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Conversion of CO_2 into Formate by Homogeneously Catalyzed Hydrogenation in Water: Tuning Catalytic Activity and Water Solubility through the Acid–Base Equilibrium of the Ligand

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This Microreview focuses on the recently developed hydrogenation of CO_2 and hydrogen carbonate catalyzed by half-sandwich complexes with 4,4′-dihydroxy-2,2′-bipyridine (dhbp) and 4,7-dihydroxy-1,10-phenanthroline (dhpt). An unprecedented high catalytic activity and reusability of the catalyst without waste generation were achieved by automatic tuning of the catalytic activity and water solubility of the catalyst through the acid–base equilibrium of the catalyst ligand. The oxyanion generated from the phenol hydroxy group played significant roles in the electronic effect and polarity. The catalyst design concept and the excellent properties of the ligands are expected to have significantly broader implications for the design of new homogeneous catalysts.

Introduction

The conversion of CO_2 into useful organic products still remains an intriguing and challenging subject.[1–6] In nature, an enormous amount of CO_2 is transformed into carbohydrate in metal centers of enzymatic systems in an aqueous environment. However, the industrial application of CO_2 as a source of C_1 instead of carbon monoxide and phosgene is limited: a recent topic of interest is polycarbonate production by using CO_2 as a starting material.[7] From an academic viewpoint, the activation of inert CO_2 has attracted considerable interest. Many attempts to convert CO_2 by using transition-metal catalysts have focused on the photochemical[8–13] and electrochemical[14–16] reduction of CO_2. In addition, there have been significant advances in the homogeneously catalyzed hydrogenation of CO_2 in the last decade, although the primary products are limited, in general, to formic acid and its derivatives (Table 1).

The homogeneous hydrogenation of CO_2 to formic acid was first reported by Inoue et al. in 1976.[17] They used phosphane complexes of group 8, 9, and 10 metals, including Wilkinson's catalyst, in benzene in the presence of water and base. Recently, Ezhova and co-workers studied the hydrogenation by Wilkinson's catalyst in detail.[18] They reported that the rhodium catalysts required phosphane ligands for the hydrogenation of CO_2, whereas the complex with bipyridine as a ligand was inactive.

In 1994, Noyori and co-workers reported that the use of supercritical carbon dioxide ($scCO_2$) greatly improved the catalytic efficiency of Ru^{II}–phosphane complexes in the presence of amine.[19,20] They obtained TOFs (Please see the list of abbreviations at the end.) up to 95000 h^{-1} at 19 MPa by the use of pentafluorophenol as the additive.[21] The good results are explained by the characteristic properties of $scCO_2$, such as its extremely high miscibility with H_2 and its good mass-transfer capability. However, a $scCO_2$-soluble catalyst and a relatively high pressure are required.

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Yuichiro Himeda was born in 1966 in Ehime, Japan. He studied organic chemistry at the School of Science, Osaka University (1984–1991). Then, he moved to the present National Institute of Advanced Industrial Science and Technology. He received his Ph. D. degree from Osaka University under the supervision of Prof. Ikuo Ueda in 1994. After a postdoctoral stay with Prof. Andrew D. Hamilton at the University of Pittsburgh (1995–1996), he worked on the development of homogeneous catalysis for CO_2 conversion. His research is focused on the development of new and potentially useful catalytic reactions.

Table 1. Homogeneous catalyst precursors for the hydrogenation of CO_2 to formic acid.

Catalyst precursor	Solvent	Additives	$P(H_2/CO_2)$/MPa	T/°C	t/h	TON	TOF/h^{-1}	Ref.
$RuH_2(PPh_3)_4$	C_6H_6	NEt_3, H_2O	2.5/2.5	r.t.	20	87	4	[17]
$RuH_2(PMe_3)_4$	$scCO_2$	NEt_3, H_2O	8.5/12	50	1	1400	1400	[19]
$RuCl(OAc)(PMe_3)_4$	$scCO_2$	NEt_3/C_6F_5OH	7/12	50	0.3	31700	95000	[21]
K[RuCl(edta-H)]	H_2O	–	0.3/1.7	40	0.5		250	[24]
$RhCl(tppts)_3$	H_2O	$NHMe_2$	2/2	81	0.5		7260	[22]
			2/2	r.t.	12	3439		[23]
$[RuCl_2(tppms)_2]_2$	H_2O	$NaHCO_3$	6/3.5	80	0.03	320	9600	[29]
			0.2/0.8	50	1		50	[29]
$RuCl_2(pta)$	H_2O	$NaHCO_3$	6/–	80			807[a]	[31]

[a] The initial TOF was calculated by nonlinear least-squares fitting of the experimental data obtained from the initial part of the reaction.

Leitner and co-workers reported that the water-soluble analogue of Wilkinson's catalyst, $[RhCl(tppts)_3]$ (Ligand abbreviations are in lowercase letters according to IUPAC recommendations; they may be in capital letters in some of the articles cited in this review.), serves as an effective catalyst in water.[22,23] In aqueous systems, an amine additive is required, and the final concentration of formic acid never exceeds that of the added amine. Moreover, the problem of separating the base from the reaction medium still exists. Khan and co-workers reported that $[RuCl(edta-H)]^+$ catalyzed the hydrogenation of CO_2 in pure water.[24] Although the initial rate of the reaction was relatively high (TOF of 250 h^{-1}), the decomposition of formic acid and formaldehyde as a reverse reaction occurred readily. Joo and Katho performed extensive studies on the hydrogenation of CO_2 and hydrogen carbonate in amine-free aqueous solutions. The use of rhodium and ruthenium complexes with widely used water-soluble phosphane ligands (i.e., tppms, tppts, and pta) were investigated in detail.[25–32] The rate of hydrogenation strongly depends on the central metal, the phosphane ligand, and the pH of the reaction solution. A high TOF of 9600 h^{-1} was obtained by using $[RuCl_2(tppms)_2]_2$ at 9.5 MPa and 80 °C. More interestingly, in the hydrogenation of $CaCO_3$, the final formate concentration reached 143% (the calculation is based on the amount of added base). It was revealed that the hydrogenation proceeds in the absence of base. Their detailed kinetic, mechanistic, and theoretical investigations[25] provided useful information on the hydrogenation of CO_2 and hydrogen carbonate in water.

According to excellent reviews encompassing the literature until 2003,[5,33–35] almost all the active catalysts for the hydrogenation of CO_2 to formic acid are rhodium- and ruthenium-based complexes with phosphane ligands. On the other hand, there are a few, less active examples of other metals (e.g., Ir,[17] Pd,[36] and Ni[37]) and ligands (e.g., edta-H,[24] 6,6′-dichloro-2,2′-bipyridine[38]). Although an aqueous-phase catalyst might not be expected to be active on the basis of mass-transfer rates, a number of active catalysts were found from aqueous systems. On the other hand, an active catalyst promotes the decomposition of formic acid as a reverse process.[27,39] Therefore, the yield of formate is strongly dependent on the equilibrium between formic acid and CO_2. Furthermore, recovery and reusability of catalyst are serious concerns from the viewpoint of process cost, because highly active catalysts are restricted to the complexes of precious metals.[37] Several attempts have been made by Baiker and Ikariya to achieve reusability by immobilizing the catalyst for dmf synthesis under $scCO_2$.[40–44]

This Microreview focuses on aqueous catalysts containing rhodium, ruthenium, and, in particular, iridium with 4,4′-dihydroxy-2,2′-bipyridine (dhbp) and 4,7-dihydroxy-1,10-phenanthroline (dhpt) as ligands. In addition, catalyst recycling as well as improvement in catalytic efficiency is considered. For a more sophisticated process, the catalytic activity and water solubility of the metal complexes are controlled through the acid–base equilibrium of the catalyst ligand.

The Use of Water as a Solvent

Water is innocuous, abundant, and cheap. Furthermore, in the hydrogenation of CO_2 and hydrogen carbonate into formic acid and formate, water serves not only as a bulk solvent but also as a participant. The solvation effect of water can significantly influence the thermodynamics of the reaction. Although the hydrogenation of CO_2 into formic acid [Equation (1)] in the gas phase is endergonic ($\Delta G°_{298}$ = +33 kJ mol^{-1}), the reaction in the aqueous phase is exergonic ($\Delta G°_{298}$ = –4 kJ mol^{-1}).[22] Similarly, on the basis of theoretical calculation, the hydrogenation of a hydrogen carbonate into formate in water [Equation (2)] is exergonic.[25] Thus, water is believed to be an ideal reaction medium for the hydrogenation of CO_2 and hydrogen carbonate.

$$CO_2 + H_2 \rightleftharpoons HCO_2H \quad (1)$$

$$HCO_3^- + H_2 \rightleftharpoons HCO_2^- + H_2O \quad (2)$$

The equilibriums of both CO_2 and formic acid in water must be considered [Equations (3) and (4)].

