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COMMUNICATION

## Direction to practical production of hydrogen by formic acid dehydrogenation with Cp\*Ir complexes bearing imidazoline ligand†

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**A Cp\*Ir complex with a bidentate pyridyl-imidazoline ligand achieved the evolution of 1.02 m<sup>3</sup> of H<sub>2</sub>/CO<sub>2</sub> gases by formic acid dehydrogenation without any additives or adjustments of the solution system. The pyridyl-imidazoline moieties provided the optimum pH to be 1.7, resulting in high activity and stability even at very acidic conditions.**

Hydrogen (H<sub>2</sub>) is considered as a clean energy source because it produces only water at the time of combustion.<sup>1</sup> However, due to the difficulties associated with storage and transport of H<sub>2</sub> gas, simple and safe methods to handle it easily are desired. One such approach is the storage of H<sub>2</sub> gas by incorporating it into a liquid organic compound. Formic acid (FA) is viewed as one of the promising hydrogen storage materials because it can be interconverted with H<sub>2</sub>/CO<sub>2</sub>.<sup>2-6</sup> Based on this idea, much recent attention has been focused on the transition metal-catalysed interconversion between H<sub>2</sub>/CO<sub>2</sub> and FA.

In 2008, two distinct studies on FA dehydrogenation under mild reaction conditions without CO contamination were reported independently by Beller and Laurenczy.<sup>7,8</sup> After these discoveries, other catalysts for the dehydrogenation of FA have been studied extensively. Fe<sup>9-11</sup>, Ru<sup>12,13</sup>, and Ir<sup>14-17</sup> complexes were shown to be effective catalysts in the presence of amines and/or organic solvents. However, for the amine system, the control of FA concentration with periodic additions of FA to maintain the reaction rate was needed, as the reaction rate decreased with the change in FA to amine ratio because of FA consumption. Furthermore, due to the loss of volatile amines during the hydrogen release process, the turnover numbers (TONs) in the amine systems were limited.<sup>13</sup>

Catalysts that function in aqueous solutions without any base can avoid these problems, although their catalytic activities and durabilities are generally unsatisfactory.<sup>8,18</sup>

Pentamethylcyclopentadienyl (Cp\*) iridium complexes with aromatic N^N bidentate ligands (*e.g.*, consisting of pyridine, pyrimidine, orazole moieties) have been found to show high catalytic activity for the dehydrogenation of FA in aqueous solutions.<sup>19-23</sup> Furthermore, previous studies have revealed that both hydrogenation of CO<sub>2</sub> and dehydrogenation of FA are catalytically activated by an increase of electron donation from the N^N bidentate ligand to the Ir centre. Recently, we have reported that electron-rich azole moieties such as imidazole are also very effective ligands for FA dehydrogenation.<sup>21</sup> Similarly, Xiao *et al.* have reported FA dehydrogenation by a Cp\*Ir complex with a phenyl-imidazoline derivative, which was the C-C saturated analogue ofazole, in a FA-amine (5:2) azeotrope.<sup>14</sup> Although the catalyst showed excellent activity for the dehydrogenation reaction in 10 s, with a turnover frequency (TOF) corresponding to 145,000 h<sup>-1</sup>, the repeated addition of FA at short intervals was required for sustained FA dehydrogenation. We have also reported that an imidazoline derivative, dihydroxypyrimidyl-imidazoline, displayed high activity owing to the presence of a pendent OH group as a proton donor site.<sup>24</sup> Very recently, Li reported that Cp\*Ir complexes with imidazoline and tetrahydropyrimidine moieties were highly efficient in small-scale experiments under reaction conditions similar to ours.<sup>25</sup> Based on these reports, imidazoline moieties could be concluded to be promising ligands for FA dehydrogenation as well as CO<sub>2</sub> hydrogenation.<sup>26</sup>

A significant challenge for FA dehydrogenation catalysts is to satisfy both high catalytic efficiency and durability requirements.<sup>10,12,13</sup> In our previous report, 50 L of H<sub>2</sub> (total volume: 100 L, TON of 2,050,000) was evolved from 200 ml of 6 M FA solution although the reaction rate decreased gradually.<sup>24</sup> Further efforts in the development of efficient and robust catalysts for the supply of large amounts of H<sub>2</sub> are required to enable the use of FA dehydrogenation on a practical scale.

