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CO_2 Hydrogenation Catalyzed by Iridium Complexes with a Proton-Responsive Ligand

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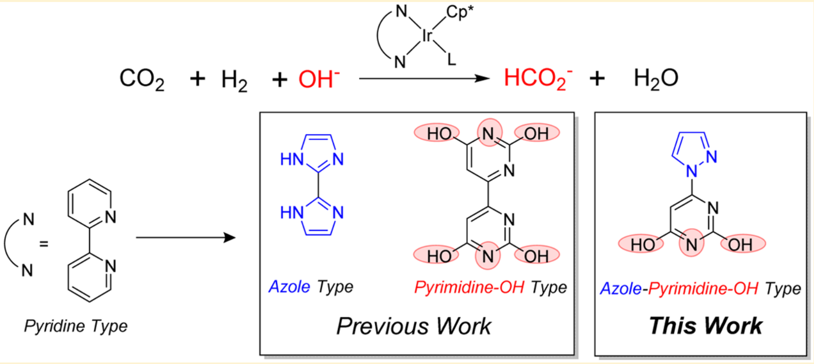

ABSTRACT: The catalytic cycle for the production of formic acid by CO_2 hydrogenation and the reverse reaction have received renewed attention because they are viewed as offering a viable scheme for hydrogen storage and release. In this Forum Article, CO_2 hydrogenation catalyzed by iridium complexes bearing sophisticated N^N-bidentate ligands is reported. We describe how a ligand containing hydroxy groups as proton-responsive substituents enhances the catalytic performance by an electronic effect of the oxyanions and a pendent-base effect through secondary coordination sphere interactions. In particular, $[(Cp^*IrCl)_2(TH2BPM)]Cl_2$ (Cp* = pentamethylcyclopentadienyl; TH2BPM = 4,4′,6,6′-tetrahydroxy-2,2′-bipyrimidine) enormously promotes the catalytic hydrogenation of CO_2 in basic water by these synergistic effects under atmospheric pressure and at room temperature. Additionally, newly designed complexes with azole-type ligands were applied to CO_2 hydrogenation. The catalytic efficiencies of the azole-type complexes were much higher than that of the unsubstituted bipyridine complex $[Cp^*Ir(bpy)(OH_2)]SO_4$. Furthermore, the introduction of one or more hydroxy groups into ligands such as 2-pyrazolyl-6-hydroxypyridine, 2-pyrazolyl-4,6-dihydroxypyrimidine, and 4-pyrazolyl-2,6-dihydroxypyrimidine enhanced the catalytic activity. It is clear that the incorporation of additional electron-donating functionalities into proton-responsive azole-type ligands is effective for promoting further enhanced hydrogenation of CO_2.

■ INTRODUCTION

Carbon dioxide (CO_2) emissions from the combustion of fossil fuels have increased recently owing to rising energy consumption in the world. Therefore, the conversion of thermodynamically stable CO_2 into useful materials has become a challenging research area. Mimicking the carbon cycle in nature, the reduction of CO_2 to 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 the activation of CO_2 molecules.[1−4]

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.[5] 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.[6,7] At the moment, ammonia borane,[8] organic hydrides,[9] and formic acid[7] are considered as hydrogen storage media. 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 CO_2 in aqueous solution with only a slight free-energy change ($\Delta G°_{298} = -4$ kJ/mol). To exploit these advantages, the combination of

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CO_2 hydrogenation with the dehydrogenation of formic acid for H_2 generation under mild conditions is essential for the development of a hydrogen storage cycle. Furthermore, because CO_2 is an abundant and cheap resourse, we view formic acid, synthesized by CO_2 hydrogenation, as a better hydrogen storage medium than any other proposed alternative.

The interconversion (reversible reaction) between CO_2 and formic acid in aqueous solution (Figure 1) is strongly affected by the pH value (eq 1). In the hydrogenation of CO_2, 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. However, previous "conventional" hydrogenation catalysts have required high pressure, high temperature, and some organic additives such as amines.[10−12] 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.

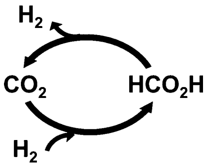

Figure 1. Hydrogen storage system by interconversion between CO_2 and formic acid.

