CO₂ Hydrogenation Catalyzed by Iridium Complexes with a Proton-responsive Ligand

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ABSTRACT

The catalytic cycle for the production of formic acid by CO₂ hydrogenation and the reverse reaction has received renewed attention because they are viewed as offering a viable scheme for hydrogen storage and release. In this Forum Article, CO₂ hydrogenation catalyzed by iridium complexes bearing N^N-bidentate ligands is reported. We describe how a ligand containing hydroxyl groups as proton-responsive substituents enhances catalytic performance by an electronic effect of the oxyanions and a pendant-base effect through secondary coordination sphere interaction. In particular, [(Cp*IrCl)₂(TH2BPM)]Cl₂ (Cp* = pentamethyl cyclopentadienyl, TH2BPM = 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) promotes enormously the catalytic hydrogenation of CO₂ by these synergistic effects under atmospheric pressure and at room temperature. Additionally, newly designed complexes with azole-type ligands are applied to CO₂ hydrogenation. The catalytic efficiencies of the azole-type complexes are much higher than that of the unsubstituted bipyridine complex [Cp*Ir(bpy)(OH₂)]SO₄. Furthermore, the introduction of one or more hydroxyl groups into ligands such as 2-pyrazolyl-6-hydroxypyridine, 2-pyrazolyl-4,6-dihydroxypyrimidine, and 4-pyrazolyl-2,6-dihydroxypyrimidine enhanced catalytic activity. It is clear that the incorporation of electron-donating hydroxyl groups into proton-responsive ligands is effective for promoting the hydrogenation of CO₂.

INTRODUCTION

Carbon dioxide (CO₂) emissions from the combustion of fossil fuels have increased recently owing to rising energy consumption in the world. Therefore, the conversion of thermodynamically stable CO₂ into useful materials has become a challenging research area.

Mimicking the carbon cycle in the nature, the reduction of CO₂ as an energy storage medium is a promising possible solution to this problem. Therefore, a great deal of effort has been directed toward the development of catalysts for activation of CO₂ molecules.

Hydrogen is considered as an alternative energy source for the next generation because its gravimetric energy density is high and water is the only product of its oxidation.¹ However, to handle and transfer hydrogen is very difficult owing to its explosive nature and low volumetric energy density, so the development of alternative hydrogen storage media has become an active area of research.^{2,3} In particular, formic acid, regarded as a hydrogen carrier, has gathered attention because it is a liquid under ambient conditions, is nontoxic toward the human body and the environment, and contains 4.4 wt% hydrogen. In addition, formic acid can be produced by hydrogenation of CO₂ in aqueous solution with only a slight free-energy change ($\Delta G^{\circ}_{298} = 4$ kJ/mol). To exploit these advantages, the combination of CO₂ hydrogenation with the dehydrogenation of formic acid for H₂ generation under mild conditions is essential for the development of a hydrogen storage cycle.

The interconversion (reversible reaction) between CO₂ and formic acid in aqueous solution is strongly affected by the pH value (Eq. 1). In the hydrogenation of CO₂, the reaction is promoted by the presence of a base (Eq. 2). On the other hand, under acidic conditions, the equilibrium is reversed and the dehydrogenation reaction of formic acid is preferred (Eq. 3). However, previous “conventional” hydrogenation catalysts have required high-pressure, high temperature, and some organic additives such as amines. Furthermore, in the case of the dehydrogenation of formic acid, the evolution of CO gas as a byproduct caused by dehydration of formic acid should be avoided. To develop hydrogen storage systems, high energy-efficiency

and clean reaction systems are desirable. For this goal, we have targeted the development of highly efficient and water-soluble catalysts without the use of organic additives.

Since CO₂ hydrogenation using homogenous catalysts was reported by Inoue in 1976,⁴ many chemists have pursued the development of more efficient catalysts.⁵⁻⁹ To improve catalyst performance, systematic investigations using rhodium- and ruthenium-based complexes with phosphine ligands in the presence of an organic base were reported by Jessop^{5,10-13}, and Leitner^{6,14}. Aqueous catalysis without organic additives was first achieved by Joo.^{15,16} Recently, the structure-reactivity relationship of a pyridinylazolate ligand using a ruthenium-based complex has been investigated by Thiel.¹⁷ Very recently, Laurenczy reported the base-free production of highly concentrated formic acid (> 1.9 M) catalyzed by a ruthenium PTA complex (PTA: 1,3,5-triaza-7-phosphaadamantane) in DMSO at 10 MPa.¹⁸ The direct production of formic acid without any additive is very attractive from the viewpoint of hydrogen storage.

