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Efficient Cp*Ir Catalysts with Imidazoline Ligands for **CO₂ Hydrogenation**

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We report newly developed iridium catalysts with electrondonating imidazoline moieties as ligands for the hydrogenation of CO₂ to formate in aqueous solution. Interestingly, these new complexes promote CO₂ hydrogenation much more effectively than their imidazole analogues and exhibit a 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 com-

Introduction

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 hydrogenation of CO₂ 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] There has been a marked development of Ir catalysts for CO_2 hydrogenation in recent years. There is

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plex is comparable to that of a dinuclear complex (70 h^{-1} , highest TOF reported) [Nat. Chem. 2012, 4, 383], which incorporates proton-responsive ligands with pendent-OH groups in the second coordination sphere. The catalytic activity of the complex with an N-methylated imidazoline moiety is much the same as that of 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.

a wide variety of ligand backbones that link to the iridium center: phosphine-type,^[9] pincer-type,^[10] N-heterocycliccarbene-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.



Scheme 1. CO₂ Hydrogenation catalyzed by Cp*Ir^{III} complexes (1-8) incorporating various bidentate ligands (N^N), where N^N is Bpy, 4DHBP, 6DHBP or one of L4-L8.

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 improves the catalytic activity for hydrogenation of CO₂ and dehydrogenation of FA. In particu-



lar, 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 accelerates catalytic CO₂ hydrogenation.^[12c,14a] On the other hand, the introduction of a ligand with a fivemembered ring (e.g., azole) significantly improves the catalytic efficiency relative to 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 shows extremely high catalytic activity (TOF up to $322,000 \text{ h}^{-1}$) compared to those of its imidazole analogues for dehydrogenation of FA.^[16] In addition, Xiao et al. reported that the phenylimidazoline analogue effectively catalyzes dehydrogenation of FA by 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.

Results and Discussion

As shown in Scheme 1, we synthesized the new iridium complexes 6-8 with imidazoline derivatives (see Detailed Procedure in the Supporting Information and Figures S1 and S2 for calculated DFT geometries of the six- and fivecoordinate complexes of 7). The results of complexes 6-8for catalytic CO_2 hydrogenation {conditions: [cat] = 0.02 mм, [KHCO₃] = 2.0 м, 50 °С, 1 MPa of H₂/CO₂ (1:1), 1 h} are shown in Table 1 along with those of the previously reported complexes 1-5 (see Scheme 1) for comparison. These complexes are able to catalyze hydrogenation in aqueous solution without any organic additives. Complex 6 shows 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 increases the catalytic activity, we also examined complex 7 having two imidazoline moieties. The TOF of $1290 h^{-1}$ of 7 is 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, complex 7 shows slightly lower catalytic activity than 3, which also has two proton-responsive OH groups, but the synthesis of ligand 4 is easier because of commercially available precursors. In other words, complex 7 is simple yet effective. Although the TOF value of complex 6 increases as the temperature is increased from 50 to 100 °C, that of complex 7 decreases (Table S1). This result suggests that the pyridyl moiety enhances the heat endurance of the complex.

Table 1. Results of CO₂ hydrogenation.^[a]

| Entry | Catalyst | <i>T</i> [°C] | TOF $[h^{-1}]$ | Ref. |
|-------------------|----------|---------------|----------------|-----------|
| 1 | 1 | 50 | 1 | [12b] |
| 2 | 2 | 50 | 650 | [12b] |
| 3 | 3 | 50 | 1400 | [12b] |
| 4 | 4 | 50 | 9 | [15] |
| 5 | 5 | 50 | 20 | [15] |
| 6 | 6 | 50 | 168 | this work |
| 7 ^[b] | 6 | 25 | 4 | this work |
| 8 | 6 | 80 | 400 | this work |
| 9 | 6 | 100 | 593 | this work |
| 10 | 7 | 50 | 1290 | this work |
| 11 ^[b] | 7 | 25 | 43 | this work |
| 12 | 7 | 80 | 1520 | this work |
| 13 | 7 | 100 | 842 | this work |
| 14 | 8 | 50 | 181 | this work |
| 15 ^[b] | 8 | 25 | 5 | this work |
| 16 | 8 | 80 | 464 | this work |
| 17 | 8 | 100 | 413 | this work |

[a] Conditions: 1 h, $P_{\text{H2}}/P_{\text{CO2}} = 1.0$ MPa (1:1), [KHCO₃] = 2.0 M, [cat] = 20 μ M in aqueous solution under pH 8.3. All numbers are the average of two runs. [b] Conditions: H₂/CO₂ = 1:1 (0.1 MPa) at 25 °C by **6** and **8** (0.05 mM), and **7** (0.025 mM) in 1 M NaHCO₃.

