

# Highly efficient conversion of carbon dioxide catalyzed by half-sandwich complexes with pyridinol ligand: The electronic effect of oxyanion

Yuichiro Himeda<sup>\*</sup>, Nobuko Onozawa-Komatsuzaki, Hideki Sugihara, Kazuyuki Kasuga

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan

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## Abstract

Half-sandwich complexes with 4,4'-dihydroxy-2,2'-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) are highly efficient catalysts for the hydrogenation of bicarbonate in an alkaline aqueous solution without an amine additive. The generation of an oxyanion by the deprotonation of the two hydroxy substituents on the catalyst ligand caused a dramatic enhancement of catalytic activity due to the strong electron-donating ability of the oxyanion. Turnover frequencies (TOF) up to 42,000 h<sup>-1</sup> and turnover numbers (TON) up to 222,000 have been obtained by using iridium catalysts under 6 MPa at 120 °C. The production of formate (TOF = 3.5 h<sup>-1</sup>) was observed even under ambient conditions (0.1 MPa, 30 °C).

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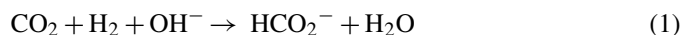
**Keywords:** CO<sub>2</sub> conversion; Electronic effect; Aqueous reaction; Hammett substituent constant; Oxyanion

## 1. Introduction

The efficient conversion of CO<sub>2</sub> into useful organic products still remains an intriguing and challenging subject [1–3]. Since an artificial photosynthesis system consisting of a sacrificial electron donor, a photosensitizer, and a reduction catalyst has been reported by Lehn and co-workers [4], various attempts have been made to convert CO<sub>2</sub> by using light energy [5–7]. Although the photochemical properties of the systems used in these studies were interesting, we were disappointed by the environmental load, high cost, and poor catalytic performance in the CO<sub>2</sub> conversion process. Therefore, our focus turned to the development of a CO<sub>2</sub> conversion process because one of the solutions may be the improvement in the catalytic activity in the dark reaction.

The conversion of CO<sub>2</sub> by using a homogeneous catalyst has improved remarkably since the development of a system using supercritical CO<sub>2</sub> by Noyori and co-workers [8,9]. Recently, Joo and co-workers [10] reported that the highly efficient catalysis proceeded in an amine-free aqueous solution (Eq. (1)). However, elevated pressure and temperature are required for efficient conversion. The purpose of our study is to develop an efficient hydrogenation catalyst that is active even at ambient conditions

like the dark reaction in photosynthesis, ideally, by using the hydrogen gas produced by photocatalytic water decomposition [11].



In our previous study [12], we reported the highly efficient hydrogenation of bicarbonate in water without an amine additive. We found that the introduction of a hydroxy group into the pyridine ring as a catalyst ligand dramatically improves the catalytic efficiency. This observation prompted us to investigate the electronic effect of the catalyst ligand on the catalytic activity and the role of the oxyanion.

## 2. Experimental

### 2.1. General considerations

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All aqueous solutions were degassed prior to use. The formate concentration was monitored by an HPLC on an anion-exclusion column (Tosoh TSK gel SCX (H<sup>+</sup>)) with an aqueous phosphate solution (20 mM) as an eluent and a UV detector ( $\lambda = 210$  nm). Research grade CO<sub>2</sub> (>99.999%), H<sub>2</sub> (>99.9999%), and CO<sub>2</sub>/H<sub>2</sub> (>99.999%) were used. Complexes 4–6 were prepared according to the procedure described in literature [12]. All new

<sup>\*</sup> Corresponding author. Tel.: +81 29 861 9344; fax: +81 29 861 4687.  
E-mail address: [himeda.y@aist.go.jp](mailto:himeda.y@aist.go.jp) (Y. Himeda).

compounds were characterized by elemental analyses,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and mass spectra.

## 2.2. Procedure for catalytic hydrogenation of bicarbonate under pressurized conditions

A degassed aqueous KOH solution (50 mL) of the complex was saturated with  $\text{CO}_2$  in a 100 mL stainless-steel reactor equipped with a sampling device. The reactor was heated and then repressurized to the desired  $\text{CO}_2\text{:H}_2$  (1:1) pressure. The initial TOFs were calculated by nonlinear least-squares fits of the experimental data obtained from the initial part of the reaction [20].