$$CO_2 + H_2 \leftrightarrows HCO_2H \tag{1}$$

$$CO_2 + H_2 + OH^- \rightarrow HCO_2^- + H_2O \tag{2}$$

Since CO_2 hydrogenation using homogeneous catalysts was reported by Inoue et al. in 1976,[13] many chemists have pursued the development of more efficient catalysts.[14−18] To improve the catalyst performance, systematic investigations using rhodium- and ruthenium-based complexes with phosphine ligands in the presence of an organic base were reported by Jessop et al.[14,19−22] and Leitner et al.[15,23] Aqueous catalysis without organic additives was first achieved by Joó et al.[24,25] Recently, the structure−reactivity relationship of a pyridinylazolate ligand using a ruthenium-based complex has been investigated by Thiel et al.[26] Very recently, Laurenczy reported the base-free production of highly concentrated formic acid (>1.9 M) catalyzed by a ruthenium 1,3,5-triaza-7-phosphaadamantane complex in dimethyl sulfoxide at 10 MPa.[27] 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,[24,28] we found that the electronic effect of a substituent in a N^N bidentate ligand significantly improved the catalytic activity in aqueous solution (vide infra).[29] Several iridium complexes for efficient CO_2 hydrogenation have been reported as aqueous catalysts without the use of an organic additive.[30,31]

In 2009, Nozaki et al. reported that an iridium trihydride complex with a PNP pincer-type ligand effectively hydrogenated CO_2 to formate with a turnover frequency (TOF) of 150000 h^{-1} at 200 °C and a turnover number (TON) of 3500000 at 120 °C in H_2O/tetrahydrofuran (THF; 5:1) under 8 MPa. After that, iridium complexes with a pincer-type ligand became widely used as catalysts for CO_2 hydrogenation. Hazari et al. reported a PNP pincer-type iridium complex with a hydrogen-bond donor that can form a secondary coordination sphere.[32] That analogue exhibited a TON of 348000 and a TOF of 18780 h^{-1} at 185 °C under 5.5 MPa. A ruthenium complex with a PNP pincer-type ligand provided the highest TOF value of 1100000 h^{-1} at 120 °C under 4 MPa in CO_2 hydrogenation as well as in the dehydrogenation of formic acid (vide infra), although catalysis was carried out in *N*,*N*-dimethylformamide (DMF) in the presence of an organic amine.[33]

The development of non-precious-metal-based catalysts has also been pursued since the pioneering work by Inoue et al.[13] Beller et al. reported iron[34,35] and cobalt[36] complexes with tetradentate ligands [PP_3 = $P(CH_2CH_2PPh_2)_3$]. The well-defined cobalt−dihydrogen complex provided a TON of 3877 in 20 h in an aqueous methanol (MeOH) solution at 120 °C under 6 MPa. Efficient CO_2 hydrogenation catalyzed by $Co(dmpe)_2H$ [dmpe = 1,2-bis(dimethylphosphino)ethane] was achieved by Linehan et al.[37] Although catalysis showed a remarkable TOF of 3400 h^{-1} at room temperature and atmospheric pressure of CO_2/H_2 (1:1) in THF, a superstrong base (i.e., Verkade's base; pK_a = 33.7) was required as a sacrificial reagent for the cobalt catalyst regeneration step. Fujita et al. reported aqueous CO_2 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.[38] An iron complex with a pincer-type ligand reported by Milstein et al. resulted in a TON of 788 at 1 MPa and 80 °C in H_2O/THF (10:1).[39] This high activity under low pressures implied an enormous potential for non-precious-metal-based catalysts.

Meanwhile, Peris et al. reported transfer hydrogenation of CO_2 to formate using *i*PrOH as a hydrogen donor catalyzed by water-soluble iridium complexes with a N-heterocyclic carbene.[40−42] Afterward, the production of formate by transfer hydrogenation of CO_2 using MeOH in aqueous media was reported by Beller et al.[43] 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 CO_2 hydrogenation is essential to a hydrogen storage system using formic acid.[44−46] However, since the pioneering work by Coffey,[47] the study of homogeneous catalysts for the dehydrogenation of formic acid had not developed significantly until the impressive work by Beller et al.[48] and Laurenczy et al.[49] 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 those of heterogeneous catalysts. Numerous other efficient homogeneous catalysts, which in most cases require an organic amine and solvent, have been reported.[50−56] For example, Pidko et al. reported the highest TOF of 257000 h^{-1} in DMF/NEt_3 at 90 °C catalyzed by a ruthenium-based complex, which was also the most effective catalyst for CO_2 hydrogenation.[33] An efficient and robust iron catalyst with a PP_3 ligand in propylene carbonate was reported by Beller et al.[52] A TON as high as 92000 and the high TOF of 9400 h^{-1} were obtained at 80 °C for 16 h. They also achieved continuous long-term hydrogen production toward a practical system using the in situ catalyst $[RuCl_2(C_6H_6)]_2$/dppe in

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dimethyloctylamine.[57] In this system, the highest catalyst productivity (TON = 1000000 and TOF = 1080 h^{-1}) was performed for 45 days. Recently, non-precious-metal-based catalysts incorporating iron,[52,58] aluminum,[59] and nickel[60] were reported. In addition, attempts to develop an efficient catalyst in water without an organic additive were also made.[31,49,61−64] Using iridium complexes with N^N bidentate ligands, we have succeeded in the aqueous dehydrogenation of formic acid with high catalytic performance (vide infra).[65−67]

