru(bpy)_2(CO)Cl]^+$	150	10	3.2	197	75
5	$[Ru(bpy)_2(CO)Cl]^+$	150	20	3.2	502	203
6	$[Ru(bpy)_2(CO)Cl]^+$	150	10	0	1.1	0.7
7	$[Ru(bpy)_2(CO)_2]^{2+}$	70	10	3.2	4.1	1.1
8	$[Ru(bpy)_2(CO)_2]^{2+}$	100	3	3.2	10.8	0.4
9	$[Ru(bpy)_2(CO)_2]^{2+}$	100	10	3.2	147	82.7
10	$[Ru(bpy)_2(CO)_2]^{2+}$	150	10	3.2	198	75
11	$[Ru(bpy)_3]^{2+}$[d]	150	20	3.2	16	15

[a] PF$_6$ salt, 0.05 mmol in H$_2$O (15 cm^3). [b] Quantity of KOH initially added. [c] Mol/(mol of catalyst·20 h). [d] Cl salt.

and an aqueous KOH solution (0.21 mol·dm^{-3}, 15 cm^3) were placed. After being degassed by three 10 kg/cm^2 pressurization/depressurization cycles with CO, the bomb was pressurized with 3–20 kg/cm^2 of CO and kept at the reaction temperature for 20 h with magnetic stirring. After the bomb was cooled to room temperature, gaseous products in the vapor phase were sampled with a gas syringe through a septum cap attached to the exit of the tap and analyzed with a Shimazu GC-7A gas chromatography equipped with TCD using a 60/80 mesh Unibeads 1S under N$_2$ carrier gas. A Shimazu Chromatopack C-E1B digital integrator was used to integrate the output from the gas chromatograph.

Physical Measurements. Electronic and infrared spectra were measured with Union SM-401 and Hitachi 215 spectrophotometers, respectively. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer. The pH value of the reaction mixture was measured with a Toa Denpa Model GS-135 pH electrode. Equilibrium constants were determined by spectrophotometry or potentiometric titration at 25 °C. The kinetic measurement for the nucleophilic attack of OH$^-$ to $[Ru(bpy)_2(CO)_2](PF_6)_2$ was carried out in H$_2$O under the pseudo-first-order conditions with at least 5-fold excess amounts of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (2.63×10^{-4} mol·dm^{-3}) in an aqueous KOH solution. The rate of reactions was followed by monitoring the absorbance at 440 nm due to $[Ru(bpy)_2(CO)C(O)OH]^+$ and $[Ru(bpy)_2(CO)(COO^-)]^+$ in the reaction mixture, using a Union RA-413 stopped-flow spectrophotometer equipped with a 0.2-cm length quartz cell in a cell holder thermostated within 25.0 ± 0.2 °C. Pseudo-first-order rate constants were obtained from the slope of plots of log $|A_t - A_\infty|$ against time, which were found to be linear for at least 3 half-lives, where A_t and A_∞ are absorbances at a time t and at the end of the reaction, respectively.

Results and Discussion

Catalytic Reactions and the Isolation of $[Ru(bpy)_2(CO)_2](PF_6)_2$. It has been reported that $[Ru(bpy)_2(CO)Cl]Cl$ and $[Ru(phen)_2(CO)Cl]Cl$ (phen = 1,10-phenanthroline) catalyze the photochemical WGS reaction in aqueous solutions under mild conditions (1–3 kg/cm^2 of CO, 100–160 °C).[10] We have, however, found that $[Ru(bpy)_2(CO)Cl](PF_6)$ is still active for the WGS reaction without irradiation in aqueous alkaline solutions. Although the turnover number for the H$_2$ formation in the present study using $[Ru(bpy)_2(CO)Cl](PF_6)$ in the presence of KOH (3.2 mmol) was only 3.8 for 20 h under a pressure of 3 kg/cm^2 of CO at 100 °C (entry 1, Table I), it increases with increases in the reaction temperature and the CO pressure (compare entry 1 with 2, entries 3 and 4 with 5, and entry 2 with 4, Table I). The maximum turnover number in the present study was 502 under 20 kg/cm^2 of CO at 150 °C (entry 5, Table I), while the theoretical one expected from the volume of the bomb used in this study is 800 under the initial pressure of 20 kg/cm^2 of CO. No further attempt to increase the turnover number has been made, since the purpose of this work is to explore the active species in the WGS reaction.[11]

