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Article

Mechanistic Studies on the Reversible Hydrogenation of Carbon Dioxide Catalyzed by an Ir-PNP Complex

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Supporting Information

ABSTRACT: The PNP-ligated iridium(III) trihydride complex 1 exhibited the highest catalytic activity for hydrogenation of carbon dioxide in aqueous KOH. The catalytic hydrogenation can be tuned to be a reversible process with the same catalyst at the expense of the activity, when triethanolamine was used as a base. Theoretical studies on the hydrogenation of carbon dioxide using DFT calculations suggested two competing reaction pathways: either the deprotonative dearomatization step or the hydrogenolysis step as the rate-determining step. The results nicely explain our experimental observations that the catalytic cycle is dependent on both the strength of the base and hydrogen pressure.



INTRODUCTION

Formic acid is widely used as a preservative, as an insecticide, for tanning leathers, etc.¹ The major synthetic route for formic acid in industry is carbonylation of methanol catalyzed by a basic catalyst such as sodium methoxide and subsequent hydrolysis of the obtained methyl formate.² Formic acid is also obtained as a byproduct in the production of acetic acid via oxidation of butane or naphtha.³ Although direct carbonylation of water is not a practical process, due to the lower thermodynamic stability of formic acid compared to water and CO,⁴ an aqueous solution of sodium hydroxide is effectively carbonylated to give sodium formate, which is acidified to produce formic acid.^{3,5} A potentially alternative and attractive process for the formation of formic acid is hydrogenation of carbon dioxide, the most important greenhouse gas.^{6–10}

In the past few years, the hydrogenation of carbon dioxide was spotlighted as a possible method for hydrogen storage, due to the global energy crisis.^{11–15} Several transition-metal (e.g., Ru,^{16–28} Ir,^{22,29,30} Rh,^{24,31–33} Mo, Ni,³⁴ Pd,³⁵ and Fe^{36,37}) catalysts were used for the hydrogenation of carbon dioxide. When we initiated our project in 2008, the two highest catalytic activities for hydrogenation of CO2 were documented: Noyori and Jessop used ruthenium phosphine complexes to catalyze reaction of supercritical carbon dioxide with tertiary amines with a turnover frequency (TOF) of 95 000 h^{-1} ,¹⁹ and Himeda applied cationic iridium complexes for the first example of the hydrogenation of carbon dioxide in basic aqueous phase under ambient pressure with a turnover number (TON) of 222 000.²⁹ Formation of formic acid from carbon dioxide and hydrogen in the gas phase is highly endoergic because of a large entropy loss due to the decreasing number of molecules.⁶ Greater stabilization to the polar product, formic acid, than to the two gaseous and nonpolar substrates by hydration promotes

the reaction in water solution to be an exergonic process (eqs 1 and 2). Nevertheless, the advantage of the free energy gain for the formation of formic acid from aqueous hydrogen and carbon dioxide is only 4 kJ/mol,⁸ suggesting that the equilibrium toward formic acid is only slightly favorable. In fact, catalytic hydrogenation of carbon dioxide under neutral or acidic conditions exhibits rather low activities.^{21,22} Thus, basic conditions are often employed for the hydrogenation, taking advantage of the stability of a formate salt being higher than that of a free acid (eq 3).^{6–8}

$$H_{2}(gas) + CO_{2}(gas) \rightarrow HCOOH(liq)$$
$$\Delta G(298 \text{ K}) = 33 \text{ kJ/mol}$$
(1)

$$\Delta G(298 \text{ K}) = -4 \text{ kJ/mol}$$
(2)

$$H_{2}(aq) + CO_{2}(aq) + NH_{3}(aq)$$

$$\rightarrow NH_{4}^{+}HCOO^{-}(aq)$$

$$\Delta G(298 \text{ K}) = -35 \text{ kJ/mol}$$
(3)

Dehydrogenation of formic acid or its salt, which is the reverse reaction of the hydrogenation of CO_2 , is also an important process for hydrogen storage to release a hydrogen source. Ruthenium,^{38–47} rhodium,^{48–50} iridium,^{48,51–53} platinum,^{54,55} molybdenum,⁵⁶ and iron^{57,58} complexes were reported to catalyze the dehydrogenation of formic acid. Ruthenium catalysts were the most intensely studied catalysts and led to the highest activity (TOF = 18 000 h⁻¹) using a 5:2 mixture of formic acid and triethylamine, as reported by

