



# ChemSusChem

Chemistry–Sustainability–Energy–Materials

 **Chemistry  
Europe**

European Chemical  
Societies Publishing

## Accepted Article

**Title:** Synthesis of Dicarboxylic Acids from Aqueous Solutions of Diols  
Accompanied by the Evolution of Hydrogen Catalyzed by an  
Iridium Complex Bearing a Bipyridonate Ligand

**Authors:** Genki Toyooka and Ken-ichi Fujita

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

**To be cited as:** *ChemSusChem* 10.1002/cssc.202001052

**Link to VoR:** <https://doi.org/10.1002/cssc.202001052>

WILEY-VCH

# Synthesis of Dicarboxylic Acids from Aqueous Solutions of Diols Accompanied by the Evolution of Hydrogen Catalyzed by an Iridium Complex Bearing a Bipyridonate Ligand

Genki Toyooka and Ken-ichi Fujita\*

[a] G. Toyooka, Prof. Dr. K. Fujita  
Graduate School of Human and Environmental Studies  
Kyoto University  
Sakyo-ku Kyoto 606-8501 (Japan)  
E-mail: fujita.kenichi.6a@kyoto-u.ac.jp

Supporting information for this article is given via a link at the end of the document.

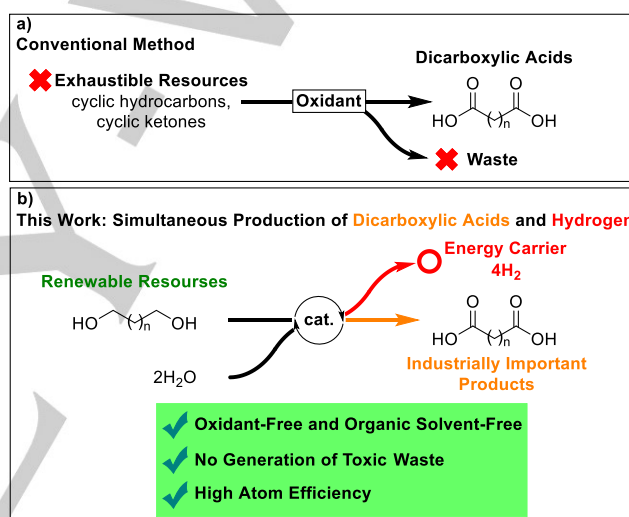
**Abstract:** A catalytic system for the synthesis of dicarboxylic acids from aqueous solutions of diols accompanied by the evolution of hydrogen was developed. An iridium complex bearing a functional bipyridonate ligand with *N,N*-dimethylamino substituents exhibited a high catalytic performance for this type of dehydrogenative reaction. For example, adipic acid was synthesized from an aqueous solution of 1,6-hexanediol in 97% yield accompanied by the evolution of four equivalents of hydrogen by the present catalytic system. It should be noted that the simultaneous production of industrially important dicarboxylic acids and hydrogen, which is useful as an energy carrier, was achieved. In addition, the selective dehydrogenative oxidation of vicinal diols to give  $\alpha$ -hydroxycarboxylic acids was also accomplished.

Dicarboxylic acids are industrially important compounds for the synthesis of a wide variety of materials including polymers, plasticizers, and lubricants.<sup>[1]</sup> Conventional methods for the production of dicarboxylic acids are mainly based on the oxidation of cyclic hydrocarbons, cyclic ketones, or fatty acids using stoichiometric amounts of harmful oxidants (Scheme 1a).<sup>[1,2]</sup> For example, adipic acid, which is one of the most important dicarboxylic acids and whose worldwide production scale is approximately 4 million tons per year,<sup>[3]</sup> is manufactured industrially by the oxidation of KA oil (i.e., a mixture of cyclohexanone and cyclohexanol prepared by the oxidation of cyclohexane) using nitric acid.<sup>[4]</sup> This method is problematic because of its low atom efficiency, the usage of a harmful oxidant, and the generation of nitrous oxide, which is a greenhouse gas. Related methods for the production of other industrially important dicarboxylic acids also suffer from similar problems.