The discrepancy in the amounts of H$_2$ and CO$_2$ evolved in the gas phase (Table I) may result from the higher solubility of CO$_2$ than H$_2$ in addition to the formation of the carbonate ion in alkaline solutions as suggested previously.[12] In fact, the amount of CO$_2$ dissolved in the final solutions obtained after releasing the pressures in the bomb was determined as 20–30 wt % of that in the gas phase by gas chromatography. The $[Ru(bpy)_2(CO)Cl](PF_6)$ complex was gradually decomposed in the course of the WGS reaction for 20 h, finally giving a solution of $[Ru(bpy)_3]^{2+}$, as confirmed from the electronic absorption spectrum, with a pale green precipitate. The catalytic activity of $[Ru(bpy)_3]Cl_2$ in the WGS reaction is, however, much lower than that of $[Ru(bpy)_2(CO)Cl](PF_6)$ (compare entry 5 with 11, Table I), suggesting that $[Ru(bpy)_3]^{2+}$ is not the actual catalyst in the WGS reaction.

In the absence of KOH, the WGS reaction catalyzed by $[Ru(bpy)_2(CO)Cl](PF_6)$ is slow even under 10 kg/cm^2 of CO at 150 °C for 20 h (entry 6, Table I); an almost colorless solution of the Ru(II) salt was obtained without any decomposition after the reaction for 20 h. The addition of NH$_4$PF$_6$ to the resulting colorless solution afforded a known dicarbonyl complex, $[Ru(bpy)_2(CO)_2](PF_6)_2$,[13] in a 70% yield. This complex isolated also catalyzes the WGS reaction under similar conditions (entries 7–10, Table I); the turnover numbers at 100 and 150 °C are essentially the same as those in the case with $[Ru(bpy)_2(CO)Cl](PF_6)$ (compare entries 9 and 10 with 2 and 4, respectively, Table I), indicating that $[Ru(bpy)_2(CO)Cl]^+$ may be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ under CO pressure in an alkaline solution.

Solvolysis of $[Ru(bpy)_2(CO)Cl]^+$ To Give $[Ru(bpy)_2(CO)(H_2O)]^{2+}$. It has been suggested that $[Ru(bpy)_2(CO)Cl]^+$ undergoes thermal and photochemical solvolyses in H$_2$O to give $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ (eq 4) and $[Ru(bpy)_2(H_2O)Cl]^+$ (eq 5), respectively.[14] However, there

$$[Ru(bpy)_2(CO)Cl]^+ + H_2O \xrightarrow{\Delta} [Ru(bpy)_2(CO)(H_2O)]^{2+} + Cl^- \quad (4)$$

$$[Ru(bpy)_2(CO)Cl]^+ + H_2O \xrightarrow{h\nu} [Ru(bpy)_2(H_2O)Cl]^+ + CO \quad (5)$$

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[10] (a) Choudhury, D.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1885. (b) Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1213.

[11] Gas sampling in the course of WGS reactions affected the turnover numbers significantly due to small volume of the bomb. Therefore, kinetic studies for the WGS reaction were not performed.

[12] King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028.

[13] Choudhury, D.; Jones, R. F.; Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1143.

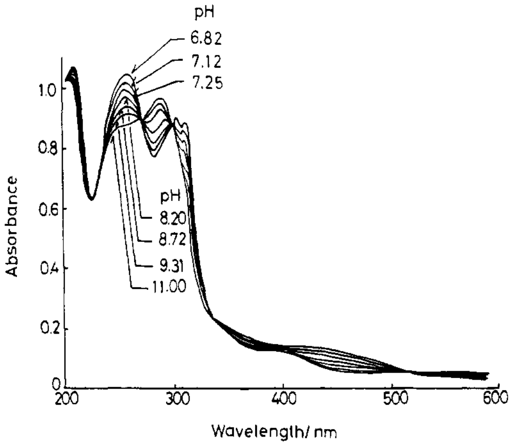

Figure 1. Electronic absorption spectra of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ (1.0×10^{-4} mol dm^{-3}) in H_2O at various pHs (25 °C).

is no difference between the electronic absorption spectra of aqueous solutions of $[Ru(bpy)_2(CO)Cl](PF_6)$ after irradiation with a 500-W Xe lamp ($\lambda > 360$ nm) at room temperature for 10 h and after refluxing for 1 h. In addition, the spectra coincided with that of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ formed in the reaction of $[Ru(bpy)_2(CO)H](PF_6)$ with H_3O^+ in water (pH 4.0) for 1 h at room temperature (eq 6).[9] In fact, the addition of $NaBPh_4$ to

$$[Ru(bpy)_2(CO)H]^+ + H_3O^+ \rightarrow [Ru(bpy)_2(CO)(H_2O)]^{2+} + H_2 \quad (6)$$

the solution after the hydrolysis of $[Ru(bpy)_2(CO)Cl]^+$ afforded $[Ru(bpy)_2(CO)(H_2O)](BPh_4)_2$ as a yellow precipitate. Thus, $[Ru(bpy)_2(CO)Cl]^+$ is subject to a thermal solvolysis in water to give $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, which may undergo the substitution of CO under CO pressure, yielding $[Ru(bpy)_2(CO)_2]^{2+}$.

