

# Aqueous Transformation of a Metal Diformate to a Metal Dihydride Carbonyl Complex Accompanied by H<sub>2</sub> Evolution from the Formate Ligands

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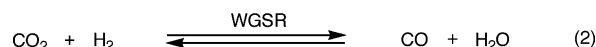
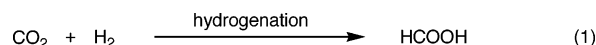
Received May 25, 2005

The rhodium diformate complex [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**, tacn = 1,4,7-triazacyclononane, OTf<sup>-</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) reacts with HCOONa at pH 6–7 at 80 °C in water to form a rhodium dihydride CO complex, [Rh<sup>III</sup>(tacn)(H)<sub>2</sub>(CO)](OTf) (**5**), with H<sub>2</sub> evolution from the formate ligands of **2**. This is the first example of H<sub>2</sub> evolution from hydrogen atoms of formate ligands of a metal diformate complex. Complex **2** was synthesized from the reaction of a rhodium aqua complex, [Rh<sup>III</sup>(tacn)(H<sub>2</sub>O)<sub>3</sub>](OTf)<sub>3</sub> (**1**), with HCOONa in water. Recrystallization of **2** with HCOONa in water gave crystals of a rhodium triformate complex, [Rh<sup>III</sup>(tacn)(HCOO)<sub>3</sub>] (**3**), whose structure was unequivocally determined by X-ray analysis. The key intermediate in the transformation from **2** to **5** is a rhodium hydride formate complex, [Rh<sup>III</sup>(tacn)H(HCOO)](OTf) (**4**), which was obtained by heating of an aqueous solution of the rhodium diformate complex **2** with 10 equiv of dimethyl sulfoxide (DMSO) at pH 6–7 in water. Complex **4** was well characterized by isotopic labeling measurements of <sup>1</sup>H NMR, electrospray ionization mass spectrometry (ESI-MS), and GC.

## Introduction

Early attempts to develop the catalytic reduction of CO<sub>2</sub> under mild conditions have focused on photochemical or electrochemical reduction of CO<sub>2</sub> with transition metal complexes acting as catalysts.<sup>1–3</sup> Recently, transition metal-catalyzed hydrogenation of CO<sub>2</sub> into formic acid (HCOOH) has attracted increasing attention (eq 1) because HCOOH is a valuable material in organic synthesis<sup>4,5</sup> and in fuel cells<sup>6,7</sup> and also is an important

intermediate in water gas shift reaction (WGSR, eq 2).<sup>8–12</sup>



Thus, the two-electron reduction of CO<sub>2</sub> generally results in formation of HCOOH (eq 1)<sup>13,14</sup> and/or CO (eq 2).<sup>15–24</sup> HCOOH is obtained by CO<sub>2</sub> insertion into the metal–H bond of a metal hydride complex to yield a metal formate complex, followed by protonation (eq 3, where M = metal ion, superscript n = oxidation number).<sup>14,25,26</sup> The reverse reaction is dehydrogenation (or decarboxylation) of HCOOH to produce CO<sub>2</sub> and H<sub>2</sub>

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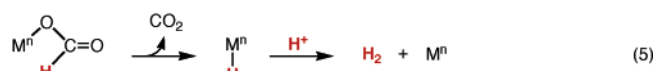
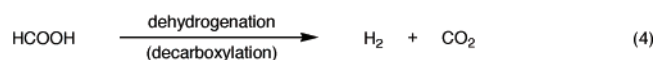
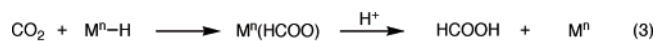
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(eq 4).<sup>4–12,27–31</sup> The H<sub>2</sub> evolution usually results from the reaction of proton with metal hydride, which is generated from a metal formate complex through  $\beta$ -hydrogen elimination (eq 5).<sup>25</sup>



On the other hand, CO is obtained via binding of CO<sub>2</sub> with a low-valent metal complex (e.g., M<sup>n-2</sup> in eq 6) and subsequent protonation to yield CO and H<sub>2</sub>O.<sup>32</sup> CO is

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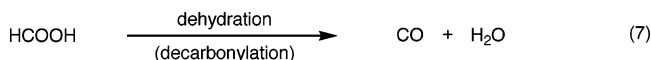
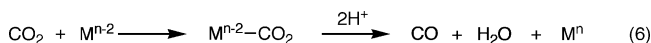
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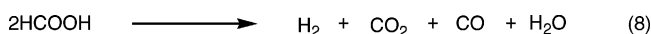
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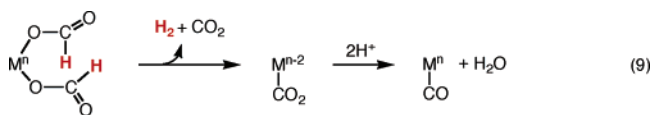
also obtained from HCOOH by dehydration (or decarbonylation) as shown in eq 7.<sup>5–11,29–31,33,34</sup>



Both types of reactions (eqs 4 and 7) of HCOOH have been extensively investigated in the gas phase,<sup>5,8,29</sup> in supercritical water,<sup>4,9,10,30</sup> on the surface of metals,<sup>6,7,11,31</sup> and in the homogeneous phase with metal complexes.<sup>12,27,28,33,34</sup> In any case, the dehydrogenation and dehydration of HCOOH reported so far are two independent processes. In such a case, the H<sub>2</sub>/CO ratio has never been unity even if two processes are both operating.<sup>7b</sup> Thus, there has been no report on the stoichiometric reaction as shown in eq 8, which is the exact sum of eqs 4 and 7.<sup>35,36</sup>



The absence of the stoichiometric reaction is related to the absence of an example of the direct transformation between a metal diformate complex with a metal–O bond and the corresponding metal–CO<sub>2</sub> complex with a metal–C bond, accompanied by H<sub>2</sub> evolution from the formate ligands, followed by protonation to yield a metal–CO complex (eq 9).