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \overset{pK_1 = 6.35}{\rightleftharpoons} HCO_3^- + H^+ \overset{pK_2 = 10.33}{\rightleftharpoons} CO_3^{2-} + 2H^+ \quad (3)$$

$$HCO_2H \overset{pK_a = 3.6}{\rightleftharpoons} HCO_2^- + H^+ \quad (4)$$

CO_2 reaches an equilibrium with hydrogen carbonate and carbonate, and this is strongly dependent on pH, temperature, and CO_2 pressure.[45,46] It is believed that, in acidic conditions, hydrogenation converts CO_2 into formic acid [Equation (1)], whereas in alkaline conditions, it converts hydrogen carbonate into formate [Equation (2)]. The presence of the base makes the hydrogenation of CO_2 more favorable.[33,39] Thus, the hydrogenation usually fails or provides only a small yield in the absence of a base, because the decomposition of formic acid as a reverse reaction might occur easily under acidic conditions. Joo reported an interesting result: the generation of formate exceeds the amount of added base, in other words, the product mixture contains formic acid, and the reaction solution changes from a basic solution into an acidic one.[27]

On the other hand, the catalysis in water requires the development of water-soluble ligands. Thus far, imparting water solubility to complexes for aqueous catalysis can be achieved by the introduction of charged or polar substituents such as acidic (-SO_3H, -CO_2H) and basic (-NR_2) functionalities into the ligands.[47,48] Although various phosphane ligands (e.g., tppms, tppts, and pta) have been the subject of considerable research in the area of aqueous catalysts, other types of water-soluble ligands have hardly been investigated.

Background

Numerous studies have investigated half-sandwich bipyridine complexes $[(C_nR_n)M(ppy)X]^{k+}$ [ppy = 2,2′-bipyridine or 1,10-phenanthroline; R = H, Me, and alkyl; X = halogen, H_2O; M = Rh, Ir (n = 5); M = Ru (n = 6)], which are isoelectronic complexes of each other, because of their interesting properties.[49–55] In particular, the transfer hydrogenation of NAD catalyzed by rhodium complexes in water by using a formate as the hydrogen donor was extensively investigated by Steckhan et al.[56–60] The reaction of rhodium complexes with a formate provides the corresponding hydrido complex $[Cp^*RhH(bpy)]^+$ through a β-elimination reaction to produce CO_2. Direct hydride transfer from the hydrido complex to a ketone results in low yields under neutral conditions.[60] However, we found that transfer hydrogenation is strongly dependent on the pH value, and the yields were significantly improved under acidic formate conditions.[61,62] In addition, the decomposition of formic acid to CO_2 and H_2 (i.e., the reverse reaction of the hydrogenation of CO_2) catalyzed by $[Cp^*Rh(bpy)Cl]Cl$ proceeded smoothly with a TOF of 238 h^{-1} at 40 °C.[63]

Caix and co-workers reported that rhodium and iridium complexes $[Cp^*MCl(bpy)]^+$ (M = Rh, Ir) serve as electrocatalysts for the reduction of CO_2 to formate in an aqueous organic medium.[16,64] It has been observed that the electrochemical reduction involves the formation of hydrido complexes $[Cp^*MH(bpy)]^+$, followed by the insertion of CO_2 into the metal–hydrogen bond.

Previous studies by us and others prompted us to investigate the hydrogenation of CO_2 or hydrogen carbonate by using the half-sandwich bipyridine complexes in water. Table 2 shows the results of the hydrogenation of CO_2 or hydrogen carbonate; the reaction proceeded in aqueous solution without the use of amine additives.[65] Interestingly, the hydrogenation proceeded under neutral and acidic conditions (entries 2 and 3), although these conditions are less suitable for activity than basic conditions. However, the decomposition of the formate as a reverse reaction occurred easily after pressure release, particularly in acidic solutions. It is noteworthy that the iridium complexes showed a catalytic activity similar to those of the rhodium and ruthenium complexes (entry 4). However, the catalytic activities of the half-sandwich bipyridine complexes were far from satisfactory.

Table 2. Hydrogenation catalyzed by half-sandwich bipyridine complexes in aqueous solution.[a]

Entry	Complex	Solution	TON
1	$[Cp^*Rh(bpy)Cl]Cl$	1 M KOH aq.	216
2	$[Cp^*Rh(bpy)Cl]Cl$	1 M NaH_2PO_4 aq.	76
3	$[Cp^*Rh(bpy)Cl]Cl$	H_2O	31
4	$[Cp^*Ir(bpy)Cl]Cl$	1 M KOH aq.	105
5	$[(C_6Me_6)Ru(bpy)Cl]Cl$	1 M KOH aq.	68[b]

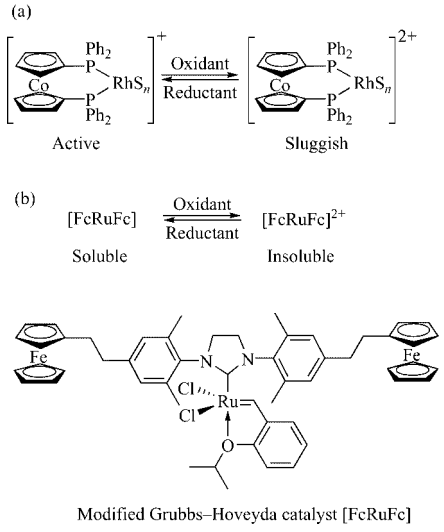
[a] The reaction was carried out by using a catalyst (0.1 mM) at 4 MPa (CO_2/H_2 = 1:1) and 80 °C for 20 h. [b] The catalyst concentration was 0.2 mM.

Sakaki's theoretical studies[66] and Jessop's experimental results[67] had the important implication that electron-donating ligands would improve the catalytic efficiency. The electronic substituent effect in a bipyridine ligand, in which the coordinated nitrogen atoms are incorporated in the aromatic ring, may have a stronger influence on the central metal atom than that in a triphenylphosphane ligand. In order to improve the catalytic activity and recover the catalyst, we designed a novel catalyst based on bipyridine complexes.

Catalyst Design

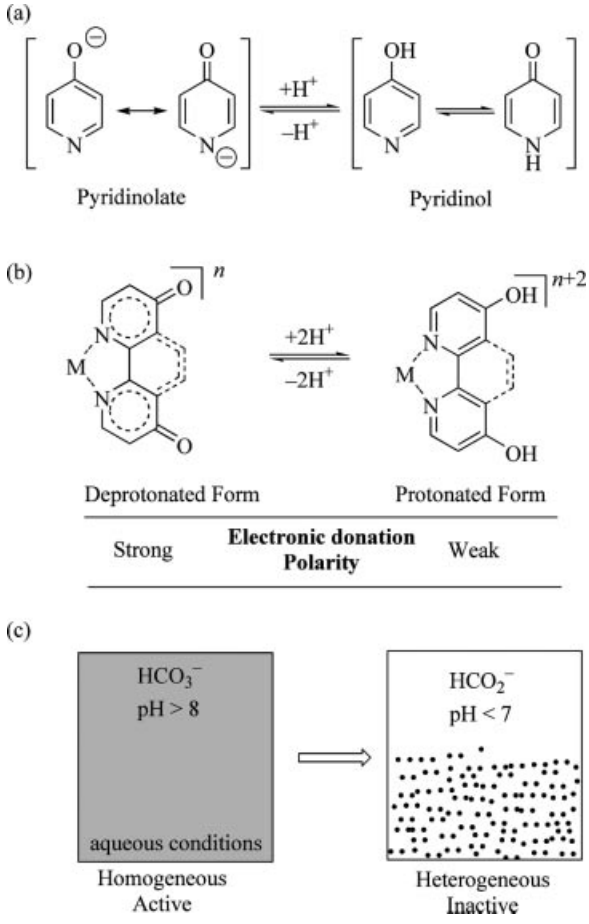
Recently, extensive efforts have been undertaken to optimize an entire chemical process consisting of reaction and separation steps in order to minimize economical and environmental costs.[68–70] Control or switching of catalyst properties (e.g., reactivity and solubility) is one of the strategies employed for this purpose.[71] The pioneering reports of Wrighton demonstrated that catalytic activity can be electrochemically controlled by changing the oxidation state of the redox-active ligand by addition of stoichiometric amounts of simple redox reagents (Scheme 1a).[72,73] In the

hydrogenation of cyclohexene, the reduced form of the diphosphanylcobaltocene-stabilized rhodium complex is approximately 16 times faster than its oxidized form. On the other hand, there are many reports of the use of an amphiphilic ligand for controlling the solubility of the complexes by varying the pH of the system.[74] For example, catalyst recycling was achieved by addition of acid or base to the solution after the reaction, followed by extraction or filtration.[75,76] Recently, the interesting work of Sussner demonstrated the recycling of the Grubbs–Hoveyda catalyst with two ferrocene moieties by using the redox-switching concept (Scheme 1b).[77] However, the simultaneous and effective control of two or more functions of a catalyst has never been demonstrated.