Although there are reports that iridium-based catalysts with phosphine ligands showed unsatisfactory catalytic performance,^{15,19} we found that the electronic effect of a substituent in a N^N bidentate ligand significantly improved catalytic activity in aqueous solution (*vide infra*).²⁰ Several iridium complexes for efficient CO₂ hydrogenation have been reported as aqueous catalysts without the use of an organic additive.^{21,22}

In 2009, Nozaki reported that an iridium trihydride complex with a PNP pincer-type ligand effectively hydrogenated CO₂ to formate with a turnover frequency (TOF) of 150,000 h⁻¹ at 200 °C and a turnover number (TON) of 3,500,000 at 120 °C in H₂O/THF (5/1) under 8 MPa. After that, iridium complexes with a pincer-type ligand became widely used as catalysts for CO₂ hydrogenation. Hazari reported a PNP pincer-type iridium complex with an H-bond donor that can form a secondary coordination sphere.²³ That analog exhibited a TON of 348,000 and TOF of 18,780 h⁻¹ at 185 °C under 5.5 MPa. A ruthenium complex with a PNP pincer type ligand provided the highest TOF value of 1,100,000 h⁻¹ at 120 °C under 4 MPa in CO₂ hydrogenation as well as in dehydrogenation of formic acid (vide infra), although catalysis was carried out in DMF in the presence of an organic amine.²⁴

The development of non-precious metal-based catalysts has also been pursued since the pioneering work by Inoue.⁴ Beller reported Fe^{25,26} and Co²⁷ complexes with tetradentate ligands (PP₃: P(CH₂CH₂PPh₂)₃). The well-defined cobalt dihydrogen complex provided TON of 3877 in 20 h in an aqueous MeOH solution at 120 °C under 6 MPa. Efficient CO₂ hydrogenation catalyzed by Co(dmpe)₂H (dmpe = 1,2-bis(dimethylphosphino)ethane) was achieved by Linehan.²⁸ Although the catalysis showed the remarkable TOF of 3400 h⁻¹ at room temperature and atmospheric pressure of CO₂:H₂ (1:1) in THF, a superstrong base (i.e., Verkade's base; pK_a = 33.7) was required as a sacrificial reagent for the Co catalyst regeneration step. Fujita reported aqueous CO₂ hydrogenation using Cp*Co complexes with bipyridine derivatives without the use of an organic base or organic solvent, but these complexes are relatively unstable in water.²⁹ A Fe complex with a pincer-type ligand reported by Milstein resulted in a TON of 788 at 1 MPa and 80 °C in H₂O/THF (10/1).³⁰ This high activity under low pressures implied an enormous potential for non-precious-metal-based catalysts.

Meanwhile, Peris reported transfer hydrogenation of CO₂ to formate using *i*PrOH as a hydrogen donor catalyzed by water-soluble iridium complexes with a N-heterocyclic carbene.³¹⁻³³ Afterwards, production of formate by transfer hydrogenation of CO₂ using MeOH in aqueous media was reported by Beller.³⁴ The catalysis using ruthenium complexes with a PNP pincer-type ligand showed excellent TON (> 18000), TOF (> 1300 h⁻¹), and yield (>90 %) at 150 °C in an autoclave.

The dehydrogenation of formic acid as a companion reaction to CO₂ hydrogenation is essential to a hydrogen storage system using formic acid.³⁵⁻³⁷ However, since the pioneering work by Coffey,³⁸ the study of homogenous catalysts for dehydrogenation of formic acid had not developed significantly until the impressive work by Beller³⁹ and Laurenczy⁴⁰ appeared. The merits of homogeneous catalysts for the dehydrogenation of formic acid are generally their high selectivity (i.e., without CO contamination) and mild reaction conditions compared to heterogeneous catalysts. Numerous other efficient homogenous catalysts, which in most cases require an organic amine and solvent, have been reported.⁴¹⁻⁴⁷ For example, Pidko reported the highest TOF of 257,000 h⁻¹ in DMF/NEt₃ at 90 °C catalyzed by a ruthenium-based complex, which was also the most effective catalyst for CO₂ hydrogenation.²⁴ An efficient and robust iron catalyst with a PP₃ ligand in propylene carbonate was reported by Beller.⁴³ The TON as high as 92,000 and the high TOF of 9400 h⁻¹ was obtained at 80 °C for 16 h. They also achieved continuous long-term hydrogen production toward a practical setup using the *in situ* catalyst [RuCl₂(C₆H₆)]₂/dppe in dimethyloctylamine.⁴⁸ In this system, the highest catalyst productivity (TON: 1,000,000 and TOF: 1080 h⁻¹) was performed for 45 days. Recently non-precious-metal-based catalysts such as Fe,^{43,49} Al,⁵⁰ and Ni⁵¹ were reported. In addition, attempts to develop an efficient catalyst in water without an organic additive were also attempted.^{22,40,52-55} Using iridium

complexes with N^N bidentate ligands, we have succeeded in the aqueous dehydrogenation of formic acid with high catalytic performance (vide infra).⁵⁶⁻⁵⁸