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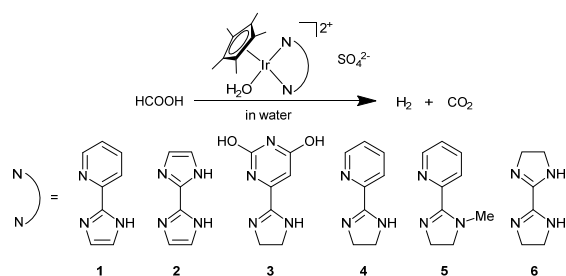
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**Scheme 1.** Catalytic dehydrogenation of FA by catalysts **C1** through **C6** bearing bidentate ligands **1** through **6**, respectively.

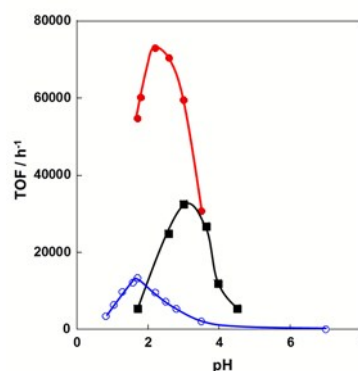
**Table 1.** Dehydrogenation of FA in water<sup>a</sup>

Run	Cat./ $\mu\text{M}$	Time/h	TOF <sup>c</sup> / $\text{h}^{-1}$	TON	Conv	Ref
1	<b>C1</b> /500	4	800	2000	98	22
2	<b>C2</b> /100	5	4000	10,000	100	22
3	<b>C3</b> /100	3	5500	10,000	100	24
4	<b>C4</b> /50	2.5	13,300	20,000	100	This work
5	<b>C5</b> /50	2.5	15,000	20,000	100	This Work
6	<b>C6</b> /10	4	54,700	100,000	100	This Work
7	<b>C6</b> /10 <sup>b</sup>	4	81,900	784,000	98	This Work

<sup>a</sup> The reaction was carried out in 1 M aqueous FA solution at 60 °C. <sup>b</sup> The reaction was carried out in 8 M aqueous FA solution. <sup>c</sup> Average TOF over the initial 10 min.

Herein we report effective catalysts bearing imidazoline derivatives for the dehydrogenation of FA that can produce a large volume of  $\text{H}_2$  and can sustain their activities for extended periods of time in water without any organic additives. Particularly effective and stable  $\text{H}_2$  production at highly acidic conditions (e.g., pH 1.7) was achieved by the incorporation of a bidentate ligand that combines an imidazoline and a pyridine moiety.

We have previously reported on FA dehydrogenation using imidazole complexes **C1**, **C2**,<sup>22</sup> and imidazoline complex **C3**<sup>24</sup> (Scheme 1) in acidic aqueous solutions (Table 1, Runs 1, 2 vs 3). The results indicated that the non-aromatic imidazoline moiety could be more efficient than the aromatic imidazole one. Based on this hypothesis, we recently prepared imidazoline complexes **C4**–**C6**, and demonstrated their high catalytic activity for  $\text{CO}_2$  hydrogenation under basic conditions.<sup>27</sup> First the dehydrogenation of FA for  $\text{H}_2$  evolution using **C4**–**C6** is investigated at standard conditions (1 M aqueous FA solution at 60 °C). In comparing TOF values of **C1** with **C4**, the imidazoline moiety was concluded to be more effective than the imidazole moiety for FA dehydrogenation (Run 1 vs 4). This result showed a similar trend as in the hydrogenation of  $\text{CO}_2$ .<sup>27</sup> Additionally, FA dehydrogenation by N-methylated complex **C5** (Run 5) was almost the same as that of **C4**. From this result, it can be concluded that the proton in the N-H functionality has little involvement in the dehydrogenation reaction.<sup>14</sup> This conclusion is further supported by density functional theory (DFT) calculations of free-energy profiles of the catalytic reactions (see ESI). A high TOF by bisimidazoline complex **C6** was observed similar to the results of Li.<sup>25</sup> Previously, we have shown that it is necessary to increase electron donation ability from the N atom of the ligand to the Ir center in order to improve catalytic activity for FA dehydrogenation.<sup>20</sup> Based on



