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Hydrogenation/Hydrolytic Ring Opening of 5-HMF by Cp*-Iridium(III) Half-Sandwich Complexes for Bioketones Synthesis

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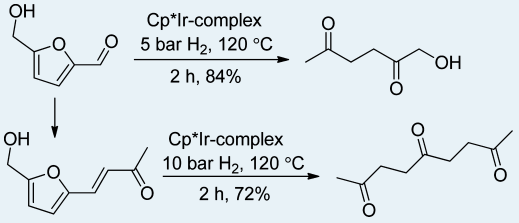
Supporting Information

ABSTRACT: A new method for one-step synthesis of ketones from biobased 5-hydroxymethylfurfural (5-HMF) and its derivatives is reported. Bipyridine coordinated Cp*-Iridium(III) complexes (Cp*, 1,2,3,4,5-pentamethylcyclopenta-1,3-diene) exhibit highly efficient catalytic performance for hydrogenation/hydrolytic ring opening of 5-HMF and derivatives to produce ketones. The catalytic mechanism is proposed to proceed via carbonyl hydrogenation, hydroxyl group promoted and directed hydrolytic furan ring opening, followed by hydrogenation of α,β-unsaturated carbonyl compound based on the experimental and independent events' statistical calculation results.



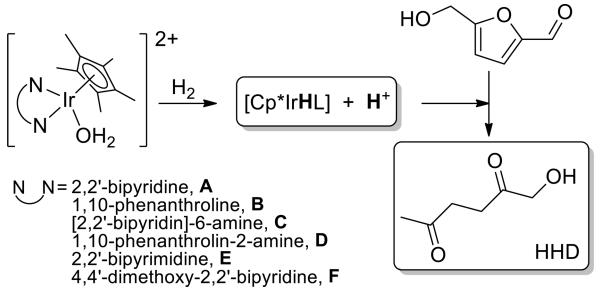
KEYWORDS: *homogeneous catalysis, hydrogenation, iridium catalyst, 5-HMF, ketones*

A sustainable production of biobased chemicals of the future depends on the development of new technologies with desired functional specificity in the transformation of available bioresources. 5-Hydroxymethylfurfural (5-HMF), a versatile platform feedstock, is available from selective dehydration of fructose and isomerization/dehydration of glucose.[1−8] 5-HMF is regarded as one of the most promising building blocks to produce valuable chemicals and fuels.[9] Starting with 5-HMF, numerous important chemicals have become available. For example, 2,5-bis(hydroxymethyl)furan, 2,5-dimethylfuran, levulinic acid, alcohols, among others, have been obtained by hydrogenation and/or hydrolysis of 5-HMF, and these chemicals have been further converted to prepare polymers, fuel additives, dyestuffs, and pharmaceutical compounds.[10−18] 2,5-Furandicarboxylic acid, which can be obtained by the oxidation of 5-HMF, is an alternative to terephthalic and isophthalic acid for polymer production.[19] Aldol condensation of 5-HMF with acetone furnishes a precursor for biofuels.[20−22] The above 5-HMF-derived chemicals are produced mainly based on heterogeneous catalysts and processes. Homogeneous catalysis is in principle anticipated to offer catalyst-specific products and high selectivity under mild conditions, but only a comparatively few are applied to the hydrogenation of 5-HMF.[23−27]

Diketone derivatives have been used to prepare valuable chemicals, such as alcohols, amines, cycloketones, pyrrolidine, and so forth.[28,29] Very recently, the direct conversion of 5-HMF[30,31] and its derivatives to produce biodiketone derivatives 1-hydroxyhexane-2,5-dione (HHD) by hydrogenation/hydrolytic ring opening reaction was reported on the basis of a Pd/C heterogeneous catalyst system with CO_2/H_2O as the acid for the ring opening of furan, resulted in 77% yield HHD from 5-HMF.[32] Ohyama et al. reported supported Au nanoparticles, another heterogeneous catalyst, that converted 5-HMF to HHD (60% yield) with the aid of H_3PO_4.[33] Generally, heterogeneous catalysts in the synthesis of diketones from 5-HMF proceeds in two steps, hydrogenation and acid-promoted opening of furan ring. However, addition of excess acid required for furan ring opening reaction may cause humin formation.[34−36] Moreover, the reported results were obtained in long reaction time, high reaction pressure, and/or high temperature, suggesting lower efficiency of the heterogeneous catalysts.

