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ARTICLE

Hydrogen generation from formic acid decomposition on a highly efficient iridium catalyst bearing diaminoglyoxime ligand

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A new iridium catalyst bearing dioxime derived ligand has been developed for aqueous formic acid (FA) dehydrogenation. This catalyst features the high stability and high efficiency for dehydrogenation of FA in aqueous solution without any additives. With the in situ formed catalysts, TONs of up to 3,900,000 (average rate: 65000 h^{-1}) at 90 °C was achieved. At 70 °C, an even higher TON of 5,020,000 was obtained, which are the highest TON ever reported. More interestingly, this catalyst can also give a TON of 400,000 and an average rate of 1053 h^{-1} even at room temperature. Electron-rich amine substitutes and the dioxime structure of the ligand are beneficial to the high stability and high efficiency of the catalyst.

Introduction

Formic acid (FA), one of the promising hydrogen storage materials,[1] has attracted a considerable attention because of its stability, transportability and biodegradability under normal conditions. From a view of practical application, an ideal catalyst system for large amount of hydrogen generation from FA decomposition should be easily available and can work with high efficiency, high selectivity and long-term stability in any concentration of aqueous FA solution in the absence of any additives. For this purpose, significant efforts have been devoted toward developing new catalysts for the production of hydrogen from FA decomposition.[2]

In homogeneous catalysis, complexes of non-noble metals of iron,[3] aluminum[4] and nickel[5] have been developed for FA dehydrogenation. Though the metals are cheap and abundant, most of these reactions were carried out in organic solvents. Some complexes of rhodium[6] or ruthenium[7] have also been applied for FA dehydrogenation but often in the presence of bases. Compared with other metal catalysts, iridium complexes are capable of dehydrogenating FA to hydrogen in water without any additives, which makes them more applicable. In recent years, a series of iridium complexes containing pyrimidine, imidazoline, pyridine and other type of N,N-ligands have been found highly effective for upscaled hydrogen generation from FA with high selectivity.[8] For example, Himeda, Fujita, Muckerman and their coworkers achieved a TON of 2,050,000 by using imidazoline derived iridium catalyst at 60 °C, but as long as 580 hours of reaction time was needed.[8k] Later, they used an iridium complex of pyridine-imidazoline N,N-ligand for the reaction and shortened the reaction time to 363 hours for a TON of 2,000,000 at 50 °C.[8l] More recently, Kawanami group reported an extremely high TON of up to 5,000,000 in water at 60 °C by using an iridium complex containing 1,10-phenanthroline-4,7-diol as a chelating ligand for FA dehydrogenation.[8j] However, 2600 hours were needed to complete the decomposition. In addition, Williams group decomposed pure FA in the presence of sodium formate with an iridium catalyst bearing a N,P-ligand, achieving a TON of 2,160,000 at 87 °C by repeatedly charging FA into the reaction system.[9] Although the highly desirable reaction of decomposing pure FA is feasible here, it takes over four months to obtain this TON.

In the absence of any additives, several iridium catalysts have shown to be quite stable for long-term continuous upscaled hydrogen generation from FA. However, the efficiencies of these catalysts are needed to be improved because most of them provided an average rate of no higher than 6000 h^{-1} at a TON of > 2,000,000 (ESI, Scheme 1), which is insufficient for the applications of fast and large amount of hydrogen supply in situ. Raising the reaction temperature is one of the most effective methods to enhance the rate of FA dehydrogenation, but the prerequisite is the catalysts must be stable at high temperature. Thus, developing a catalyst to make it workable under high temperature with high catalytic activity and long-term stability is challenging and desirable. On the other hand, most of the reported catalysts were used under protection and the reactions were performed in deaerated FA solution, which brings inconvenience for the