## 2.3. Procedure for catalytic hydrogenation of bicarbonate under ambient conditions

A degassed aqueous  $\text{K}_2\text{CO}_3$  solution (20 mL) of the complex (4.0  $\mu\text{mol}$ ) was saturated with  $\text{CO}_2$  at ambient pressure. The reaction mixture was heated and stirred vigorously under an atmosphere of  $\text{CO}_2\text{:H}_2$  (1:1). All gases were passed through an oxygen trap prior to use.

## 2.4. NMR observation of iridium hydride complex

The solution of **1c** in  $\text{D}_2\text{O/KOD}$  was allowed to stand under 2 MPa of  $\text{H}_2$  for 4 days.  $^1\text{H}$  NMR ( $\text{D}_2\text{O/KOD}$ )  $\delta$  8.15 (d,  $J=6.6$  Hz, 2 H), 7.15 (d,  $J=2.7$  Hz, 2 H), 6.58 (dd,  $J=6.6$ , 2.7 Hz, 2 H), 1.75 (s, 15 H),  $-11.09$  (s, 1 H, Ir-H).

## 3. Results and discussion

It is known that Hammett constants are useful reference values for the electronic effect of a substituent [13]. The electronic effect of substituent of a catalyst ligand on the catalytic performance has been widely investigated in the range from nitro to amine groups [14–17]. The theoretical study by calculation predicts that the strongly donating ligand would improve the catalytic efficiency in the hydrogenation of  $\text{CO}_2$  [18].

In order to investigate the influence of the electronic properties of the bipyridine ligand on the catalytic activity, we prepared a series of iridium complexes  $[\text{Cp}^*\text{Ir}(4,4'\text{-X}_2\text{-2,2'}\text{-bpy})\text{Cl}]\text{Cl}$  **1** by reacting  $[\text{Cp}^*\text{IrCl}_2]_2$  with the corresponding disubstituted

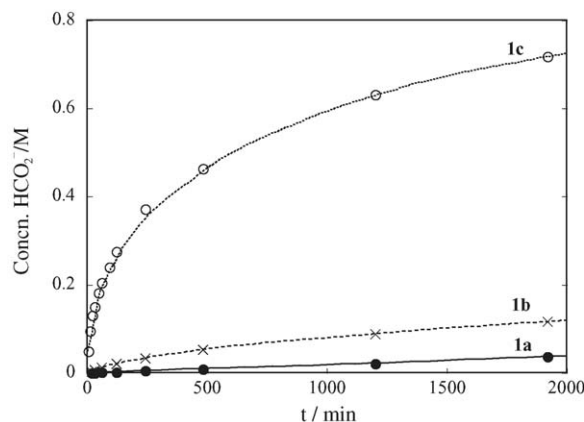


Fig. 1. Time course of formate concentration in the hydrogenation of bicarbonate catalyzed by **1a–c** (0.2 mM) under 4 MPa ( $\text{H}_2\text{:CO}_2 = 1:1$ ) at  $80^\circ\text{C}$  in 1 M aqueous KOH.

2,2'-bipyridine (Chart 1). Fig. 1 shows the time course of formate generation catalyzed by **1a–c**. The catalytic performance of the hydroxy catalyst **1c** was considerably more effective than that of the methoxy one **1b**, whose Hammett constant is slightly higher than that of the hydroxy group. The remarkable difference in the catalytic performance among the three catalyst **1a–c** suggests that the hydroxy group on **1c** changed to an oxyanion, which has a strong electron-donating ability.