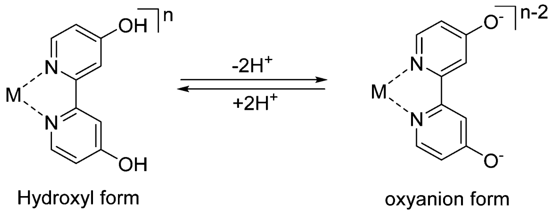
Recent success in CO_2 hydrogenation and the dehydrogenation of formic acid made it possible to demonstrate a hydrogen storage/release system. In 1994, Leitner et al. reported the first example of a hydrogen storage system that combined CO_2 hydrogenation with formic acid and dehydrogenation using a rhodium-based complex with a phosphine ligand.[23] Storage and release of H_2/CO_2 were controlled by the reaction pressure and temperature in NEt_3/acetone. However, until recently only a few attempts have been made at hydrogen storage using CO_2[68,69] because a suitable catalyst that can work under mild conditions could not be exploited. In 2011, in situ catalysts $[RuCl_2(C_6H_6)]_2$/1,2-bis(diphenylphosphino)methane (DPPM) were reported for CO_2 hydrogenation in H_2O/THF and the dehydrogenation of formic acid in H_2O/DMF by Beller et al.[70] Although the combination of both reactions led to a reversible hydrogen storage system, an exchange of solvent was required for each reaction. Joó et al. demonstrated a charge/discharge device for a hydrogen storage system using $[RuCl_2(TPPMS)_2]_2$ [TPPMS = 3-(diphenylphosphino)-benzenesulfonate sodium salt] in aqueous solution without an organic additive.[71] The storage of hydrogen by hydrogenation of CO_2 was carried out at 10 MPa to give formate with a yield of 90%. Subsequently, dehydrogenation at atmospheric pressure led to the release of H_2 with only 40−50% conversion of formate. Beller et al. demonstrated eight consecutive cycles of hydrogen storage/release by the $[RuCl_2(DPPM)_2]$-catalyzed interconversion between CO_2/H_2 and formic acid in the presence of NEt_3.[11] Unfortunately, the 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/1,8-diazabicyclo[5.4.0]-undec-7-ene at 100 °C.[12] Up to five cycles were performed without CO contamination or degradation of the storage capacity. In contrast, we demonstrated a pH-controlled hydrogen storage system combining H_2 storage under ambient conditions and high-pressure H_2 production (vide infra).[66]

We first focus on previously reported iridium catalysts bearing N^N bidentate ligands for formate production by the hydrogenation of CO_2 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 iridium 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 pendent-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 of increasing the electron density of iridium by its own strong electron donor performance, has been applied to the catalytic hydrogenation of CO_2.

RESULTS AND DISCUSSION

Dihydroxybipyridine as a Proton-Responsive Ligand: Electronic and Pendent-Base Effects. We have developed catalysts having pyridine and pyrimidine ligands with hydroxy groups that are reversibly deprotonated to generate an oxyanion (O^-). The acid−base equilibrium of the phenolic hydroxy groups in the pyridine and pyrimidine ring imparts some unique properties to the complexes coordinated with these ligands (Scheme 1).[72−77] First, according to the Hammett substituent constant, the oxyanion generated from deprotonation of the hydroxy group is strongly electron-donating ($\sigma_p^+ = -2.30$). Although some complexes having hydroxy groups were studied,[78] they have not yet been applied to catalysis. Second, a phenolic hydroxy group, which can generate an oxyanion as a polar substituent under basic conditions, has been used as a water-soluble moiety.[79,80] 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 hydroxy groups in their ligand are attractive for catalysis.[81]

Scheme 1. Acid−Base Equilibria of a Complex with 4DHBP



We have previously studied transfer hydrogenation using formic acid in water catalyzed by half-sandwich bipyridinylrhodium and -iridium complexes [Cp*M(bpy)Cl]Cl (M = Rh, Ir).[82] In this study, the evolution of a H_2 and CO_2 gas mixture was observed during the course of the reaction under acidic conditions. Furthermore, when the pH of the solution was changed to basic, it was found that the bipyridine complexes hydrogenated CO_2 at 4 MPa of H_2/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.[21,83]

On the basis of our results and the existing reports mentioned above, we designed and synthesized a complex with 4,4′-dihydroxy-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). UV−vis titration of iridium aqua complex **1** and the change in absorbance at 265 nm as a function of the pH are shown in Figures 2 and 3a, respectively. The two absorbance changes were caused by deprotonation of the hydroxy groups on the bipyridine and aqua ligands. 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 hydroxy groups. The results showed that the iridium complex will change to the oxyanion form under the reaction conditions of CO_2 hydrogenation (pH 8.3). This suitable property encouraged us to investigate CO_2 hydrogenation using the proton-responsive catalyst with 4DHBP.