In contrast, the transformation of aqueous solutions of diols to give dicarboxylic acids based on a catalytic dehydrogenation reaction is an attractive potential route (Scheme 1b). Indeed, this method is oxidant-free and organic solvent-free, and generates no toxic waste. It could be therefore provide a new synthetic protocol for the synthesis of dicarboxylic acids in an atom-economical and environmentally benign manner.

Moreover, this process is also advantageous in that hydrogen is produced as a by-product. Thus, to meet the enormous demand for hydrogen as an energy carrier,<sup>[5]</sup> the simultaneous evolution of hydrogen and the large-scale production of industrially indispensable chemicals are desirable from the viewpoint of hydrogen supply. Actually, hydrogen is already produced as a by-product in various industrial processes, such as sodium hydroxide production, steelmaking, and petroleum refining.<sup>[6-8]</sup> The production of dicarboxylic acids from aqueous solutions of

diols is therefore of particular interest since dicarboxylic acids are also produced industrially on a large scale, and using the proposed method, four equivalents of hydrogen would also be obtained.



Scheme 1. Methods for the Production of Dicarboxylic Acids.

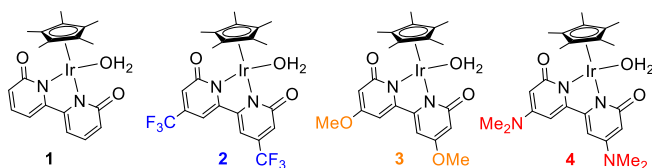
Furthermore, from the standpoint of sustainability, the replacement of petroleum-derived materials with renewable materials is of particular interest in modern chemistry. As such, diols are attractive as sources of dicarboxylic acids, since they can be obtained from renewable feedstocks, such as carbohydrates, glycerol, or fatty acids.<sup>[9-11]</sup> Recently, biological processes have received growing attention as environmentally friendly routes to diols,<sup>[11-13]</sup> since they tend to be energy-conserving reactions that operate under mild conditions without the discharge of toxic waste. However, such biological processes are usually conducted under aqueous conditions, and so the energy-intensive and costly process of water removal has been a major bottle-neck in the utilization of diols produced in typical organic reactions.<sup>[12a,14]</sup> In this context, the production of dicarboxylic acids through the dehydrogenation of aqueous solutions of diols would be ideal, since the mixture of diol and water can be directly employed as a starting material for the production of dicarboxylic acids.

To date, several examples have been reported in the synthesis of monocarboxylic acids from primary alcohols in aqueous media based on catalytic dehydrogenation.<sup>[15]</sup> However, the preparation of dicarboxylic acids remains a challenge, and

although aliphatic diols have been used as substrates in a few previous publications, the yields of the corresponding dicarboxylic acids were moderate to low.<sup>[15a,15d,15i,16,17]</sup>

Meanwhile, we previously developed catalytic systems for the dehydrogenative transformation of alcohols using iridium catalysts **1-4** (Figure 1).<sup>[18,19]</sup> In the course of our research, we found that an iridium catalyst **4** bearing a functional bipyridonate ligand with *N,N*-dimethylamino substituents exhibited a high catalytic performance in the synthesis of acetic acid from an aqueous solution of ethanol.<sup>[20]</sup>

Herein, we report a new catalytic system for the synthesis of dicarboxylic acids from aqueous solutions of diols via catalytic dehydrogenation using **4**. In addition, the catalytic production of synthetically important  $\alpha$ -hydroxycarboxylic acids from vicinal diols is also presented.