Recent success in CO₂ hydrogenation and dehydrogenation of formic acid made it possible to demonstrate a hydrogen storage/release system. In 1994, Leitner reported the first example of a hydrogen storage system that combined CO₂ hydrogenation with formic acid dehydrogenation using a rhodium-based complex with a phosphine ligand.¹⁴ Storage and release of H₂/CO₂ were controlled by the reaction pressure and temperature in NEt₃/acetone. However, until recently only a few attempts have been made at hydrogen storage using CO₂^{59,60} because a suitable catalyst that can work under mild conditions could not be exploited. In 2011, *in situ* catalysts [RuCl₂(C₆H₆)]₂/DPPM (DPPM: 1,2-bis-(diphenylphosphino)methane) were reported for CO₂ hydrogenation in H₂O/THF and dehydrogenation of formic acid in H₂O/DMF by Beller.⁶¹ Although the combination of both reactions led to a reversible hydrogen storage system, the exchange of solvent was required in each reaction. Joó demonstrated a charge/discharge device for a hydrogen storage system using [RuCl₂(TPPMS)₂]₂ (TPPMS: 3-(diphenylphosphino)-benzenesulfonate sodium salt) in aqueous solution without an organic additive.⁶² The storage of hydrogen by hydrogenation of CO₂ was carried out at 10 MPa to give formate with a yield of 90%. Subsequently, dehydrogenation at atmospheric pressure led to the release of H₂ with only 40-50% conversion of formate. Beller and Laurenczy demonstrated eight consecutive cycles of hydrogen storage/release by the [RuCl₂(DPPM)₂]-catalyzed interconversion between CO₂/H₂ and formic acid in the presence of NEt₃.⁶³ Unfortunately, addition of an amine base was required after each cycle, and slight deactivation was observed after seven cycles. Very recently, almost complete interconversion was achieved using a Ru-PNNP complex controlled by pressure in toluene/DBU at 100 °C.⁶⁴ Up to five cycles were performed without CO contamination or

degradation of storage capacity. In contrast, we demonstrated a pH-controlled hydrogen storage system combining H₂ storage under ambient conditions and high-pressure H₂ production (vide infra).⁵⁷

We first focus on previously reported iridium catalysts bearing N^N bidentate ligands for formate production by the hydrogenation of CO₂ under basic conditions. With respect to the development of our target catalyst, the necessary feature is water-solubility with no additives. In our previous work we have shown that the efficiency of the catalytic reaction is improved by increasing the electron donating strength toward the Ir center. In this Forum Article, our success in the investigation of iridium catalysts bearing a proton-responsive ligand that can enhance the catalytic activity by such an electronic effect and a pendant-base effect is reported. Additionally, a novel type of N^N-bidentate ligand consisting of a proton-responsive moiety and an azole moiety, which has the possibility to increase the electron density of Ir by its own strong electron donor performance, has been applied to the catalytic hydrogenation of CO₂.

DIHYDROXYL BIPYRIDINE AS A PROTON-RESPONSIVE LIGAND: ELECTRONIC AND PENDENT BASE EFFECTS

We have developed catalysts having pyridine and pyrimidine ligands with hydroxyl groups, which are reversibly deprotonated to generate an oxyanion (-O^-). The acid-base equilibrium of the phenolic hydroxyl groups in the pyridine and pyrimidine ring imparts some unique properties to the complexes coordinated with these ligands (Scheme 1).⁶⁵⁻⁷⁰ First, according to the Hammett substituent constant, the oxyanion generated from the deprotonation of the hydroxyl group is strongly electron-donating ($\sigma_p^+ = -2.30$). Although some complexes having hydroxyl groups were studied,⁷¹ they have not yet been applied to catalysis. Second, a phenolic hydroxyl group, which can generate an oxyanion as a polar substituent under basic conditions, has been used as a water-soluble moiety.^{72,73} Third, an oxyanion as a pendent base may form in the second coordination sphere to mimic the active site of the hydrogenases. Finally, these properties can be tuned by the solution pH. These distinct features of complexes having proton-responsive phenolic hydroxyl groups in their ligand are attractive for catalysis.⁷⁴