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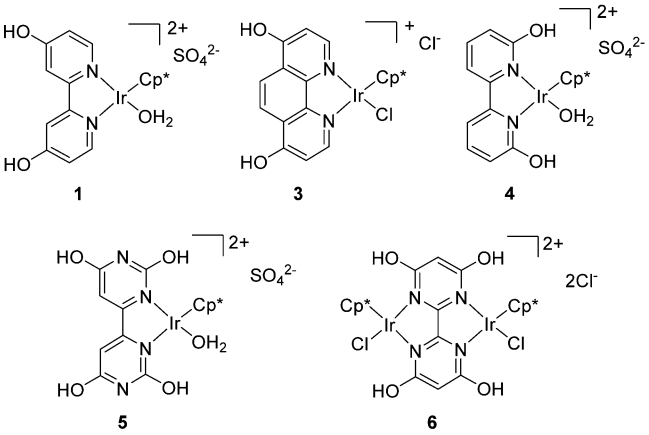
Chart 1. Iridium Complexes with Proton-Responsive Ligands



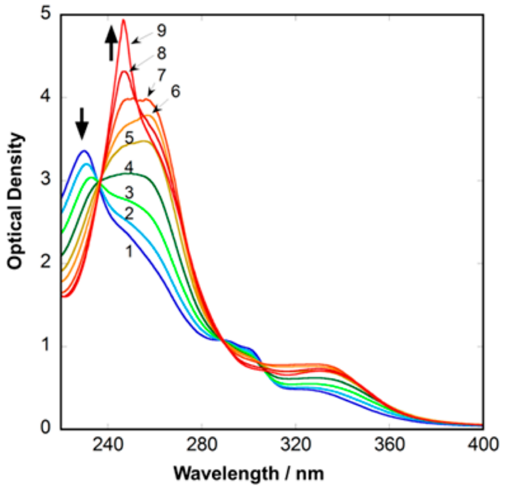


Figure 2. UV−vis absorption spectra of **1** in pH titration. Curves 1−9 were obtained at pH 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 8.0, 9.0, and 10.0, respectively.

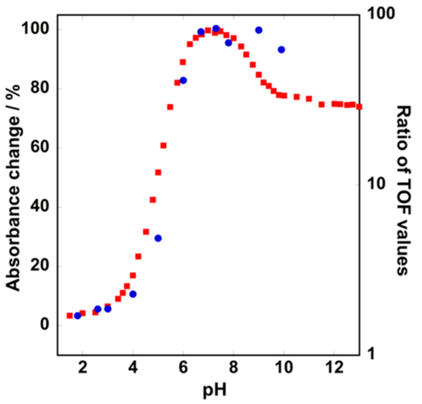


Figure 3. Correlation between (a) the absorbance change of **1** at 265 nm as a function of the pH (red closed squares) and (b) the TOF ratio of **1** versus the methoxy analogue as a function of the pH on a logarithmic scale (blue closed circles).

In CO_2 hydrogenation, the proton-responsive complex **1** has significantly improved the catalytic performance compared to the bipyridine complex $[Cp^*Ir(bpy)(H_2O)]SO_4$ (**2**; entry 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 that 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 CO_2 under atmospheric pressure and room temperature (entry 3). Considerable activation by the electronic effects of the oxyanion was also observed for the analogous rhodium, ruthenium,[84,85] and cobalt[38] complexes. It is reasonable to conclude that the strong electron-donating oxyanion generated by deprotonation of the hydroxy group caused catalytic activation.

We confirmed that the electronic substituent effect of the proton-responsive hydroxy group was affected by the pH of the solution owing to equilibrium of the hydroxy 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 analogue **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 hydroxy group, i.e., its electronic effect. In fact, the shift of the pH-dependent activity of **1** relative to the methoxy analogue $[Cp^*Ir(4,4'\text{-}(OMe)_2\text{-}2,2'\text{-bpy})(H_2O)](SO_4)$ (Figure 3b) correlates well with the change in the pH-dependent absorbance of **1** (Figure 3a).[86] 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 hydroxy groups.

Furthermore, the water solubility of catalysts with proton-responsive ligands can be tuned by the pH of the solution.[87] A recyclable self-precipitation/filtration catalyst system was achieved under optimal reaction conditions using the iridium catalyst **3** with 4,7-dihydroxy-1,10-phenenthroline as a ligand on the basis of its tunable water solubility (Figure 5). As the CO_2 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 a 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 above pH 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 a high efficiency of 93% simply via filtration. Moreover, the pure product (HCO_2K) could be obtained by evaporating the water. The recovered catalyst retained the 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 hydrogenase[88] provided a bioinspired catalyst design concept for reversible H_2 oxidation (i.e., H_2 heterolysis and generation) through a hydrogen-bonding interaction and a second coordination sphere interaction involving the hydroxy moieties. We also examined the positional effects of the hydroxy groups by placing them at the 3,3′, 4,4′, 5,5′, and 6,6′ positions on the catalytic activities for CO_2 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.[89] Surprisingly, the transfer of hydroxy groups from the para position to the ortho position significantly improved the catalytic performance

