Efficient Cp*Ir Catalysts with Imidazoline Ligands for CO₂ Hydrogenation

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Abstract: We report newly developed iridium catalysts with electron-donating imidazoline moieties as ligands for CO₂ hydrogenation to formate in aqueous solution. Interestingly, these new complexes promote CO₂ hydrogenation much more effectively than their imidazole analogues, exhibiting the turnover frequency (TOF) of 1290 h⁻¹ for the bisimidazoline complex compared to that of 20 h⁻¹ for the bisimidazole complex at 1 MPa and 50 °C. In addition, the hydrogenation proceeds smoothly even under atmospheric pressure at room temperature. The TOF of 43 h⁻¹ for the bisimidazoline complex was comparable to that of a dinuclear complex (70 h⁻¹, highest TOF reported) [*Nat. Chem.* **2012**, *4*, 383], which incorporated proton-responsive ligands with pendent-OH groups in the second coordination sphere. The catalytic activity of the complex with an N-methylated imidazoline moiety was much the same as the corresponding pyridylimidazoline analogue. This result and the UV-vis titrations of the imidazoline complexes indicate that the high activity is not attributable to the deprotonation of NH on the imidazoline under the reaction conditions.

For a future hydrogen-based economy, the development of hydrogen storage and transfer technology is highly desired in terms of energy and cost efficiency as well as safety. One of the promising solutions is conversion of hydrogen gas to a liquid chemical compound.^[1] From the late 1970s, the combination of CO₂ hydrogenation and dehydrogenation of formic acid (FA) has been regarded as a viable hydrogen storage system.^[2] Furthermore, CO₂ hydrogenation has attracted attention from the viewpoint of small molecule activation as well as CO₂ utilization.^[3] A number of transition metal catalysts for CO₂ hydrogenation to formate and FA have been reported for Cp*Ir complexes (Scheme 1) as well as for complexes of Fe,^[4] Ru,^[5] Cu,^[6] Co,^[7] and Rh.^[8] The development of Ir catalysts for CO₂ hydrogenation has been especially marked in recent years. There is a wide variety of ligand backbones that link to the iridium center: phosphine-type,^[9] pincer-type,^[10] NHC carbene-type,^[11] bipyridine-type,^[12] and so on.^[13] In addition, the realization of a hydrogen storage system in aqueous solution is

desirable from the viewpoint of green chemistry.

Recently, a series of water-soluble Cp*Ir(N[^]N) complexes has been found to have good catalytic efficiency for CO₂ hydrogenation.^[12c, 14] Our previous reports demonstrated that the introduction of electron-donating ligands toward the Ir center improved the catalytic activity for hydrogenation of CO₂ and dehydrogenation of FA. In particular, an acidic hydroxy moiety on a ligand, which provides an electron-donating oxyanion by deprotonation under basic conditions (a so called "proton-responsive" ligand), dramatically accelerated catalytic CO₂ hydrogenation.^[12c, 14a] On the other hand, the introduction of a ligand with a five-membered ring, i.e., azole, significantly improved the catalytic efficiency in comparison with a complex with an unsubstituted bipyridine reference ligand, [Cp*Ir(Bpy)(H₂O)]SO₄, which was attributed to the strong electron donation of the azole moiety.^[14c, 15] Very recently, we developed an Ir complex having a pyrimidyl-imidazoline moiety that showed extremely high catalytic activity (TOF up to 322,000 h⁻¹) compared to its imidazole analogues for dehydrogenation of FA.^[16] In addition, Xiao et al. reported that the phenylimidazoline analogue effectively catalyzed dehydrogenation of FA using NEt₃.^[17] Similar to the hydrogenation of CO₂, the catalytic efficiency of FA dehydrogenation with Cp*Ir complexes was thought to be improved by an increase in electron donation by the ligand.^[18] These results led to the hypothesis that the imidazoline moiety would be the proper ligand backbone for CO₂ hydrogenation. Herein, we report the efficient hydrogenation of CO₂ using simple imidazoline complexes in basic water.