**Figure 1.** Iridium catalysts **1-4** used in this study.

Initially, the catalytic activities of a series of iridium catalysts **1-4** bearing functional bipyridonate ligands for the dehydrogenation of an aqueous solution of 1,6-hexanediol were investigated. Results are summarized in Table 1. When the solution of 1,6-hexanediol (3.0 mmol) and NaOH (6.3 mmol) in water (6.0 mL) was heated under reflux for 18 h in the presence of iridium catalyst **1** (0.20 mol%Ir) bearing a simple bipyridonate ligand, disodium adipate was obtained in 14% yield (entry 1). The effect of the substituents on the functional bipyridonate ligand was then examined (entries 2-4). More specifically, reaction in the presence of iridium catalyst **2** bearing an electron deficient bipyridonate ligand with trifluoromethyl groups resulted in a lower yield (3%) of disodium adipate (entry 2). In contrast, catalyst **3**, bearing an electron rich bipyridonate ligand with methoxy groups, exhibited a higher catalytic activity to give disodium adipate in 37% yield (entry 3). Finally, catalyst **4**, bearing an extremely electron rich bipyridonate ligand with *N,N*-dimethylamino groups, which is known to be strongly electron donating in character, exhibited the highest catalytic activity, leading to the quantitative yield of disodium adipate (entry 4). During these reactions, the concomitant evolution of four equivalents of pure hydrogen gas was observed (see Table S1 and Figure S2(a) in the Supporting Information). Upon a simple acidic work-up of the produced disodium adipate using 2 M aqueous H<sub>2</sub>SO<sub>4</sub>, the desired adipic acid was isolated in 97% yield (entry 4). Other iridium catalysts without a functional ligand showed no catalytic activity for the dehydrogenative transformation of an aqueous solution of 1,6-hexanediol (entries 5-7). We also investigated the effect of the base on the reaction efficiency. On the survey of hydroxide salts of alkali metals (entries 4, 8, and 9), quantitative yields were accomplished when NaOH or KOH were employed (entries 4 and 9), and we expect that NaOH would be preferable in terms of mildness and cost. Reactions using other sodium salts were also examined (entries 10-12). While NaOtBu was effective (entry 10), Na<sub>3</sub>PO<sub>4</sub> was found to be an inferior base, leading to a lower yield (entry 11). Furthermore, the cheap Na<sub>2</sub>CO<sub>3</sub> was effective, giving a

quantitative yield of the desired product (entry 12), however, the evolution of carbon dioxide along with hydrogen was also observed (see Table S1 and Figure S2(c) in the Supporting Information). In the absence of base, only trace amounts of product were obtained (entry 13).

**Table 1.** Optimization of the reaction conditions for the dehydrogenative oxidation of 1,6-hexanediol to disodium adipate.<sup>[a]</sup>

Entry	Catalyst	Base	Yield [%] <sup>[b]</sup>
1	<b>1</b>	NaOH	14
2	<b>2</b>	NaOH	3
3	<b>3</b>	NaOH	37
4	<b>4</b>	NaOH	100 (97) <sup>[c]</sup>
5	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	NaOH	0
6	[Cp*Ir(H <sub>2</sub> O) <sub>3</sub> ][OTf] <sub>2</sub>	NaOH	0
7	[Cp*Ir(bpy)(H <sub>2</sub> O)] <sub>2</sub> [OTf] <sub>2</sub>	NaOH	0
8	<b>4</b>	LiOH	88
9	<b>4</b>	KOH	100
10	<b>4</b>	NaOtBu	98
11 <sup>[d]</sup>	<b>4</b>	Na <sub>3</sub> PO <sub>4</sub>	22
12 <sup>[e]</sup>	<b>4</b>	Na <sub>2</sub> CO <sub>3</sub>	100
13	<b>4</b>	none	5

[a] The reaction was carried out with 1,6-hexanediol (3.0 mmol), iridium catalyst (0.20 mol%Ir), and base (6.3 mmol) under reflux in water (6.0 mL) for 18 h. [b] Yield of disodium adipate determined by <sup>1</sup>H NMR under basic conditions using an internal standard. [c] Isolated yield after acidic work-up. [d] Na<sub>3</sub>PO<sub>4</sub> (2.1 mmol) was used. [e] Na<sub>2</sub>CO<sub>3</sub> (3.15 mmol) was used.