Scheme 1. Control of catalytic properties by switching of the redox-active ligand: (a) Electrochemical control of catalytic activity.[72] (b) Control of solubility for recyclability of catalyst.[77]

We focused our attention on catalyst tuning through the acid–base equilibrium between pyridinol and pyridinolate (Scheme 2). The interconversion leads to simultaneous changes in both electronic and polar properties, which are attributed to the difference between the hydroxy group in pyridinol and the oxyanion in pyridinolate (Scheme 2a). In comparison with the acid–base equilibrium of carboxylic acid and sulfonic acid, the interconversion of the phenol hydroxy group causes a drastic change in the electronic status on the benzene ring through the resonance structure. From the Hammett constant,[78] a substantial difference in the electronic effects of the oxyanion ($\sigma_p^+ = -2.30$) and the hydroxy group ($\sigma_p^+ = -0.91$) can be observed. Thus, the control of the electronic effect through the acid–base equilibrium of catalyst ligands provides a desirable reactivity of the catalyst, i.e., activation in the reaction step and deactivation in the separation step in order to prevent the reverse reaction. In addition, it should be noted that the σ_p^+ value of the oxyanion is much lower than those of the amine and alkoxy groups, which are widely used electron-donating substituents. On the other hand, it is known that the dipole moment of pyridone is much greater than that of pyridinol.[79,80] Accordingly, when pyridinol is used as a part of a complex ligand, the interconversion will provide an excellent opportunity for controlling the electronic effect and polarity of a catalyst by varying only the pH (Scheme 2b).



Scheme 2. Catalyst design for catalyst tuning: (a) Acid–base equilibrium between pyridinol and pyridinolate. (b) Interconversion between the deprotonated and protonated forms. (c) Catalyst state at the beginning and at the end of the hydrogenation of hydrogen carbonate in water.

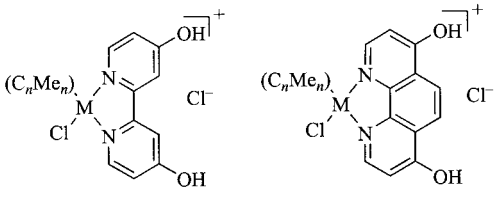
It is noteworthy that our catalyst design based on the acid–base equilibrium of catalyst ligands is closely correlated with the change in the pH of the reaction solution during the hydrogenation of hydrogen carbonate. In other words, as the reaction proceeds, the reaction solution changes from basic to acidic. Therefore, it is expected that the catalyst may spontaneously transform from the homogeneous and active deprotonated form at the beginning of the reaction into the heterogeneous and inactive protonated form at the end (Scheme 2c). Our system has the advantages of heterogeneous catalysis (i.e., the simplicity of catalyst separation) and biocatalysis (i.e., aqueous reaction and pH dependence) as well as those of homogeneous catalysis (i.e., high catalytic performance).

This paper reviews catalysis with complexes of the 4,4′-dihydroxy-2,2′-bipyridine (dhbp: H_2L^1) and 4,7-dihydroxy-1,10-phenanthroline (dhpt: H_2L^2) ligands that succeeded in the activation and reusability of the catalyst for the hydro-

genation of CO_2 and hydrogen carbonate in water. In addition, our studies on catalyst tuning through the acid–base equilibrium of the catalyst ligand can be expected to provide valuable insights into the development of homogeneous catalysts.

Properties of dhbp and dhpt Complexes

The most significant feature of dhbp and dhpt is that they have two acidic phenol hydroxy groups. While both ligands are soluble in an alkaline aqueous solution, dhpt is insoluble in water and common organic solvents except dmf and dmso. Hence, half-sandwich dhbp complexes $[(C_nMe_n)M(H_2L^1)Cl]Cl$ **1**–**3** [M = Rh, Ir (n = 5), M = Ru (n = 6)] were prepared from $[(C_nMe_n)MCl_2]_2$ in water or alcohol, but dhpt complexes $[(C_nMe_n)M(H_2L^2)Cl]Cl$ **4**–**6** were prepared in dmf.



1: M = Rh (n = 5)
2: M = Ir (n = 5)
3: M = Ru (n = 6)

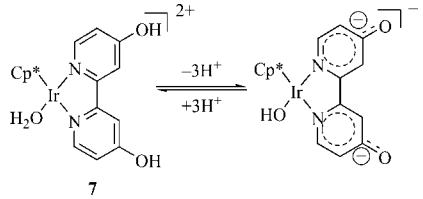
4: M = Rh (n = 5)
5: M = Ir (n = 5)
6: M = Ru (n = 6)

The ^1H and ^{13}C NMR spectra of aqua complex $[Cp^*Ir(H_2O)(H_2L^1)]^{2+}$ (**7**) were strongly dependent on the pH of the environment (Table 3).[81] The substantial shifts are attributed not only to the transformation from the aqua ligand to the hydroxido ligand,[82] but also to the deprotonation of the hydroxy groups (Scheme 3).[83] The downfield shift in the ^{13}C NMR signal for the carbon atoms attached to oxygen strongly suggests the generation of the oxyanion. On the other hand, the complex with 3,3′-dihydroxy-2,2′-bipyridine (**8**) allows the formation of an intramolecular O–H–O hydrogen bond.[84]

Table 3. ^1H and ^{13}C NMR spectroscopic data for iridium complexes in D_2O (chemical shifts in ppm).

Signal	In acidic solution	In basic solution
C-4,4′ in **7**	170.37	178.59
3,3′-*H* in **7**	7.24	6.63
5,5′-*H* in **7**	7.77	7.13
6,6′-*H* in **7**	8.77	8.25
6,6′-*H* in $[Cp^*Ir(H_2O)bpy]^{2+}$ [a]	9.14	9.00
6,6′-*H* in $[Cp^*Ir(H_2O)(Me_2L^1)]^{2+}$ [a]	8.88	8.76

[a] Ref.[82]



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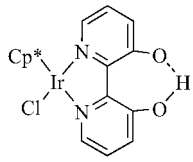
Scheme 3. Acid–base equilibrium of **7**.



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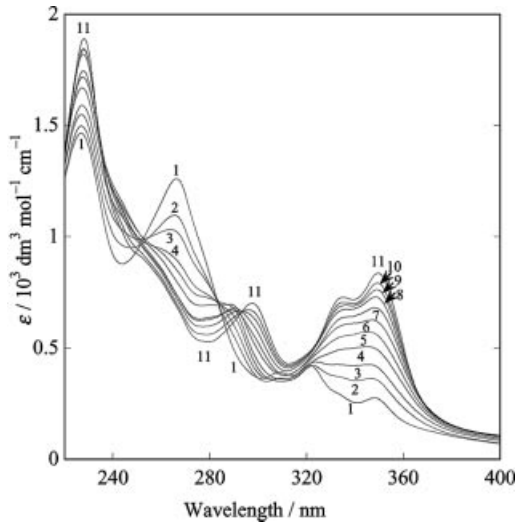


Figure 1. Absorption spectra of rhodium complex **4** (50 μM) in an aqueous solution containing 2.5% methanol at pH values of 1.9–2.3 (1), 3.3 (2), 3.6 (3), 4.0 (4), 4.2 (5), 4.5 (6), 4.8 (7), 4.9 (8), 5.2 (9), 5.5 (10), and 5.6–9.0 (11).