We have previously studied transfer hydrogenation using formic acid in water catalyzed by half-sandwich bipyridine rhodium- and iridium complexes $[\text{Cp}^*\text{M}(\text{bpy})\text{Cl}]\text{Cl}$ ($\text{M} = \text{Rh}, \text{Ir}$).⁷⁵ In this study, evolution of a H_2 and CO_2 gas mixture was observed during the course of the reaction under acidic conditions. Furthermore, by changing the pH of the solution to basic, it was found that the bipyridine complexes hydrogenated CO_2 at 4 MPa of $\text{H}_2\text{:CO}_2$ to give formate although the catalytic performance was poor. On the other hand, there are some reports that an electron-rich ligand improved the catalytic activity of the catalyst in CO_2 hydrogenation.^{12,76}

Based on our results and the existing reports mentioned above, we designed and synthesized a complex with 4,4'-dihydroxyl-2,2'-bipyridine (4DHBP) on the basis of our catalyst design concept of proton-responsive ligands that can generate a strong electron-donating oxyanion (Chart 1). The UV-vis titration of iridium aqua complex **1** and the change in absorbance at 265 nm as a function of pH are shown in Figure 2 and Figure 3a, respectively. The two absorbance changes were caused by the deprotonation of the aqua ligand and the hydroxyl groups on the bipyridine ligand. The change in the region from pH 4 to 7 accompanied by a bathochromic effect is attributed to a change in the electronic properties of the ligand by deprotonation of the hydroxyl groups. The results showed that the iridium complex will change to the oxyanion form under the reaction conditions of CO₂ hydrogenation (pH 8.3). This suitable property encouraged us to investigate CO₂ hydrogenation using the proton-responsive catalyst with 4DHBP.

In CO₂ hydrogenation, the proton-responsive complex **1** significantly improved catalytic performance compared to the bipyridine complex [Cp*Ir(bpy)(H₂O)]SO₄ (**2**) (Entries 1 vs 2 in Table 1). The electronic effect on the catalytic activity was confirmed by a Hammett plot using a series of complexes with various substituted bipyridine ligands which exhibited a good correlation between the Hammett constants (σ_p^+) and the initial TOF on a logarithmic scale (Figure 4). The catalytic activation by the electronic effect made it possible to hydrogenate CO₂ under atmospheric pressure and room temperature (Entry 3). Considerable activation by the electronic effects of the oxyanion were also observed for rhodium-, ruthenium-,^{77,78} and cobalt²⁹ complexes. It is reasonable to conclude that the strong electron-donating oxyanion generated by deprotonation of the hydroxyl group caused the catalytic activation.

We confirmed that the electronic substituent effect of the proton-responsive hydroxyl group was affected by the pH of the solution owing to equilibrium of the hydroxyl groups. In transfer hydrogenation of 2-cyclohexen-1-one in an aqueous formic acid/formate solution, the ratio of the TOF of **1** to that of the unsubstituted analog **2** was 19 at pH 2.6, while that same ratio was 1330 at pH 7.3. The change in the ratio is attributed to the status of the protonated/deprotonated hydroxyl group, i.e., its electronic effect. In fact, the shift of the pH-dependent activity of **1** relative to the methoxy analog [Cp*Ir(4,4'-OMe-2,2'-bpy)(H₂O)](SO₄) (Figure 3b) correlates well with the change in the pH-dependent absorbance of **1** (Figure 3a).⁷⁹ It was concluded that the catalytic activity of the catalyst with the proton-responsive substituents was affected by the electronic effect of the status of the protonated/deprotonated hydroxyl groups.

Furthermore, the water-solubility of catalysts with proton-responsive ligands can be tuned by the pH of the solution.⁸⁰ A recyclable self-precipitation/filtration catalyst system was achieved under optimal reaction conditions using the iridium catalyst **3** with 4,7-dihydroxy-1,10-phenanthroline as a ligand on the basis of its tunable water solubility (Figure 5). As the CO₂ hydrogenation reaction proceeded, the pH of the reaction solution gradually decreased by consumption of the base. At the end of the reaction, the pH of the solution was approximately 5. Examination of the pH-dependent water solubility in formate solution showed that complex **3** was negligibly soluble (~ 100 ppb) at pH 5 (i.e., similar to the pH of the solution at the end of the reaction) and highly soluble at pH above 7.5 (i.e., similar to the pH of the solution at the beginning of the reaction). When the reaction was carried out using complex **3** in 0.1 M KOH at 6 MPa and 60 °C, the catalyst was spontaneously precipitated at the end of the reaction and could be recovered at the high efficiency of 93% simply via filtration. Moreover, the pure product (HCO₂K) could be obtained by evaporating the water. The recovered catalyst retained activity

for four cycles. The three components (i.e., catalyst, product, and solvent) in the reaction solution can all be easily separated by filtration and evaporation without waste generation.