Interconversion between $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ and $[Ru(bpy)_2(CO)(OH)]^+$ in Weak Alkaline Solutions. The addition of an aqueous KOH solution to a weak acidic solution of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ resulted in the disappearance of the electronic absorption bands of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ (λ_{max} 259, 304, 314, and 390 nm) and in the appearance of new bands at 292, 350, and 444 nm with isosbestic points at 270, 304, and 340 nm, as shown in Figure 1. At pHs higher than 11, a limiting spectrum was obtained. In addition, the pH dependence of the spectra is reversible. Thus, an equilibrium may exist between $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ and $[Ru(bpy)_2(CO)(OH)]^+$ (eq 7). The equilibrium constant (K_7) calculated from the

$$[Ru(bpy)_2(CO)(H_2O)]^{2+} + OH^- \xrightleftharpoons{K_7} [Ru(bpy)_2(CO)(OH)]^+ + H_2O \quad (7)$$

change of the absorbance at 260 nm was 5.06×10^5 $mol^{-1}\cdot dm^3$ at 25 °C. The rate of eq 7, however, is too fast to be determined by a stopped-flow method probably because of a diffusion controlled reaction. The existence of the equilibrium (eq 7) is compatible with the fact that $[Ru(bpy)_2(CO)(OH)](PF_6)$ has been isolated on the addition of excess NH_4PF_6 to a concentrated aqueous alkaline solution of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$.

Nucleophilic Attack of OH^- to Coordinated CO of $[Ru(bpy)_2(CO)_2]^{2+}$. The absorption spectrum of an aqueous solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ also changed reversibly depending on the pH value. The electronic spectrum of $[Ru(bpy)_2(CO)_2]^{2+}$ in an acidic solution shows two absorption maxima at 253 and 307 nm, which gradually disappear upon the addition of an aqueous KOH solution; instead four new bands at 248, 274, 344, and 430 nm appear with three isosbestic points at 260, 302, and 329 nm, as shown in Figure 2a. It should, however, be noted that in a weak alkaline medium there appears a weak shoulder at 400 nm, which is concealed by an absorption at 430 nm appearing at a pH value higher than 9.0 (Figure 2b). The absorption band at 430 nm attained a maximum intensity around pH 11.0 and was almost unchanged at the higher pH values. Moreover, $[Ru(bpy)_2(CO)_2](PF_6)_2$ (5.15×10^{-3} $mol\cdot dm^{-3}$) in H_2O behaves as a dibasic acid upon titration with an aqueous KOH solution (0.2 $mol\cdot dm^{-3}$), as shown in Figure 3. Thus, there may exist two successive equilibria in an aqueous alkaline solution of $[Ru(bpy)_2(CO)_2]^{2+}$.

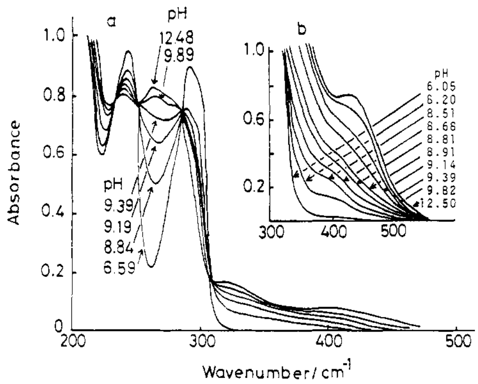

Figure 2. Electronic absorption spectra of $[Ru(bpy)_2(CO)_2](PF_6)_2$ ((a) 2.84×10^{-5} mol dm^{-3} and (b) 2.84×10^{-4} mol dm^{-3}) in H_2O at various pHs (25 °C).