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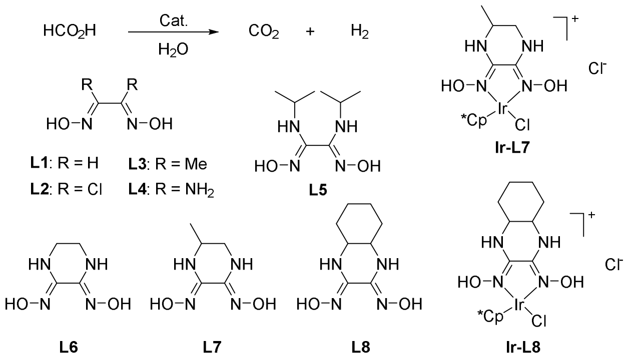
practical manipulation. Recently, we reported a stable and efficient iridium catalyst generated in situ from 2,2'-tetrahydrobipyrimidine and $[IrCp^*Cl_2]_2$ (Ir/L = 1/5), which can catalyze the FA dehydrogenation in water without any additives.[8m] Through repeatedly charging FA into the reaction system, a TON of 2,400,000 was obtained at 80 °C (average rate: 171,000h^{-1}). As part of our continuing work and to develop more practical catalyst systems, here we present another new type of efficient catalyst systems, which are highly active for FA dehydrogenation in one batch. Furthermore, all the manipulations can be conducted without any protection and degas.

Results and Discussion

Table 1 Catalysts screening for FA dehydrogenation[a]



Entry	Cat.	TOF (h^{-1})	H_2 (mL)	TON (20 min)
1	Ir/**L1**	625[b]	5.5	208
2	Ir/**L2**	0[c]	/	/
3	Ir/**L3**	3125[b]	25	1042
4	Ir/**L4**	23750	157	6542
5	Ir/**L5**	5625	38	1583
6	Ir/**L6**	28750	186	7750
7	Ir/**L7**	27500	178	7417
8	Ir/**L8**	26250	171	7125
9	**Ir-L7**	33750	200	8333
10	**Ir-L8**	31250	196	8167

[a] General reaction conditions: $[IrCp^*Cl_2]_2$ (0.5 µmol), Ir/**L** = 1/1.2, FA (1.0 M, 10.0 mL), 60 °C, 20 minutes; TOF was calculated based on the conversion in the first 3 minutes unless otherwise noted; [b] The reaction rate was very slow and TOF was calculated on the conversion in 20 minutes; [c] No readable gas volume was collected in 20 minutes.

In our previous work, iridium catalysts bearing 2,2'-biimidazoline and 2,2'-bi-tetrahydropyrimidine diimine ligands are proved to be effective for aqueous FA dehydrogenation[8m] and CO_2 hydrogenation reactions,[10] but the complexes are not stable when the reactions were carried out at high temperature.[11] The reason is maybe due to the easily hydrolyzing of imine motif in such a cyclic structure under the reaction conditions.[12] To avoid such a problem, a different type of dioxime ligands with the diimine structure being outside of the cycles were prepared and applied for FA dehydrogenation. The similar reaction procedure as our previous reported work was followed where no protection and degas were necessary during the manipulation. The catalysts were prepared in situ from $[IrCp^*Cl_2]_2$ and **L1-8** in water and their catalytic performance were investigated in aqueous FA solution (1.0 M, 10.0 mL) at 60 °C. As shown in Table 1, most of the in situ prepared catalysts were active and the diaminoglyoximes derived catalysts have higher activity. Using $[IrCp^*Cl_2]_2$ as the metal precursor and **L1** as the ligand, the formed catalyst gave too low initial reaction rate that no measurable amount of gas can be collected in the first 3 minutes (Table 1, entry 1). When **L2** with two chloride substitutes on the glyoxime structure was used as the ligand, no activity can be found (Table 1, entry 2). However, when **L3** with two methyl groups on the glyoxime structure was applied, the reaction gave a TOF of 3125 h^{-1} (Table 1, entry 3), which indicated that the substitutes on the glyoxime are important for the reactivity and electron donating groups are beneficial for the reaction. This is further demonstrated by the catalytic performance of using **L4** as the ligand which bears two amine groups on the glyoxime structure. Due to the electron-rich properties of amine group, a much higher TOF of 23750 h^{-1} was obtained (Table 1, entry 4). However, **L5** with two iso-propyl amine groups gave a lower TOF (Table 1, entry 5), which is possibly due to the difficult coordinating of iridium center to **L5** caused by the bulky *iso*-propyl group. Other catalysts derived from substituted diaminoglyoximes ligands **L6-8** all gave the similar initial TOF of over 26000 h^{-1} (Table 1, entries 6-8) and the catalyst from L6 gave the highest initial TOF of 28750 h-1 (Table 1, entry 6).