Bipyridine coordinated Cp*Ir-complexes show excellent catalytic performance for hydrogenation of ketones, esters, acids, *N*-heterocycles, etc.[37−40] We anticipate the Cp*Ir-complexes to serve as bifunctional catalysts (Scheme 1), as the Cp*Ir-complexes may catalyze the hydrogenation of 5-

Scheme 1. Strategy of This Work to Produce Bio-Diketone from 5-HMF



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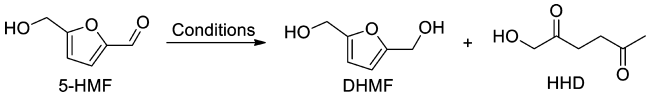
HMF under H_2, and in situ generated acid may facilitate the furan ring opening reaction. To the best of our knowledge, the catalytic hydrogenation/hydrolytic ring opening of 5-HMF into diketones using Cp*Ir-complex as a homogeneous catalyst has not been reported. In this study, we report on the efficient synthesis of HHD and 2,5,8-nonanetrione by homogeneous Cp*Ir-complexes catalyzed hydrogenation/hydrolytic ring opening of 5-HMF and its derivatives in aqueous solution under mild conditions. We further investigated this transformation through quantitative isotope marked GC-MS results, which led to a mechanism in this work based on the statistical rationalization of the GC-MS results. This strategy represents a significant advancement for understanding the homogeneous Cp*Ir-complexes catalyzed hydrogenation/hydrolysis in aqueous solution.

The catalytic activities of Cp*Ir-complexes with different bidentate ligands **A**–**F** were tested in the hydrogenation/hydrolytic ring opening reaction of 5-HMF in a homogeneous aqueous phase. As seen in Table 1, the reactions were first carried out at 110 °C under 20 bar of H_2 by using 2,2′-bipyridine coordinated Cp*Ir-**A**. After 1 h, 89.0% of 5-HMF was converted to HHD in 60.8% yield and dihydroxymethylfuran (DHMF) in 8.2% yield (entry 1). A similar result was observed when using phenanthroline coordinated Cp*Ir-**B** (entry 2). To achieve full conversion of 5-HMF, longer reaction time was required (1.5 h, entries 3 and 4), and the yield of HHD was increased to 72.6–77.8%. When Cp*Ir-complexes coordinated by [2,2′-bipyridin]-6-amine, 1,10-phenanthrolin-2-amine, 2,2′-bipyrimidine, 4,4′-dimethoxy-2,2′-bipyridine (**C**–**F**) were used as the catalysts, although full conversion of 5-HMF was achieved after 1 h (entries 5–8), the yield of HHD did not further increase compared with entry 3. Thus, Cp*Ir-**A** was used as the catalyst for the subsequent optimization. When the reaction was carried out at 120 °C, the yield of HHD was increased to 82.5% (entry 9). The yield of HHD did not increase any further at elevated temperature, 130 °C (entry 10). The highest yield was obtained under 7 bar of H_2 (85.8%, entry 11). The formation of HHD remains in high yield under 5 bar of H_2 (84.1%, entry 12). Compared with the reported heterogeneous catalysis system,[30−33] the homogeneous Cp*Ir-complex exhibited superior catalytic performance in converting 5-HMF to HHD with higher yield under lower H_2 pressure and temperature.

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	conversion (%)[b]	yield of DHMF (%)[b]	yield of HHD (%)[b]
1	**A**	89.0	8.2	60.8
2	**B**	90.6	8.1	61.8
3[c]	**A**	>99	<1	77.8
4[c]	**B**	>99	<1	72.6
5	**C**	>99	<1	64.3
6	**D**	>99	7.9	60.4
7	**E**	>99	6.7	66.5
8	**F**	>99	7.8	57.2
9[d]	**A**	>99	<1	82.5
10[e]	**A**	>99	<1	83.9
11[d,f,g]	**A**	>99	<1	85.5
12[d,f,h]	**A**	>99	<1	84.1

[a]Reaction conditions: 5-HMF (0.95 mmol), catalyst (0.0025 mmol, 0.26 mol % to 5-HMF), and water (4.0 mL), under 20 bar of H_2, at 110 °C, for 1.0 h. [b]GC-MS yield, *N*,*N*-dimethylformamide was the internal standard. [c]1.5 h. [d]120 °C. [e]130 °C. [f]2.0 h. [g]7 bar H_2. [h]5 bar H_2.