Therefore, we systematically examined the electronic effect of the substituent on the catalyst activity on the basis of Hammett rule. The TON and initial TOF of complexes **1a–e** are summarized in Table 1. Since phenolic hydroxyl and carboxyl are acidic, the deprotonation of these groups on **1c** [19] and **1d** will occur under basic reaction conditions. Thus, the Hammett constant ( $\sigma_p^+$ ) values for **1c** and **1d** can be inferred to be  $-2.30$  and  $-0.02$ , corresponding to oxyanion ( $-\text{O}^-$ ) and carboxylate ( $-\text{CO}_2^-$ ), respectively [13]. A plot of  $\log(\text{initial TOF})$  versus the  $\sigma_p^+$  of X in **1** presented in Fig. 2 shows a good correlation ( $R=0.997$ ). It is apparent that the extremely high catalytic activity of **1c** was attributed to the strong electron-donating ability of the oxyanion generated from the phenolic hydroxy group. These results are consistent with Sakaki's theoretical prediction [18]. To the best of our knowledge, this is the first example applicable to the oxyanion on a catalyst ligand.

Since the introduction of a hydroxy group into the pyridine ring led to a dramatic improvement in the catalytic

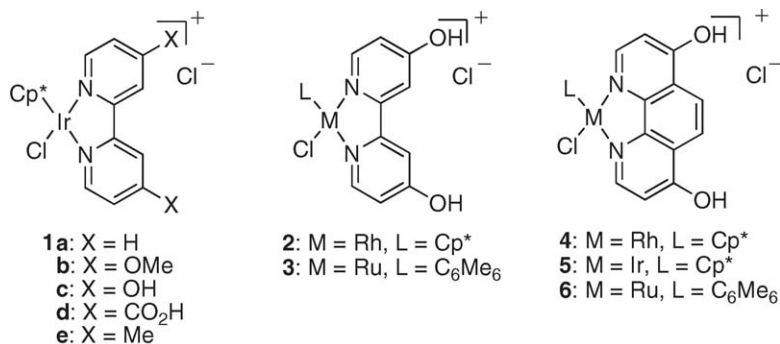


Chart 1.

Table 1  
Hydrogenation of bicarbonate catalyzed by iridium complexes with para-substituted bipyridine [Cp\*Ir(4,4'-X<sub>2</sub>-2,2'-bpy)Cl]Cl **1**<sup>a</sup>

Entry	Catalyst/ concentration (mM)	X	$\sigma_p^+$	Initial TOF <sup>b</sup> (h <sup>-1</sup> )	TON
1	<b>1a</b> /0.2	H	0	6	105
2	<b>1d</b> /0.2	CO <sub>2</sub> H	-0.02 <sup>c</sup>	9	137
3	<b>1e</b> /0.2	Me	-0.31	13	128
4	<b>1b</b> /0.2	OMe	-0.78	72	444
5	<b>1c</b> /0.05	OH	-2.30 <sup>d</sup>	7960	6770

<sup>a</sup> The reaction was carried out under 4 MPa of CO<sub>2</sub>:H<sub>2</sub> (1:1) at 80 °C for 20 h.

<sup>b</sup> The initial TOFs were calculated by nonlinear least-squares fits of the experimental data obtained from the initial part of the reaction [20].

<sup>c</sup> The carboxylic acid group is regarded as a carboxylate (-CO<sub>2</sub><sup>-</sup>).

<sup>d</sup> The hydroxy group is regarded as an oxyanion (-O<sup>-</sup>).

performance, the reactions were carried out by using complexes with 4,4'-dihydroxy-2,2'-bipyridine (DHBP) or 4,7-dihydroxy-1,10-phenanthroline (DHPT) as a catalyst ligand. The results obtained by using rhodium and ruthenium analogs are shown in Table 2. The iridium complexes were superior to the corresponding rhodium analogs (entries 1 versus 3 and 2 versus 7). In the iridium complexes, the highest TOF, 42,000 h<sup>-1</sup> (entry 5) and TON, 220,000 (entry 9), were obtained at 6 MPa and 120 °C in a highly diluted concentration of the catalyst (<2 × 10<sup>-6</sup> M). Furthermore, the hydrogenation proceeded under ambient pressure (entries 6, 10, and 11). The production of formate (TOF = 3.5 h<sup>-1</sup>) was observed even at 30 °C. To the best of our knowledge, there is only one other report on homogeneous catalytic hydrogenation occurring under ambient pressure at room temperature [21]. The arene-ruthenium complexes **3** and **6** yielded a higher equilibrium concentration of formate, although their TOF and TON were moderate (entries 12–14). As a result, it was shown that the catalytic performances (TOF, TON, and equilibrium concentration) were strongly affected by the central metals. On the other hand, it appears that the differ-