The iridium complexes **Ir-L7** and **Ir-L8** were prepared and obtained in good yield from $[IrCp^*Cl_2]_2$ and **L7**/**L8**, respectively. The complexes are air-stable and water-soluble. The crystal structures of **Ir-L8** were determined by X-ray diffraction and a distorted octahedral coordination geometry was formed (see ESI). Under the identical conditions, the performance of complexes **Ir-L7** and **Ir-L8** were evaluated and slightly higher TOF than that of the in situ formed corresponding catalysts were obtained (Table 1, entries 9-10 vs 7-8). To further understand the decomposition behavior of the reaction with these catalysts, other reaction conditions were investigated using complex **Ir-L7** as the catalyst.

The pH-dependence of dehydrogenation with **Ir-L7** was firstly examined in FA and sodium formate (SF) mixture solution with a total FA-SF concentration fixed at 1.0 M. As shown in Fig. S1 and Table S1 in electronic supporting information (ESI), in the pH range between 1.78 and 8.01, the maximum initial TOF of 33750 h^{-1} was found in pure FA solution (pH = 1.75). It is different from the previous reported 2,2'-biimidizoline derived catalyst, whose maximum activity was achieved in FA-SF solution with a pH value of 2.8. To check the effect of more acidic FA solution on the reaction, we carried out the reaction in the mixture of methanesulfonic acid and FA solution (pH value from 0.71 to 1.59). Nevertheless, no more even higher TOF than 33750 h^{-1} was found, which

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demonstrates the importance of the concentration of both hydronium ion (H_3O^+) and HCO_2^- species in this reaction.

The temperature dependence of the dehydrogenation reaction with **Ir-L7** was examined in FA solution and the initial reaction rate increased with the temperature increasing and a TOF of more than 210,000 h^{-1} was obtained at 90 ^oC (ESI, Table S2). The apparent activation energy (Ea) was calculated to be 66.9 kJ mol^{-1} (ESI, Fig. S2), which is slightly lower than the reported value obtained with 2,2'-biimidizoline derived catalyst (72.1 kJ mol^{-1}). The rate dependence on concentrations of complex **Ir-L7** and FA were examined. The double logarithmic plots of the initial rate against the concentration of complex **Ir-L7** in the range of 25 to 200 μM indicate a linear dependence (ESI, Fig. S3 and Table S3) and show a similar behavior as our previous reported results of 2,2'-biimidizoline derived catalyst. The initial TOF dependence on FA concentration from 0.5 to 20.0 M indicated that at 60 ^oC and with 1.0 μmol of **Ir-L7** in 10.0 mL of FA solution, the reaction rate increased firstly with the increasing of FA concentration then decreased when it further increased, showing a highest activity at 4.0 M of FA concentration (ESI, Table S4). Obviously, high concentrated FA solution is detrimental for the reaction, so 20.0 M of FA solution could not be decomposed completely.

Then the stabilities and efficiencies of the iridium catalysts were evaluated at high temperature in high concentrated and large amount of FA solution, still without any protection and deaeration. Using 1.0 μmol of the iridium catalysts, either the in situ formed catalysts from **L4** and **L6-8** or the complexes **Ir-L7** and **Ir-L8**, can all decomposed 0.9 mole of FA smoothly at 90 ^oC, producing hydrogen and CO_2 without CO contaminated. As shown in Table S5 in ESI, all these catalysts dehydrogenated FA with high conversion of over 99.9%. With the same FA amount, the time to finish the decomposition is different and the stabilities and efficiencies of these catalyst systems have been revealed initially. The in situ formed catalyst from **L4** has the lowest efficiency and over 9 hours of reaction time are needed to finish the reaction (ESI, Table S5, entry 1). The other three of the in situ formed catalysts have the similar activity, which finished the decomposition reaction in less than 6 hours (ESI, Table S5, entries 3, 6, 9). The catalyst with **L7** as the ligand has the highest average reaction rate of 171,000 h^{-1} and the reaction finished in a much shorter reaction time of 5.25 hours. The complexes **Ir-L7** and **Ir-L8** have the similar activities as those of the in situ formed catalysts, finishing the reaction in 6.0 and 5.8 hours (ESI, Table S5, entries 12 and 15), respectively.