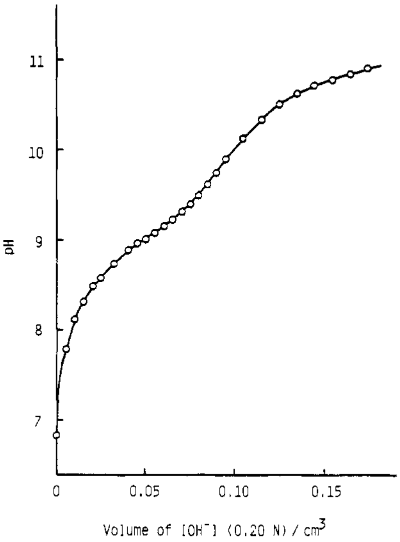

Figure 3. Titration of $[Ru(bpy)_2(CO)_2](PF_6)_2$ (1.03×10^{-5} mol) in H_2O (20 cm^3) by an aqueous KOH solution (0.2 mol dm^{-3}) at 25 °C.

When an aqueous solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with pH 9.5 ± 0.5 was concentrated under reduced pressures, the ruthenium hydroxycarbonyl complex $[Ru(bpy)_2(CO)C(O)OH](PF_6)$ was obtained as a yellow precipitate, suggesting that the nucleophilic attack of OH^- on CO of $[Ru(bpy)_2(CO)_2](PF_6)_2$ takes place in weak alkaline media. Thus, $[Ru(bpy)_2(CO)_2]^{2+}$ may exist as an equilibrium mixture with $[Ru(bpy)_2(CO)C(O)OH]^+$ in weak alkaline solutions (eq 8).

$$[Ru(bpy)_2(CO)_2]^{2+} + OH^- \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [Ru(bpy)_2(CO)C(O)OH]^+ \quad (8)$$

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(14) 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.

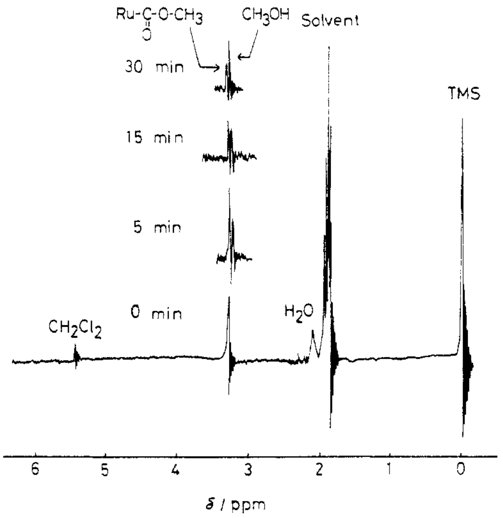

Figure 4. Time dependence of the ^1H NMR spectrum of $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6)$ after dissolved in CD_3CN containing a small amount of H_2O at 25 °C. A CH_2Cl_2 signal arose from a solvated molecule.

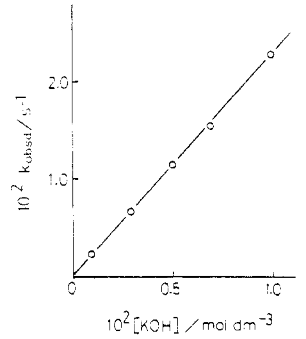

Figure 5. A plot of k_{obsd} vs. [KOH] for the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with KOH in H_2O at 25 °C.

The formation of the monoohydroxycarbonyl complex from $[Ru(bpy)_2(CO)_2]^{2+}$ in alkaline solutions (eq 8) may be consistent with the fact that the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with $NaOCH_3$ in dry CH_3OH afforded a monomethoxycarbonyl derivative, $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6)$, whose ^1H NMR spectra shown in Figure 4 reveal that $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6)$ readily undergoes a hydrolysis reaction in the presence of a small amount of water to give CH_3OH and $[Ru(bpy)_2(CO)_2]^{2+}$. Thus, $[Ru(bpy)_2(CO)C(O)OCH_3]^+$ and $[Ru(bpy)_2(CO)_2]^{2+}$ may exist as an equilibrium mixture in solution, as expressed by eq 9. A similar equilibrium is known for $[Ru_3(CO)_{11}C(O)OCH_3]^-$, which partly dissociates into $Ru_3(CO)_{12}$ and CH_3O^- in methanol.[15]

$$[Ru(bpy)_2(CO)_2]^{2+} + CH_3O^- \rightleftharpoons [Ru(bpy)_2(CO)C(O)OCH_3]^+ \quad (9)$$

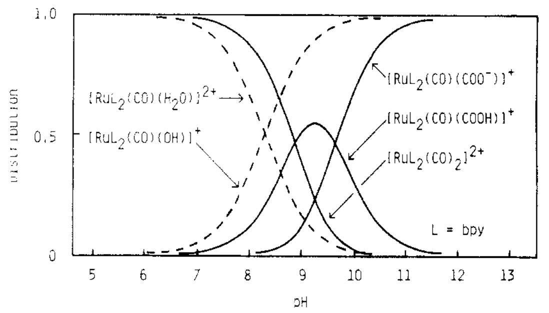

Figure 6. Distribution of the ruthenium species in H_2O at various pHs at 25 °C.