To reveal the possible mechanism of Cp*Ir-complex-catalyzed hydrogenation/hydrolytic ring opening of 5-HMF, the time course of the conversion of 5-HMF to HHD was followed as shown in Figure 1. As 5-HMF was consumed, the yield of HHD was increased. However, DHMF maintained at nearly 10% yield during the reaction and disappeared near the end of the reaction. In addition, the selective hydrogenative ring opening of DHMF was also studied (Table 2). Full conversion of DHMF and 38% yield of HHD were observed. On the basis of the results, we propose that 5-HMF is first hydrogenated to produce highly reactive intermediate DHMF,[30,31] followed by hydrolytic ring opening of DHMF and a final hydrogenation to form HHD.

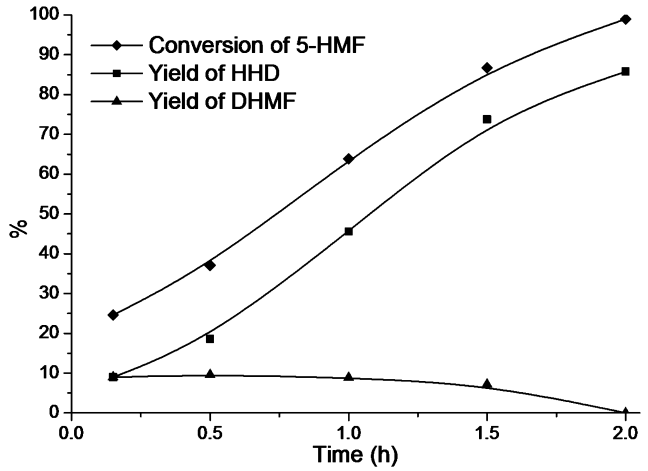
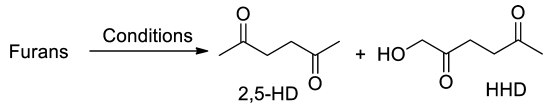


Figure 1. Time course of the conversion of 5-HMF to HHD. Reaction conditions: 5-HMF (0.95 mmol), catalyst Cp*Ir-**A** (0.0025 mmol, 0.26 mol % to 5-HMF), and water (4.0 mL), under 7 bar of H_2, at 120 °C.

Table 2. Reaction of Furans Catalyzed by Cp*Ir-A Catalyst[a]



entry	furans	yield of 2,5-HD (%)[b]	yield of HHD (%)[b]
1	2,5-DMF	4.5	–
2	5-MF	35.6	0
3	DHMF	0	38.9

[a]Reaction conditions: furans (0.5 mmol), catalyst (0.00125 mmol, 0.25 mol % to substrate), and water (2.0 mL), under 7 bar of H_2, at 120 °C, for 0.5 h. [b]GC-MS yield, *N*,*N*-dimethylformamide was the internal standard.

We then studied the reaction of 2,5-dimethylfuran (2,5-DMF) and 5-methylfufural (5-MF) by homogeneous Cp*Ir-**A** catalyst (Table 2). Interestingly, the ring opening product of 5-MF (35.6%, entry 2) is nearly 9 times of that from 2,5-DMF (4.5%, entry 1). These results may be rationalized on the basis that 5-MF is first hydrogenated to form (5-methylfuran-2-