The electronic spectra of ruthenium dhpt complexes $[Ru(dhpt)(ppy)_2]^{2+}$ were studied in detail.[83,85,86] As a result of an acid–base equilibrium of the phenol hydroxy group in dhpt, the absorption spectra of the complexes are dependent on the pH of the environment. Similarly, in half-sandwich complexes **1**–**6**, spectral changes were observed with variations in the pH. Representative absorption spectra of rhodium dhpt complex **4** as a function of pH are shown in Figure 1. Plots of percent change in optical density against pH for iridium and ruthenium complexes are shown in Figure 2. Although the complexes have two acidic protons, only one inflection point is observed in the plots. The values of the overall dissociation constant pK_a estimated from the pH at the inflection point are given in Table 4.[83] The result indicates that the dhpt complexes were obviously more acidic than the dhbp complexes, and the iridium complexes were slightly acidic relative to other complexes.

The structural features of ruthenium complex **3** obtained by single-crystal X-ray crystallographic analysis are similar to those of its 4,4′-dimethoxy-2,2′-bipyridine and bipyridine analogs (Figure 3).[87,88]

The water solubilities of chlorido complexes **1**–**6** are pH dependent: chlorido complexes are highly soluble in basic solution but poorly soluble under acidic and neutral conditions (Scheme 4). When an alkaline solution of deprotonated complexes **1**–**6** was acidified, it precipitated as the protonated complexes. However, the complexes remained par-

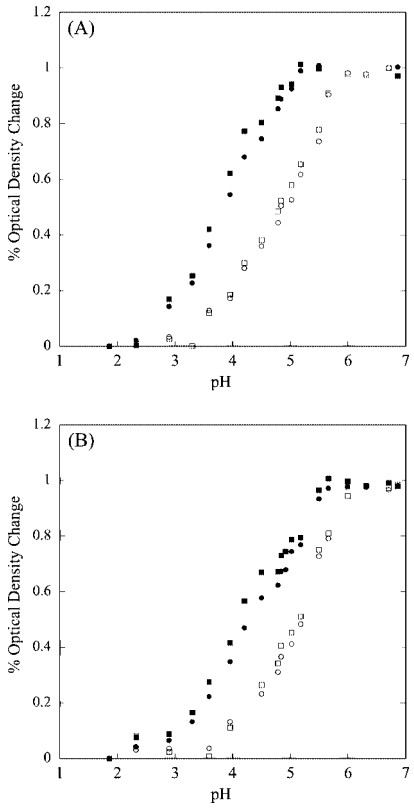


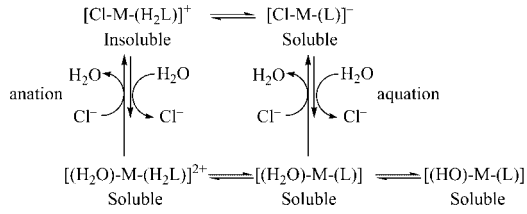
Figure 2. Absorbance change as a function of pH for: (A) iridium complexes **2** at 328 (empty circle) and 258 nm (empty square) and **5** at 353 (filled circle) and 340 nm (filled square); (B) ruthenium complexes **3** at 318 (empty circle) and 247 nm (empty square) and **6** at 358 (filled circle) and 345 nm (filled square).

Table 4. pK_a for complexes with dhbp or dhpt.

Complex	pK_a[a]
2	9.6
3	10.2
4	8.4
5	7.7
6	8.4

[a] Observed pK_a is twice the pH at the inflection point in the curve.

tially in the mother liquor as a result of the generation of aqua complexes by the aquation of the chlorido complexes. It is highly probable that the dhpt complexes could be recovered more efficiently than the dhbp complexes. On the other hand, aqua complex **7** is water soluble. However, when HCl was added to a solution of **7**, chlorido complex **2** precipitated as a result of the anation of the aqua complex. This result shows that anation is preferable to aquation in half-sandwich bipyridine complexes.[53,89]



Scheme 4. Behavior of the dhbp and dhpt complexes in aqueous solution. [M = Cp*Rh, Cp*Ir, or (C_6Me_6)Ru; L = L^1 or L^2].

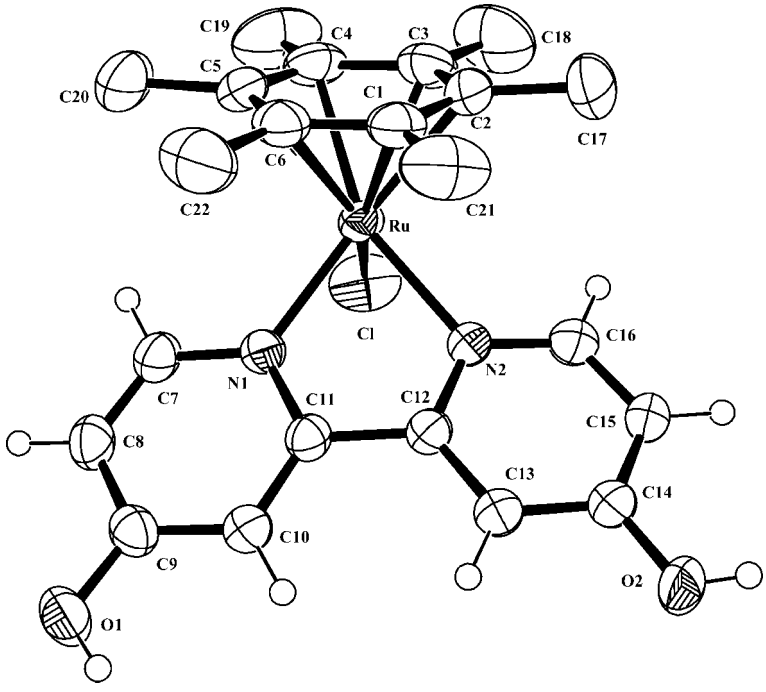


Figure 3. ORTEP view of **3**. The counteranion (Cl^-), methanol, and hydrogen atoms of η_6-C_6Me_6 are omitted for clarity.

The pH-dependent solubility of the complexes in formate solutions was investigated.[90] An alkaline solution of the complex was added to the formate solution at various pH values. After the resulting solution was allowed to stand overnight, the metal concentrations of the filtrates were measured by ICP-MAS. Figure 4 shows the iridium concentrations of **2** and **5** at various pH values. In both of the complexes, the solubility decreased sharply below pH 8. In particular, the concentration of dhpt complex **5** was as low as 0.12 ppm in the pH range 4.5 to 5.5, which is almost one seventh that of the dhbp complex **2** (0.80 ppm at pH 7.4). Since it is known that half-sandwich bipyridine complexes form hydrido complexes under certain conditions in a formate solution,[61] the recovered solids may be mixtures of hydrido complexes, which consist of monoprotonated and fully protonated complexes. On the other hand, at pH 3.5 and below, the solubility of both the complexes increased; this was probably due to the generation of aqua complexes.[91,92] In the rhodium and ruthenium complexes, precipitation was not observed under these conditions, probably because of the instability of the hydrido complexes.

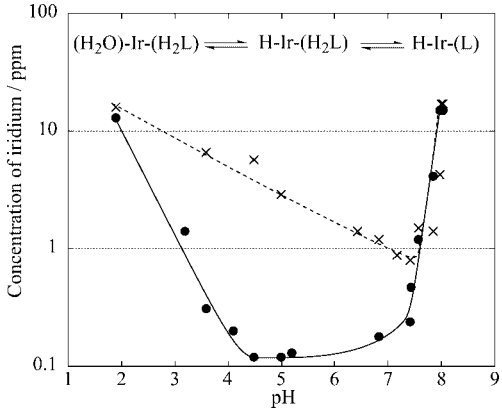


Figure 4. Iridium concentration in an aqueous formate solution (1 M) of **2** (crosses/dotted line) and **5** (filled circles/solid line). Ir = Cp*Ir, H_2L = dhbp(H_2L^1), dhpt(H_2L^2).

Electronic Effect on Catalytic Activity

Numerous studies have established a dependence of both stoichiometric and catalytic activity on electronic substituent effects in the range from the electron-withdrawing nitro group to the electron-donating amine groups.[93–95] The substituent effects on the electrochemical properties of the half-sandwich bipyridine rhodium and iridium complexes have been investigated.[59,96] Sakaki[66] and Jessop[67] suggested that electron-donating ligands would improve the catalytic efficiency for the hydrogenation of CO_2. On the other hand, a high catalytic activity might promote the reverse reaction after the release of pressure.[27,39] Such a conflicting requirement can be satisfied by controlling the electronic properties of the catalyst ligand (i.e., the catalytic activity) through the acid–base equilibrium of pyridinol.