Table 1. Hydrogenation of CO_2 Catalyzed by Iridium Catalysts

entry	catalyst/μM	time (h)	*P* (MPa)	*T* (°C)	initial TOF (h^{-1})	TON	final concn of formate (M)	ref
1	**2**/200	30[b]	1.0	80	4.5	125	0.023	85
2	**1**/20	30[b]	1.0	80	5100	11000	0.220	85
3	**1**/50	24[c]	0.1	25	7	92	0.005	66
4	**4**/20	9[c]	1.0	50	1650	5150	0.103	90
5	**4**/50	33[c]	0.1	25	27	330	0.016	90
6	**5**/20	8[c]	1.0	50	3060	28000	0.560	91
7	**5**/50	24[c]	0.1	25	66	193	0.009	91
8	**6**[a]/20	8[c]	1.0	50	4200	24000	0.480	90
9	**6**[a]/50	336[d]	0.1	25	64	7200	0.360	66
10	**6**[a]/250	216[d]	0.1	25	70	2230	0.560	66

[a] The bimetallic complex **6** concentration was calculated by 1 mol of **6** (which includes two iridium metals) divided by the solvent volume. [b] 1 M aqueous KOH. [c] 1 M aqueous $NaHCO_3$. [d] 2 M aqueous $KHCO_3$.

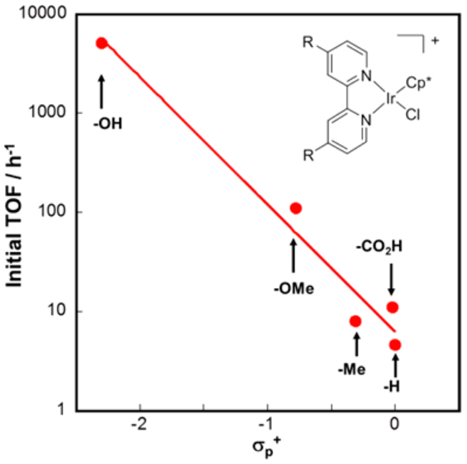


Figure 4. Correlation between the σ_p^+ values of the substituent (R = H, CO_2H, Me, OMe, OH) and the initial TOF in CO_2 hydrogenation at 1 MPa ($H_2/CO_2 = 1/1$) in a 1 M KOH aqueous solution at 80 °C using iridium catalysts (M = Ir; *n* = 5).[85]

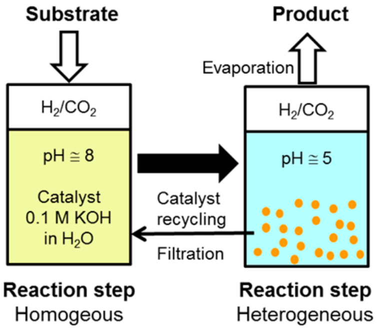
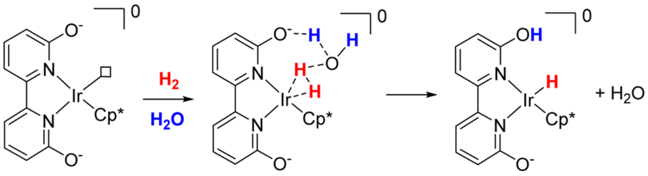


Figure 5. Recycling system of hydrogenation of CO_2 using **3** via spontaneous precipitation.

for CO_2 hydrogenation (entries 3 and 5).[90,91] It was found that 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.[91,92] The results of the kinetic isotopic effect strongly suggested that a water molecule was involved in the rate-limiting heterolysis of H_2 through a second coordination sphere interaction in **4**.[90] Accordingly, along the reaction coordinate for heterolysis, the water molecule may form hydrogen bonds with the approaching H_2 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 heterolysis of the hydrogen molecule.[91,92] Consequently, we obtained useful information regarding efficient formation of the hydride complex as an active species in CO_2 hydrogenation.

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



We examined the tetrahydroxy-substituted mononuclear complex **5** and dinuclear complex **6**, in order to evaluate the synergistic effects of the electronic and pendent-base effects.[66] 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 10000-fold activation over the unsubstituted complex **2** for CO_2 hydrogenation. A comparison between mononuclear and dinuclear complexes with four hydroxy groups shows that the catalytic activity for CO_2 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 CO_2 hydrogenation under basic conditions (Table 2). It was found that the salient features of catalysis using the iridium complexes with the bipyridine derivatives were efficient, producing CO-free H_2 without an organic additive. Furthermore, high-pressure H_2 can be supplied when catalysis is carried out in a closed reaction vessel. Similar to their role in CO_2 hydrogenation, the electron-donating substituents enhanced the catalytic activity in the dehydrogenation of formic acid. Because 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 hydroxy group ($\sigma_p^+ = -0.91$; entry 1 vs 2).[65] Complex **4**, in which the hydroxy groups are transferred from the para positions to the ortho positions, improved the catalytic performance and exhibited a different