The understanding of the pendent amine effect in hydrogenase⁸¹ provided a bio-inspired catalyst-design concept for reversible H₂ oxidation (i.e., H₂ heterolysis and generation) through a hydrogen bonding interaction and a second coordination sphere interaction involving the hydroxyl moieties. We also examined the positional effects of the hydroxyl groups by placing them at 3,3'-, 4,4'-, 5,5'- and 6,6'-positions on the catalytic activities for CO₂ hydrogenation, formic acid dehydrogenation, and transfer hydrogenation of cyclohexanone and 2-cyclohexen-1-one using formate/formic acid as a hydrogen source at pH 7.2 and 2.6, respectively.⁸² Surprisingly, the transfer of hydroxyl groups from the *para* to the *ortho* position significantly improved catalytic performance for CO₂ hydrogenation (Entries 6 and 7).^{83,84} It was found that the formation of the corresponding hydride complex from *ortho*-positioned complex **4** was much faster than that of the *para*-positioned complex **1** under basic conditions. The difference in the activities could be explained by clear evidence of an experimental kinetic isotopic effect and theoretical DFT calculations.^{84,85} The results of the kinetic isotopic effect strongly suggested that a water molecule was involved in the rate-limiting heterolysis of H₂ through a second coordination sphere interaction in **4**.⁸³ Accordingly, the water molecule may form hydrogen bonds with the approaching H₂ along the reaction coordinate for heterolysis and the pendent base (i.e., oxyanion) (Scheme 2). Furthermore, DFT calculations demonstrated that participation of a water molecule in a proton-relay could stabilize the transition state and facilitate the heterolysis of the hydrogen molecule.^{84,85} Consequently, we obtained useful information regarding the efficient formation of the hydride complex as an active species in CO₂ hydrogenation.

We examined the tetrahydroxyl-substituted mononuclear complex **5** and dinuclear complex **6**, in order to evaluate the synergistic effects of the electronic and pendent-base effects.⁵⁷ In particular, the dinuclear catalyst **6** showed unprecedented catalytic performance under ambient conditions (TON of up to 7200 (Entry 9) and TOF of up to 70 h⁻¹ (Entry 10)). The modification based on our catalyst design concept leads to more than a 10,000-fold activation over the unsubstituted complex **2** for CO₂ hydrogenation. Comparison between mononuclear and dinuclear complexes with four hydroxyl groups shows that the catalytic activity for CO₂ hydrogenation is not significantly affected by the number of metal centers.

The newly-developed proton-responsive catalysts can be applied to the dehydrogenation of formic acid under acidic conditions as the reverse reaction of CO₂ hydrogenation under basic conditions (Table 2). It was found that the salient features of the catalysis using the iridium complexes with the bipyridine derivatives were efficient, producing CO-free H₂ without an organic additive. Furthermore, high pressure H₂ can be supplied when the catalysis is carried out in a closed reaction vessel. Similar to their role in CO₂ hydrogenation, the electron-donating substituents enhanced the catalytic activity in the dehydrogenation of formic acid. Since the proton-responsive substituents will be in their protonated form under acidic conditions, the TOF of **1** showed 80 times higher activity than that of **2** by the electronic effect of the hydroxyl group ($\sigma_p^+ = -0.91$) (Entries 1 vs 2).⁵⁶ Complex **4**, in which the hydroxyl groups are transferred from the *para*-positions to the *ortho*-positions, improved catalytic performance and exhibited a different pH-dependence, which is explained by the pendent-base effect through kinetic isotopic effect studies (entries 3 and 4).⁸⁶ The tetrahydroxyl-substituted complex **6** provided the highest TOF for dehydrogenation of formic acid in aqueous media without an organic additive (Entries 7

and 8).⁵⁷ It was clarified that the electronic and pendent-base effects played useful roles in the catalyst for CO₂ hydrogenation as well as dehydrogenation of formic acid in aqueous media.

Reversible and recyclable hydrogen storage was achieved using complex **6**, which is pH-switchable between CO₂ hydrogenation and dehydrogenation of formic acid (Figure 6). In a proof of concept study, H₂ storage by CO₂ hydrogenation was carried out in 2 M KHCO₃ under atmospheric pressure of a 1:1 CO₂: H₂ gas mixture to give 0.48 M formate. The reaction solution was acidified to protonate the catalyst. Warming the solution in a glass autoclave led to H₂ release and resulted in a final pressure of 2.3 MPa without CO contamination. The cycle could be repeated by alkalization. This reversible and recyclable system demonstrated that atmospheric H₂ gas can be stored as aqueous formate, and then high-pressure CO₂ and H₂ gas without CO contamination can be regenerated for a possible fuel application.