To further evaluate these catalysts durability, we increased the FA amount to 1.8 mole and kept the other reaction conditions unchanged. The reaction with **L4** as ligand was deactivated slowly after the reaction started and low FA dehydrogenating conversion was found (ESI, Table S5, entry 2). Obviously, the catalyst from **L4** cannot tolerate the high temperature of 90 ^oC with large amount of FA. Nevertheless, under such conditions, other three of the in situ formed iridium catalysts from **L6-8** can all complete the decomposition smoothly. With **L6** as the ligand, the reaction finished in 18 hours. While for **L7** and **L8**, finishing the FA decomposition needed a much shorter time of 13.5 hours (ESI, Table S5, entries 4, 7, 10). The complexes of **Ir-L7** and **Ir-L8** have the similar activities as the corresponding in situ formed catalysts, finishing the decomposition in 15 and 16 hours (ESI, Table S5, entries 13 and 16), respectively.

When FA amount was increased to 2.2 mole (10.0 M, 220 mL), the reaction proceeded to the end by using either in situ formed catalysts from ligands of **L6**, **L7** and **L8** (ESI, Table S5, entries 5, 8, 11) or the complexes of **Ir-L7** and **Ir-L8** (ESI, Table S5, entries 14, 17). With this FA amount, the catalyst using **L8** as the ligand completed the decomposition in 17.5 hours, giving an average reaction rate of 126,000 h^{-1}, higher than that of the other four catalysts which performed with the similar activity.

After comparing the results of in situ formed catalyst of **L8** with that of the complex **Ir-L8** for the decomposition of 0.9, 1.8 and 2.2 moles of FA (ESI, Fig. S4), we found that the former one always has a slightly higher efficiency than the latter one. For the catalyst of **L7** and the complex **Ir-L7**, it shows a same trend except for the result obtained from the decomposition of 2.2 mole of FA. It seems that the little excess of ligand (**L**/Ir = 1.2) in the in situ formed catalyst has some good effects on the reaction. To verify this, we investigated the effect of ligand amount on the reaction by using the situ formed catalyst. As shown in Figure 1a and Table S6 in ESI, under the other identical conditions, with the increasing **L**/Ir ratio, the average rate of reaction with **L6** as the ligands firstly increased and then decreased slightly. At the ratio of 4.4/1, it achieved a highest average rate of 176,000 h^{-1}(the reaction finished in 12.5 hours). As the **L6**/Ir ratio increased to 7/1, the efficiency of the reaction was not enhanced further, which indicates that too more ligand cannot improve the efficiency of the reaction further. For the reaction with **L8** as the ligand, the similar results were observed. Obviously, the appropriate excess amount of ligand plays an important role of possibly stabilizing the active iridium center thus improving the efficiency of the catalyst.

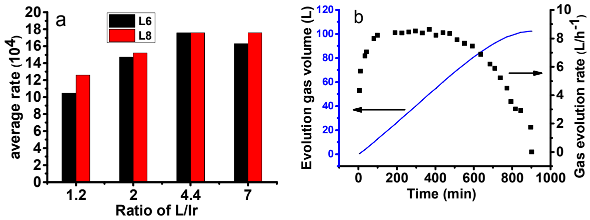

Figure 1 (a) The effect of the L/Ir ratio on FA dehydrogenation; (b) The time courses of the released gases volumes/evolution gas rate; Reaction conditions: FA (10.0 M, 220 mL), 90 ^oC, in situ formed catalyst from $[IrCp^*Cl_2]_2$ (0.5 μmol) and **L6**/**L8** for (a); using **L6** (**L6**/Ir = 2) as the ligand for (b).