As shown in Scheme 1, we synthesized the new iridium complexes **6-8** with imidazoline derivatives (see Detailed Procedure in Supporting Information and Figures S1 and S2 for calculated DFT geometries of the six- and five-coordinate complexes of **7**). The results of complexes **6-8** for catalytic CO₂ hydrogenation (conditions: [cat] = 0.02 mM, [KHCO₃] = 2.0 M, 50 °C, 1 MPa of H₂/CO₂(1/1), 1 hr) are shown in Table 1 along with those of the previously reported complexes, **1-5** (see Scheme 1) for comparison. These complexes were able to catalyze hydrogenation in aqueous solution without any organic additives. Complex **6** showed good catalytic activity (entry 6), which is better than conventional complexes such as **1**, **4** and **5**. Since the introduction of one imidazoline moiety in a ligand increased the catalytic activity, we also examined complex **7** having two imidazoline moieties. The TOF of 1290 h⁻¹ of **7** was much higher than that of complex **2** with the proton-responsive ligand with OH groups (pK_a = 5.2).^[12b] To the best of our knowledge, this is the first report that a ligand such as an imidazoline without a proton-responsive OH group was more effective for CO₂ hydrogenation in aqueous solution than the proton-responsive ligand **4DHBP**. This is attributable to the powerful electron-donation of an imidazoline moiety. In addition, the complex **7** showed slightly lower catalytic activity than **3** which also has two proton-responsive OH groups, but the synthesis of the ligand **4** was easier because of commercially available precursors. In other words, complex **7** was simple yet effective. Although the TOF

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Figure 2. (a) UV-Vis absorption spectra of complex **7** (0.2 mM) in a pH titration and (b) absorbance change at a single wavelength as a function of pH. Boltzmann fits are depicted by the red lines.

The reason that an imidazoline ligand is effective in promoting the hydrogenation of CO₂ is attributable to the influence of the amidine backbone in the imidazoline moiety. The imine substituent in the amidine structure has a resonance structure in which it is partially converted to an amide form. The electron density of the Ir center is increased by ligation of the amide that is more electron rich than the imine. However, in aromatic imidazole, which has an amidine backbone the same as an imidazoline, its π -electrons are delocalized over the entire ligand. By contrast, π -electrons on non-aromatic imidazoline are delocalized within the amidine moieties, leading to an increase in the electron density of the N atom coordinating the Ir center in comparison with imidazole. As described in the Introduction, the catalytic efficiency of CO₂ hydrogenation is improved by an increase in electron donation from the ligand to the Ir center. Hence, the bisimidazoline complex **7** is an outstanding complex for CO₂ hydrogenation.

Comparing the electronic ligand effects of the 4- or 6-hydroxy group in a pyridinol moiety with those of an imidazoline moiety, in the former there is a moderate σ donation effect at low pH, but at the higher pH at which deprotonation of the hydroxy group occurs the resulting oxyanion has a keto resonance structure that is a strong π -donor. This effect is enhanced by the strong π -acceptor property of the metal center in the Cp*Ir(III) moiety. This causes the weakening or detachment of the aqua ligand, creating a site for H₂ heterolysis, the rate-determining step in CO₂ hydrogenation. In the case of the imidazoline moiety, the restricted conjugation of the double bonds is extended by a

resonance structure that places negative charge on the π -accepting Ir(III) center through π -donation even at low pH.

In conclusion, we have reported that imidazoline ligands improve the Ir-catalyzed hydrogenation of CO₂ to formate. In particular, the bisimidazoline complex **7** achieved a high TOF value under both pressurized and ambient conditions. There are many N^N-bidentate ligands that have been linked to Cp*Ir complexes for CO₂ hydrogenation, but a ligand such as bisimidazoline that is not completely conjugated has not previously been reported as an effective ligand for catalytic CO₂ hydrogenation. This is a potentially important finding for expanding the “toolbox” for the design of improved complexes for CO₂ hydrogenation.

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Novel complex having imidazoline ligand showed much higher catalytic activity than that conventional one having imidazole ligand for the CO₂ hydrogenation. Only change from double bond in imidazole to single bond in imidazoline increased catalytic activity in 60 times.