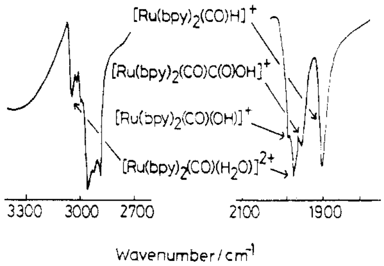

Figure 7. Infrared absorption spectrum of the thermolysis products of $[Ru(bpy)_2(CO)_2](PF_6)_2$ in H_2O (pH 8.09) at 100 °C.

The hydroxycarbonyl complex formed in eq 8 is known to undergo deprotonation reactions in strong alkaline solutions.[16] Another equilibrium existing in alkaline solutions may, therefore, be expressed by eq 10. The existence

$$[Ru(bpy)_2(CO)C(O)OH]^+ + OH^- \overset{K_{10}}{\rightleftharpoons} [Ru(bpy)_2(CO)(COO^-)]^+ + H_2O \quad (10)$$

of the equilibria shown by eq 8 and 10 may be consistent with the fact that the reaction of $[PtH(CO)(P(i\text{-}Pr)_3)_2]^+$ with an excess KOH in a mixture of THF and H_2O gives $PtH(COOK)(P(i\text{-}Pr)_3)_2$.[16] The equilibrium constants of eq 8 ($K_8 = k_8/k_{-8}$) and 10(K_{10}) were determined as 1.32×10^5 and 2.27×10^4 $mol^{-1}\cdot dm^3$, respectively, by the potentiometric method.[17] The rate of the reaction of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with KOH at 25 °C, k_{obsd}, is plotted against the concentration of KOH, as shown in Figure 5, which indicates a linear relation between those with a small nonzero intercept. The forward rate constant (k_8) of eq 8 determined from the slope of the plot is 2.3×10^4 $s^{-1}\cdot mol^{-1}\cdot dm^3$. The backward rate constant (k_{-8}) was calculated as 0.17 s^{-1} from K_8 and k_8, since the intercept of the plot (Figure 5) is too small to determine this value accurately. The reaction rate of eq 10 has not been determined by the stopped-flow technique owing to a diffusion-controlled reaction.

Distribution of the Ruthenium Species in Water. In the WGS reaction under aqueous alkaline conditions, CO readily reacts with OH^- quantitatively to form a formate ion, which may function as a buffer to some extent, adjusting the pH of the initial solution around 8.5.[12] However, the pH value of the solution is lowered gradually to about 7.5 due to the formation of carbonate ion arising from CO_2 evolved in the course of the WGS reaction.[12] Thus, the reaction in alkaline media actually proceeds at pH 7.5–8.5. The distribution of several Ru(II) species at various pHs, calculated from the equilibrium constants K_7, K_8, and K_{10}, are shown in Figure 6, which indicates that the Ru(II) species existing in the pH range of the present reaction (pH 7.5–8.5) are $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)_2(CO)C(O)OH]^+$, $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, and $[Ru(bpy)_2(CO)(OH)]^+$. Although a hydroxyplatinum complex, $Pt(CH_3)(OH)L$ [L = bis(tertiary phosphine)], has been reported to undergo an insertion reaction of CO to afford the hydroxycarbonyl derivatives $Pt(CH_3)(C(O)OH)L$,[18] a substitution reaction of CH_3CN, but not CO, for the hydroxy group of $[Ru(bpy)_2(CO)(OH)](PF_6)$ occurred when the hydroxyruthenium(II) complex was heated in CH_3CN under 10 kg/cm^2 of CO at 100 °C.

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(15) Gross, D. C.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 1702.

(16) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(17) Speakman, J. C. *J. Chem. Soc.* **1940**, 855.

(18) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88.