Received: October 31, 2011 Published: November 30, 2011 Morris.⁴⁶ For practical hydrogen storage, the reaction in both directions needs to take place with reasonably high TOFs. Successful reversible hydrogenation/dehydrogenation of formic acid or its salt catalyzed by the same ruthenium or iridium catalyst was reported (Figure 1).^{18,20,24,31,32,47}



Figure 1. Recent examples for dehydrogenation of formic acid and its salts.

In 2009, we communicated that the iridium trihydride complex 1 containing a PNP-pincer ligand⁵⁹ catalyzed the hydrogenation of carbon dioxide. The highest catalytic activity ever reported was accomplished when aqueous KOH was used as a base.⁶⁰ We also proposed a possible mechanism of hydrogenation of carbon dioxide catalyzed by 1 by observing the intermediates 2 and 3 and several elementary reactions in the proposed catalytic cycle. For the catalytic cycle of this reaction, Ahlquist⁶¹ and Yang⁶² suggested another reaction pathway of hydrogen activation using theoretical calculations (vide infra).

Herein we report our detailed studies on this highly active catalytic hydrogenation reaction. The reversibility of the reaction was realized by optimizing the reaction conditions. In order to shed light on the reaction mechanism, the effect of hydrogen pressure, base, and isotope were further studied. We also estimated the energy profile of the reaction pathways and elucidated that the existence of water molecules is essential for the catalytic cycle by using DFT calculations. Experimental and theoretical studies both suggested that the two reaction pathways previously proposed by us⁵⁸ and others^{59,60} can compete with each other under the reaction conditions.

RESULTS AND DISCUSSION

1. Hydrogenation of Carbon Dioxide Catalyzed by the Ir(III) Complexes 1 and 4. As previously reported, hydrogenation of carbon dioxide using the Ir(III) complex 1 afforded potassium formate in aqueous KOH solution with a TOF of 150 000 h^{-1} (Table 1, entry 1) and a TON of 3 500 000 (entry 3), both of the values being the highest ever reported.⁶⁰ Here we further investigated the reaction with varied reaction conditions. The reaction could be scaled up to a 10 times larger scale (entry 2). A significant pressure effect was also observed as, under ambient pressure of dihydrogen and carbon dioxide, the catalytic activity was decreased to a TON of 43 at 100 °C in 40 h (entry 4). Moreover, the reaction did not proceed at room temperature, even under pressurized conditions (entry 5). A higher concentration of KOH (5.0 M) leading to higher pH conditions resulted in lower activity (entries 1 and 6).⁶³ In the presence of tertiary amines such as triethylamine in an ethanol solution, ammonium formate was obtained, although the catalytic activity was lower than that in aqueous KOH (entry 7). The presence of a very polar solvent is essential for the reaction, as the reaction did not proceed in THF (entry 8). In comparison, the reaction with triethanolamine in water showed higher catalytic activity than with triethylamine in EtOH (entries 9 and 7). Importantly, when D₂O was used as a solvent instead of H₂O, the TOF was lowered (entries 10 and 1), indicating that proton transfer is involved in the key reaction of the catalytic cycle. It is notable that treatment of 1 in KOH/D₂O at room temperature for 18.5 h led to H–D exchange at the py- CH_2 -PⁱPr₂ position (Scheme 1), suggesting that most of the active species in D_2O partially

Table 1. Hydrogenation of Carbon Dioxide Catalyzed by Ir(III)-Pincer Complexes 1 and 4