**Figure 1.** pH-dependence of FA dehydrogenation at 60 °C in 1 M FA/SF solution (pH 1.7–7.0) or 1 M FA containing  $\text{H}_2\text{SO}_4$  (pH 0.8–1.6). The pH of the solution is adjusted by changing the ratio of FA and SF while keeping their total concentration constant. Black solid line, **C3** (100  $\mu\text{M}$ ); blue solid line, **C4** (50  $\mu\text{M}$ ); red solid line, **C6** (10  $\mu\text{M}$ ).

our recent papers,<sup>22,27</sup> we suggested that an imidazoline moiety would show the highest activity compared to imidazole and pyridine. In fact, **C6** with two imidazoline moieties was confirmed by activity studies at standard conditions to exhibit the highest TOF among all employed catalysts (Table 1).

Next, we examined the pH-dependence of the dehydrogenation with **C4** adjusted by changing the ratio of FA and sodium formate (SF) with total concentration of FA + SF fixed at 1 M or by adding  $\text{H}_2\text{SO}_4$  (Figure 1). In our previous report, **C3** showed a maximum catalytic activity at pH 3.0 by the influence of a pendent OH group on a pyrimidine moiety (Figure 1, black solid line).<sup>24</sup> However, this result meant that a pH adjustment would be needed for maximum performance of **C3**. For practical use in a hydrogen storage system, complicated operations such as adding compounds for pH adjustment should be avoided. On the other hand, the reaction rate and conversion by **C4** between pH 0.8 and 7.0 were found to maximize at pH 1.7 (Figure 1, blue solid line, Figure S2(a), and Table S1). The maximum in the activity vs. pH profile of **C4** is shifted to lower pH than that of **C6** (pH 2.2, Figure 1, red solid line). Based on these results, we investigated the pH-dependent rate-determining step (RDS) of **C4** and **C6** via kinetic isotope effect (KIE) studies (Table S2 and S3) and DFT calculations.<sup>21,24,25</sup> FA dehydrogenation using a homogeneous catalyst generally proceeds through three steps: (i) formation of a formate complex; (ii) release of  $\text{CO}_2$  by  $\beta$ -hydride elimination to generate a metal-hydride complex,  $[\text{M}]-\text{H}$ ; and (iii) production of  $\text{H}_2$  from the reaction of  $[\text{M}]-\text{H}$  and a proton.<sup>21</sup> This plausible mechanism for FA dehydrogenation using the imidazoline-type catalysts was supported by NMR studies in which **C4**–**C6** reacted with SF to generate the inferred Ir–H complex (Figure S3–S5). From the KIE studies, the formation of the  $[\text{Ir}]-\text{H}$  complex was found to be the RDS at low pH where the activity is rising, switching to the formation of  $\text{H}_2$  at higher pH for both **C4** and **C6** (Figure 1 and Figure S2), where the activity is decreasing. This switchover is further supported by free-energy profiles generated by DFT calculations at the M06 level of theory<sup>28</sup> (Schemes S1–S14 and Table S3). In our previous reports, we have demonstrated that the presence of proton responsive sites in an *ortho*-pyridinol

moiety in the bidentate ligand and their associated  $pK_a$  values play a significant role in the switching of the RDS from  $\beta$ -hydride elimination to  $H_2$  formation.<sup>24</sup> However, in the case of **C4** and **C6**, there are no proton responsive sites in the associated pH range, and the change in RDS occurs at more acidic pH (1.7 for **C4** and 2.2 for **C6**) compared to our previously reported catalysts (e.g., the switchover point for **C3** is  $pH \approx 3.0$ ). As a consequence of this, **C4** and **C6** display their optimum activity at more acidic conditions rendering them more efficient catalysts for  $H_2$  generation via FA dehydrogenation.