Table 2. Dehydrogenation of Formic Acid Catalyzed by Iridium Catalysts

entry	catalyst/ μM	time (h)	pH	T (°C)	tnitial TOF (h^{-1})	convn (%)	ref
1	**2**/200	12	1.7	60	30		65
2	**1**/200	4	1.7	60	2400	100	65
3	**4**/100	8	1.7	60	2450	100	93
4	**4**/100	4.5	3.5	60	5440	46	93
5	**5**/100	6	3.5	60	12200	37	93
6	**6**/50	4	1.7	60	12000	100	66
7	**6**/50	18	3.5	60	31600	84	66
8	**6**/3.1	7	3.5	90	228000	52	66

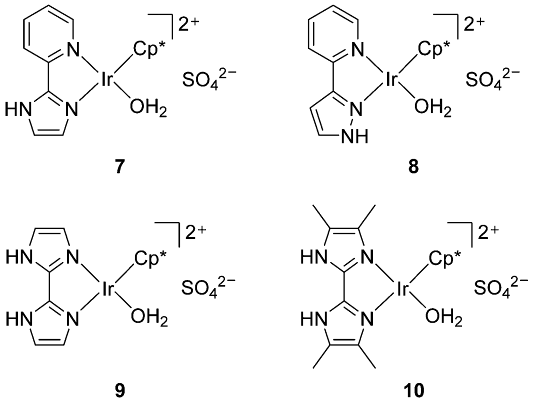
The reaction was carried out in a 1 M formic acid/sodium formate solution.

pH dependence, which is explained by the pendent-base effect through kinetic isotopic effect studies (entries 3 and 4).[93] The tetrahydroxy-substituted complex **6** provided the highest TOF for the dehydrogenation of formic acid in aqueous media without an organic additive (entries 7 and 8).[66] It was clarified that the electronic and pendent-base effects played useful roles in the catalyst for CO_2 hydrogenation as well as the dehydrogenation of formic acid in aqueous media.

Reversible and recyclable hydrogen storage was achieved using complex **6**, which is pH-switchable between CO_2 hydrogenation and the dehydrogenation of formic acid (Figure 6).[66] In a proof of concept study, H_2 storage by CO_2 hydrogenation was carried out in 2 M $KHCO_3$ under atmospheric pressure of a 1:1 CO_2/H_2 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 H_2 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 H_2 gas can be stored as aqueous formate, and then high-pressure CO_2 and H_2 gas without CO contamination can be regenerated for a possible fuel application.

CO_2 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.[67] Especially, the activities of bis(imidazole) complexes **9** and **10** were higher than those of the proton-responsive catalysts with bipyridine derivatives such as **1** and **4**.[65,93] The reason why azole-type complexes were effective for dehydrogenation is explained below. We reported that electron donation to the iridium center affects the catalytic activity for the hydrogenation of CO_2 and the dehydrogenation of formic acid and a highly electron-donating ligand promoted the 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 enhancement of the catalytic activity.

Chart 2. Iridium Complexes with Azole-Type Ligands



Therefore, we evaluated the catalytic activities of the azole-type complexes in CO_2 hydrogenation (Table 3). By the replacement of one pyridine ring by an imidazole ring, the activity for the pyridylimidazole complex **7** was significantly improved compared with that for bipyridine complex **2** (entry 1 vs 2). The pyridylpyrazole complex **8** was also more effective than **2** (entry 3). The results showed that the azole ring is more

Table 3. Hydrogenation of CO_2 Using Azole Complexes[a]

entry	catalyst	concn of catalyst (μM)	average TOF for 1 h (h^{-1})	ref
1	**2**	500	1	89
2	**7**	400	9	67
3	**8**	500	26	67
4	**9**	500	20	67
5	**10**	500	87	67

[a] The reaction was carried out for 1 h in 10 mL of a 2.0 M $KHCO_3$ aqueous solution (pH 8.5) at 50 °C under 1.0 MPa H_2/CO_2 (1:1) with stirring (1500 rpm).