			H ₂ + CO ₂ I (1 : 1) Base (Solver THF	r cat. 5.0 mmol) ht (5.0 mL) (0.1 mL)	H HCOOH • Base ⁱ Pr ₂ P	P ⁱ Pr ₂ 1 (X = 4 (X =	H) CI)		
entry	cat. (amt (μ mol))	solvent	base	temp (°C)	total pressure a (MPa)	time (h)	yield (%)	TON (10^3)	TOF $(10^3 h^{-1})$
1^b	1 (0.010)	H_2O	КОН	200	8.0 ^{<i>c</i>,<i>d</i>}	2	60	300	150
2	1 (0.1)	H_2O	КОН	200^{e}	6.6 ^e	2	15	76	38
3 ^b	1 (0.0010)	H_2O	КОН	120	8.0 ^{c,f}	48	70	3500	73
4	1 (1.0)	H_2O	КОН	100	0.13	40	1	0.043	0.001
5	1 (1.0)	H_2O	КОН	25	5.0 ^c	48	0	0	0
6	1 (0.010)	H_2O	КОН ^g	200	$8.0^{c,d}$	2	12	58	29
7	1 (10)	EtOH	Et ₃ N	200	8.0 ^{<i>c</i>,<i>d</i>}	2	15	0.075	0.38
8	1 (0.010)	THF	N(CH ₂ CH ₂ OH) ₃	200	8.0 ^{<i>c</i>,<i>d</i>}	2	0	0	0
9	1 (0.010)	H_2O	N(CH ₂ CH ₂ OH) ₃	200	8.0 ^{<i>c</i>,<i>d</i>}	2	6	29	14
10	1 (0.010)	D_2O	КОН	200	8.0 ^{<i>c</i>,<i>d</i>}	2	21^{h}	110	53
11	1 (0.010)	H_2O	КОН	200	5.6 ^{<i>c</i>,<i>i</i>}	2	13	63	32
12^{b}	4 (0.010)	H_2O	КОН	200	8.0 ^{<i>c</i>,<i>d</i>}	13	20	100	7.7
13	4 (0.010)	H_2O	КОН	200	5.6 ^{<i>c</i>,<i>i</i>}	13	13	63	4.8
14	4 (0.010)	H ₂ O	КОН	200	$3.2^{c_{,j}}$	13	10	48	3.7

^{*a*} Total pressure of inside of the reactor when the system reached the reaction temperature. ^{*b*} Data taken from ref 58. ^{*c*} A 50 mL autoclave was used, and the whole apparatus was heated by an aluminum block. ^{*d*} The initial total pressure was 5.0 MPa at 24 °C. ^{*c*} A 300 mL autoclave was used, and only the bottom part was heated by an oil bath. The pressure at 24 °C was 5.0 MPa. ^{*f*} The initial total pressure was 6.0 MPa at 24 °C. ^{*g*} A 25 mmol portion of KOH was used. ^{*h*} Total yield of HCOOK and DCOOK. ^{*i*} The pressures of H₂ and of CO₂ were 1.0 and 2.5 MPa, respectively, at 24 °C. ^{*j*} The pressures of H₂ and of CO₂ were 1.0 and 1.0 MPa, respectively, at 24 °C.





incorporates deuterium in the methylene groups. Lowering the H_2 pressure decelerated the reaction even on maintaining the CO_2 pressure (entries 1/11 and 12/13). Lowering the CO_2 pressure also decelerated the reaction under the same H_2 pressure (entries 13 and 14). Therefore, it was revealed that the reaction rate is dependent on the H_2 and CO_2 pressures, the strength of the base, and the use of very polar solvents.

2. Dehydrogenation of Formic Acid and Its Salt Catalyzed by the Ir(III) Complex 1. Dehydrogenation of formic acid or its salt using the Ir(III) complex 1 as a catalyst was also investigated. The aqueous solution of formic acid was found to decompose and form dihydrogen, which was collected by water replacement and analyzed by GC. The catalytic activity was calculated by assuming that all the collected gas was dihydrogen, and thus the TON of the reaction was estimated to be 890 (Table 2, entry 1).⁶⁴ However, dehydrogenation did not proceed when sodium formate was used (entry 2). The use of triethylammonium formate greatly improved the catalytic activity, and its initial TOF reached 120 000 h^{-1} (entry 3), which is 6 times higher than the previously reported value by the best Ru catalyst.⁴⁶ The starting material was completely consumed after 4 h, and the TOF for this condition was calculated to be at least 1200 h^{-1} (entry 4). The TOF is about the same order as those with previously reported catalysts.³⁸⁻⁵⁸ When triethanolamine was used, the TON reached 4900 at 60 °C (entry 5). It should be noted that, with triethanolamine as the base, the hydrogenation of carbon dioxide also proceeded smoothly (TOF = $14\,000 \text{ h}^{-1}$; Table 1, entry 9), showing that the iridium catalyst 1 can be used for reversible hydrogen storage.