The time courses of the released gases volumes by using L6 as the ligand (**L6**/Ir = 2/1) for dehydrogenation of 2.2 mole of FA were recorded and shown in Fig. 1b. After the reaction started, the reaction rate increased rapidly from 4.32 L•h^{-1} for the first 5 minutes to 7.99 L•h^{-1} at 80 minutes. In the time

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range of 1.5 to 8.0 hours, the reaction proceeded at a rate of over 8.0 L•h^{-1}. After that, the reaction rate gradually slowed down until the gas evolution stopped. The final TON value was calculated around 2,200,000 (the residual FA was measured to be 0.115 mmol by ion chromatograph). It means totally around 102 liter of H_2 and CO_2 gas released during the whole process; and 3.4 liter of H_2 was produced per hour with 1.0 μmol catalyst loading.

To check the best performance of these catalysts, we further increased the FA amount. At the **L**/Ir ratio of 2/1, when 2.64 mole of FA (12.0 M, 220 mL) was submitted, the reaction with **L6** as the ligand could not proceed to the end and the reaction stopped after 28 hours with large amount of FA left. However,when we increase the ratio of **L6**/Ir to 4.4/1, the in situ formed catalyst system can finish the decomposition reaction in 17.3 hours (Table 2, entry 1), giving an average reaction rate of 152,000 h^{-1}, which demonstrates the obvious and beneficial effect of excess ligand on the reaction again. When the FA amount further increased to 2.82 mole (12.0 M, 235 mL), the reaction still proceeded to the end in 19 hours (Table 2, entry 2). When to 3.0 mole (12.0 M, 250 mL), the reaction proceeded smoothly and completed after 26 hours (Table 2, entry 3). When **L7** was used as the ligand for the decomposition of 2.82 mole FA, as long as 29 hours was needed to finish the reaction (Table 2, entry 4), showing a much lower catalytic efficiency than that of **L6**. Under the same conditions, the catalyst from **L8** decomposed 2.82 mole and 3.0 mole of FA completely in 18.8 and 29.3 hours (Table 2, entries 5 and 6), showing a similar catalytic efficiency as the catalyst from **L6**. From these results, we can conclude that the catalysts from **L6** and **L8** are more stable and efficient than the catalyst from **L7** for large amount of FA decomposition. When 4.0 mole of FA was added in the reaction, the catalysts from **L6** (Ir/L6 = 1/6) could not finish the decomposition and stopped after 34 hours (Table 2, entry 7), achieving a TON of around 3,390,000. For **L8**, a TON of 3,900,000 and an average rate of 65000 h^{-1} was achieved (Table 2, entry 8).

Table 2 Large amount of FA decomposition with iridium catalysts at 90 ^{o}C^{a}

Entry	Cat.	FA (mol)	Time (h)	TON ($\times10^4$)	Average rate ($\times10^4$ h^{-1})
1	**Ir/L6**	2.64	17.3	264	15.2
2	**Ir/L6**	2.82	19.0	282	14.3
3	**Ir/L6**	3.00	26.0	300	11.5
4	**Ir/L7**	2.82	29.0	282	9.72
5	**Ir/L8**	2.82	18.8	282	15.0
6	**Ir/L8**	3.00	29.3	300	10.2
7	**Ir/L6**^{b}	4.0	34.0	339	9.97
8	**Ir/L8**^{b}	4.0	60.0	390	6.50

$^{a:}$ General reaction conditions: $[IrCp^*Cl_2]_2$ (0.5 μmol), Ir/**L** = 1/4.4; 90 ^{o}C, FA (12.0 M); $^{b:}$ Ir/**L** = 1/6，FA (10.0 M, 400 mL).

The reaction was also carried out at low temperature, such as 70 ^{o}C, to control the gas release in a relatively low rate and to satisfy different requirements. When we carried out the reaction in 220 mL of FA solution (10.0 M) at 70 ^{o}C, the reaction can still proceed to the end with almost full conversion in 45 hours when **L6** was used as the ligand (Table 3, entry 1). The similar results were obtained when **L7** and **L8** were used as the ligands and the reactions proceeded to the end in 46 and 47 hours, respectively (Table 3, entries 2 and 3). It is noted that the catalyst of **L4** was unable to complete 1.8 mole of FA at 90 ^{o}C, but it can decompose 2.2 mole FA smoothly at 70 ^{o}C in 93 hours (Table 3, entry 4). Obviously, under lower reaction temperature, the catalyst stability is higher. As expected, 5.02 mole of FA can be decomposed at 70 ^{o}C with the catalyst from **L6** in 175 hours (Table 3, entry 5), achieving a TON of 5,020,000, the highest values ever reported (ESI, Scheme S1). With **L8** as the ligand, a TON of 4,470,000 was obtained.