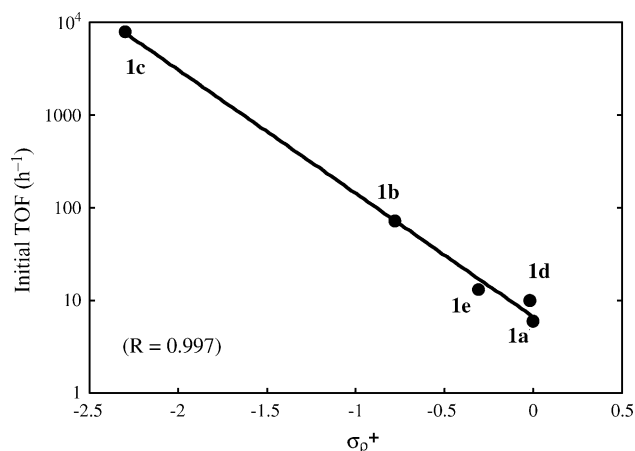


Fig. 2. Hammett plot for the hydrogenation of bicarbonate catalyzed by **1a–e**. The reactions were carried out with **1** (0.2–0.05 mM) under 4 MPa of CO<sub>2</sub>:H<sub>2</sub> (1:1) at 80 °C in 1 M aqueous KOH.

ence in the ligand effects of DHBP and DHPT on the catalytic efficiency was relatively small.

The absorption spectra of **1c** as a function of pH are shown in Fig. 3. The spectral change is a result of an acid-base equilibrium of the complexes attributable to 4-hydroxypyridine (pK<sub>a</sub> = 11.1)[22] as part of ligand. The pK<sub>a</sub> value of the **1c** was estimated to be ca. 9.6 calculated from change in optical density against pH [19].

The proposed mechanism for the hydrogenation of bicarbonate catalyzed by the complexes with DHBP or DHPT ligands is shown in Scheme 1. The deprotonation of the pyridinol form **A** converts to the pyridinolate form **B** under basic reaction conditions. The hydride complex **C** is generated in the presence of H<sub>2</sub>. In fact, the complex **C** generated from **1c** exhibited a singlet at  $\delta$  -11.09 in <sup>1</sup>H NMR and reduced the bicarbonate into formate under an atmospheric pressure of H<sub>2</sub>. We suggest that the deprotonated hydride complexes **C** are the actual catalysts and

Table 2  
Hydrogenation of bicarbonate using the complexes with DHBP or DHPT ligand<sup>a</sup>

Entry	Catalyst/ concentration (μM)	Temperature (°C)	P (MPa)	Time (h)	Initial TOF (h <sup>-1</sup> )	TON	Final concentration of formate (M)
1	<b>2</b> /100	80	4	12	790	1800	0.18
2	<b>4</b> /100	80	4	32	270	2400	0.24
3	<b>1c</b> /100	80	4	140	4000	8000	0.80
4	<b>1c</b> /20	120	6	32	41000	33500	0.67
5	<b>1c</b> /0.5	120	6	57	42000	190000	0.095
6	<b>1c</b> /200 <sup>b</sup>	60	0.1	50	33	376	0.075
7	<b>5</b> /100	80	4	116	3000	7300	0.73
8	<b>5</b> /20	120	6	32	35000	26000	0.52
9	<b>5</b> /2	120	6	48	33000	222000	0.44
10	<b>5</b> /200 <sup>b</sup>	30	0.1	30	3.5	81	0.016
11	<b>5</b> /200 <sup>b</sup>	60	0.1	50	32	444	0.089
12	<b>3</b> /100 <sup>c</sup>	120	6	8	4400	13620	1.36
13	<b>6</b> /100 <sup>c</sup>	80	4	165	370	12500	1.25
14	<b>6</b> /100 <sup>c</sup>	120	6	24	3600	15400	1.54

<sup>a</sup> The reaction was carried out in an aqueous 1 M KOH solution under the desired CO<sub>2</sub>:H<sub>2</sub> (1:1) pressure.