We report herein a transformation of a metal diformate complex, [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**, tacn =

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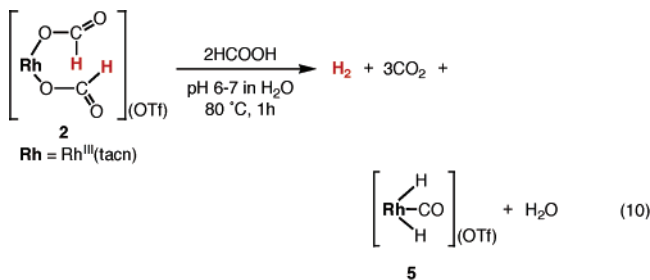
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1,4,7-triazacyclononane,  $\text{OTf}^- = \text{CF}_3\text{SO}_3^-$ ), to a metal dihydride CO complex,  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H})_2(\text{CO})](\text{OTf})$  (**5**), in the presence of formic acid,<sup>37</sup> accompanied by  $\text{H}_2$  evolution from the formate ligands of **2** in water (eq 10).



## Experimental Section

**Materials and Methods.** All experiments were carried out under an Ar atmosphere by using standard vacuum line techniques.  $\text{D}_2\text{O}$  (99.9% D),  $\text{DCOONa}$  (99% D), and  $\text{H}^{13}\text{COONa}$  (99%  $^{13}\text{C}$ ) were purchased from Cambridge Isotope Laboratories. These reagents were used as received. The water-soluble rhodium aqua complex  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H}_2\text{O})_3](\text{OTf})_3$  (**1**) was prepared by the method described in the literature.<sup>38</sup> Purification of water (18.2 M $\Omega$  cm) was performed with a Milli-Q system (Millipore; Milli-RO 5 plus and Milli-Q plus).  $\text{H}_2$  gas (99.9999%) was purchased from Taiyo Toyo Sanso Co., Ltd.,  $\text{D}_2$  gas (99.5%) was purchased from Sumitomo Seika Chemicals Co., Ltd., and HD gas (HD 97%,  $\text{H}_2$  1.8%,  $\text{D}_2$  1.2%) was purchased from Isotec Inc.; these were used without further purification.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on JEOL JNM-AL300 and Varian UNITY INOVA600 spectrometers at 20  $^\circ\text{C}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments in  $\text{H}_2\text{O}$  were performed by dissolving the samples in  $\text{H}_2\text{O}$  in a NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3- $d_4$  acid sodium salt (TSP, 50 mM, as the reference with the methyl proton or carbon resonance set at 0.00 ppm) dissolved in  $\text{D}_2\text{O}$  (for deuterium lock). IR spectra were recorded on a Thermo Nicolet NEXUS 870 FT-IR instrument using 2  $\text{cm}^{-1}$  standard resolution at ambient temperature. The ESI-MS data were obtained by an API 365 triple-quadrupole mass spectrometer (PE-Sciex) in the positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of + 5.0 kV, and compressed  $\text{N}_2$  was employed to assist liquid nebulization. The orifice potential was maintained at +20 V.  $\text{H}_2$ , HD,  $\text{D}_2$ , and  $\text{CO}_2$  gases were determined by Shimadzu GC-14B {He carrier, 10%  $\text{MnCl}_2$ -alumina 100/120 column (4.0 m  $\times$  3.0 mm i.d.) at  $-196$   $^\circ\text{C}$  (liquid  $\text{N}_2$ )} and Shimadzu GC-8A {He carrier, active charcoal, 60/80 column (2 m  $\times$  3 mm i.d.), GL Sciences Inc.} equipped with a thermal conductivity detector. A Nissin magnetic stirrer (model SW-R700) was used. The pH values of solutions were determined by a pH meter (TOA, HM-25G) equipped with a pH combination electrode (TOA, GST-5725C).

**$[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_2](\text{OTf})$  (**2**).** The rhodium aqua complex **1** (303 mg, 0.414 mmol) reacts with  $\text{HCOONa}$  (563 mg, 8.28 mmol) at pH 6–7 in  $\text{H}_2\text{O}$  (15 mL) at 50  $^\circ\text{C}$  for 15 min to yield a yellow solution of **2** (yield: 90% based on **1** by  $^1\text{H}$  NMR).  $^1\text{H}$  NMR (300 MHz, in  $\text{H}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$  2.89–3.08 (m,  $\text{NCH}_2$ , 6H), 3.20–3.40 (m,  $\text{NCH}_2$ , 6H), 7.93

(s, NH, 3H), 8.19 (d,  $^3J_{\text{Rh,H}} = 1.8$  Hz,  $\text{HCOO}$ , 2H).  $^{13}\text{C}$  NMR (600 MHz, in  $\text{H}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$  53.59 (s,  $\text{NCH}_2$ ), 53.82 (s,  $\text{NCH}_2$ ), 54.27 (s,  $\text{NCH}_2$ ), 176.44 (s,  $\text{HCOO}$ ). ESI-MS (in  $\text{H}_2\text{O}$ ),  $m/z$  322.0 [**2** –  $\text{OTf}^+$ ]; relative intensity ( $I$ ) = 100% in the range of  $m/z$  100–2000.

**$[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_3]$  (**3**).** Complex **1** (303 mg, 0.414 mmol) reacted with  $\text{HCOONa}$  (563 mg, 8.28 mmol) at pH 6–7 in  $\text{H}_2\text{O}$  (15 mL) at ambient temperature for 1 h to give a yellow solution of **2**, which was evaporated to give a yellow powder. After stirring of the yellow powder in dimethyl sulfoxide (DMSO) for 10 min, the precipitate of  $\text{HCOONa}$  was removed by filtration. The filtrate was evaporated to yield a yellow powder of **3**. Recrystallization of the yellow powder in  $\text{H}_2\text{O}$  gave yellow crystals of the rhodium triformate complex **3**· $\text{CF}_3\text{SO}_3\text{Na}$ , which were dried in vacuo (isolated yield: 84% based on **1**).  $^1\text{H}$  NMR (300 MHz, in  $\text{H}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$  2.89–3.08 (m,  $\text{NCH}_2$ , 6H), 3.20–3.40 (m,  $\text{NCH}_2$ , 6H), 8.08 (s, NH, 3H), 8.17 (d,  $^3J_{\text{Rh,H}} = 2.2$  Hz,  $\text{HCOO}$ , 2H).  $^{13}\text{C}$  NMR (600 MHz, in  $\text{H}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$  53.59 (s,  $\text{NCH}_2$ ), 53.82 (s,  $\text{NCH}_2$ ), 54.27 (s,  $\text{NCH}_2$ ), 176.71 (s,  $\text{HCOO}$ ). ESI-MS (in  $\text{H}_2\text{O}$ ),  $m/z$  390.0 [**3** +  $\text{Na}^+$ ]; relative intensity ( $I$ ) = 17% in the range of  $m/z$  100–2000}. Anal. Calcd for **3**· $\text{CF}_3\text{SO}_3\text{Na}$ :  $\text{C}_{10}\text{H}_{18}\text{N}_3\text{F}_3\text{NaO}_9\text{RhS}$ : C, 22.27; H, 3.36; N, 7.79. Found: C, 22.07; H, 3.23; N, 7.72.