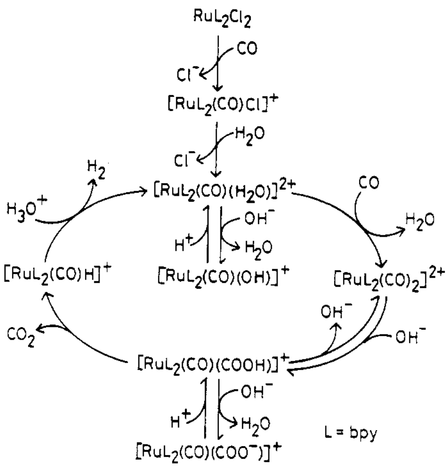
The Decarboxylation from $[Ru(bpy)_2(CO)C(O)OH]^+$. When an aqueous solution of $[Ru(bpy)_2(CO)_2](PF_6)_2$ at pH 8.09 ($KOH-H_3BO_3$ buffer) was kept at 100 °C for 2 h under 10 kg/cm^2 of N_2 in a bomb, CO_2 and H_2 were evolved. To the resulting solution was added an aqueous solution of $NaBPh_4$ to precipitate all the cationic ruthenium species[19] as the BPh_4^- salts. After collection by filtration, washing with water, and drying in vacuo, the precipitate in Nujol mulls exhibits four IR bands at 1910 (s), 1960 (m), 1980 (s), and 1990 (sh) cm^{-1} due to $\nu(C{\equiv}O)$, as shown in Figure 7. The former two bands are assigned to $[Ru(bpy)_2(CO)H](BPh_4)$ and $[Ru(bpy)_2(CO)C(O)OH](BPh_4)$, respectively, by comparing the frequencies with those of the authentic samples. Of the latter two, the intense band is associated with $[Ru(bpy)_2(CO)(H_2O)](BPh_4)_2$ and the shoulder is assignable to $[Ru(bpy)_2(CO)(OH)](BPh_4)$, based on the infrared spectra of the authentic samples. On the other hand, appreciable thermolysis of $[Ru(bpy)_2(CO)(COO^-)]^+$ did not take place when an aqueous solution (pH 11.0, $KOH-H_3PO_4$ buffer) of $[Ru(bpy)_2(CO)_2](PF_6)_2$ was heated at 100 °C for 2 h under 10 kg/cm^2 of N_2.[20] These results indicate that $[Ru(bpy)_2(CO)C(O)OH]^+$ existing as an equilibrium mixture with $[Ru(bpy)_2(CO)_2]^{2+}$ in a weak aqueous alkaline solution undergoes a decarboxylation to give $[Ru(bpy)_2(CO)H]^+$ (eq 11), which further reacts with H_3O^+ to produce H_2 and

$$[Ru(bpy)_2(CO)C(O)OH]^+ \rightarrow [Ru(bpy)_2(CO)H]^+ + CO_2 \qquad (11)$$

$[Ru(bpy)_2(CO)(H_2O)]^{2+}$ (eq 6), as described in the previous section. In fact, the hydrolysis of $[Ru(bpy)_2(CO)H](PF_6)$ in water at pH 8.05 ($KOH-H_3BO_3$ buffer) under 10 kg/cm^2 of N_2 at 100 °C has evolved H_2. The reaction of $[Ru(bpy)_2(CO)H]^+$ with H_2O in place of H_3O^+ may also produce H_2 together with $[Ru(bpy)_2(CO)(OH)]^+$, though the contribution of this reaction to the H_2 formation has not been evaluated because of a rapid equilibrium between $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ and $[Ru(bpy)_2(CO)(OH)]^+$ in weak alkaline solutions. However, $[Ru(bpy)_2(CO)H]^+$ may be one of the actual catalysts in the reaction, since using $[Ru(bpy)_2(CO)H](PF_6)$ in the presence of KOH under 10 kg/cm^2 of CO at 100 °C for 20 h gave the turnover number 179, which is essentially the same value as that with $[Ru(bpy)_2(CO)Cl](PF_6)$ as a catalyst under the same conditions (entry 2 in Table I).

The WGS Reaction Using $Ru(bpy)_2Cl_2$ as a Catalyst Precursor. It has been reported that $Ru(bpy)_2Cl_2$ in CH_2Cl_2 under CO pressures at 80 °C is converted to $[Ru(bpy)_2(CO)_2]^{2+}$.[13] The same reaction occurred also when $Ru(bpy)_2Cl_2$ (0.05 mmol) was allowed to stand under 10 kg/cm^2 of CO at 100 °C in water (15 cm^3) for 20 h.[21] As expected from this, a large turnover number (243) was obtained in the reaction using $Ru(bpy)_2Cl_2$ (0.05 mmol) as a catalyst precursor in the presence of KOH (3.2 mmol) under 10 kg/cm^2 of CO at 100 °C for 20 h. It should be noted that the turnover number is considerably larger than that obtained in the reaction using the PF_6^- salt of $[Ru(bpy)_2(CO)Cl]^+$ or $[Ru(bpy)_2(CO)_2]^{2+}$ (see entry 2 or 9, Table I). On the other hand, the addition of NH_4PF_6 (0.10 mmol) to an aqueous solution containing $Ru(bpy)_2Cl_2$ (0.05 mmol) and KOH (3.2 mmol) under 10 kg/cm^2 of CO at 100 °C has reduced the turnover number of the reaction to 149. This result may be interpreted by a weak poisoning effect of PF_6^- on the WGS reaction.