Next, we investigated the catalytic CO₂ hydrogenation under ambient conditions { $[NaHCO_3] = 1.0 \text{ M}, 25 ^{\circ}C,$ 0.1 MPa of H₂/CO₂ (1:1), Figure 1 and Entries 7, 11, and 15 in Table 1}. Complex 7 achieves a TOF of 43 h^{-1} after the first 1 h, and a TON of 298 after 1 d (Table S2). Compared to complex 6, complex 7 demonstrates higher catalytic activity. The catalytic activity of 7 is comparable to those of the complexes with proton-responsive ligands with pendent-OH groups (e.g., 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine^[12c] and 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine),^[14b] which achieves the highest activity for CO₂ hydrogenation under ambient conditions among all the complexes we have studied. In addition, complex 7 is more active than Fukuzumi's complex (TOF = 6.8 h^{-1}), which is



Figure 1. Time course for the hydrogenation of CO_2 under H_2/CO_2 = 1:1 (0.1 MPa) at 25 °C by 6 and 8 (0.05 mM), and 7 (0.025 mM) in 1 M NaHCO₃.



the only other example apart from ours that can work well under these conditions.^[13]

An imidazoline moiety has an acidic proton on NH, which may deprotonate to form an N-anion under basic conditions. We have already reported that the tetramethylbisimidazole analogue has proton-responsive NH moieties $(pK_a = 8.8)$.^[15] As a follow-up investigation of the imidazole analogue, we measured the UV/Vis spectrum of bisimidazoline complex 7 under various pH conditions (Figure 2). The UV/Vis spectrum for the titration of 7 exhibits a redshift in the region from pH 8 to 10, which is attributed to a change in the electronic properties of the ligand by deprotonation of NH.^[12b] The pK_a value of 7 was determined to be 8.94, and this value is close to that of the tetramethylbisimidazole analogue.^[15] However, the results suggest that deprotonation of complex 7 does not significantly affect its catalytic behavior because the pH used in CO_2 hydrogenation was 8.3. Based on this result, we sought to determine whether or not the deprotonation of the NHproton has a significant effect on the catalytic activity of 7.



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 *N*-methylated pyridyl–imidazoline complex **8** reacts with CO_2 under both pressurized and ambient conditions. The measured TOF value is almost the same as that of the non-methylated complex **6** (Entries 6 vs. 14 in Table 1, and Figure 1). These results confirm that deprotonation of the NH moiety has hardly any effect on this catalytic system.

The reason that an imidazoline ligand is effective in promoting the hydrogenation of CO_2 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, which is more electron rich than the imine. However, in aromatic imidazole, which has an amidine backbone the same as in imidazoline, its π -electrons are delocalized over the entire ligand. By contrast, π -electrons on non-aromatic imidazoline are delocalized within the amidine moieties, which leads to an increase in the electron density of the N atom coordinating the Ir center in comparison with those of 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, bisimidazoline complex 7 is an outstanding catalyst for CO₂ hydrogenation.

Comparing the electronic ligand effects of the 4- or 6hydroxy 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.

Conclusions

We have reported that imidazoline ligands improve the Ir-catalyzed hydrogenation of CO_2 to formate. In particular, bisimidazoline complex 7 achieves 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 CO_2 hydrogenation, but a ligand such as bisimidazoline that is not completely conjugated has not previously been reported as an effective ligand for catalytic CO_2 hydrogenation. This is a potentially important finding for expanding the "toolbox" for the design of improved complexes for CO_2 hydrogenation.

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