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Supporting Information

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Experimental section

General. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox, and all aqueous solutions were degassed prior to use. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers using tetramethylsilane or sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal standard. Elemental analyses were performed by a CE Instruments EA1110 elemental analyzer. pH values were measured on an Orion 3-Star pH meter with a glass electrode after calibration with standard buffer solutions. ESI-MS data were collected on a Shimadzu LCMS-2020. Formate concentrations were monitored by an HPLC on an anion-exclusion column (Tosoh TSKgel SCX(H^+)) using an aqueous H_3PO_4 solution (20 mM) as an eluent and a UV detector ($\lambda = 210$ nm). Water used in the reactions was obtained from a Simplicity water purification system. 2,2'-Bisimidazoline was purchased (Molport) and used without further purification. $[\text{Cp}^*\text{Ir}(\text{OH}_2)_3][\text{SO}_4]$ was synthesized according to a previous report.¹

General procedure for catalytic hydrogenation of CO_2 : A KHCO_3 aqueous solution (2.0 M, pH 8.3, 10 mL) with complexes (2×10^{-4} mmol) was degassed by three cycles of Freeze-Pump-Thaw in a flask, and was transferred into a stainless autoclave. After 10 min. stabilization at 50 °C under 1.0 MPa of 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.

Hydrogenation of CO_2 under ambient conditions: A NaHCO_3 aqueous solution (20 mL) with a complex (see Table S2) was degassed by three cycles of Freeze-Pump-Thaw in a flask. The solution was vigorously stirred at atmospheric pressure (0.1 MPa of H_2/CO_2 (1:1)) and temperature (25 °C). At appropriate intervals, samples were removed and analyzed by HPLC.

1. Synthesis of ligands.

Synthesis of ligands **L6** and **L8** for complexes **6** and **8**: The ligands were synthesized according to the reported processes.²

1.1. Synthesis of 4,5-dihydro-2-(pyridin-2-yl)-1H-imidazole (**L6**).

tert-Butyl isocyanide (170 μ L, 1.5 mmol) was added to a mixture of cesium carbonate (423 mg, 1.3 mmol), anhydrous toluene (5 mL), 2-bromopyridine (158 mg, 1.0 mmol), ethylenediamine (334 μ L, 5 mmol), palladium(II) chloride (8.9 mg, 0.05 mmol), and dppp (41.2 mg, 0.1 mmol). The reaction mixture was stirred at 120 $^{\circ}$ C under N_2 atmosphere for 24 h. After cooling to room temperature, the mixture was filtered through celite and washed with water (5 mL $\times$ 2). The filtrate was extracted by dichloromethane (DCM, 10 mL $\times$ 3). The combined organic phase was washed with brine (10 mL $\times$ 3), dried over anhydrous Na_2SO_4 , and concentrated to give the crude product as a black solid. It was then purified by column chromatography on silica gel using DCM/MeOH (10:1) as eluent to give the product (0.14 g, 0.95 mmol, yield: 95 %) as a yellow solid. 1H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, J = 4.8 Hz, 1H), 8.19 (t, J = 7.6 Hz, 1H), 7.78 (td, J = 7.6, 1.6 Hz, 1H), 7.36 (dd, J = 7.6, 4.8 Hz, 1H), 3.86 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.30, 148.58, 148.51, 136.60, 125.07, 122.30, 50.51.

1.2 Synthesis of 4,5-dihydro-2-(pyridin-2-yl)-1-methyl-imidazole (**L8**).

The title compound was synthesized by using *N*-methylethylenediamine as diamine according to the method described in procedure 1.1. The crude product was purified by column chromatography on silica gel using dichloromethane/methanol (10:1) as eluent to give the product (yield: 80 %) as a yellow oil. 1H NMR ($CDCl_3$, 400 MHz): δ 8.63 (d, J = 4.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.75 (td, J = 7.6, 1.6 Hz, 1H), 7.34-7.27 (m, 1H), 3.89 (t, J = 10.0 Hz, 2H), 3.50 (t, J = 10.0 Hz, 2H), 3.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.62, 150.59, 148.44, 136.48, 124.22, 124.03, 54.31, 53.00, 35.59.