Scheme I



Catalytic Cycle of the WGS Reaction. The WGS reaction catalyzed by some metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W), in alkaline media has been reported to proceed preferentially by decomposition of the formate ion (eq 12) which is produced at the beginning of the reac-

$$HCOO^- + H_2O \xrightarrow{M(CO)_6} H_2 + CO_2 + OH^- \qquad (12)$$

tion.[22-24] For example, $HCOO^-$ reacts with $M(CO)_5$ resulting from the dissociation of a CO ligand of $M(CO)_6$ to afford $M(CO)_5OC(O)H^-$, which undergoes a decarboxylation to generate $M(CO)_5H^-$, as proposed by King et al.[23,25,26] A similar thermal decarboxylation has been reported for $[Ru(bpy)_2(CO)OC(O)H]^+$ in 2-methoxyethanol, giving $[Ru(bpy)_2(CO)H]^+$.[27,28] Therefore, we have examined the H_2 evolution arising from the decomposition of $HCOO^-$ in the presence of the Ru(II) complexes. The thermal decomposition of HCOOH (13 mmol) in the presence of $[Ru(bpy)_2(CO)X](PF_6)$ (X = H, Cl) (0.05 mmol) in H_2O at pH 8.0–9.0 (KOH–HCOOH buffer) evolved 0.5–1.0 mmol of H_2 under 10 kg/cm^2 of N_2 at 100 °C for 20 h. The amount of H_2 evolved, however, was much smaller than that in the WGS reaction at 100 °C (see entries 2 and 9 in Table I), despite the presence of a large amount of $HCOO^-$ in the solution. Thus, the decomposition of HCOOH may not be the main pathway for the H_2 evolution in the present WGS reaction.

A plausible catalytic cycle of the reaction is depicted in Scheme I; $Ru(bpy)_2Cl_2$ in an aqueous KOH solution under CO pressures at elevated temperatures may be converted to $[Ru(bpy)_2(CO)_2]^{2+}$ probably through $[Ru(bpy)_2(CO)Cl]^+$ and $[Ru(bpy)_2(CO)(H_2O)]^{2+}$ successively, followed by the substitution reaction by CO. The nucleophilic attack of OH^- to one of the coordinated CO of $[Ru(bpy)_2(CO)_2]^{2+}$ at pH 8.0–9.0 affords $[Ru(bpy)_2(CO)C(O)OH]^+$, which undergoes the decarboxylation to give $[Ru(bpy)_2(CO)H]^+$.

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[19] Has not been precipitated by adding a large amount of $NaPF_6$ dissolved in H_2O.

[20] The final solution was treated with HCl to regenerate $[Ru(bpy)_2(CO)_2]^{2+}$, which was confirmed by the electronic absorption spectrum.

[21] A crude product obtained by evaporation of solvent water was $[Ru(bpy)_2(CO)_2]^{2+}$ contaminated with a small amount of $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, as confirmed by the infrared spectrum.

[22] King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* 1981, *103*, 2699.

[23] King, A. D., Jr.; King, R. B.; Sailers, E. L., III *J. Am. Chem. Soc.* 1981, *103*, 1867.

[24] Weiller, B. H.; Liu, J.-P.; Grant, E. R. *J. Am. Chem. Soc.* 1985, *107*, 1595.

[25] Slegeir, W. A. R.; Sapienza, R. S.; Rayford, R.; Lam, L. *Organometallics* 1982, *1*, 1728.

[26] Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* 1981, *103*, 1297.

[27] Caspar, J. V.; Sullivan, B. P; Meyer, T. J. *Organometallics* 1983, *2*, 551.

[28] Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* 1984, *3*, 1241.

The hydride complex thus formed reacts with H_3O^+ to evolve H_2 with regenerating $[Ru(bpy)_2(CO)(H_2O)]^{2+}$, while the reaction of $[Ru(bpy)_2(CO)H]^+$ with H_2O may participate into the production of H_2 to some extent. These reaction-pathways are strongly supported by the isolation or characterization of all the intermediates.