<sup>b</sup> The reaction was carried out in 0.1 M aqueous K<sub>2</sub>CO<sub>3</sub> solution.

<sup>c</sup> The reaction was carried out in 2 M aqueous KOH.

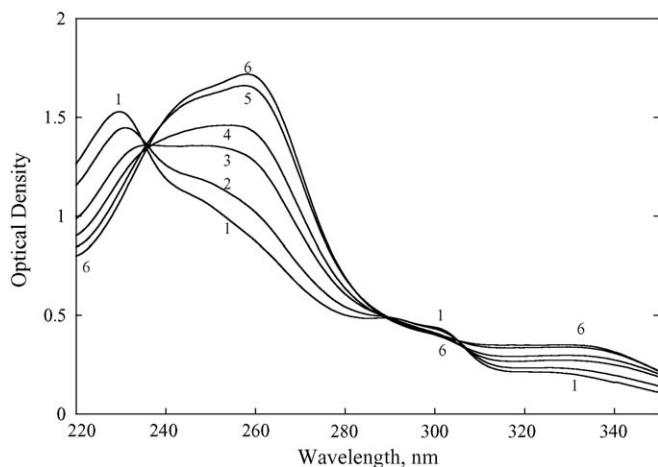
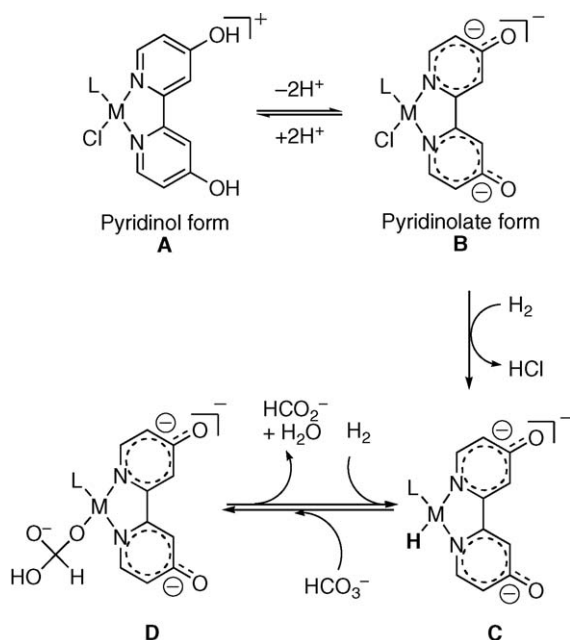


Fig. 3. Absorption spectra of **1c** (50  $\mu\text{M}$ ) in aqueous solution containing 2.5% methanol as a function of pH; curves, 1, 2, 3, 4, 5, and 6 are at pH 2.36, 3.93, 4.64, 5.15, 5.65, and 5.96, respectively.



Scheme 1. The proposed mechanism of the hydrogenation of bicarbonate into formate.

the bicarbonate is the actual substrate. It is reasonable to assume that the bicarbonate is inserted into the metal-hydride bond to generate the formate intermediate with the release of the hydroxide ion, as suggested by Joo and co-workers [23]. In our catalytic system, none of the reactions showed a significant induction period, and neither CO nor any other carbon-containing products were detected by GC, LC, or NMR analysis.

#### 4. Conclusion

The half-sandwich complexes with DHBP or DHPT serve as highly efficient catalysts for the hydrogenation of bicarbonate in

an aqueous solution without an amine additive. The extremely high catalytic activity is attributed to the strong electronic effect of the oxyanion. The log of the initial TOFs is linearly correlated with the  $\sigma_p^+$  values of the substituent on the bipyridine ligand. In addition, catalyst recycling was achieved by self-precipitation without waste generation by taking advantage of the interconversion of the catalyst ligand [24]. Our catalyst design concept may hold significantly broader implications and can be applied to a wide range of homogeneous catalysts with a simple modification.

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