**$[\text{Rh}^{\text{III}}(\text{tacn})\text{H}(\text{HCOO})](\text{OTf})$  (**4**).** An aqueous solution of **2**, which was prepared by dissolving **3**· $\text{CF}_3\text{SO}_3\text{Na}$  (41.3 mg, 76.6  $\mu\text{mol}$ ) at pH 6–7 in  $\text{H}_2\text{O}$  (2 mL) at 50  $^\circ\text{C}$ , was heated with 10 equiv of DMSO (54.6  $\mu\text{L}$ , 0.766 mmol) at 80  $^\circ\text{C}$  for 1 h under Ar atmosphere to give a yellow solution of the rhodium hydride formate complex **4** (yield: 80% based on **2** by  $^1\text{H}$  NMR). Isolation of **4** is difficult because complex **4** is not only sensitive to air but also unstable without DMSO.  $^1\text{H}$  NMR and ESI-MS only detect **4** in solution with DMSO.  $^1\text{H}$  NMR (300 MHz, in  $\text{H}_2\text{O}/\text{DMSO}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$   $-13.0$  (d,  $^1J_{\text{Rh,H}} = 16.5$  Hz,  $\text{RhH}$ , 1H), 2.89–3.03 (m,  $\text{NCH}_2$ , 6H), 3.20–3.40 (m,  $\text{NCH}_2$ , 6H), 7.90 (d,  $\text{HCOO}$ ,  $^3J_{\text{Rh,H}} = 1.8$  Hz, 1H). ESI-MS (in  $\text{H}_2\text{O}/\text{DMSO}$ ),  $m/z$  278.0 [**4** –  $\text{OTf}^+$ ];  $I$  = 100% in the range of  $m/z$  100–2000.

**$[\text{Rh}^{\text{III}}(\text{tacn})(\text{H})_2(\text{CO})](\text{OTf})$  (**5**).** **Method A.** An aqueous solution of **2** with  $\text{HCOONa}$ , which was prepared by dissolving **3**· $\text{CF}_3\text{SO}_3\text{Na}$  (41.3 mg, 76.6  $\mu\text{mol}$ ) and  $\text{HCOONa}$  (0.104 g, 1.53 mmol) at pH 6–7 in  $\text{H}_2\text{O}$  (2 mL) at 50  $^\circ\text{C}$ , was heated without excess DMSO at 80  $^\circ\text{C}$  for 1 h under Ar atmosphere to give a deep brown solution with evolution of  $\text{H}_2$ . Addition of  $\text{NH}_4\text{PF}_6$  into the brown solution provides a brown powder of  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H})_2(\text{CO})](\text{PF}_6)$  (isolated yield: 70% based on **1**).  $^1\text{H}$  NMR (300 MHz, in  $\text{H}_2\text{O}$ , reference to TSP in  $\text{D}_2\text{O}$ , 25  $^\circ\text{C}$ ):  $\delta$   $-13.6$  (d,  $^1J_{\text{Rh,H}} = 23.2$ ,  $\text{RhH}$ , 2H), 2.65–2.92 (m,  $\text{NCH}_2$ , 6H), 3.03–3.31 (m,  $\text{NCH}_2$ , 6H). ESI-MS (in  $\text{H}_2\text{O}$ ),  $m/z$  262.2 [**5** –  $\text{OTf}^+$ ];  $I$  = 100% in the range of  $m/z$  100–2000). FT-IR (in  $\text{H}_2\text{O}$ ):  $\nu(\text{CO}) = 2047$   $\text{cm}^{-1}$ . **Method B.** The aqueous solution of the rhodium hydride formate complex **4** (61.3  $\mu\text{mol}$ ), which was prepared from **2** (76.6  $\mu\text{mol}$ ) in the presence of DMSO (54.6  $\mu\text{L}$ , 0.766 mmol), reacted with 20 equiv of  $\text{HCOONa}$  (80.8 mg, 1.22 mmol) at pH 6–7 in  $\text{H}_2\text{O}$  (2 mL) at 80  $^\circ\text{C}$  for 3 h to give the solution of the rhodium dihydride CO complex **5** with evolution of  $\text{H}_2$  and  $\text{CO}_2$  (yield: 84% based on **4** by  $^1\text{H}$  NMR).

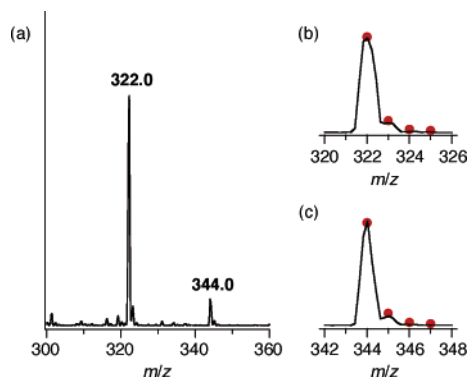
**X-ray Crystallographic Analysis.** A yellow crystal of the rhodium triformate complex **3** used for the X-ray analysis was obtained from an aqueous solution of the rhodium diformate complex **2** with  $\text{HCOONa}$  at pH 7 in  $\text{H}_2\text{O}$ . Crystallographic data for  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_3]\cdot\text{CF}_3\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$  (**3**· $\text{CF}_3\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$ ) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-266289. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK {fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk}. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.7107$   $\text{\AA}$ ). Data were collected and processed using the CrystalClear program (Rigaku). All cal-

(35) Heterogeneous: (a) Ying, D. H. S.; Madix, R. J. *Inorg. Chem.* **1978**, *17*, 1103–1108. (b) Xu, C.; Goodman, D. W. *J. Phys. Chem.* **1996**, *100*, 1753–1760.

(36) Homogeneous: (a) Elliott, D. C.; Hallen, R. T.; Sealock, L. J., Jr. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 431–435. (b) Elliott, D. C.; Sealock, L. J., Jr.; Butner, R. S. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 541–549.

(37) A large excess of formic acid is required to isolate the dihydride CO complex **5**, which contains two hydrido ligands.

(38) Galsboel, F.; Petersen, C. H.; Simonsen, K. *Acta Chem. Scand.* **1996**, *50*, 567–570.