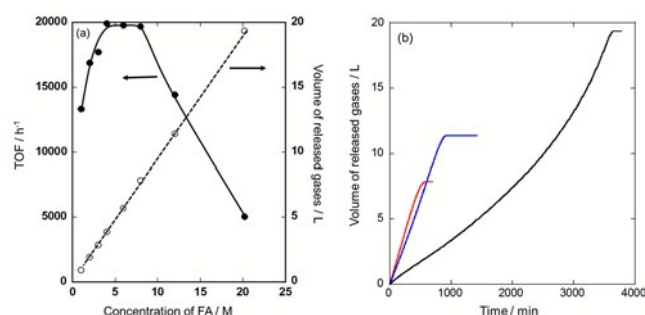
We also examined the temperature dependence of the dehydrogenation reaction by **C4** (Figure S6(a) and Table S4). By analysing the Arrhenius plot (Figure S6(b)), the activation energy ( $E_a$ ) was calculated to be  $72.0 \text{ kJ mol}^{-1}$ , which is almost the same as the value obtained using the bisimidazoline analogue **C6**.<sup>25</sup>

The dependence on the concentration of FA in the range from 1 M to 20 M was investigated using **C4** at  $60^\circ\text{C}$ . The TOFs and the volume of released gases are shown in Figure 2a (detailed data in Table S5). The time courses of the volumes of released gases are shown in Figure 2b. In 8 M and 12 M FA solution, the gases were released at a constant rate by the end of the reaction. Interestingly, although the reaction rate was slow at the beginning of the reaction in the 20 M solution, it increased gradually due to the decrease in FA concentration

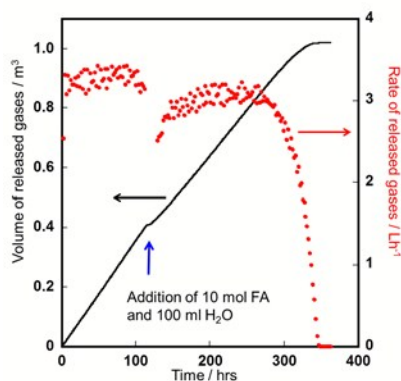
and the solution becoming closer to the optimal pH. In all cases, FA was completely decomposed by the end of the reaction. Furthermore, the percentage of the components in the released gases measured by GC was about 1:1 of  $H_2:CO_2$  during the reaction (Figure S7). On the other hand, although **C6** showed an excellent activity in 1 M FA solution, 2 % of the FA remained in the 8 M FA solution after 4 hrs (Table 1, run 6 vs 7). In fact, **C6** was clearly degraded in larger scale experiments, while use of **C4** led to complete conversion under the same conditions (Figure S8). Since high stability and activity of catalysts are prerequisites for practical use in hydrogen storage, **C4** would be more useful than **C6**. In addition, a significant observation is that **C4** showed the highest TOF at pH 1.7 in the presence of only FA in the reaction solution, which indicates that adjustment of solution pH is not required to achieve optimum activity for **C4**. This indicates that although a pyridyl moiety does not further enhance the catalytic activity, it gives much higher tolerance and provides more stability than an imidazoline moiety.

For the production of a larger volume of  $H_2$ , the dehydrogenation reaction catalysed by **C4** was carried out in 1 L of 10 M FA solution at  $50^\circ\text{C}$  (Figure 3). After the reaction started, it maintained a very high TOF value of  $7340 \text{ h}^{-1}$  on average. The total volume of the released gases reached about  $0.4 \text{ m}^3$  after 114 hrs. After the reaction rate became slow owing to the decrease in substrate concentration, 10 mol of FA in 100 mL of  $H_2O$  was added to the reaction solution (Figure 3). This second stage of reaction maintained high catalytic activity for a total of 363 hrs, and the TOF value on average was  $6250 \text{ h}^{-1}$ . This means that the catalyst was still active in the second stage of reaction. Overall,  $1.02 \text{ m}^3$  of gases ( $H_2:CO_2$  1:1) were released from 20 mol of FA. HPLC analysis of the reaction solution showed that the FA was completely converted to  $H_2$  and  $CO_2$  gases, and the final TON was 2,000,000. Although this epoch-making value was obtained only on the laboratory scale, **C4** could be a promising catalyst for a future chemical hydrogen storage system. Furthermore, these reaction conditions (*i.e.*, aqueous FA solution without any additives) can be assumed to be optimal because the gas evolution was sustained as long as the FA concentration remained in a suitable range. For example, addition of SF to the FA solution led to a significant decrease in the rate owing to the increase in pH caused by consumption of FA (Figure S1). Practical production of  $H_2$  requires an ease in handling (e.g., no need for any additives) and control of the reaction system, both of which were achieved in FA dehydrogenation by **C4**.