CO₂ HYDROGENATION USING AZOLE-TYPE CATALYSTS

Previously, we have reported that azole-type iridium complexes **7-10** (Chart 2) catalyze the dehydrogenation of formic acid with high efficiency.⁵⁸ Especially, the activities of bisimidazole complexes **9** and **10** were higher than the proton-responsive catalysts with bipyridine derivatives such as **1** and **4**.^{56,86} The reason why azole-type complexes were effective for the dehydrogenation is explained below. We reported that electron donation to the Ir center affects the catalytic activity for the hydrogenation of CO₂ and dehydrogenation of formic acid, and a highly electron-donating ligand promoted catalytic efficiency. The π -electron rich azole-type complexes have considerable electron density even in their unsubstituted form, so the N-donor ability of azole is higher than that of pyridine, which results in the enhancement of catalytic activity.

Therefore, we evaluated the catalytic activities of the azole-type complexes in CO₂ hydrogenation (Table 3). By the replacement of one pyridine ring by an imidazole ring, the activity for pyridylimidazole complex **7** was significantly improved compared with bipyridine complex **2** (Entries 1 vs 2). Pyridylpyrazole complex **8** was also more effective than **2** (Entry 3). The results showed that the azole ring is more effective than the pyridine ring for the hydrogenation of CO₂. Consequently, we synthesized bisimidazole complex **9**, which showed a TON of 20 (Entry 4). Furthermore, incorporating four methyl groups as electron-donating groups to the bisimidazol ligand significantly improved the activity (Entry 5), clearly indicating the effect of increasing the electron donation ability of the ligand. This tendency is consistent with the case of dehydrogenation of formic acid. However, the activities of the azole-type complexes were lower than that of the proton-responsive complex **1**. Due to the high pK_a (8.8) of protonic

NH on the imidazol ligand in **10**,⁵⁸ it seems that the limited increase of the electron-donation by deprotonation led to the some activation of the catalyst under the reaction conditions.

On the basis of our catalyst-design concept, the hydroxyl substituents were incorporated into the ligands.⁸⁷ The novel complexes **11-13** with hydroxyl groups on a pyridine or pyrimidine moiety linked with an azole moiety were newly synthesized by the reaction of [Cp*Ir(OH₂)₃]SO₄ with the corresponding ligands in good yield and identified by ¹H, ¹³C NMR and elemental analysis (Chart 3). The detailed preparation of ligands and the corresponding Ir complexes are described in the SI. The hydroxyl groups can be deprotonated and protonated reversibly. The UV-vis titration of complex **11** in Figure 7 showed a bathochromic effect in the region from 3 to 6, which is attributed to a change in the electronic properties of the ligand by deprotonation of the hydroxyl groups. The p*K*_a of complex **11** (3.9) was slightly lower than that of analogue **6**.⁸²

The results for hydrogenation of CO₂ catalyzed by **11-13** are shown in Table 4. All reactions were carried out in aqueous solution without organic additives. The hydroxyl-pyridine complexes **11** outperformed the non-proton-responsive complexes with the azole-type ligands **7-10** under similar reaction conditions (1 MPa, H₂/CO₂ = 1:1, 50 °C, 1 h). This finding is consistent with our previous results that the hydroxyl group as an electron donating substituent was effective for CO₂ hydrogenation under basic conditions. Furthermore, the dihydroxyl-pyrimidine complexes **12** and **13** were more effective than hydroxyl-pyridine complex **11** (Entries 3 *vs* 4 and 8). As expected, the ligands containing multiple hydroxyl groups were effective for catalyzing the reaction.

The N-positional effect of the pyrimidine ring was shown in the complexes **12 vs 13**. The TON of **13** was approximately 1.5 times higher than that of **12** (Entries 4 *vs* 8). However, as

mentioned below, while **12** showed good temperature tolerance (Entries 5-7), **13** decomposed to an inactive species above 80 °C (Entries 12-13). Nevertheless, the difference in N-position on the pyrimidine ring was demonstrated to affect catalytic activity.

In order to build an optimal reaction system, we carried out the hydrogenation of CO₂ under various conditions including temperature, gas pressure, and reaction time using **13**. First, the temperature dependence was examined. The reaction at 80 °C resulted in a TON of 2090 (Entry 12). The fact that the TON value at 100 °C was lower than that at 80 °C suggests that the catalyst decomposes above 80 °C. Next, the pressure dependence was examined. As expected, the most effective result was obtained at the highest pressure (Entry 15). Additionally, prolongation of reaction time increased the TON (1230 to 8080) (Entries 16-18). In the case of catalyst **12**, the TON value escalated with the increase of reaction time as well as catalyst **13** (Entries 8-10).