3. Theoretical Studies on the Hydrogenation of Carbon Dioxide using 1. Scheme 2 summarizes the mechanistic studies of the hydrogenation with the Ir complex 1 in our previous communication.⁶⁰ The key findings are briefly discussed as follows. (1) Exposure of 1 to 1 atm of CO_2 led to a 1:1 mixture of 1 and the dihydridoformatoiridium complex 2, which were unable to be isolated due to the equilibrium between 1 and 2. (2) The chloroiridium dihydride complex 4, an analogue of 2, was treated with CsOH·H₂O to give the amidoiridium dihydride complex 3, which was formed by

Scheme 2. Summary of Our Previous Mechanistic Investigations for Hydrogenation of CO₂ using Iridium Complex 1



deprotonation from Ar– CH_2 -PⁱPr₂ and subsequent dearomatization of the pyridine ring.^{65–70} (3) Exposure of amidoiridium dihydride complex 3 to 1 atm of hydrogen resulted in the regeneration of 1. Therefore, a catalytic cycle which consists of three elementary reactions, insertion of CO_2 into 1, deprotonative dearomatization with dissociation of formate ligand in 2, and hydrogenation of 3 to regenerate the trihydride complex 1, was proposed as shown in Scheme 3.⁶⁰ Very recently, the catalytic cycle of the reaction was studied theoretically by Ahlquist⁶¹ and Yang,⁶² suggesting another reaction pathway of hydrogen activation (vide infra).

Herein we report our DFT calculations for possible intermediates, including 1–3 and transition states. The B3LYP^{71–73} method and Lanl2dz^{74–76} on iridium and 6-31++G(d,p) on the other atoms as basis sets were employed for the calculations. The polarizable continuum model (PCM)^{77–80} was used to estimate bulk solvent effects using water as the solvent. The energies in the gas phase were also calculated to estimate the solvent effects, and this will be discussed in section 3.5.

It appears that a reliable method for evaluation of free energy in solution has not been fully established. The gas-phase free energy plus solvation free energy is often used. However, some gas-phase entropy, in particular the translational entropy, should in part be "quenched" in solution. Several scaling methods have been proposed.^{81–89} In the present paper, we show the calculated energy and entropy values in Table S1 and evaluated several "scaled" as well as unscaled free energies in

Table 2. (Catalytic I	Dehydroge	nation of	f Formic	Acid or	Its	Salt t	ising I	r Com	plex 1	1
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		HCOOH (1 mr	• Base	→ H ₂ + CO ₂	+ Base ⁱ Pr ₂ P-	HH -r-P ⁱ Pr ₂ N 1		
entry	solvent	base	amt of $1 \ (\mu mol)$	temp (°C)	time (h)	yield (%)	TON (10^3)	TOF $(10^3 h^{-1})$
1	H_2O	none	1.0	60	43	18	0.89	0.020
2	H_2O	NaOH	1.0	60	48	0	0	0
3 ^{<i>a</i>}	^t BuOH	Et ₃ N	1.0	80	0.016	40	2.0	120
4 ^{<i>a</i>}	^t BuOH	Et ₃ N	1.0	80	4	100	5.0	1.2
5 ^{<i>a</i>}	H_2O	$N(CH_2CH_2OH)_3$	0.10	60	5	10	4.9	1.0

^{*a*}A 5 mmol portion of HCOOH (base) was used.

Scheme 3. Our Proposed Mechanism for Hydrogenation of CO_2 using Iridium Complex 1⁵⁸



solution in Table S2 (see the Supporting Information). In the following discussion, we simply adopt the values in which the gas-phase vibrational and rotational entropies are retained, but the gas-phase translational entropy is assumed to be totally quenched (set to zero). Because of these uncertainties, we avoid quantitative comparison and limit ourselves to qualitative comparison of reaction free energy profiles within such uncertainties. The energies for all stationary points were calculated relative to the iridium trihydride complex 1 and isolated substrates. In Schemes 4–7, the values in water and in the gas phase are drawn as solid lines and dotted lines, respectively. Our theoretical results will be compared with the experimental data in section 3.6.