The electronic substituent effect on the hydrogenation of hydrogen carbonate was investigated by using a series of iridium complexes [Cp*Ir(4,4′-X_2-2,2′-bpy)Cl]Cl [X = H, CO_2H, Me, OMe, OH(**2**)].[90,97,98] The time courses of formate generation are shown in Figure 5. The catalytic activities of the iridium complexes are strongly dependent on the substituent on the bipyridine ligand. The correlation between the substituent and the initial TOF can be explained on the basis of Hammett's rule. Note that the deprotonation of the phenol hydroxy group and the carboxyl group occurs under basic reaction conditions. Thus, the σ_p^+ value for the hydroxy complex is –2.30 and that for the carboxylic acid complex is –0.02, and they correspond to the oxyanion (-O^-) and carboxylato (-CO_2^-) values, respectively.[78] The Hammett plots of the initial TOF vs. the σ_p^+ value of X in [Cp*Ir(4,4′-X_2-2,2′-bpy)Cl]Cl at 4 MPa and 1 MPa and 80 °C are shown in Figure 6. Both plots have high correlation coefficients, and the reaction constants (ρ) are very similar. The electronic trend is in agreement with Sakaki's theoretical prediction[66] and Jessop's experimental results[67] for the catalytic hydrogenation of CO_2. The large σ_p^+ value of –2.30 and the ρ value of –1.3 resulted in a remarkably high initial TOF for **2**, which was ca. 100 times greater than that of a methoxy complex (X = OMe) and over 1000 times greater than that of an unsubstituted complex (X = H). Similarly, a similar reactivity trend (H < OMe < OH) was observed for the series of disubstituted phenanthroline complexes.[63] This was the first example of a strong electronic oxyanion effect on catalytic activity in the field of complex catalysts.

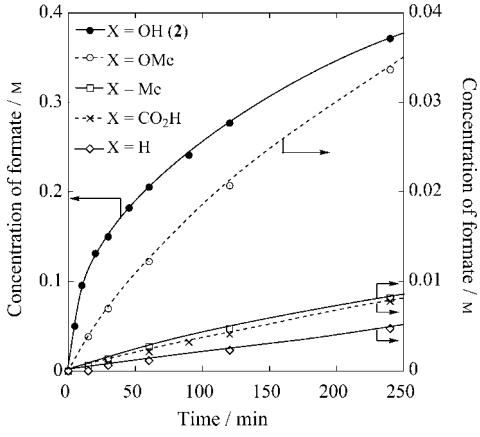


Figure 5. Time course of formate concentration during the hydrogenation of hydrogen carbonate catalyzed by [Cp*Ir(4,4′-X_2-2,2′-bpy)Cl]Cl (0.2 mM) at 4 MPa (H_2:CO_2 = 1:1) and 80 °C in an aqueous KOH solution (1 M).

Surprisingly, no significant activation was observed in *meta*-substituted analogue **8**, although one negative charge existed on the ligand.[63] One possible explanation is that the resonance structures of 3-hydroxypyridine cannot increase the π-electron density on the nitrogen atoms. This hypothesis is consistent with the data reported for the nucleophilicity of the nitrogen atom in the 3- and 4-hydroxypyridine anions.[99]

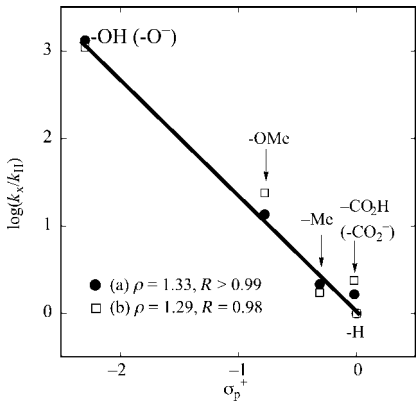


Figure 6. Hammett plot of initial TOF (= k) vs. the σ_p^+ value of substituent (X) in [Cp*Ir(4,4′-X_2-2,2′-bpy)Cl]Cl. The reaction was carried out with the catalyst (0.02–0.2 mM) at 80 °C in an aqueous KOH solution (1 M) at (a) 4 MPa and (b) 1 MPa.

Table 5 summarizes the results for the iridium complexes with dhbp, **2**, and dhpt, **5**, under various conditions. The catalysts were relatively stable at a high temperature. Unprecedented high activities [TOF = 42000 h^{-1} (entry 3) and TON = 222000 (entry 11)] were obtained at 6 MPa and 120 °C in a highly diluted solution of the catalyst (<2 μM). As compared with $[RuCl_2(tppms)_2]_2$ under the same conditions (TOF = 30–50 h^{-1} at 1 MPa and 50 °C),[29] **2** showed a far superior catalytic activity [TON = 740 after 1 h (entry 5)].[81] Furthermore, the hydrogenation of hydrogen carbonate proceeded at ambient pressure and 60 °C (entries 6 and 9) and even at 30 °C (entry 10). The results show that the corresponding hydrido complexes can be easily generated at ambient pressure, because the color of the solution changed immediately from pale yellow into deep yellow when H_2 was admitted. To the best of our knowledge, there is only one other report on homogeneously catalyzed hydrogenation of CO_2 that occurs at ambient pressure at room temperature (TON = 3 per day).[22]

Activation by the introduction of the hydroxy group into the bipyridine ligand as a catalyst ligand were also observed in ruthenium and rhodium complexes (Table 6).[63] In the (arene)ruthenium complexes $[(C_6Me_6)Ru(L)Cl]Cl$, the TONs for complexes with dhbp, **3**, and dhpt, **6**, were ca. 60 times greater than those of the unsubstituted ones. The detailed results under various conditions are summarized in Table 7. The ruthenium complexes yielded higher concentrations of formate relative to the iridium complexes, although their TOF and TON values were moderate (entries 2–5). The formate concentrations increased steadily with increasing pressure from 1.08 M at 2 MPa to 1.54 M at 6 MPa (entries 3–5). The TOFs increased with an increase in the

Table 6. Substituent effect on TON for the hydrogenation of hydrogen carbonate.[a]

Cat.[b] L =	TON bpy	dhbp	phen	TON dhpt
Ru	68	4400	78[c]	5100
Rh	216[c]	1800	220	2300

[a] The reactions were carried out at 4 MPa (CO_2/H_2 = 1:1) and 80 °C for 20 h in an aqueous KOH solution (1 M) containing the complex (0.1 mM). [b] Catalyst: Rh = [Cp*Rh(L)Cl]Cl, Ru = $[(C_6Me_6)Ru(L)Cl]Cl$. [c] The catalyst concentration was 0.2 mM.

Table 7. Hydrogenation of hydrogen carbonate using the rhodium and ruthenium complexes with the dhbp or dhpt ligand.[a]

Entry	Catalyst	T /°C	P /MPa	t /h	Initial TOF[b] /h^{-1}	TON	Final conc. of formate /M
1	**3**	80	4	20	720	4400	0.44
2	**3**[c]	120	6	8	4400	13620	1.36
3	**6**[c]	80	4	165	370	12500	1.25
4	**6**[c]	120	6	24	3600	15400	1.54
5	**6**[c]	100	2	92	600	10800	1.08
6	**1**	80	4	12	790	1800	0.18
7	**1**	80	1	24	170	1200	0.12
8	**1**	50	1	30	24	500	0.05
9	**4**	80	4	32	270	2400	0.24

[a] The reaction was carried out by using the catalyst (0.1 mM) in an aqueous KOH solution (1 M) at the desired CO_2/H_2 (1:1) pressure. [b] The initial TOFs were calculated by nonlinear least-squares fits of the experimental data from the initial part of the reaction.[36] [c] The reaction was carried out in an aqueous KOH solution (2 M).

Table 5. Hydrogenation of hydrogen carbonate with iridium complexes **2** and **5**.[a]

Entry	Catalyst (Conc./μM)	T/°C	P/MPa	t/h	Initial TOF[b]/h^{-1}	TON	Final conc. of formate/M
1	**2** (100)	80	4	140	4000	8000	0.80
2	**2** (20)	120	6	32	41000	33500	0.67
3	**2** (0.5)	120	6	57	42000	190000	0.095
4	**2** (20)	120	1	30	14200	13500	0.27
5	**2** (20)	50	1	30	820	9500	0.19
6	**2** (200)[c]	60	0.1	50	33	376	0.075
7	**5** (100)	80	4	116	3000	7300	0.73
8	**5** (20)	120	6	32	35000	26000	0.52
9	**5** (200)[c]	60	0.1	50	32	444	0.089
10	**5** (200)[c]	30	0.1	30	3.5	81	0.016
11	**5** (2)	120	6	48	33000	222000	0.44

[a] The reaction was carried out in an aqueous KOH solution (1 M) at the desired CO_2/H_2 (1:1) pressure. [b] The initial TOFs were calculated by nonlinear least-squares fits of the experimental data from the initial part of the reaction.[36] [c] The reaction was carried out in an aqueous K_2CO_3 solution (0.1 M).

reaction temperature from 60 to 120 °C without a decrease in the product yield (Figure 7). However, at ambient pressure, only a small amount of formate was generated (TOF = 1.8 at 60 °C).