The efficiency of catalytic hydrogenation of CO₂ increases with an increase in the number of hydroxyl groups on the bidentate (or bridging) ligand, so in order to maximally activate this catalyst system it may be useful to add additional hydroxyl groups to N^N-bidentate ligands that already showed a strong electron donation ability and pendant base effect. Therefore, in order to develop an “industrial strength” catalyst for the hydrogenation of CO₂, a further refinement of catalyst structure is needed. Our future work will synthesize novel ligands incorporating many hydroxyl groups on the azole moiety.

CONCLUSIONS

In this paper, we demonstrated that the hydrogenation of CO₂ was efficiently catalyzed by iridium complexes with various N^N-bidentate ligands, and we assessed the effect of the hydroxyl groups as proton-responsive substituents. The hydroxyl groups played an important role in tuning the strength of electron donation from an N-atom on the ligand toward the Ir center at various solution pH. By biasing toward basic conditions, the strong electron-donating oxyanion enhanced catalytic activity. Furthermore, the hydroxyl groups also worked to help the access of H₂ molecules toward the Ir center by a pendant-base effect through a proton relay. In particular, a bipyrimidine complex with four hydroxyl groups showed excellent catalytic activity from these synergistic effects. Additionally, it can be said that newly designed azole-type complexes were quite promising for CO₂ hydrogenation. It was found that the introduction of hydroxyl groups into these ligands enhanced catalytic activity. As for a pyrimidine ring, the effect of the N-position on the ring toward catalytic activity was observed. Further investigation focusing on the introduction of hydroxyl groups into ligands continues in order to develop even more effective catalysts for CO₂ hydrogenation.

EXPERIMENTAL SECTION

General. ¹H NMR spectra were recorded at 25 °C on a Bruker Avance operating at 400 MHz, where chemical shifts were determined with respect to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as an internal reference in D₂O. ESI-MS data were collected on a Waters Micromass ZQ Mass Spectrometer with a 2695/2795 HPLC Separations Module. Elemental analyses were performed using a CE Instruments EA1110. Mixed gas (CO₂/H₂ = 1/1) was used for CO₂ hydrogenation. Formate concentrations were monitored by a Tosoh HPLC

system equipped with an anion-exclusion column (Tosoh TSKgel SCX(H⁺)) and a UV detector ($\lambda = 210$ nm), using an aqueous H₃PO₄ solution (20 mM) as an eluent. The preparation procedures for complexes **11-12** are submitted to elsewhere.

Hydrogenation of CO₂ (Standard Method). To a KHCO₃ aqueous solution (2.0 M, pH 8.5, 10 mL) was added complexes as a solid. Then the mixture was degassed by three cycles of Freeze-Pump-Thaw in a flask and was transferred into a stainless autoclave. After 10 min. stabilization at 50 °C under 1.0 MPa of H₂/CO₂ (1/1) gas, the reaction was started by stirring (1500 rpm). The stirring was stopped after 1 h and the pressurized gas was released to measure the concentration of formate in the resulting solution by HPLC.

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Notes

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Figure 1. Hydrogen storage system by interconversion between CO_2 and formic acid

Figure 2. UV-Vis absorption spectra of **1** in a pH titration. Curves 1, 2, 3, 4, 5, 6, 7, 8, and 9 were obtained at pH 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 8.0, 9.0, and 10.0, respectively.

Figure 3. Correlation between (a) absorbance change of **1** at 265 nm as a function of pH (red closed squares); (b) TOF ratio of **1** vs. the methoxy analog as a function of pH on a logarithmic scale (blue closed circles).

Figure 4. Correlation between σ_p^+ values of substituent (R = H, CO_2H , Me, OMe, OH) and initial TOF in CO_2 hydrogenation at 1 MPa ($\text{H}_2/\text{CO}_2 = 1/1$) in 1 M KOH aqueous solution at 80 °C using iridium catalysts (M = Ir, n = 5).⁷⁸

Figure 5. The recycling system of hydrogenation of CO₂ using **3** via spontaneous precipitation.

Figure 6. Reversible and recyclable hydrogen storage: The hydrogenation was carried out under atmospheric conditions (0.1 MPa, 30 °C), and the dehydrogenation proceeded in a closed system to provide pressurized gas (2.3 MPa): (1) hydrogenation of CO₂/bicarbonate, (2) acidification by the addition of sulfuric acid, (3) dehydrogenation of FA, and (4) addition of solid KHCO₃ to start the next run.