3.1. Insertion of Carbon Dioxide into the Trihydridoiridium Complex. First, the theoretical investigation of the reaction of trihydridoiridium complex 1 and CO_2 is discussed (Scheme 4). In our experiment, complex 1 is in equilibrium with dihydridoformato complex 2 in THF. For this interconversion, we find that the intermediate 5, in which carbon dioxide is attacked by the weaker hydride ligand cis to the nitrogen ligand, is more stable than 1 by 8.4 kcal/mol. The energy barrier for insertion of carbon dioxide is calculated to be 4.2 kcal/mol. After a rearrangement via TS5/2, the proposed intermediate 2 is formed and calculated to be more stable than 1 by 9.9 kcal/mol. In contrast, the formate intermediate 2 is calculated to be higher in energy than 1 by 1.1 kcal/mol in the gas phase.

3.2. Deprotonation of Dihydridoformatoiridium Complex and the Following Elimination of Formate Ligand. The energetic profile for the reaction of dihydridoformatoiridium complex 2 and a base is discussed next (Scheme 5). Experimentally, the dihydridochloroiridium complex 4, a model compound of 2, was treated with an excess amount of cesium hydroxide to give the dihydridoamidoiridium complex 3 (Scheme 2). The following mechanism is suggested for the reaction of model compound 4: deprotonation on the α -carbon of the pyridine ring, dearomatization of the pyridine ring to form an amidoiridium intermediate, and finally elimination of the chloride ligand. However, the directly deprotonated anionic complex 6 is calculated to be less stable than 2 by 17.6 kcal/ mol. On the other hand, dissociation of the formate ligand of 2 to give the cationic dihydride complex 7 is a slightly endoergic process by 1.1 kcal/mol (shown in a red solid line in Scheme 5). We were unable to locate transition states connecting 2 and 7, presumably because of a low barrier. It is likely that there is an equilibrium between the intermediate 2 and hydroxide complex 8, which is about 3.0 kcal/mol lower in energy than 2. The activation energy for proton transfer to give the watercoordinated dihydridoamido complex 9 from 8 is calculated to be 14.4 kcal/mol via TS8/9. Dissociation of water from 9 to 3 was slightly endoergic by 0.4 kcal/mol. Thus, this reaction is more likely to take place via dissociation of the formate ligand followed by deprotonation: $2 \rightarrow 7 \rightarrow 8 \rightarrow 9 \rightarrow 3$.

3.3. Addition of Dihydrogen to Dihydridoamidoiridium Complex. Experimentally, addition of dihydrogen to dihydridoamidoiridium complex 3 gave 1 at ambient pressure (Scheme 2). The relative energy of the dihydrogen-coordinated complex 10 is calculated to be -10.6 kcal/mol and is less stable than 8 by 2.3 kcal/mol (Scheme 6). The heterolytic cleavage reaction of the coordinated dihydrogen of 10, leading to 1, is exoergic by





^{*a*}The vibrational and rotational entropy terms only are included in solution.

Scheme 5. Free Energy Change for Deprotonative Dearomatization of Dihydridoformatoiridium Complex 2^{a}



^aThe vibrational and rotational entropy terms only are included in solution. The more favorable path is shown in red.

17.1 kcal/mol. The activation barrier via TS10/1 is 20.3 kcal/mol relative to 8 (shown by black solid lines).