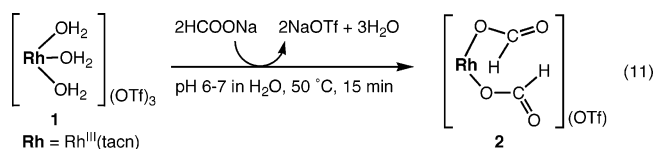


**Figure 1.** (a) Positive-ion ESI mass spectrum of **2** in H<sub>2</sub>O. The signals at *m/z* 322.0 and 344.0 correspond to [2 - OTf]<sup>+</sup> and [2 - OTf - H + Na]<sup>+</sup>, respectively. (b) The signal at *m/z* 322.0. Red circles: calculated isotopic distribution for [2 - OTf]<sup>+</sup>. (c) The signal at *m/z* 344.0. Red circles: calculated isotopic distribution for [2 - OTf - H + Na]<sup>+</sup>.

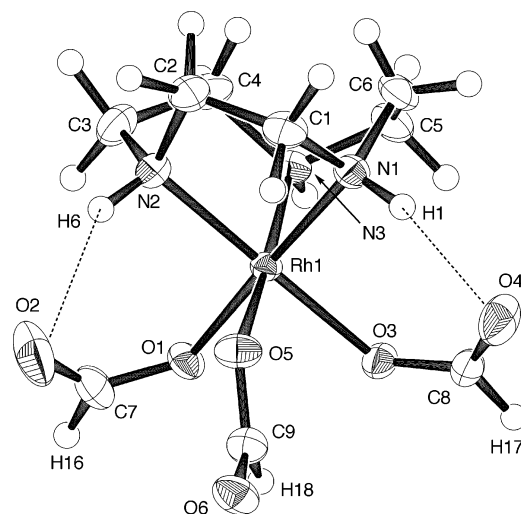
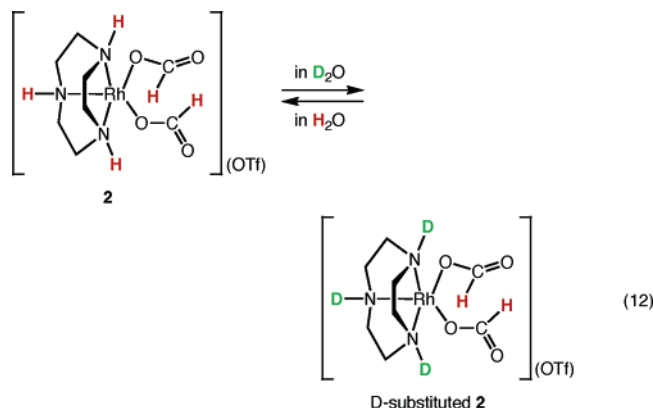
Calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystal data, data collection parameters, structure solution and refinement, atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles are given in the Supporting Information.

## Results and Discussion

**Synthesis and Characterization of the Diformate Complex [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**).** The water-soluble rhodium aqua complex [Rh<sup>III</sup>(tacn)(H<sub>2</sub>O)<sub>3</sub>](OTf)<sub>3</sub> (**1**, tacn = 1,4,7-triazacyclononane, OTf<sup>-</sup> = CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) reacts with HCOONa at pH 6–7 in H<sub>2</sub>O at 50 °C for 15 min to give a yellow solution of the rhodium diformate complex [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**) as shown in eq 11. The <sup>1</sup>H NMR spectrum of **2** in H<sub>2</sub>O



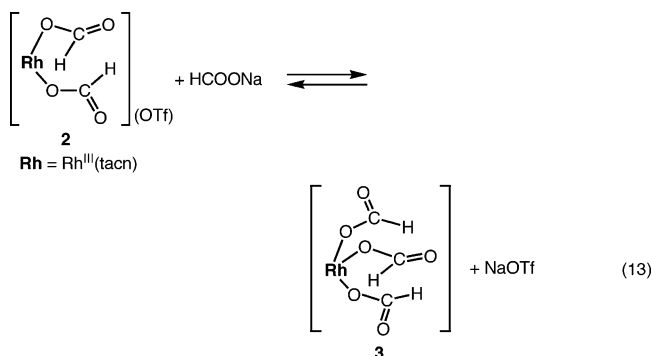
shows signals at 7.93 and 8.19 ppm due to the tacn (N-H) protons and the formate (HCOO) protons, respectively. Only the signal of the tacn protons disappears in D<sub>2</sub>O. Such disappearance of the tacn proton signal in D<sub>2</sub>O results from the exchange of the tacn protons with water protons as shown in eq 12.



**Figure 2.** ORTEP drawing of **3**. Selected bond lengths (*l*/Å) and angles (*φ*/deg): Rh1–O1 = 2.061(2), Rh1–O3 = 2.065(1), Rh1–O5 = 2.052(1), Rh1–N1 = 2.016(2), Rh1–N2 = 2.034(2), Rh1–N3 = 2.019(2), O1–Rh1–O3 = 79.37(6), O1–Rh1–O5 = 93.97(6), O3–Rh1–O5 = 93.60(6).

The ESI mass spectrum of **2** in H<sub>2</sub>O, recorded in positive ion mode,<sup>39</sup> shows prominent signals at *m/z* 322.0 and 344.0 (Figure 1a). The signals at *m/z* 322.0 {relative intensity (*I*) = 100% in the range of *m/z* 100–2000} and at *m/z* 344.0 (*I* = 11%) have characteristic distributions of isotopomers that match well with the calculated isotopic distribution for [2 - OTf]<sup>+</sup> (Figure 1b) and for [2 - OTf - H + Na]<sup>+</sup> (Figure 1c), respectively.

**Synthesis and Crystal Structure of the Triformate Complex [Rh<sup>III</sup>(tacn)(HCOO)<sub>3</sub>] (**3**).** On evaporation of the solvent of the yellow solution of **2** with HCOONa in water, a yellow powder of the rhodium triformate complex [Rh<sup>III</sup>(tacn)(HCOO)<sub>3</sub>] (**3**) was obtained (eq 13). One formate ligand of **3** was readily dissociated in water to give **2** and free formate ion, which was confirmed by <sup>1</sup>H NMR and ESI-MS measurements as shown in eq 13. The structure of **3** was



determined by X-ray analysis (Figure 2). Crystal data are summarized in Table 1. Complex **3** adopts a distorted octahedral coordination, which is surrounded by one tacn and three formate ligands. The two oxygen atoms (O2 and O4) of the formate ligands form hydrogen bonding with the N-H protons (H6 and H1) of the tacn

(39) (a) Ogo, S.; Makihara, N.; Watanabe, Y. *Organometallics* **1999**, *18*, 5470–5474. (b) Takara, S.; Ogo, S.; Watanabe, Y.; Nishikawa, K.; Kinoshita, I.; Isobe, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 3051–3053. (c) Chen, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 2832–2847.