We also investigated high pressure  $H_2$  gas production in a closed vessel. The reaction was carried out using **C4** at  $60^\circ\text{C}$  in a glass autoclave with a back pressure valve set at 1 MPa (Figure 4). After 47 min, the pressure reached 1 MPa and the gases started to be released through the back-pressure valve. Even under high pressure conditions, no significant decrease in reaction rate was observed, and the average TOF was  $17,700 \text{ h}^{-1}$ , which was almost the same as that at atmospheric pressure ( $19,700 \text{ h}^{-1}$ , Table S5). Compared to the result in Figure 3, the reaction rate appeared to decrease earlier, because a relatively small amount of FA (0.64 mol) was loaded.

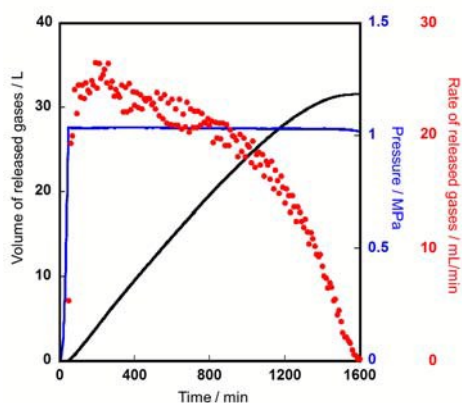


**Figure 2.** (a) The plots of the TOF versus concentration of FA (solid line) and the volumes of released gases (dashed line) for the dehydrogenation of FA by **C4** ( $50 \mu\text{M}$ ) at  $60^\circ\text{C}$ . (b) The time courses of the volumes of the released gases in various FA concentration at  $60^\circ\text{C}$  by **C4** in 8 M (red), 12 M (blue), and 20 M (black).



**Figure 3.** The time courses of the volume and the rate of released gases by FA dehydrogenation in 1 L of 10 M FA solution with **C4** ( $10 \mu\text{M}$  at the beginning of the reaction) at  $50^\circ\text{C}$  (red: rate, black: volume of released gases).





**Figure 4.** The time courses of the volume, the rate of released gases, and the pressure of the vessel for FA dehydrogenation in 8 M FA solution (80 mL) at 60 °C by **C4** (25  $\mu$ M). (red: rate of released gases, blue: pressure, black: volume of released gases, conditions: Pressure gage of back-pressure valve was set at 1 MPa)

After the gas evolution stopped, the residual FA concentration was only 0.4 mM (conversion yield, 99.995%). It is clear that the equilibrium between  $\text{CO}_2/\text{H}_2$  and FA even under high pressure conditions favours gas evolution. It was confirmed by GC that the released gases were composed of only  $\text{H}_2$  and  $\text{CO}_2$  without CO ( $< 1$  ppm, Figure S9). This result could be very important for the supply of  $\text{H}_2$  gas to devices such as fuel cells, which are easily degraded by a small amount of CO.

## Conclusions

Effective catalysts for FA dehydrogenation for  $\text{H}_2$  evolution were synthesized by the use of  $\text{Cp}^*\text{Ir}$  catalysts with imidazoline derivatives. The **C4** catalyst featuring a bidentate ligand with imidazoline and pyridine moieties displayed an improved stability and activity, especially in low pH solutions. **C4** completed FA dehydrogenation with a fixed reaction rate even under higher FA concentration conditions and as a consequence, 1.02  $\text{m}^3$  of gas production and a TON of 2 000 000 were achieved using 20 mol of FA and 10  $\mu$ mol of **C4** in 363 hrs. In this experiment, complicated operations such as frequent additions of substrate or additives, or monitoring the solution system were not required. Furthermore, the gases could be released under high pressure conditions without any significant decrease in reaction rate. An important feature of the **C4** complex is that it displays optimum activity and high stability in acidic (pH 1.7) conditions. From the viewpoint of practical use in a hydrogen storage system, these results will contribute to the development novel catalyst designs and the realization of a viable hydrogen storage system.