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Registry No. $[Ru(bpy)_2(CO)Cl](PF_6)$, 86389-99-3; $[Ru(bpy)_2(CO)_2](PF_6)_2$, 75550-97-9; $[Ru(bpy)_2(CO)(H_2O)][B(C_6H_5)_4]_2$, 100190-77-0; $[Ru(bpy)_2(CO)(OH)](PF_6)$, 100190-79-2; $[Ru(bpy)_2(CO)C(O)OH](PF_6)$, 86536-99-4; $[Ru(bpy)_2(CO)C(O)OCH_3](PF_6)$, 100190-81-6; $Ru(bpy)_2Cl_2$, 15746-57-3; $Ru(bpy)_2O_2MoO_2$, 100190-82-7; $[Ru(bpy)_2(CO)H](PF_6)$, 82414-89-9; Na_2MoO_4, 7631-95-0.

Electrophilic Attack at Pentamethylcyclopentadienyl-Substituted Germylenes

Peter Jutzi* and Bernd Hampel

Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld, West Germany

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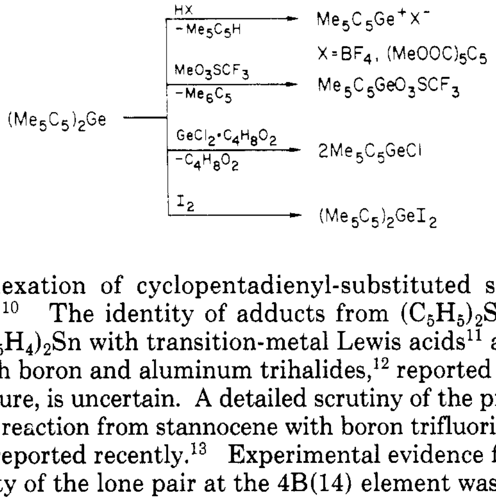
The pentamethylcyclopentadienyl-substituted germylenes $Me_5C_5GeCH(SiMe_3)_2$ (1) and Me_5C_5GeCl (2) exhibit nucleophilic reactivity at the π-system of the Me_5C_5 ligand, at the chlorine atom, and at the Ge–C σ-bond of the Ge–$CH(SiMe_3)_2$ group. Furthermore, oxidative addition reactions with alkylating and acylating agents may be rationalized in terms of electrophilic attack at the germanium center and thus suggest nucleophilic activity also of the lone pair of electrons.

Introduction

The analogous carbene species of germanium and tin possess a nonbonding pair of electrons as well as an empty p_z orbital. In the cyclopentadienyl-substituted species the π-bonded ligand partly saturates the electron deficiency at the 4B (14^{24}) element. Nucleophilic attack, however, still can take place at the metal center.[1] For an electrophilic attack the molecule provides as objectives the π-system of the cyclopentadienyl ligand, a center of electron density at the second ligand, or its σ-bond to the 4B (14) element (with the $R_5C_5El^+$ cation[2-4] acting as a leaving group) and the lone pair of electrons of the 4B (14) element.

Electrophilic attack at the π-system of the cyclopentadienyl ligand has been demonstrated upon protonation[3,5] and alkylation[6] of bis(pentamethylcyclopentadienyl)germanium, as well as in its reaction with germanium dichloride–dioxane,[7] which acts as a Lewis acid. The reactions of bis(pentamethylcyclopentadienyl)germanium with electrophiles are shown in Scheme I.

Scheme I



The existence of a nucleophilic center at the 4B(14) element to date has not clearly been demonstrated. Although analogous carbene complexes of the type $R_2Ge\rightarrow M(CO)_5$ ($R = (Me_3Si)_2CH, (Me_3Si)_2N$; M = Cr, W) are available by irradiation of hexacarbonylchromium and -tungsten[8,9] in the presence of the free germylene, the complexation of cyclopentadienyl-substituted species failed.[10] The identity of adducts from $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ with transition-metal Lewis acids[11] as well as with boron and aluminum trihalides,[12] reported in the literature, is uncertain. A detailed scrutiny of the product of the reaction from stannocene with boron trifluoride has been reported recently.[13] Experimental evidence for the activity of the lone pair at the 4B(14) element was given first by the synthesis of the complexes $Me_5C_5(Cl)Ge\rightarrow W(CO)_5$[10] and $Me_5C_5((Me_3Si)_2CH)Ge\rightarrow W(CO)_5$[14] whose structures have been confirmed by X-ray crystallography. Unfortunately, these adducts are only accessible by a synthetic detour, based on an already established 4B(14)

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