2. Synthesis of complexes.

2.1 Synthesis of complex [Cp*Ir(L6)(OH₂)]SO₄ (**6**).

A mixture of [Cp*Ir(OH₂)₃]₂SO₄ (143.7 mg, 0.3 mmol) and **L6** (44.2 mg, 0.3 mmol) in 15 mL H₂O was stirred at room temperature under Ar atmosphere for 18 h. The solution was filtered to remove the insoluble solid. The filtrate was concentrated and dried at 50 °C under vacuum for 5 h to give the product as a yellow solid (158 mg, 90 %). Purification was carried out by reprecipitation using MeOH/Et₂O (1/1). ¹H NMR (D₂O, 400 MHz): δ 8.98 (d, *J* = 5.2 Hz, 1H), 8.18 (t, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.81-7.74 (m, 1H), 4.18 (t, *J* = 10.8 Hz, 2H), 3.97 (t, *J* = 10.8 Hz, 2H), 1.61 (s, 15H). ¹³C{¹H}NMR (D₂O, 100 MHz): δ 171.37, 152.35, 146.51, 141.49, 130.37, 125.33, 87.91, 52.12, 46.03, 8.13. ESI-MS(+): *m/z* 474 [M-H₂O-SO₄²⁻]⁺. Anal. Calc. for C₁₈H₂₄IrN₃O₆S + 0.5MeOH: C 36.74, H 4.67, N 6.95. Found: C 36.59, H 4.53, N 6.58.

2.2 Synthesis of bisimidazoline complex [Cp*Ir(L7)(OH₂)]SO₄ (**7**).

Complex **7** was synthesized by using 2,2'-bisimidazoline as diamine according to the method described in procedure 2.1. ¹H NMR (D₂O, 400 MHz): δ 4.16 (t, *J* = 6.8 Hz, 4H), 4.00 (t, *J* = 6.8 Hz, 4H), 1.75 (s, 15H). ¹³C{¹H}NMR (D₂O, 100 MHz): δ 162.89, 87.55, 52.29, 47.39, 9.13. ESI-MS(+): *m/z* 465 [M-H₂O-SO₄²⁻-H]⁺. Anal. Calc. for C₁₆H₂₇IrN₄O₅S + 1.5H₂O: C 31.67, H 4.98, N 9.23. Found: C 32.06, H 4.84, N 8.94.

Caution: This compound should be stored under inert gas atmosphere because its color changed from orange to green in the air. This implies that the complex was gradually decomposed by oxygen.

2.3 Synthesis of complex [Cp*Ir(L8)(OH₂)]SO₄ (**8**).

Complex **8** was synthesized using **L8** as ligand according to the method described in procedure 2.1. ^1H NMR (D_2O , 400 MHz): δ 9.12 (d, $J = 5.6$ Hz, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 8.29 (t, $J = 8.0$ Hz, 1H), 7.90-7.86 (m, 1H), 4.12-4.08 (m, 4H), 3.44 (s, 3H), 1.70 (s, 15H). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , 100 MHz): δ 169.12, 153.59, 146.88, 141.63, 130.59, 126.86, 88.31, 55.88, 50.54, 34.85, 8.44. ESI-MS(+): m/z 486 $[\text{M}-\text{H}_2\text{O}-\text{SO}_4^{2-}-3\text{H}]^+$. Anal. Calc. for $\text{C}_{19}\text{H}_{28}\text{IrN}_3\text{O}_5\text{S} + 2.5\text{H}_2\text{O}$: C 35.23, H 5.14, N 6.49. Found: C 35.54, H 5.13, N 6.15.