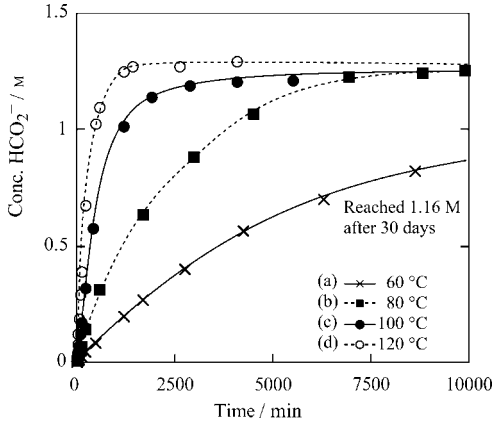


Figure 7. Time course of formate concentration during the hydrogenation of hydrogen carbonate catalyzed by ruthenium complex **6** (0.1 mM) at 4 MPa (H_2/CO_2 = 1:1) and (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) 120 °C in aqueous KOH solution (2 M).

Among rhodium complexes [Cp*Rh(L)Cl]Cl, the TOFs of the unsubstituted ones were the highest among those of all unsubstituted complexes. However, the TOFs for rhodium complexes **1** and **4** were ordinary, and the rates of increase against the unsubstituted complexes were moderate (8–10 times). In addition, the final concentrations of the formate were lower than those of the other metal complexes, probably because of the instability of the catalyst.[61]

The catalytic efficiencies (i.e., TOF, TON, and the concentration of formate) were strongly affected by the central metals. The effects of the metal in complexes with phosphane ligands were also reported.[17,31,32] Interestingly, in the series of the catalysts, the iridium complexes were superior to the rhodium and ruthenium complexes, which have so far dominated in the hydrogenation of CO_2. On the other hand, the difference between the effects of the dhbp and dhpt ligands on the catalytic efficiency is relatively small.

Interestingly, no significant decomposition of formate, which is sometimes a problem in the hydrogenation of CO_2 and hydrogen carbonate after pressure release, was observed.[39] This suggests that the catalyst activity decreases considerably at the end of the reaction, since it is highly probably that by the acidification of the reaction solution, the catalyst changes from the active deprotonated form into the sluggish protonated form, in which its activity might be lower relative to that of the methoxy analogue.

In this manner, the results demonstrated the usefulness of the concept of catalyst tuning through the acid–base equilibrium of dhbp and dhpt as a catalyst ligand for the hydrogenation of hydrogen carbonate. In other words, the catalyst in the deprotonated form showed an enormously high activity that can be attributed to the strong electron-donating ability of the oxyanion group. On the other hand, the decrease in the activity by the transformation from the deprotonated form into the protonated form restrained the reverse reaction at end of the reaction.

Catalyst Recycling

Homogeneous catalysis generally has many advantages with respect to the reaction step; however, there are considerable difficulties involved in the separation of a catalyst from the product and/or solvent as compared with heterogeneous catalysis. There have been numerous attempts to recycle catalysts by using multiphase[100–105] and immobilized[106–111] catalysts; however, these often reduce the mixing efficiency between catalyst and substrate. Recently, in order to keep homogeneity in a reaction step, significant attention has been given to stimuli-responsive catalysts such as redox-switchable,[77] magnetic-,[112] temperature-,[113] and pH-responsive,[75] and self-assembly-supported[114] catalysts.[115] However, many concerns (e.g., reduced activity and selectivity, catalyst leaching, waste generation, and use of environmentally suspected solvents) still remain. In particular, a sophisticated design generally results in increasingly expensive complexes.

Reusability of the catalyst was achieved by tuning its water solubility through the acid–base equilibrium of the ligand.[116] In the hydrogenation of hydrogen carbonate in water, it is noteworthy that the reaction solution changes from basic to acidic during the course of the reaction, because the hydrogenation of a basic hydrogen carbonate yields a formate and then formic acid after the consumption of the added base.[27] Thus, it is expected that the catalyst may spontaneously transform from the water-soluble deprotonated form at the beginning of the reaction into the poorly water-soluble protonated form at the end. In particular, iridium–dhpt complex **5** will become favorable for catalyst recycling because of its water insolubility between pH 4 and 7 (Figure 4).

The hydrogenation of hydrogen carbonate catalyzed by **5** was strongly affected by the concentration of KOH, i.e., the pH of the solution. Figure 8 shows the time course of the

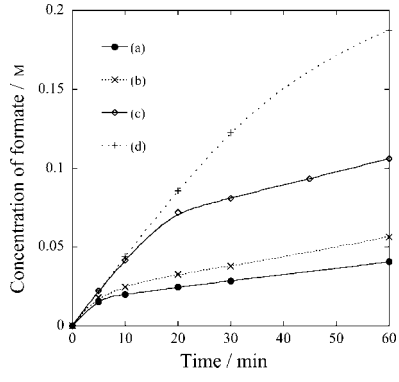


Figure 8. Time course of formate concentration during the hydrogenation of hydrogen carbonate with **5** (0.05 mM) at 6 MPa (CO_2/H_2 = 1:1) and 60 °C in (a) 0.1-M, (b) 0.2-M, (c) 0.5-M, and (d) 1.0-M aqueous KOH solution.

Table 8. Hydrogenation of hydrogen carbonate catalyzed by **5** in various KOH concentrations.[a]

KOH/M	*t*/h	Leaching [Ir][b]/ppm	Final conc. of formate/M	pH of the final solution
0.5	72	0.61	0.476	7.5
0.2	48	0.19	0.201	6.8
0.1	20	0.11	0.105	5.5

[a] The reaction was carried out by using **5** (0.05 mM) at 6 MPa (CO_2/H_2 = 1:1) and 60 °C. [b] The iridium concentration was measured by ICP-MS analysis.

formate concentration in a KOH solution (0.1–1.0 M). At the beginning of the reaction, the maximum TOFs (ca. 5000 h^{-1}) were observed in all the reactions. However, in 0.1- and 0.2-M KOH solutions, the reaction rates decreased drastically after 5 min. In a 1.0-M KOH solution, the rate was steady till 30 min, and it then decreased gradually. The results reveal that **5** exhibited high activity at the beginning of the reaction (i.e., basic conditions), in which **5** might exist in a homogeneous and activated deprotonated form.

On the other hand, prolongation of the reaction time to 72 h in 0.5-M KOH solution did not lead to complete consumption of the added base (Table 8). In other words, the reaction medium was not neutralized (pH = 7.5). Although most of the catalyst precursor was precipitated spontaneously and recovered by filtration of the obtained suspension, 0.61 ppm iridium remained in the filtrate. By using 0.2-M solutions, the added base was consumed completely, and the solution was neutralized. Hence, the remaining iridium decreased to 0.19 ppm. In particular, in 0.1-M KOH solutions, the concentration of the generated formate (0.105 M) exceeded that of the added base to give a weakly acidic suspension (pH = 5.5). The catalyst precursor was separated by filtration. As expected, the colorless filtrate was found to contain only 0.11 ppm iridium, which was 1.2% of the loaded catalyst. The value for iridium leaching was consistent with its solubility in the formate solution, as shown in Figure 4. Furthermore, the concentration of the filtrate and drying under vacuum at 100 °C resulted in pure potassium formate (>98% pure). These results imply the possibility of catalyst recycling in the conversion of CO_2 into formate without waste generation.

Subsequently, **5** was recycled in a batchwise cycle (Table 9). The above-mentioned recovered catalyst precursor was dissolved in a 0.1 M degassed aqueous KOH solution, from which 93% iridium was recovered [the loss of iridium was due to the sampling for assay (2%) and handling losses]. While all the four cycles could be performed without a significant loss of the catalytic activity, leaching increased and recovery decreased with an increase in the recycling of the catalyst. However, thermal degradation was observed. It appears that thermal stress and exposure to air lead to an increase in catalyst leaching.