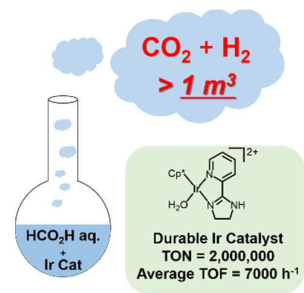
## Acknowledgements

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## Notes and references

- N. Armaroli and V. Balzani, *ChemSusChem*, 2011, **4**, 21.
- B. Loges, A. Boddien, F. Gartner, H. Junge and M. Beller, *Top. Catal.*, 2010, **53**, 902.
- Q.-L. Zhu and Q. Xu, *Energy Environ. Sci.*, 2015, **8**, 478.
- T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.*, 2010, **39**, 81.
- S. Enthaler, J. von Langermann and T. Schmidt, *Energy Environ. Sci.*, 2010, **3**, 1207.
- W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck and E. Fujita, *Chem. Rev.*, 2015, DOI 10.1021/acs.chemrev.1025b00197.
- B. Loges, A. Boddien, H. Junge and M. Beller, *Angew. Chem.-Int. Edit.*, 2008, **47**, 3962.
- C. Fellay, P. J. Dyson and G. Laurenczy, *Angew. Chem.-Int. Edit.*, 2008, **47**, 3966.
- A. Boddien, D. Mellmann, F. Gartner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 1733.
- E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Wuertele, W. H. Bernskoetter, N. Hazari and S. Schneider, *J. Am. Chem. Soc.*, 2014, **136**, 10234.
- T. Zell, B. Butschke, Y. Ben-David and D. Milstein, *Chem.-Eur. J.*, 2013, **19**, 8068.
- G. A. Filonenko, R. van Putten, E. N. Schulpen, E. J. M. Hensen and E. A. Pidko, *ChemCatChem*, 2014, **6**, 1526.
- P. Sponholz, D. Mellmann, H. Junge and M. Beller, *ChemSusChem*, 2013, **6**, 1172.
- J. H. Barnard, C. Wang, N. G. Berry and J. Xiao, *Chem. Sci.*, 2013, **4**, 1234-1244.
- S. Fukuzumi, T. Kobayashi and T. Suenobu, *J. Am. Chem. Soc.*, 2010, **132**, 1496.
- R. Tanaka, M. Yamashita, L. W. Chung, K. Morokuma and K. Nozaki, *Organometallics*, 2011, **30**, 6742.
- S. Oldenhof, B. de Bruin, M. Lutz, M. A. Siegler, F. W. Patureau, J. I. van der Vlugt and J. N. Reek, *Chem.-Eur. J.*, 2013, **19**, 11507.
- Y. Maenaka, T. Suenobu and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7360.
- Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa and K. Kasuga, *J. Mol. Catal. A-Chem.*, 2003, **195**, 95.
- Y. Himeda, *Green Chem.*, 2009, **11**, 2018.
- W.-H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *ChemSusChem*, 2014, **7**, 1976.
- Y. Manaka, W.-H. Wang, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *Catal. Sci. Technol.*, 2014, **4**, 34.
- J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman and E. Fujita, *Nat Chem*, 2012, **4**, 383.
- W.-H. Wang, M. Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita and Y. Himeda, *ACS Catal.*, 2015, **5**, 5496.
- Z. Wang, S.-M. Lu, J. Li, J. Wang and C. Li, *Chem. - Eur. J.*, 2015, **21**, 12592.
- N. Onishi, S. A. Xu, Y. Manaka, Y. Suna, W. H. Wang, J. T. Muckerman, E. Fujita and Y. Himeda, *Inorg. Chem.*, 2015, **54**, 5114.
- S. Xu, N. Onishi, A. Tsuruzaki, Y. Manaka, W.-H. Wang, J. T. Muckerman, E. Fujita and Y. Himeda, *Eur. J. Inorg. Chem.*, in press.
- 28.Y. Zhao and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2008, **120**, 215.

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Cp\*Ir complex with pyridyl-imidazoline achieved the quantity production of 1 m<sup>3</sup> H<sub>2</sub>/CO<sub>2</sub> gases from only HCO<sub>2</sub>H in water without additive.