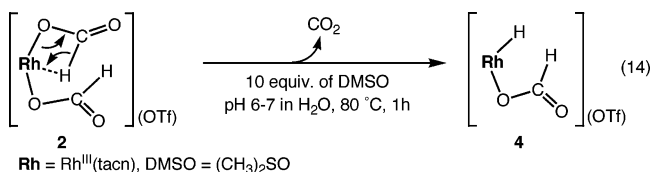
**Table 1. Crystallographic Data for 3·CF<sub>3</sub>SO<sub>3</sub>Na·H<sub>2</sub>O**

empirical formula	C <sub>10</sub> H <sub>20</sub> F <sub>3</sub> N <sub>3</sub> NaO <sub>10</sub> RhS
fw	557.23
cryst color	yellow
cryst dims (mm)	0.30 × 0.30 × 0.20
cryst syst	monoclinic
<i>a</i> (Å)	12.0327(8)
<i>b</i> (Å)	12.6956(7)
<i>c</i> (Å)	13.5546(9)
β (deg)	108.144(2)
<i>V</i> (Å <sup>3</sup> )	1967.7(2)
space group (number)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.881
<i>F</i> <sub>000</sub>	1120
μ(Mo Kα) (mm <sup>-1</sup> )	1.076
radiation (λ, Å)	0.107
temp (°C)	20.0
2θ <sub>max</sub> (deg)	55
abs corr method	numerical
no. of reflens obsd (all, 2θ < 54.95°)	4458
no. of params	262
<i>R</i> <sup>a</sup>	0.041
<i>R</i> <sub>w</sub> <sup>b</sup>	0.066
<i>R</i> <sub>1</sub> <sup>c</sup>	0.025
goodness of fit indicator, <i>S</i> <sup>d</sup>	1.00
max. shift/error in final cycle	0.003
max. peak in final diff map (e Å <sup>-3</sup> )	0.80
min. peak in final diff map (e Å <sup>-3</sup> )	-0.53

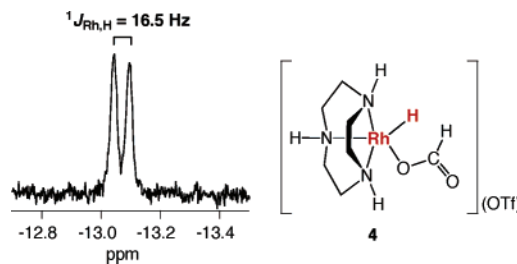
<sup>a</sup>  $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$ . <sup>b</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ . <sup>c</sup>  $R_1 = \sum||F_o^2| - |F_c^2||/\sum|F_o^2|$  for  $I > 2.0\sigma(I)$  data. <sup>d</sup> Goodness of fit indicator,  $S = [S_w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$  ( $N_o$  = number of observations,  $N_v$  = number of variables).

ligand {O2···H6 = 2.425(3) and O4···H1 = 2.095(2) Å}. Such intramolecular hydrogen bonding has also been observed in a rhodium nitrate complex with the tacn ligand, in which the NO<sub>3</sub><sup>-</sup> ligand interacts with a N-H proton on the tacn ligand.<sup>40</sup>

**Formation and Characterization of the Hydride Formate Intermediate [Rh<sup>III</sup>(tacn)H(HCOO)](OTf) (4).** The heating of an aqueous solution of the rhodium diformate complex **2** with 10 equiv of dimethyl sulfoxide (DMSO) at pH 6–7 in H<sub>2</sub>O at 80 °C for 1 h gave the rhodium hydride formate complex [Rh<sup>III</sup>(tacn)H(HCOO)](OTf) (**4**) through β-hydrogen elimination of one formate ligand of **2** (eq 14). The evolution of CO<sub>2</sub>, accompanied by formation of **4**, is detected by GC. The presence of DMSO plays a crucial role in stabilizing **4**, since the formation of **4** is hardly detected without DMSO by <sup>1</sup>H NMR and ESI-MS. The coordination of DMSO to **4** retards the further β-elimination and thereby stabilizes **4**. Thus, the characterization of **4** by <sup>1</sup>H NMR and ESI-MS was carried out in water with DMSO.



The hydride formate complex **4** exhibits a doublet <sup>1</sup>H NMR signal at -13.0 ppm due to the spin–spin coupling with the Rh atom (<sup>1</sup>*J*<sub>Rh,H</sub> = 16.5 Hz) as shown in Figure 3. The proton of the formate ligand of **4** is observed at 7.90 ppm (<sup>3</sup>*J*<sub>Rh,H</sub> = 1.8 Hz), which is apparently different

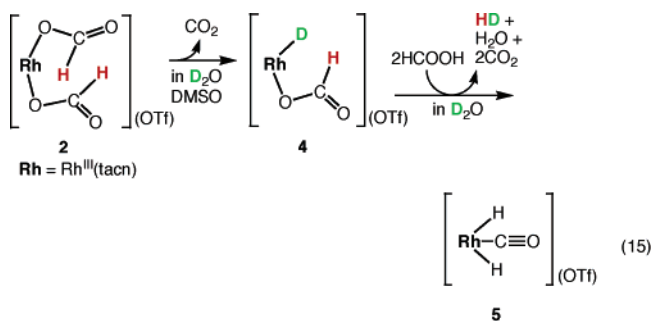


**Figure 3.** <sup>1</sup>H NMR signal at -13.0 ppm due to the spin–spin coupling with the Rh atom (<sup>1</sup>*J*<sub>Rh,H</sub> = 16.5 Hz) of **4** in H<sub>2</sub>O with 10 equiv of dimethyl sulfoxide (DMSO).

from that of **2**. These results indicate that complex **4** contains one terminal hydrido ligand and one formate ligand bound to the Rh center.