Milstein studied the addition of dihydrogen to a PNP-ligated phenylhydridoiridium complex by theoretical methods⁹⁰ and found that the activation energy is 18.2 kcal/mol, which is close to our current result. In their study, addition of two water molecules accelerates the cleavage of dihydrogen. We also examined the addition of two explicit water molecules to 10 and to 1 in order to estimate the acceleration effect of water. We found the cleavage transition state TS10/11·2H₂O, which is 5.8 kcal/mol above 10.2H2O and is featured mainly as a protonation transition state, as the distance between oxygen atom of the water molecule and hydrogen atom of the dihydrogen molecule is still long (red solid lines). TS10/ $11.2H_2O$ did not directly give the intermediate $1.2H_2O$, but intermediate 11 was located in which the pyridylmethyl position is protonated with the long distance between the oxygen atom of water and the hydrogen atom of the dihydrogen molecule (2.092 Å). Attempts to locate a transition state connecting intermediate 11 and 1.2H2O proved to be unsuccessful, probably due to the very flat potential energy surface and the very early nature of this transition state. It should be noted that TS10/11·2H₂O and 11 are very similar in energy ($\Delta\Delta G = 0.7$ kcal/mol). Therefore, TS10/11·2H₂O might be considered as a quasi-concerted, but highly asynchronous, transition state. The transition state containing one water molecule, TS10/1·H₂O, is 8.2 kcal/mol higher in energy than TS10/11·2H₂O but lower in energy than TS10/1 by 5.1 kcal/mol (blue solid lines). The free energy change ΔG from 10 to $10 \cdot H_2O$ is -0.7 kcal/mol and ΔG from TS10/1 to TS10/1·H₂O is -5.1 kcal/mol. In sharp contrast, the additional water molecule, participating in the reaction, decreased the activation barrier for the dihydrogen activation. The overall barrier via TS10/11·2H₂O relative to 8 is 7.0 kcal/mol, lower than that via TS8/9 by 7.4 kcal/mol.

3.4. Dissociation of Formate from Dihydrideformate Complex. Using a simplified model with 2,6- $(H_2PCH_2)_2C_5H_3N$, Ahlquist theoretically investigated an alternative route from 2 to 1 via dissociation of the formate ligand;⁸ namely, the formate ligand on 2 first dissociates to give

cationic dihydride complex 7, coordination of the dihydrogen molecule and hydroxide ion to 7 gives 12, and then heterolytic cleavage of the dihydrogen molecule assisted by hydrogen bond results in the formation of $1 \cdot H_2O$. Yang⁶² supported the mechanism by calculations using an exact catalyst model without consideration of the coordination of water molecules.

The reaction from 2 to 1 via 7 and 12 has to overcome the highest-energy transition state TS12/1 with a barrier of 14.4 kcal/mol relative to 8 (Scheme 7). On the basis of these results, the two routes $2 \rightarrow 7 (\rightarrow 8) \rightarrow 12 \rightarrow 1$ and $2 \rightarrow 7 \rightarrow 8 \rightarrow 9 \rightarrow 3 \rightarrow 10 \cdot 2H_2O \rightarrow 11 \rightarrow 1$ seem to compete, since the activation barrier difference is very small.

3.5. Theoretical Investigation in Gas Phase To Reveal the Solvent Effect. The relative energies for all stationary points in the gas phase were also compared to estimate the solvent effect (Schemes 4–7). The activation energy of insertion of carbon dioxide to trihydride complex 1 via TS5/2 was 23.1 kcal/mol higher than that in water. The energy difference between trihydride complex 1 and dihydrideformate complex 2 was 1.1 kcal/mol, which is less stable than that in water.

The deprotonation of **2** by hydroxide ion leading to anion intermediate **6** is highly exergonic by -45.4 kcal/mol relative to **1**, much lower in energy than in water, which originates from the high instability of the hydroxide ion in the gas phase. The succeeding elimination of the formate ligand gave the dihydridoamido complex **3** with an endoergicity of 16.7 kcal/ mol. It is notable that another intermediate 7, which was generated by dissociation of formate from **2**, was considerably destabilized to 90.8 kcal/mol with reference to **1** in the gas phase. Thus, the conversion from **2** to **3** or **8** in less polar solvents seems more likely to proceed via deprotonation to give intermediate **6** followed by dissociation of formate.⁹¹

The transition state for the heterolytic cleavage of dihydrogen on dihydridoamido dihydrogen complex TS10/1 was 36.8 kcal/mol higher in energy than intermediate 6. The transition state containing one water molecule, $TS10/1\cdot H_2O$, is almost the same in energy as TS10/1. Therefore, the reaction is unlikely to take place in a nonpolar or gas-phase environment.