At room temperature, the efficiency of the catalyst was also checked. Using the in situ formed catalyst from $[IrCp^*Cl_2]_2$ and **L6**, the effect of FA concentration on the activity was investigated. The initial TOF dependence on FA concentration from 0.5 to 12.0 M indicated that at 25~26 ^{o}C and with 1.0 μmol of catalyst in 10.0 mL of FA solution, the reaction rate increased firstly with the increasing of FA concentration then decreased when it further increased, showing a highest TOF of 1417 h^{-1} at 2.0 M of FA concentration (ESI, Table S7). When large amount of FA (10.0 M, 200 mL) was submitted to decomposition, an average rate of 1053 h^{-1} was obtained using a catalyst loading of 5 μmol. All the FA was decomposed completely in 380 h, giving a TON of 400,000 (Table 3, entry 7).

Table 3 Large amount of FA decomposition with iridium catalysts at 70 ^{o}C^{a}

Entry	Cat. Ir/L	Time (h)	TON ($\times10^4$)	Average rate ($\times10^4$ h^{-1})
1	**Ir/L6**	45	220	4.89
2	**Ir/L7**	46	220	4.78
3	**Ir/L8**	47	220	4.68
4	**Ir/L4**	93	220	2.37
5	**Ir/L6**^{b}	175	502	2.87
6	**Ir/L8**^{c}	180	447	2.48
7	**Ir/L6**^{d}	380	40	0.105

$^{a:}$ General reaction conditions: $[IrCp^*Cl_2]_2$ (0.5 μmol), Ir/**L** = 1/2.5; FA (10.0 M, 220 mL), 70 ^{o}C; $^{b:}$ Ir/**L6** = 1/6, FA (10.0 M, 505 mL); $^{c:}$ Ir/**L8** = 1/6, FA (10.0 M, 500 mL); $^{d:}$ 5 μmol catalyst, Ir/L6 = 1/1.2, FA (10.0 M, 200 mL), 25~26 ^{o}C.

Conclusions

In conclusion, we have developed a new type of diaminoglyoxime derived iridium catalyst systems for the highly efficient hydrogen generation from FA decomposition in water without any additives. These catalysts can be produced in situ from $[IrCp^*Cl_2]_2$ and dioxime ligands, and used directly without the isolation of the complexes. Amine substitutes make the dioxime ligand more electron-rich, leading to the catalyst system with high stability. It can work efficiently at high or low temperatures according to the practical

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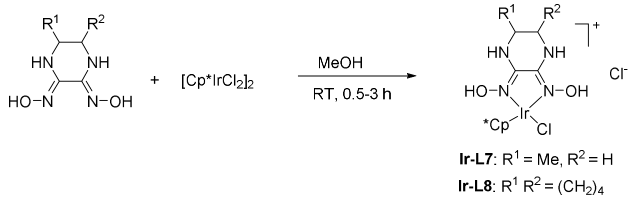
requirement, giving a TON of up to 3,900,000 at 90 °C (average rate: 65000 h^{-1}), 5,020,000 at 70 °C (average rate: ~28700 h^{-1}) and 400,000 at 25~26 °C (average rate: 1053 h^{-1}), respectively. The easily prepared catalysts and their high efficiency and long-term stability, free of protection and degas of the experimental manipulation make them more practical for FA dehydrogenation.