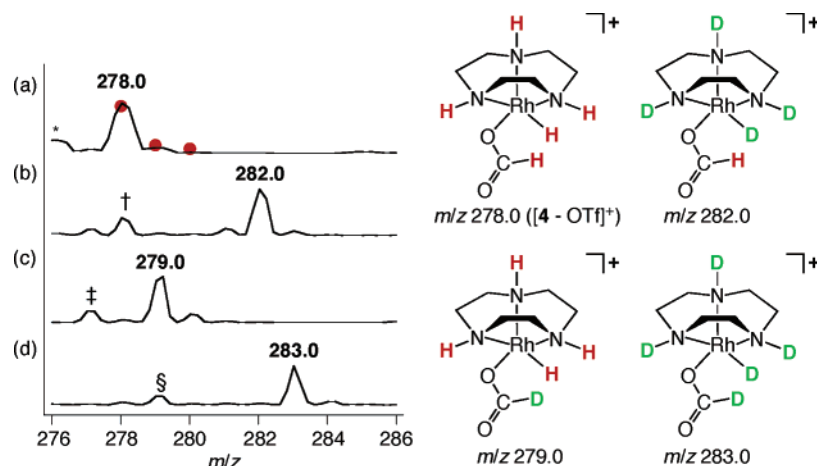
The formation of the rhodium hydride formate complex **4** from **2** was also examined by ESI-MS after heating of the solution of [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**) or [Rh<sup>III</sup>(tacn)(DCOO)<sub>2</sub>](OTf) (D-labeled **2**) in H<sub>2</sub>O or D<sub>2</sub>O with DMSO (Figure 4). The positive-ion ESI mass spectrum obtained after heating of an aqueous solution of **2** with 10 equiv of DMSO at pH 6–7 at 80 °C for 1 h exhibits a prominent signal at *m/z* 278.0, which corresponds to [Rh<sup>III</sup>(tacn)H(HCOO)]<sup>+</sup> ([**4** - OTf]<sup>+</sup>, Figure 4a). When the reaction is carried out in D<sub>2</sub>O, the ESI mass signal due to [Rh<sup>III</sup>(tacn)H(HCOO)]<sup>+</sup> is shifted from *m/z* 278.0 in H<sub>2</sub>O (Figure 4a) to 282.0 in D<sub>2</sub>O (Figure 4b) by 4. The <sup>1</sup>H NMR spectrum of [Rh<sup>III</sup>(tacn)H(HCOO)](OTf) (**4**) in D<sub>2</sub>O shows no hydride signal at -13.0 ppm. Moreover, the ESI mass signal due to [Rh<sup>III</sup>(tacn)(H/D)(DCOO)]<sup>+</sup> is also shifted from *m/z* 279.0 in H<sub>2</sub>O (Figure 4c) to 283.0 in D<sub>2</sub>O (Figure 4d) by 4. These results indicate that the H of the hydride ligand and the three tacn (N-H) protons in [Rh<sup>III</sup>(tacn)H(HCOO)]<sup>+</sup> are readily exchanged with D<sub>2</sub>O, whereas no H/D exchange occurs in the formate (HCOO) proton.

**Synthesis and Characterization of the Dihydride CO Complex [Rh<sup>III</sup>(tacn)(H)<sub>2</sub>(CO)](OTf) (5).** The aqueous solution of the rhodium hydride formate complex **4**, which was prepared from the rhodium diformate complex **2** in the presence of 10 equiv of DMSO, reacted with 20 equiv of HCOONa<sup>37</sup> at pH 6–7 in H<sub>2</sub>O at 80 °C for 3 h to give a deep brown solution of the rhodium dihydride CO complex [Rh<sup>III</sup>(tacn)(H)<sub>2</sub>(CO)](OTf) (**5**) with evolution of H<sub>2</sub> and CO<sub>2</sub>. The reaction mechanism was determined by isotopic labeling measurements of <sup>1</sup>H NMR, ESI-MS, and GC (vide infra). When the reaction of [Rh<sup>III</sup>(tacn)(HCOO)<sub>2</sub>](OTf) (**2**) was carried out in D<sub>2</sub>O, complex **5** was formed with evolution of HD via [Rh<sup>III</sup>(tacn)D(HCOO)](OTf) (D-substituted **4**) as shown in eq 15. Similarly, when the reaction of [Rh<sup>III</sup>(

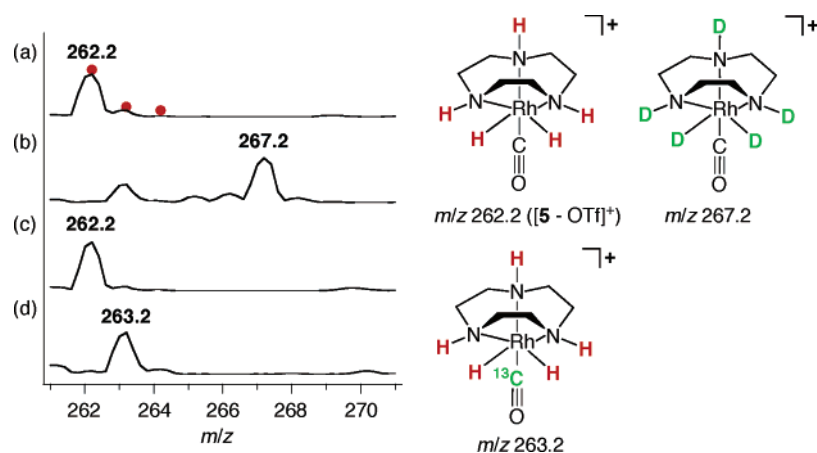


(40) Hayashi, H.; Nishida, H.; Ogo, S.; Fukuzumi, S. *Inorg. Chim. Acta* **2004**, *357*, 2939–2944.