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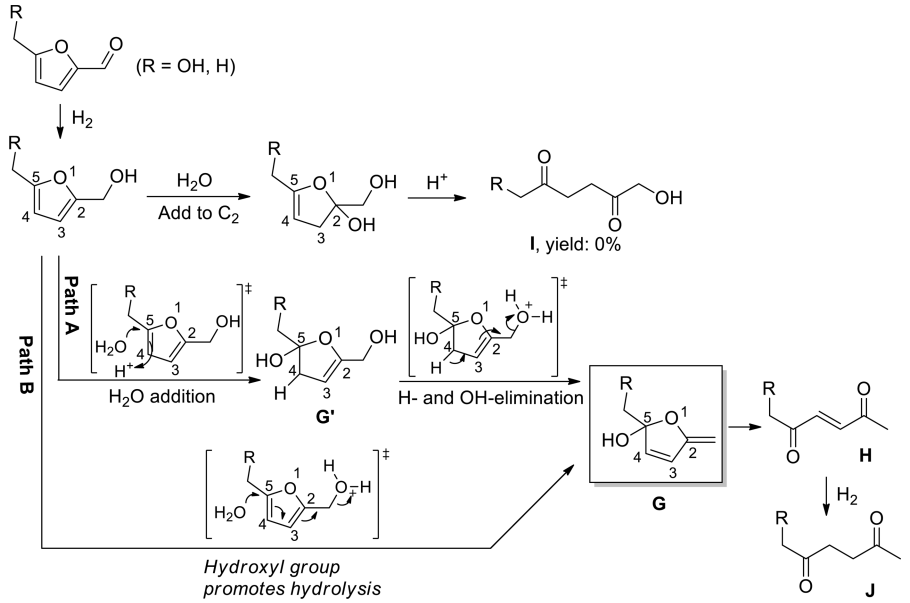
Scheme 2. Plausible Mechanism for Ring Opening of 5-MF and DHMF

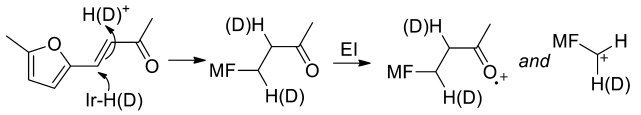


yl)methanol (5-MHF). Comparing with 2,5-DMF, the hydroxyl group of 5-MHF may have accelerated the hydrolysis reaction. The hydroxyl group of 5-MHF also controls H_2O addition direction (C_2-addition product **I** was not detected by GC-MS, Scheme 2), which led to (hexane-2,5-dione) 2,5-HD as the only product. Although heterogeneous Ir catalysts were capable of catalyzing ring opening of hydrocarbons,[41] the reaction substrates and conditions are very different from those studied in this work with the homogeneous Ir complexes. On the basis of our above results, we propose that[31,32,42,43] hydroxymethyl furans would generate intermediate **G** through Path A (two-steps reaction: water added to double bond, followed by H- and OH-elimination) or Path B (a hydroxymethyl group promoted one-step hydrolysis process). *α,β*-Unsaturated carbonyl compound **H** would be produced from hydrolysis of **G**, followed by hydrogenation to form the final product **J**.

We also studied the fundamental mechanism of H_2 activation by the Cp*Ir-A complex in catalytic hydrogenation of carbon−carbon double bond involved in Scheme 2 (step c). Compound **K** was used as the analogue of *α,β*-unsaturated carbonyl compound **H**. The hydrogenation of **K** catalyzed by Cp*Ir-**A** was carried out in D_2O, and the deuterated product **L** was analyzed by GC-MS. Molecular ion **M** and fragment ion **N** were used for the data analysis. The results shown in Table 3 were calculated on the basis of the deuteron incorporation in **M** and **N**. (Details are shown in 3.1, Tables S1 and S2, Supporting Information.) It is proposed that hydride/deuteride exchange process happened during the reaction. It was obtained by GC-MS analysis that the fraction of Ir-D is 11.2%, and the fraction of Ir−H is 88.8% (entry 1). The fraction of Ir-D did not change when H_2 pressure was varied (entries 2 and 3). The fraction of Ir-D was increased at higher temperature (entry 4) and vice versa (entry 5). For proton/deuteron exchange process, it was found that the fraction of D^+ was maintained at 97%, and the fraction of H^+ was near 3%. These results supported the expected high exchange rate between H^+ and D_2O generated D^+ in situ.

On the basis of the above results and the literatures,[44−46] a plausible mechanism of H_2 activation by Cp*Ir-**A** in D_2O is proposed as shown in Scheme 3. H_2 was activated by Cp*Ir-**A**

Table 3. Hydrogenation of K and the GC-MS Results[a]

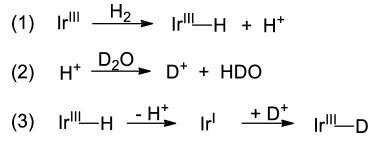


K L M N

			component of equilibrium Ir−H(D) (%)		component of equilibrium $H^+(D)^+$ (%)	
entry	temperature (°C)	pressure (bar)	Ir−H	Ir−D	H^+	D^+
1	100	5	88.8	11.2	2.9	97.1
2	100	10	86.9	13.1	2.7	97.3
3	100	15	87.8	12.1	2.8	97.2
4	80	10	91.6	8.4	2.8	97.2
5	120	10	74.1	25.9	3.3	96.7

[a]Reaction conditions: substrate **K** (0.5 mmol), catalyst (0.00125 mmol, 0.25 mol % to **K**), and D_2O (2.0 mL), for 0.5 h.