3.6. Comparison between the Theoretical and Experimental Results. Now we compare our theoretical results with

∆G_{PCM,vib+rot} + H₂O TS10/1 + 2H₂O 7.4 10*H₂O 2 **AG(kcal/mol** TS10/1*H20 -2 5 10 + H₂ -6.3 -5.9 23 -10.6 11 TS10/11 10*2H2O *2H20 -11.7 -27 7 1*2H20 -28.0 1*2H20 -29. TS10/1 10 10*H2O TS10/1*H20 1*H20 Ĥ O-H: 2.092Å 1*2H20 10*2H2O TS10/11 11 2H20 TS10/11 TS10/1*H20 ∆G_{gas} 2H20 11 -8.5 -10.9 +H20 +2H2C -11.6 TS10/1 AG(kcal/mol) 10*2H2O 8.6 -22.2 -26.9 -28. 10 10*H2O 3 1*2H20 -37.4 -24.5 1*H20 -38.9 40 1

Scheme 6. Free Energy Change for Addition of Dihydrogen to Dihydridoamidoiridium Complex 3 and Effect of Addition of Two Water Molecules^a

 a The PNP ligand was simplified in the presence of two water molecules for clarity. The vibrational and rotational entropy terms only are included in solution.

Scheme 7. Free Energy Change for Dissociation of Formate from 2 and the Following Heterolytic Cleavage of Dihydrogen^a



 ${}^{a}\mathrm{The}$ vibrational and rotational entropy terms only are included in solution.

our experimental data. For the initial CO_2 insertion into Ir trihydride 1, the intermediate 2 was calculated to be 9.9 kcal/ mol more stable than 1 in the water phase. In contrast, formate 2 was calculated to be higher in energy than 1 by 1.1 kcal/mol in the gas phase. Experimentally, we observed a 1:1 equilibrium mixture of 1 and 2 *in THF, but it was not in the real reaction media KOH*/H₂O/THF.

For the whole catalytic cycle, we propose that the reaction can take place via both/either $2 \rightarrow 7 \rightarrow 8 \rightarrow 9 \rightarrow 3 \rightarrow$ $10 \cdot 2H_2O \rightarrow 11 \rightarrow 1$ and/or $2 \rightarrow 7 \rightarrow 12 \rightarrow 1$ (Scheme 8). The rate-determining step could be the deprotonative dearomatization step $8 \rightarrow 9$ via TS8/9 for the former reaction pathway and the hydrogenolysis step $12 \rightarrow 1$ via TS12/1 for the latter pathway. The relative energies of the two ratedetermining transition states are nearly identical in solution in the present scaling scheme. The step $8 \rightarrow 9$ should be slowed down in D₂O (entry 10, Table 1), since the methylene protons in 8 are easily replaced by deuterium (Scheme 1). In addition, the equilibrium among 7, 8, 9, and 3 should be strongly affected by the concentration of base (entries 1 and 6–9). However, this step should be less affected by the hydrogen pressure. On

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Scheme 8. Proposed Mechanism for the Hydrogenation of CO_2 by the Ir(III) Complex



the other hand, the hydrogenolysis step $12 \rightarrow 1$ should be accelerated by the higher hydrogen pressure, showing good agreement with our experimental observations (entries 1, 4, and 10), although the kinetic isotope effect we observed in D₂O is not reasonably explained by this mechanism. According to the observations mentioned above, it may be suggested that these two competing pathways operate concurrently.

The overall catalytic cycle producing the free formate anion resulted in a stabilization of 27.7 kcal/mol. If the free formate anion undergoes the reversed reaction, it is required to surmount TS 1/12 or TS 9/8, that is 29.2 kcal/mol from 1.

CONCLUSION

The highly active catalytic hydrogenation of carbon dioxide to form formic acid salts and dehydrogenation of formic acid salt have been established. Both reactions were catalyzed by the PNP-ligated iridium trihydride complex **1**, and under certain conditions, the activities were higher than for any other catalyst previously reported. A theoretical investigation of the hydrogenation of carbon dioxide in the presence of aqueous base revealed two competitive pathways. The suggested ratedetermining step for each pathway was the deprotonative dearomatization step via **TS8**/9 and the hydrogenolysis step via **TS12/1**. The results nicely explained the effect of hydrogen pressure, base, and solvent. Reversible hydrogen fixation onto carbon dioxide is an attractive, safe, and inexpensive method for hydrogen storage. The current highly active catalyst could find practical application for this purpose.