The solubility behavior of **5** during the course of the reaction was visually observed by using a glass reactor. Complex **5** (0.05 mM) was completely soluble in the KOH solution with pressurized CO_2. When the reactor was recharged with 3 MPa of H_2/CO_2 (1:1) at 60 °C, the pale yellow solution immediately turned to orange, which might indicate the formation of a hydrido complex.[117] After 30 min, a yellow

Table 9. Batchwise recycling of **5** for the conversion of CO_2.[a]

Cycle	Loaded [Ir] /ppm	Recovery efficiency/%	Leaching [Ir][b] /ppm	Final conc. of formate/M
1	9.0	–	0.11	0.105
2	8.4	93	0.22	0.104
3	7.7	92	0.42	0.103
4	7.0	91	0.61	0.103

[a] The reaction was carried out at 6 MPa (CO_2/H_2 = 1:1) and 60 °C in aqueous KOH solution (0.1 M). No hydrogen carbonate was detected in all the four cycles. [b] The iridium concentration was measures by ICP-MS analysis.

precipitate was formed. After a further 2.5 h, the resulting suspension was filtered to give a clear pale yellow filtrate and yellow precipitate. The filtrate (pH = 7.9) was found to contain 0.05 M of the formate (50% conversion) and 1.0 ppm iridium (ca. 10% of the loaded iridium). The precipitate was readily converted to a deprotonated form by the addition of an aqueous base. Figure 9 shows the photographs of the reaction solution, in which ten times catalyst concentration (0.5 mM) was used for clarity. The pale yellow solution (Figure 9a) at the beginning of the reaction turned into a yellow suspension (Figure 9b) at the end of the reaction. By filtration of the suspension, a colorless solution (Figure 9c) was obtained.

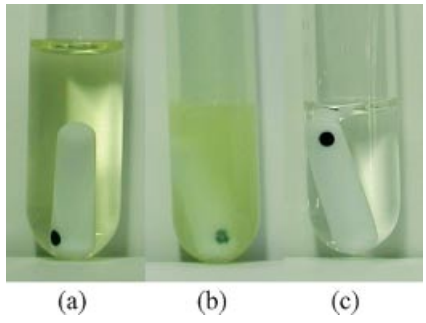
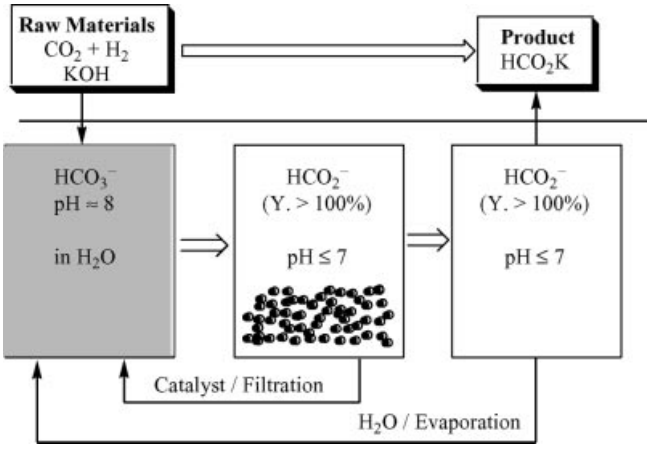


Figure 9. Photographs of the reaction solution (a) before reaction, (b) after reaction, and (c) after filtration. The reaction was carried out with **5** (0.5 mM) in an aqueous KOH solution (0.1 M) at 6 MPa (CO_2/H_2 = 1:1) and 60 °C for 15 h.

In this manner, the reusability of **5** was achieved by self-precipitation without a significant loss of catalytic activity. It is interesting to note that the three components (i.e., catalyst, product, and solvent) can be easily separated by using conventional filtration and evaporation without waste generation (Scheme 5). This catalytic system is characterized by interconversion between an active and homogeneous deprotonated form at the beginning of the reaction and an inac-

tive and heterogeneous protonated form at the end of the reaction, which is achieved through the acid–base equilibrium of the ligand; the catalyst is easily recovered, and the reverse reaction is suppressed in this system.

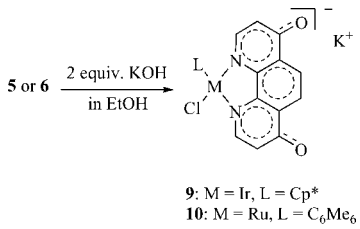


Scheme 5. Recycling system for the conversion of CO_2/H_2 and KOH into HCO_2K with **5** in water.

Mechanistic and Kinetic Studies

The mechanisms of the hydrogenation of hydrogen carbonate catalyzed by ruthenium and rhodium complexes with water-soluble phosphane ligands have been studied extensively by Joo and Katho.[26–32] Recently, a theoretical investigation with the density functional theory was reported.[25] Although these studies increased their mechanistic understanding, the pH-dependent catalysts with dhbp and dhpt ligands in our system are distinct from water-soluble phosphane complexes.

Deprotonated dhpt complexes [Cp*Ir(L^2)Cl]K (**9**) and [(C_6Me_6)Ru(L^2)Cl]K (**10**) were isolated from an alkaline ethanol solution by the addition of ethyl ether (Scheme 6). Similar to the dhbp complex **7**, significant shifts of the deprotonated forms **9** and **10** were observed in the ^1H and ^{13}C NMR spectra in [D_6]dmso relative to those of the protonated forms **5** and **6**, respectively.[63] The ^1H NMR spectrum of **9** in D_2O was nearly identical to that of **5** in KOD/D_2O (i.e., the deprotonated form of **5**).



Scheme 6. Preparation of deprotonated complexes **9** and **10**.

The properties of the hydrido complexes [(C_nR_n)-MH(ppy)]$^+$ [M = Rh, Ir (n = 5), M = Ru (n = 6)] are dependent on the central metal (M). Hydrido(iridium) complexes with bipyridine and phenanthroline were prepared by a reaction with $NaBH_3CN$ or a formate and were isolated.[92,118,119] The hydrido(iridium) complexes appear to be relatively stable.[55,117] Hydrido complexes [Cp*IrH-(L^1)]$^-$ (**11**) and [Cp*IrH(L^2)]$^-$ (**12**) were quantitatively generated under H_2 pressure. In comparison with the hydrido complexes with unsubstituted and methoxy-substituted bipyridine, significant upfield shifts of the aromatic protons in **11** and **12** were observed due to the oxyanion (Table 10). Hydrido(ruthenium) complex [(C_6Me_6)RuH(bpy)]$^+$ was isolated by Ogo.[91] Under H_2 pressure, hydrido complexes [(C_6Me_6)RuH(L^1)]$^-$ (**13**) and [(C_6Me_6)RuH(L^2)]$^-$ (**14**) were generated as a mixture of the corresponding deprotonated forms, whose ratios depended on the H_2 pressure. However, the hydrido(rhodium) complex has never been isolated. Indeed, the corresponding hydrido complexes from **1** and **4** were not detected spectroscopically.

The reaction of the hydrido(iridium) complexes with $KHCO_3$ in aqueous solution led to the production of formate in an atmosphere of H_2. However, no formate was generated in the reaction with K_2CO_3. In the hydrogenation catalyzed by **2**, there was no induction period in the solution saturated by CO_2 prior to the reaction (Figure 10).[81] Conversely, an induction period was observed in the solution saturated by H_2 prior to the reaction. This indicates that the overall rate of the generation of hydrido complexes from **2** and the subsequent reaction with hydrogen carbonate was extremely rapid, when compared with the rate of hydration of CO_2 in aqueous KOH solution.

Scheme 7 shows the proposed pathway for the generation of hydrido complexes, which is marked by the acid–base equilibrium of dhbp and dhpt. The protonated form (**PX**: X = Cl) as the catalyst precursor was transformed into the deprotonated form (**DX**) in an alkaline solution. The reaction of **DX** with H_2 yielded the deprotonated hydrido complex (**DH**), which probably is the actual catalyst. The strong electron-donating ability of oxyanion on **DH** will play a significant role in the activation of the hydrido complexes. The generation of **DH** is strongly dependent on the central metal (M): under H_2 pressure, the iridium hydrido complexes are formed quantitatively, but the ruthenium complexes attain equilibrium between **DH** and **DX**. It is likely that the hydride-formation step is one of the factors that affect the catalyst activity of the hydrogenation of hydrogen carbonate. This hypothesis is consistent with the mechanistic investigation of Ogo: the rate-determining step for the hydrogenation of CO_2 in an acidic solution by using the methoxy ruthenium analog [(C_6Me_6)Ru(Me_2L^1)(H_2O)]$^{2+}$ is the formation of a hydrido complex, whereas it is the reaction of the hydrido complex with CO_2 in the methoxy iridium analog [Cp*Ir(Me_2L^1)(H_2O)]$^{2+}$.[82]

The actual substrate could be established as hydrogen carbonate under basic conditions and as CO_2 under acidic conditions (Scheme 8).[33] It is known that CO_2 readily gets inserted into the metal–hydrogen bond to give a formato complex in nonaqueous media.[66,120–123] Similarly, the formato complex is believed to be generated by the insertion of CO_2 into the metal–hydrogen bond in an acidic aqueous solution and a water/amine mixture.[22,82] Indeed, the for-

Table 10. ^{1}H NMR spectroscopic data for hydrido complexes.