Experimental section

Synthesis and characterization of complex Ir-L7 and Ir-L8



Under an argon atmosphere, dry methanol (20 mL) was added to the mixture of $[IrCp^*Cl_2]_2$ (0.1 mmol) and **L7** (0.2 mmol) in a flask bottle and then stirred at room temperature. After approximately 5 minutes, the mixture became a yellow clear solution, and stirring was maintained for another half an hour. Then, the methanol was removed under reduced pressure. The residue was purified by flash column chromatography using CH_2Cl_2/MeOH (30:1-15:1) as the eluent to get complex 80.2 mg, Yield: 72%. ^1H NMR (400 MHz, D2O): δ (ppm) = 3.83-3.74 (m, 1H), 3.47 (dd, J = 12.4, 4.0 Hz, 1H), 3.18 (dd, J = 12.4, 8.4 Hz, 1H), 1.69 (s, 15H), 1.21 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, D2O) δ 151.6, 89.1, 45.9, 44.7, 17.3, 8.3. HRMS: calcd. for $C_{15}H_{24}IrN_4O_2$ [M-2Cl]+, 485.1529, Found 485.1553

Complex **Ir-L8** was obtained from $[IrCp^*Cl_2]_2$ (0.1 mmol) and **L8** (0.2 mmol) using the similar procedure as complex Ir-L7. Yellow solid, 80.5 mg, yield: 68%. Crystal that was suitable for X-ray diffraction was obtained from a mixture of methanol and ether. ^1H NMR (400 MHz, D2O): δ (ppm) = 3.30 (s, 2H), 2.08-2.06 (m, 2H), 1.78-1.76 (m, 10H), 1.75 (s, 15 H) 1.37-1, 38 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 152.1, 89.3, 55.2, 28.9, 23.3, 8.4. HRMS: calcd. For $C_{18}H_{28}IrN_4O_2$ [M-2Cl]+, 525.1842, Found 525.1877.

General procedure for catalytic dehydrogenation of HCO_2H in a small scale:

All of the solvents and reagents were used directly without any manipulations unless otherwise specified. The reactions were carried out without protection.

For the in situ formed catalysts from $[IrCp^*Cl_2]_2$ and ligands, we get the catalysts stock solution (5 mM) with the help of ultrasound for 5-10 minutes until the solution get clear. If the complex is used as the catalyst, we also submit the solution for ultrasonic as the in situ formed catalyst to get the catalyst stock solution.

For the reaction, aqueous formic acid solution (0.38 mL FA, 9.42 mL H_2O) and a stir bar were placed in a Schlenk tube equipped with a side branch and rubber septa. Afterwards, the tube was preheated at given temperature (e.g. 60 °C) in a water bath until the required temperature was attained. Then, freshly prepared aqueous catalyst stock solution (0.2 mL, 1.0 μmol) was injected into the reaction through the septa, and the timing started immediately. The side branch was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume). The volume of gas generated was recorded.

General procedure for catalytic dehydrogenation of HCO_2H in a large scale:

All of the solvents and reagents were used directly without any manipulations unless otherwise specified. The reactions were carried out without protection.

The aqueous in situ formed catalyst stock solution was prepared freshly before use. First, aqueous formic acid solution (10.0 M, 220 mL) and a stir bar were placed in a two necked flask (250 mL) equipped with rubber septa and reflux condenser. The upper of the reflux condenser was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume). Afterwards, the flask was preheated at given temperature (e.g. 90 °C) in a water bath for 30-90 minutes until the required temperature was attained and stable at 90 °C. Then, freshly prepared aqueous catalyst stock solution (0.2 mL, 1.0 μmol) was added into the reaction, and the timing started immediately. The volume of gas generated was recorded if necessary. The residue FA was measured by SHINEHA CIC-100 ion chromatograph.

Conflicts of interest

There are no conflicts to declare.

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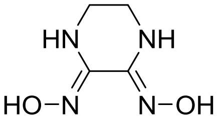
Graphical Abstract:

$$HCO_2H \xrightarrow[H_2O]{Ir/\mathbf{L}} CO_2 + H_2$$

Temp.	TON	average rate
90 °C	3,900,000	65,000 h^{-1}
70 °C	5,020,000	28,700 h^{-1}
25 °C	400,000	1053 h^{-1}



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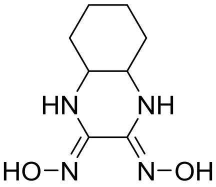

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A new iridium catalyst bearing dioxime derived ligand has been developed for aqueous formic acid (FA) dehydrogenation in the absence of any additives. These catalysts can work at high temperature or room temperature with high efficiency and stability.