(tacn)(DCOO)<sub>2</sub>](OTf) (D-labeled **2**) was carried out in

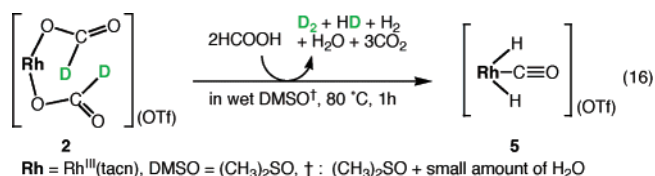


**Figure 4.** (a) Positive-ion ESI mass spectrum of **4** obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_2](\text{OTf})$  (**2**) at pH 6–7 in  $\text{H}_2\text{O}$  with 10 equiv of DMSO at  $80^\circ\text{C}$  for 1 h. The signal at  $m/z$  278.0 corresponds to  $[\mathbf{4} - \text{OTf}]^+$ . Red circles: calculated isotopic distribution for  $[\mathbf{4} - \text{OTf}]^+$ . (b) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_2](\text{OTf})$  (**2**) in  $\text{D}_2\text{O}$  under otherwise the same conditions. (c) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{DCOO})_2](\text{OTf})$  (D-labeled **2**) in  $\text{H}_2\text{O}$  under otherwise the same conditions. (d) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{DCOO})_2](\text{OTf})$  (D-labeled **2**) in  $\text{D}_2\text{O}$  under otherwise the same conditions. \*, †, ‡, and § are fragment ions. \*:  $[(m/z$  278 species)  $- 2\text{H}]^+$ . †:  $[(m/z$  282 species)  $- 2\text{D}]^+$ . ‡:  $[(m/z$  279 species)  $- 2\text{H}]^+$ . §:  $[(m/z$  283 species)  $- 2\text{D}]^+$ .



**Figure 5.** (a) Positive-ion ESI mass spectrum of **5** in  $\text{H}_2\text{O}$ . The signal at  $m/z$  262.2 corresponds to  $[\mathbf{5} - \text{OTf}]^+$ . Red circles: calculated isotopic distribution for  $[\mathbf{5} - \text{OTf}]^+$ . (b) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{HCOO})_2](\text{OTf})$  (**2**) in  $\text{D}_2\text{O}$ . (c) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{DCOO})_2](\text{OTf})$  (D-labeled **2**) in  $\text{H}_2\text{O}$ . (d) Spectrum obtained by using  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H}^{13}\text{COO})_2](\text{OTf})$  ( $^{13}\text{C}$ -labeled **2**) in  $\text{H}_2\text{O}$ .

$\text{H}_2\text{O}$ , complex **5** was also formed with evolution of HD via  $[\text{Rh}^{\text{III}}(\text{tacn})\text{H}(\text{DCOO})](\text{OTf})$  (D-labeled **4**). In these reactions, the amount of HD formed was virtually the same as the amount of **2** or **4**. It was also confirmed that when the reaction of  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{DCOO})_2](\text{OTf})$  (D-labeled **2**) was carried out in wet DMSO  $\{(\text{CH}_3)_2\text{SO} + \text{small amount of } \text{H}_2\text{O}\}$ ,  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H})_2(\text{CO})](\text{OTf})$  (**5**) was formed with evolution of  $\text{D}_2$ , HD, and  $\text{H}_2$  (eq 16). These results indicate that the evolved hydrogen gas is from two H in **4**: one is the hydride H that is readily exchanged with  $\text{D}_2\text{O}$ , and the other is the formate H that cannot be exchanged with  $\text{D}_2\text{O}$ .



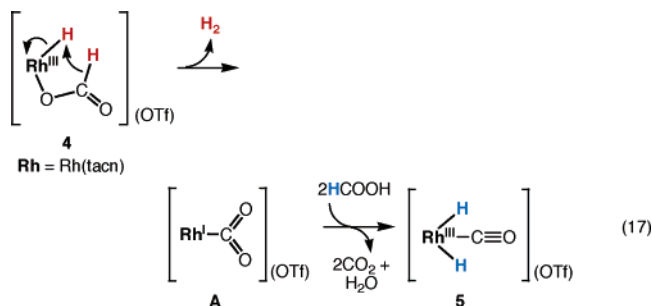
As shown in eq 17, the intramolecular elimination of  $\text{H}_2$  from **4** should leave two electrons in the rhodium

complex to give formally  $\text{Rh}^{\text{I}}\text{-CO}_2$  species **A** (equivalent to  $\text{Rh}^{\text{III}}\text{-CO}_2^{2-}$  species), which is further protonated to afford the final product **5**.<sup>41</sup> Alternatively, the rhodium hydride formate complex **4** could be reduced by its own hydrido ligand to produce the rhodium formaldehyde complex, from which  $\text{H}_2$  is evolved to afford the final product **5**.<sup>42</sup> It should be noted that under acidic conditions (below pH 5) the rhodium hydride formate complex **4** reacts with proton to release  $\text{H}_2$ , leading to regeneration of the rhodium aqua complex **1**.

The ESI mass spectrum of **5** in Figure 5a shows a signal at  $m/z$  262.2 that corresponds to  $[\text{Rh}^{\text{III}}(\text{tacn})(\text{H})_2(\text{CO})]^+ [\mathbf{5} - \text{OTf}]^+$ , and the distribution of isotopomers

(41) Importance of intramolecular elimination of  $\text{H}_2$  in nitrogenases has been pointed out: (a) Ogo, S.; Nakai, H.; Watanabe, Y. *J. Am. Chem. Soc.* **2002**, *124*, 597–601. (b) Ogo, S.; Kure, B.; Nakai, H.; Watanabe, Y.; Fukuzumi, S. *Appl. Organomet. Chem.* **2004**, *18*, 589–594. (c) Fryzuk, M. D.; MacKay, B. A.; Patrick, B. O. *J. Am. Chem. Soc.* **2003**, *125*, 3234–3235.

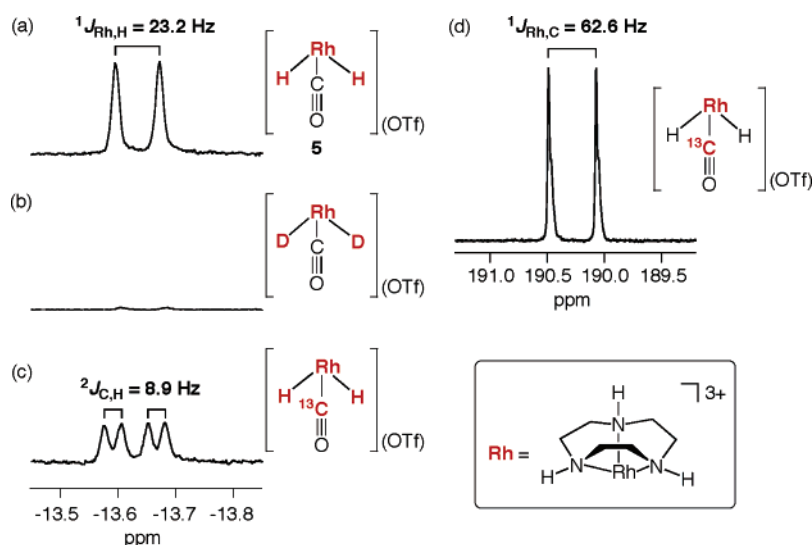
(42) For the transformation of  $\text{HCHO}$  to  $\text{CO}$  with evolution of  $\text{H}_2$ , see: (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204. The exact mechanism of the hydrogen evolution remains to be further clarified.