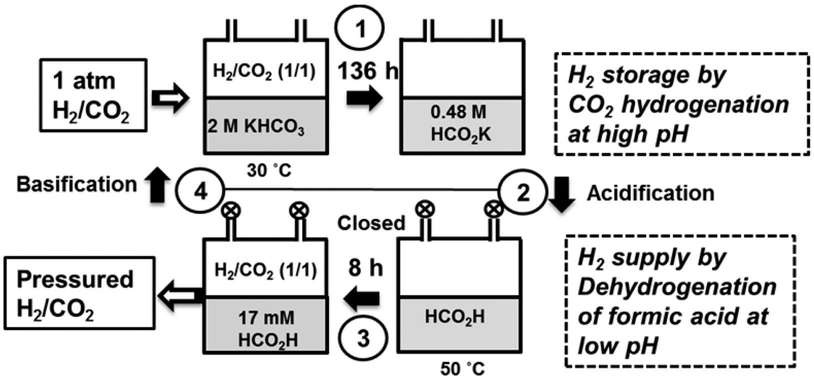


Figure 6. Reversible and recyclable hydrogen storage: (1) hydrogenation of CO_2/bicarbonate, (2) acidification by the addition of sulfuric acid, (3) dehydrogenation of FA; (4) addition of solid $KHCO_3$ to start the next run. The hydrogenation was carried out under atmospheric conditions (0.1 MPa, 30 °C), and the dehydrogenation proceeded in a closed system to provide pressurized gas (2.3 MPa).

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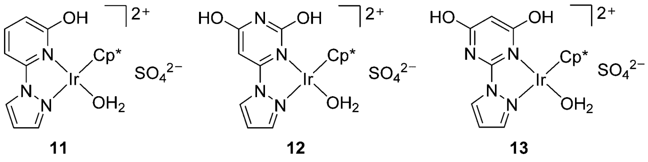
effective than the pyridine ring for the hydrogenation of CO_2. Consequently, we synthesized the bis(imidazole) complex **9**, which showed a TON of 20 (entry 4). Furthermore, incorporating four methyl groups as electron-donating groups to the bis(imidazole) ligand significantly improved the activity (entry 5), clearly indicating the effect of increasing the electron-donating ability of the ligand. This tendency is consistent with the case of the dehydrogenation of formic acid. However, the activities of the azole-type complexes were lower than that of the proton-responsive complex **1**. Owing to the high pK_a (8.8) of the protonic NH on the imidazole ligand in **10**,[67] it seems that the limited increase of electron donation by deprotonation led to some activation of the catalyst under the reaction conditions.

On the basis of our catalyst design concept, hydroxy groups were incorporated into pyridine and pyrimidine ligands to make them proton-responsive. Recently, we have found effective catalysts **11**−**13** (Chart 3), which showed high performance for H_2 generation from the dehydrogenation of formic acid.[94] These catalysts have hydroxy groups on a pyridine or pyrimidine moiety linked with an azole moiety. Therefore, these catalysts were also expected to be efficient for CO_2 hydrogenation.

Chart 3. Iridium Complexes with Hydroxy-Substituted Ligands



The hydroxy groups can be deprotonated and protonated reversibly. 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 hydroxy groups. The pK_a of complex **11** (3.9) was slightly lower than that of analogue **6**.[89]

The results for hydrogenation of CO_2 catalyzed by **11**−**13** are shown in Table 4. All reactions were carried out in aqueous solution without organic additives. The hydroxypyridine complexes **11** outperformed the non-proton-responsive complexes with the azole-type ligands **7**−**10** under similar reaction conditions (1 MPa, H_2/CO_2 = 1/1, 50 °C, 1 h). This finding is consistent with our previous results that the hydroxy group as an electron-donating substituent was effective for CO_2 hydrogenation under basic conditions. Furthermore, the dihydroxypyrimidine complexes **12** and **13** were more effective than the hydroxypyridine complex **11** (entry 3 vs 4 and 8). As expected, the ligands containing multiple hydroxy groups were effective for catalyzing the reaction.

Table 4. Hydrogenation of CO_2 Using Proton-Responsive Catalysts[a]

entry	catalyst	*P* (MPa)	*T* (°C)	average TOF for 1 h (h^{-1})	ref
1	**1**	1.0	50	650	89
2	**4**	1.0	50	1400	89
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	**13**	1.0	50	637	this work
9	**13**	1.0	80	2090	this work
10	**13**	1.0	100	610	this work
11	**13**	0.5	50	372	this work
12	**13**	2.0	50	1080	this work

[a] The reaction was carried out for 1 h in 10 mL of 20 μM catalyst in a 2.0 M $KHCO_3$ aqueous solution (pH 8.5).

The N-positional effect of the pyrimidine ring was shown in complex **12** versus **13**. The TON of **13** was approximately 1.5 times higher than that of **12** (entry 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 9 and 10). Nevertheless, the difference in the N position on the pyrimidine ring was demonstrated to affect the catalytic activity.

In order to build an optimal reaction system, we carried out the hydrogenation of CO_2 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 9). 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 12).