Figure 7 (a) UV-vis absorption spectra of complex **11** in a pH titration and (b) absorbance changes at single wavelengths (315 and 350 nm) as a function of pH, Boltzmann fits are depicted.

Table 1. Hydrogenation of CO₂ Catalyzed by Iridium Catalysts

Entry	Catal. / μM	Time / h	P / MPa	T / °C	Initial TOF / h ⁻¹	TON	Final. Conc. Formate / M	ref
1	2 / 200	30 ^a	1.0	80	4.5	125	0.023	⁷⁸
2	1 / 20	30 ^a	1.0	80	5100	11000	0.220	⁷⁸
3	1 / 50	24 ^b	0.1	25	7	92	0.005	⁵⁷
4	4 / 20	9 ^b	1.0	50	1650	5150	0.103	⁸³
5	4 / 50	33 ^b	0.1	25	27	330	0.016	⁸³
6	5 / 20	8 ^b	1.0	50	3060	28000	0.560	⁸⁴
7	5 / 50	24 ^b	0.1	25	66	193	0.009	⁸⁴
8	6 / 20	8 ^b	1.0	50	4200	24000	0.480	⁸³
9	6 / 50	336 ^b	0.1	25	64	7200	0.360	⁵⁷
10	6 / 250	216 ^c	0.1	25	70	2230	0.560	⁵⁷

^a 1 M KOH aq., ^b 1 M NaHCO₃ aq., ^c 2 M KHCO₃ aq.

Table 2. Dehydrogenation of Formic Acid Catalyzed by Iridium Catalysts

Entry	Catal. / μM	Time / h	pH	T / °C	Initial TOF / h ⁻¹	Conv. / %	ref
1	2 / 200	12	1.7	60	30	-	⁵⁶
2	1 / 200	4	1.7	60	2400	100	⁵⁶
3	4 / 100	8	1.7	60	2450	100	⁸⁶
4	4 / 100	4.5	3.5	60	5440	46	⁸⁶
5	5 / 100	6	3.5	60	12,200	37	⁸⁶
6	6 / 50	4	1.7	60	12,000	100	⁵⁷
7	6 / 50	18	3.5	60	31,600	84	⁵⁷
8	6 / 3.1	7	3.5	90	228,000	52	⁵⁷

The reaction was carried out in 1 M formic acid/sodium formate solution.

Table 3. Hydrogenation of CO₂ using Azole Complexes^a

Entry	Catalyst	Conc. Cat. / μM	Average TOF for 1 h / h ⁻¹	Ref.
1	2	500	1	82
2	7	400	9	58
3	8	500	26	58
4	9	500	20	58
5	10	500	87	58

^a The reaction was carried out for 1 h in 10 mL of 2.0 M KHCO₃ aqueous solution (pH 8.5) at 50 °C under 1.0 MPa H₂/CO₂ (1/1) with stirring (1500 rpm).

Table 4. Hydrogenation of CO₂ using Proton-Responsive Catalysts^a

Entry	Catalyst	Pressure/ MPa	Temp / °C	Average TOF for 1 h / h ⁻¹	Ref.
1	1	1.0	50	650	⁸²
2	4	1.0	50	1400	⁸²
3	11	1.0	50	388	This work
4	12	1.0	50	440	This work
5	12	1.0	80	4050	This work
6	12	1.0	100	5990	This work
7	12	1.0	120	6440	This work
8	12	1.0	50	(1290) ^b	This work
9	12	1.0	50	(6360) ^c	This work
10	12	1.0	50	(7680) ^d	This work
11	13	1.0	50	637	This work
12	13	1.0	80	2090	This work
13	13	1.0	100	610	This work
14	13	0.5	50	372	This work
15	13	2.0	50	1080	This work
16	13	1.0	50	(1230) ^b	This work
17	13	1.0	50	(6920) ^c	This work
18	13	1.0	50	(8080) ^d	This work

^a The reaction was carried out for 1 h in 10 mL of 20 μM catalyst in 2.0 M KHCO₃ aqueous solution (pH 8.5). ^b The reaction was carried out for 2 h. Value in parentheses is total TON. ^c The reaction was carried out for 24 h. Value in parentheses is total TON. ^d The reaction was carried out for 48 h. Value in parentheses is total TON.

Scheme 1. Acid-Base Equilibria of Complex with 4,4'-Dihydroxy-2,2'-Bipyridine

Scheme 2. Proposed Mechanism for Heterolysis of Hydrogen Molecule by Pendent Base Effect through Proton-Relay with Water Assist.

Chart 1. Iridium Complexes with Proton-Responsive Ligands

Chart 2. Iridium Complexes with Azole-type Ligands

Chart 3. Iridium Complexes with Hydroxyl Substituted Ligands

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