matches well with the calculated isotopic distribution. When the reaction is carried out in  $D_2O$ , the ESI mass signal due to the dihydride CO complex is shifted from  $m/z$  262.2 in  $H_2O$  to 267.2 in  $D_2O$  (Figure 5b) by 5 because of the H/D exchange of the three tacn (N-H) protons and two hydride (Rh-H) protons with  $D_2O$ . When the reaction is started from the D-labeled difor-

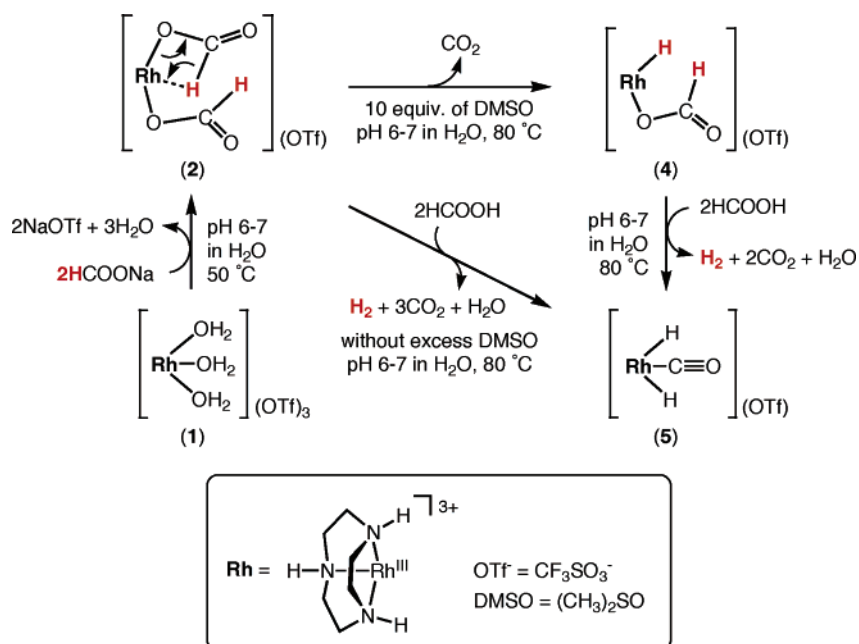
mate complex  $[Rh^{III}(tacn)(DCOO)_2](OTf)$  (D-labeled **2**) in  $H_2O$ , the same shift in the ESI mass signal is observed (Figure 5c), since the deuteride is readily exchanged with  $H_2O$  as well as  $D_2O$ . To establish the origin of the CO ligand of **5**,  $^{13}C$ -labeled **2**  $\{[Rh^{III}(tacn)(H^{13}CO)_2](OTf)\}$ . ESI-MS results show that the signal at  $m/z$  262.2 shifts to  $m/z$  263.2, which corresponds to  $[Rh^{III}(tacn)(H)_2(^{13}CO)]^+ [^{13}C\text{-labeled } \mathbf{5} - OTf]^+$  as shown in Figure 5d.

The dihydride CO complex **5** exhibits doublet  $^1H$  NMR signals at  $-13.6$  ppm ( $^1J_{Rh,H} = 23.2$  Hz), which are attributable to the terminal hydrido ligands bound to the Rh center (Figure 6a). The hydride signals disappeared in the  $^1H$  NMR spectrum of **5** in  $D_2O$  as shown in Figure 6b. Moreover, when the  $^{13}C$  isotopomer of **5** is used, the doublet signals in the  $^1H$  NMR spectrum of **5** in  $H_2O$  further split into double doublet signals ( $^2J_{C,H} = 8.9$  Hz, Figure 6c). The presence of the CO ligand in



**Figure 6.** (a)  $^1H$  NMR spectrum of **5** in  $H_2O$ . The signals correspond to the hydrido ligands of **5**. (b)  $^1H$  NMR spectrum of **5** in  $D_2O$ . (c)  $^1H$  NMR spectrum of  $[Rh^{III}(tacn)(H)_2(^{13}CO)](OTf)$  ( $^{13}C$ -labeled **5**) in  $H_2O$ . (d)  $^{13}C$  NMR spectrum of  $[Rh^{III}(tacn)(H)_2(^{13}CO)](OTf)$  ( $^{13}C$ -labeled **5**) in  $H_2O$ .

### Scheme 1



**5** is also confirmed by  $^{13}\text{C}$  NMR and IR spectra of the aqueous solution of **5**. The  $^{13}\text{C}$  NMR spectrum shows a signal at 190.3 ppm ( $^1J_{\text{Rh,C}} = 62.6$  Hz) as shown in Figure 6d. The IR spectrum of **5** in  $\text{H}_2\text{O}$  shows a CO stretching vibration at  $2047\text{ cm}^{-1}$  that shifts to  $2001\text{ cm}^{-1}$  by using the  $^{13}\text{C}$  isotopomer.<sup>43</sup>

### Conclusions

On the basis of the above results, the transformation of the diformate complex **2** to the dihydride CO complex **5** at pH 6–7 in water is summarized in Scheme 1. Although  $\text{H}_2$  evolution usually results from the reaction of a metal hydride complex with proton (the reaction of hydride and proton), the present study provides a unique pathway for the  $\text{H}_2$  evolution from the formate

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(43) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley: New York, 1997, and references therein.

ligands of the metal diformate complex. Isotopic labeling measurements of  $^1\text{H}$  NMR, ESI-MS, and GC have indicated that the evolved hydrogen gas is from the hydride formate complex **4**, whose H of the hydrido ligand is readily exchanged with  $\text{D}_2\text{O}$ , whereas H of the formate ligand is not exchanged with  $\text{D}_2\text{O}$ .

**Acknowledgment.** This work was supported by grants in aid (15036242, 15350033, 16205020, and 16655022) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and a CREST program (Nano-Structured Catalysts and Materials) by JST. We thank emeritus Professor M. Misono (University of Tokyo) and emeritus Professor A. Nakamura (Osaka University) for valuable discussions.

**Supporting Information Available:** Crystallographic data (CIF) for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0504147