Scheme 3. Proposed Activation Mode of H_2 by Cp*Ir-A Complex in D_2O



to generate Ir^{III}−H and H^+ intermediate, followed by H^+ exchange with D_2O to produce D^+ (step 2), and Ir^{III}−H equilibrium with Ir^{III}-D through an Ir^I intermediate (step 3).

To verify the pathway to generate intermediate **G** shown in Scheme 2, the hydrogenation/hydrolysis ring opening of DHMF catalyzed by Cp*Ir-**A** was also studied in D_2O solution. Statistical calculation based on independent events (Detailed statistical calculations based on Path **A** are shown in Table S4 and Scheme S2; Detailed statistical calculations based on Path **B** are shown in Table S3 and Scheme S1, Supporting Information.) was used to estimate the composition of deuterated fragment ion **O** (m/z = 101, 102, 103, 104). The calculated values (ω) are summarized in Table 4. It became

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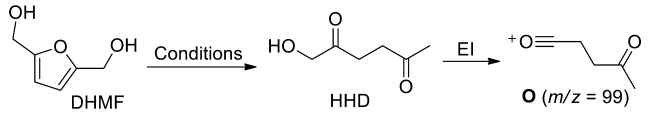
Table 4. Statistical Calculation and Experimental Results[a]



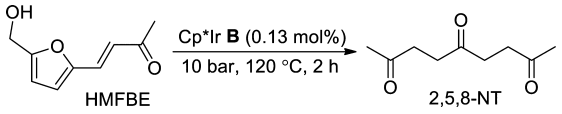
data resource	D_1–N m/z = 100	D_2–N m/z = 101	D_3–N m/z = 102	D_4–N m/z = 103
GC-MS	5.8%	70.1%	20.8%	2.7%
calcd (path **A**, Scheme 2)	0.2%< ω <2.5%	6.9%<ω <38.9%	46.8%< ω <69.4%	11.7%< ω <23.5%
calcd (path **B**, Scheme 2)	4.7%	70.7%	24.5%	0%

[a]Reaction conditions: DHMF (0.5 mmol), catalyst (0.00125 mmol, 0.25 mol % to DHMF), and D_2O (2.0 mL), under 10 bar of H_2, at 120 °C, for 0.5 h.

evident that the calculated data based on path **B** and the experimental data agree well. Thus, the calculated data support that the formation of HHD from DHMF is mainly through hydroxymethyl group promoted hydrolysis process (Path **B**, Scheme 2).

Inspired by the above results, 4-(5-(hydroxymethyl)furan-2-yl)but-3-en-2-one (HMFBE) was synthesized through condensation of 5-HMF with acetone. Cp*Ir-**B** was the most effective catalyst for this reaction. Compared with the results of 5-HMF, the lower solubility of HMFBE in water may have attributed to the decrease in catalytic reactivity, and nonane-2,5,8-trione (2,5,8-NT) was obtained with 72% yield (Scheme 4).

Scheme 4. Synthesis of 2,5,8-NT



In conclusion, we have demonstrated a highly efficient homogeneous catalytic system for the hydrogenation/hydrolytic ring opening reaction of 5-HMF to produce biodiketones HHD. High yield of HHD was achieved by using CP*Ir-**A** as catalyst in water under mild conditions. This represents a powerful addition to the suite of fundamental organic transformations from biobased platform 5-HMF. The mechanistic study based on the results of MS analysis and statistical calculation not only allow us to rationalize our results but also may broadly impact on the transformation of 5-HMF by homogeneous catalysts. Further improvement of the catalyst efficiency and developing a homogeneous catalytic process for economic production of bioketones from 5-HMF are underway.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501874v.

Full experimental details and calculation details (PDF)

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Notes

The authors declare no competing financial interest.

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