EXPERIMENTAL SECTION

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out by using standard Schlenk techniques or a glovebox under argon that was purified by passing through a hot column packed with BASF catalyst R3-11. All the organic solvents used for reactions were distilled under argon after drying over an appropriate drying agent or passed through solvent purification columns. Water was degassed by two freeze—thaw—pump cycles before use. Most of the reagents were used without further purification unless otherwise specified. NMR spectra were recorded on 500 MHz spectrometers. GC analysis was performed by using N_2 as carrier gas and TCD as a detector.

Standard Procedure for Hydrogenation of Carbon Dioxide. Iridium trihydride complex 1 (10.7 mg, 20 μ mol) was dissolved in THF (4.00 mL) and diluted to 100 μ mol/L. In a 50 mL stainless autoclave the mixture of catalyst (100 μ L, 0.010 μ mol), base (5.0 mmol), and solvents was charged and pressurized by a 1:1 mixture of CO₂ and H₂. The reaction mixture was heated by an aluminum block to 200 °C and stirred for 2 h. Sodium 3-(trimethylsilyl)-1-propanesulfonate (11.3 mg, 51.8 μ mol) was added to the reaction mixture as an internal standard, and an aliquot of the mixture was dissolved in D₂O or CDCl₃ for an estimation of the yield by using ¹H NMR measurement. DMSO-*d*₆ was used as an internal standard to estimate the yield of DCOOK by using ²H NMR measurements. The same reaction was repeated at least twice to confirm the reproducibility.

Procedure for Hydrogenation of Carbon Dioxide on a Large Scale. In a 300 mL stainless autoclave the mixture of catalyst (1.0 mL, 0.10 μ mol) and 1 M aqueous solution of KOH (50 mL, 50 mmol) were charged and pressurized by a 1:1 mixture of CO₂ and H₂. The reaction mixture was heated by an oil bath to 200 °C and stirred for 2 h. The entire reaction vessel cannot be heated, and the temperature at the top of the autoclave is lower than that estimated. Sodium 3-(trimethylsilyl)-1-propanesulfonate (11.5 mg, 52.6 μ mol) was added to the reaction mixture as an internal standard, and an aliquot of the mixture was dissolved in D₂O for an estimation of the yield by using ¹H NMR measurements. A 7.64 mmol amount (15%) of HCOOK was obtained.

Observation of H–D Exchange of 1. In an NMR sample tube, **1** (10 mg) in C_6D_6 (0.5 mL) was introduced and 1 M KOH solution in D_2O (0.1 mL) was added. The solution was stored at room temperature for 18.5 h. The integral ratio of the py- CH_2 - $PiPr_2$ position decreased from 4 to 0.92.

Standard Procedure for Dehydrogenation of Ammonium Formate. In a 20 mL Schlenk tube was charged a THF solution of 1 (10 mmol/L, 100 μ L, 1.0 μ mol) and warmed to 60 °C. The reaction was started by adding a solution of triethylammonium formate (736 mg, 5.00 mmol) in 'BuOH (4.0 mL). The gas that evolved during reaction was collected by water replacement. The catalytic activity was calculated from the volume of the collected gas, supposing that all the gas consists of hydrogen only. The content of the collected gas was confirmed to be hydrogen by GC analysis.

Theoretical Calculations. Geometry optimization and vibrational frequency calculation of all reactants, intermediates, transition states, and products were performed by using the Gaussian 03 program⁹² and the B3LYP^{71–73} method with combined basis sets (Lanl2DZ^{74–76} basis sets for iridium atom and 6-31G++(d,p) basis sets for the other atoms). IRC^{93,94} calculations were also performed. The solvent effect was estimated by single-point energy calculations of all intermediates and transition states using PCM^{77–80} with water as the solvent, in which the UAHF radius was used to build the cavity of the solute and the nonelectrostatic terms were also included. The HF/6-31+G(d) method was tested and gave a solvation energy similar to that for the key step in the B3LYP method. Since the entropy in the solution is well-known to be overestimated by the gas-phase calculations, the vibrational and rotational entropy terms only are included in the free energy in solution.

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ASSOCIATED CONTENT

S Supporting Information

Text, tables, and figures giving experimental procedures, the complete ref 88, and calculated structures of all intermediates and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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