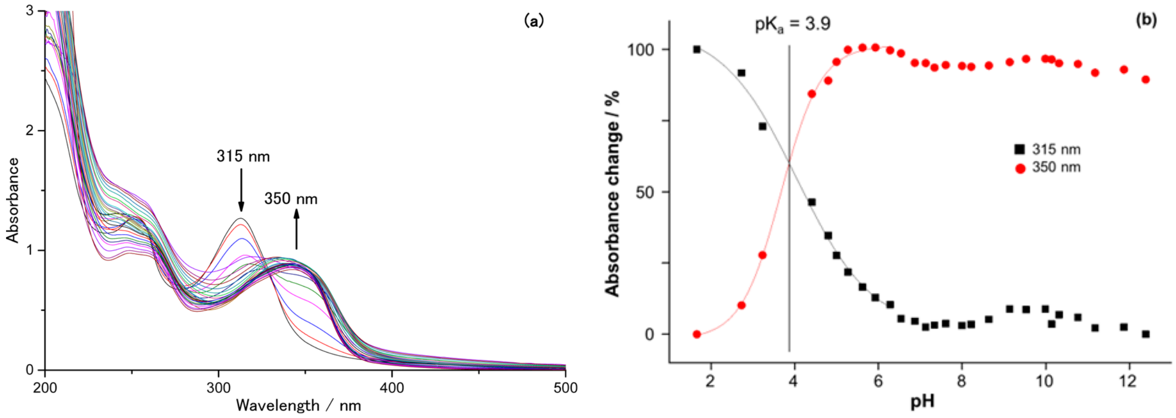


Figure 7. (a) UV−vis absorption spectra of complex **11** in a pH titration and (b) absorbance changes at single wavelengths (315 and 350 nm) as a function of the pH. Boltzmann fits are depicted.

Additionally, prolonging the reaction time increased the TON (from 1230 to 8080; Table 5, entries 4−6). In the case of catalyst **12** as well as **13**, the TON value escalated with an increase of the reaction time (Table 5, entries 1−3).

Table 5. Reaction Time Study of the Hydrogenation of CO_2 Using Proton-Responsive Catalysts[a]

entry	catalyst	time (h)	TON
1	**12**	2	1290
2	**12**	24	6360
3	**12**	48	7680
4	**13**	2	1230
5	**13**	24	6920
6	**13**	48	8080

[a]The reaction was carried out in 10 mL of 20 μM catalyst in a 2.0 M $KHCO_3$ aqueous solution (pH 8.5) at 50 °C under 1.0 MPa H_2/CO_2 (1:1) with stirring (1500 rpm).

The efficiency of the catalytic hydrogenation of CO_2 increases with an increase in the number of hydroxy groups on the bidentate (or bridging) ligand, so in order to maximally activate this catalyst system, it may be useful to add additional hydroxy groups to N^N-bidentate ligands that already showed a strong electron-donating ability and pendent-base effect. Therefore, in order to develop an "industrial strength" catalyst for the hydrogenation of CO_2, a further refinement of the catalyst structure is needed. Our future work will synthesize novel ligands incorporating many hydroxy groups on the azole moiety.

CONCLUSIONS

In this paper, we demonstrated that the hydrogenation of CO_2 was efficiently catalyzed by iridium complexes with various N^N-bidentate ligands, and we assessed the effect of the hydroxy groups as proton-responsive substituents. The hydroxy groups played an important role in tuning the strength of electron donation from an N atom on the ligand toward the iridium center at various solution pH values. By biasing toward basic conditions, the strong electron-donating oxyanion enhanced the catalytic activity. Furthermore, the hydroxy groups also worked to help the access of H_2 molecules toward the iridium center by a pendent-base effect through a proton relay. In particular, a bipyrimidine complex with four hydroxy groups showed excellent catalytic activity from these synergistic effects. Additionally, it can be said that newly designed azole-type complexes were quite promising for CO_2 hydrogenation. It was found that the introduction of hydroxy groups into these ligands enhanced the catalytic activity. As for a pyrimidine ring, an effect of the N position on the ring toward the catalytic activity was observed. Further investigation focusing on the introduction of hydroxy groups into ligands continues in order to develop even more effective catalysts for CO_2 hydrogenation.

EXPERIMENTAL SECTION

General Procedures. Mixed gas ($CO_2/H_2 = 1/1$) was used for CO_2 hydrogenation. The formate concentrations were monitored by a Tosoh high-performance liquid chromatography (HPLC) system equipped with an anion-exclusion column [Tosoh TSKgel SCX(H^+)] and a UV detector ($\lambda = 210$ nm), using an aqueous H_3PO_4 solution (20 mM) as the eluent. The preparation procedures for complexes **11**−**13** are submitted elsewhere.[93]

Hydrogenation of CO_2 (Standard Method). To a $KHCO_3$ aqueous solution (2.0 M, pH 8.5, 10 mL) were added the complexes as solids. Then the mixture was degassed by three cycles of freeze−pump−thaw in a flask. After that, the flask was moved into a glovebox under argon, and then the reaction mixture was transferred into a stainless steel autoclave. After 10 min of stabilization at 50 °C under 1.0 MPa of H_2/CO_2 (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

The authors declare no competing financial interest.

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