Complex	Solvent	M–*H*	Cp*/C_6Me_6	δ/ppm [bpy(3,3′;4,4′;5,5′;6,6′)/ phen(2,9;3,8;4,7;5,6)]	Ref.
$[Cp^*IrH(bpy)]^+$	$[D_6]$acetone	–11.45	1.93	8.55; 8.16; 7.72; 9.11	[118]
$[Cp^*IrH(phen)]^+$	$[D_6]$acetone	–11.35	2.00	9.48; 8.10; 8.80; 8.28	[118]
$[Cp^*IrH(bpy)]^+$	D_2O	–11.80	1.78	8.29; 8.11; 7.62; 8.90	[92]
$[Cp^*IrH(Me_2L^1)]^+$	dmso	–11.25	1.79	8.33; –; 7.33; 8.65	[82]
$[Cp^*IrH(L^1)]^-$ (**11**)	KOD/D_2O	–11.09	1.75	7.15; –; 6.58; 8.15	[90]
$[Cp^*IrH(L^2)]^-$ (**12**)	KOD/D_2O	–11.10	1.69	8.40; 6.75; –; 7.92	[90]
$[(C_6Me_6)RuH(bpy)]^+$	D_2O	–7.45	2.14	8.19; 7.93; 7.48; 8.57	[91]
$[(C_6Me_6)RuH(L^1)]^-$ (**13**)	KOD/D_2O	–7.46	2.03	7.03; –; 6.49; 7.83	[90]
$[(C_6Me_6)RuH(L^2)]^-$ (**14**)	KOD/D_2O	–7.58	2.02	8.12; 6.66; –; 7.83	[90]

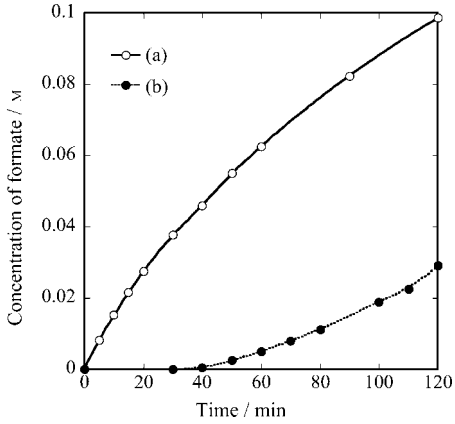
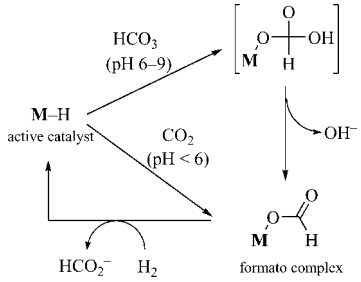


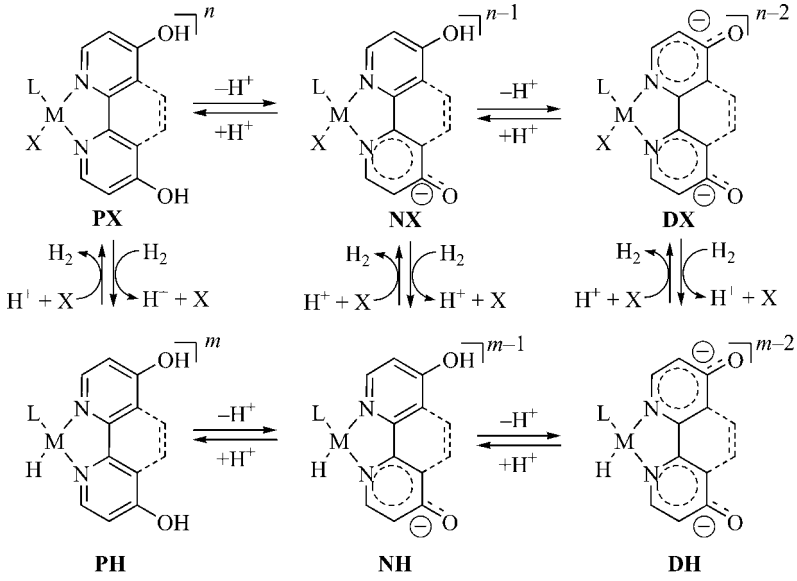
Figure 10. Time course of formate concentration during the hydrogenation of hydrogen carbonate catalyzed by **2** (20 μM) at 1 MPa (CO_2/H_2 = 1:1) and 80 °C after the reaction solution was saturated by (a) CO_2 and (b) H_2.[81]

mato(ruthenium) complex was isolated in aqueous formate solution.[87] In contrast, the key intermediate has not been observed experimentally in the basic aqueous solution. However, it is assumed that the hydrogen carbonate is inserted into the metal–hydrogen bond, after which a formato intermediate is generated with the accompanying release of a hydroxide ion.[29,31]



Scheme 8. Suggested pathway for the hydrogenation steps of HCO_3^-/CO_2 in water.

During the course of the reaction, the acidification due to formate generation might cause the deprotonated form (**D**) to transform into the monoprotonated (**N**) or fully protonated form (**P**). Hence, this results in less catalytic activity and prevention of the decomposition of the formate as a reverse reaction. In particular, iridium–dhpt complexes,



Scheme 7. Proposed pathway for the generation of hydrido complexes in the hydrogenation of HCO_3^-/CO_2 in water.

whose solubility is negligible under weak acidic formate conditions, can be recovered almost quantitatively at the end of the reaction. Further studies are required to clarify the interesting catalytic system for the conversion of CO_2 in detail.

Summary and Outlook

The CO_2 conversion system that uses the half-sandwich complexes with dhbp and dhpt has significant features (high efficiency, catalyst recycling by self-precipitation, easy isolation of product, waste-free process, aqueous reaction, and prevention of reverse reaction); further, the system overcomes almost all of the problems occurring in the homogeneously catalyzed hydrogenation of CO_2 into formate. It should be noted that over a 1000-fold increase in catalytic activity was achieved as a result of the strong electron-donating ability of the oxyanion on the catalyst ligand. In addition, the three components (i.e., catalyst, product, and solvent) could be easily separated by conventional filtration and evaporation without waste generation. Our next goal will be the conversion of CO_2 into products other than formate (e.g., methanol or oxalic acid) by the homogeneously catalyzed hydrogenation of CO_2.

More importantly, the tuning of the catalyst through the acid–base equilibrium of dhbp or dhpt as a catalyst ligand offers a novel tool for the simultaneous control of the activity and water solubility of complex catalysts. It was shown that the properties of iridium complexes were strongly dependent on the pH of the aqueous solution. These significant features are attributed to the electronic effect and polarity of the oxyanion generated from the phenol hydroxy group. Consequently, the system combines the advantages of homogeneous catalysis (i.e., high catalytic performance) with those of heterogeneous catalysis (i.e., simplicity of catalyst separation) and biocatalysis (aqueous reaction and pH dependence). The control of catalyst properties through the acid–base equilibrium between pyridinol and pyridinolato as a ligand has not been explored previously in catalyst systems. For these features to appear, only the introduction of a hydroxy group into the pyridine and subsequent pH control are required. This catalyst design concept is expected to have significantly broader implications for the design of new homogeneous catalysts (e.g., strong electronic effect and water-soluble ligand). The idea of catalyst tuning will become increasingly important and will be an extremely challenging field of study.

Abbreviations: dhbp, 4,4′-dihydroxy-2,2′-bipyridine; dhpt, 4,7-dihydroxy-1,10-phenanthroline; edta-H, protonated ethylenediaminetetraacetic acid; pta, 1,3,5-triaza-7-phosphaadamantane; TON, turnover number (mole product per mol catalyst); TOF, turnover frequency (TON per hour); tppms, sodium 3-(diphenylphosphanyl)benzenesulfonate; tppts, triphenylphosphane-3,3′,3′′-trisulfonic acid trisodium salt.

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