Table S1. CO₂ Hydrogenation using complexes **6-8**^a

Entry	Cat.	Temp (°C)	Time (h)	TOF (h ⁻¹)	1 st TON	2 nd TON	Average TON
1	6	50	1	168	170	166	168
2	6	50	2	149	316	280	298
3	6	50	4	131	550	505	525
4	6	50	24	81	2000	1870	1940
5	6	80	1	400	395	405	400
6	6	100	1	593	600	585	593
8	7	50	1	1290	1290	1280	1290
9	7	50	2	920	1900	1770	1840
10	7	50	4	728	2910	2900	2910
11 ^b	7	50	4	450	1800	-	-
12	7	50	24	168	4200	3850	4030
13	7	80	1	1520	1520	1520	1520
14	7	100	1	842	859	825	842
15	8	50	1	181	175	186	181
16	8	50	2	155	318	302	310
17	8	50	4	147	600	574	587
18	8	50	24	86	2100	2030	2070
19	8	80	1	464	468	460	464
20	8	100	1	413	410	415	413

^a Carried out with catalyst (0.2 μmol) in 10 mL of 2.0 M KHCO₃ aqueous solution (pH 8.3) under 1.0 MPa H₂/CO₂ (1/1) with stirring (1500 rpm). The TOF is calculated as TON/time. TONs and avg TONs are shown with 3 significant digits.

^b pH of 10 was adjusted by a small amount of KOH solid.

Table S2. CO₂ Hydrogenation using complexes **6-8** under ambient conditions.^a

Entry	Cat.	Time	TON	TOF (h ⁻¹)
1	6	30 min	3	6
2	6	1 h	4	4
3	6	2 h	6	3
4	6	4 h	11	3
5	6	1 d	44	2
6	6	2 d	76	1.6
7	6	3 d	96	1.6
8	7	30 min	27	53
9	7	1 h	43	43
10	7	2 h	75	37
11	7	4 h	121	30
12	7	1 d	298	12
13	7	2 d	352	7
14	7	3 d	356	5
15	8	30 min	4	8
16	8	1 h	5	5
17	8	2 h	7	4
18	8	4 h	14	4
19	8	1 d	48	2
20	8	2 d	65	1.4
21	8	3 d	79	1.1

^a Carried out with catalyst (1.0 μmol for complexes **6** and **8**, 0.5 μmol for complex **7**) in 20 mL of 1.0 M NaHCO₃ aqueous solution (pH 8.3) under 0.1 MPa H₂/CO₂ (1/1). The TOF is calculated as TON/time.

Figure S1. Calculated DFT structure of $[\text{Cp}^*\text{Ir}(\text{L7})(\text{OH}_2)]^{2+}$ (**7**) from two views: (a) from the side, and (b) from the front. [B3LYP functional/LANL2DZ basis/SMD continuum solvation model.]

Figure S2. Calculated DFT structure of 5-coordinate $[\text{Cp}^*\text{Ir}(\text{L7})]^{2+}$ (**7**) from two views: (a) from the side, and (b) from the front. [B3LYP functional/LANL2DZ basis/SMD continuum solvation model.]

UV-vis Spectra

We have measured the UV-vis spectra for all three complexes **6-8** to characterize the deprotonation of the proton-responsive ligands. The result for catalyst **8**, which doesn't have an acidic proton on the ligand, exhibited a pK_a of 7.7 (Figure S5). This deprotonation corresponds to the deprotonation of the aqua ligand. The same phenomenon was observed in the result for catalyst **6** (Figure S3). On the other hand, as described in the text, a red shift was observed for catalyst **7** at pH from 8 to 10, and the proton on NH was deprotonated. However, the peak at near 600 nm suddenly increased by adjusting the pH up to 11, implying that Ir(III) was reduced to Ir(I) under strong basic conditions.³ Although this result means that the deprotonation of the aqua ligand in catalyst **7** was hardly observed, the reaction conditions in the present work corresponded to a pH of 8.3.

Figure S3. (a) UV-vis absorption spectra of complex **6** (0.1 mM) in a pH titration and (b) absorbance change at single wavelength as a function of pH with Boltzmann fits depicted by red lines.

Figure S4. (a) UV-vis absorption spectra of complex **7** (0.2 mM) in a pH titration and (b) absorbance change at single wavelength as a function of pH with Boltzmann fits depicted by red lines.

Figure S5. (a) UV-vis absorption spectra of complex **8** (0.2 mM) in a pH titration and (b) absorbance change at single wavelength as a function of pH with Boltzmann fits depicted by red lines.

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