With the optimal conditions in hand, we subsequently investigated the scope of the present catalytic system (Table 2). A variety of dicarboxylic acids were obtained by acidic work-up after the reaction of the aqueous solutions of diols using iridium catalyst **4** and NaOH. Aliphatic diols with carbon chain lengths of C5 to C8 were converted into the corresponding dicarboxylic acids in excellent to almost quantitative yields accompanied by the evolution of hydrogen (entries 1-4). In addition, the reaction of 1,10-decanediol leading to the formation of sebacic acid, which is one of the starting materials for the synthesis of nylon-6,10, proceeded well by the reaction for 44 h (entry 5). An aliphatic branched diol was also converted to the corresponding dicarboxylic acid in an excellent yield with a catalyst loading of 0.40 mol%Ir (entry 6).<sup>[21]</sup> When the reactions were performed starting from *meta*- and *para*-xylylene glycol, isophthalic acid and terephthalic acid were obtained in 97 and 98% yields, respectively (entries 7 and 8). Furthermore, the oxygen-containing diol diethylene glycol was tolerated to give diglycolic acid (entry 9). Interestingly, the tertiary amino moiety remained intact under the optimal conditions, whereby *N*-phenyldiethanolamine was found to be a good substrate for the synthesis of *N*-phenyliminodiacetic acid (entry 10). A chloro-substituted substrate was also applicable in this catalytic system (entry 11). Interestingly, a diol containing a furan ring was easily converted into the 2,5-furandicarboxylic acid (entry 12). Recently, much attention has been paid to 2,5-furandicarboxylic acid as a platform molecule for the preparation of bio-based materials for packaging applications such as polyethylene 2,5-


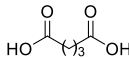
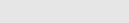
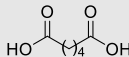
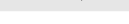
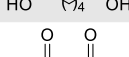

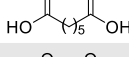
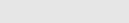
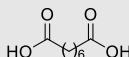
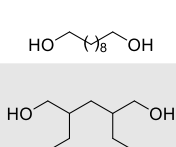
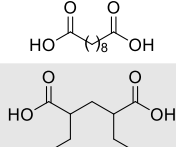
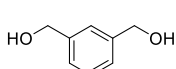
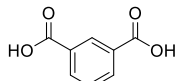
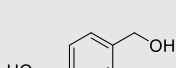
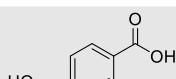

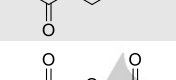
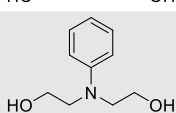
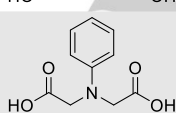
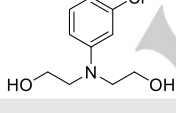
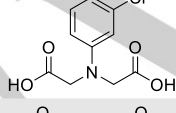

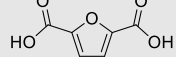
furandicarboxylate (PEF),<sup>[22]</sup> which is considered as an interesting alternative instead of polyethylene terephthalate (PET).

We believe that the mechanism of the present catalytic system must be similar to that of the dehydrogenative transformation of a mixture of primary alcohols and water into carboxylic acids catalyzed by **4**, as we previously reported.<sup>[20]</sup> A plausible catalytic mechanism is therefore illustrated in Scheme S2 in the Supporting Information.

**Table 2.** Synthesis of various dicarboxylic acid derivatives from aqueous solutions of diols catalyzed by **4**.<sup>[a]</sup>

$$\text{HO}-(\text{CH}_2)_n-\text{OH} + \text{H}_2\text{O} \xrightarrow[\text{2) acidic work-up}]{\text{1) cat. 4 (0.20 mol\%Ir), NaOH (2.1 eq.) reflux, 18 h}} \text{HO}-(\text{CH}_2)_n-\text{COOH} + 4\text{H}_2$$

3.0 mmol                      6.0 mL

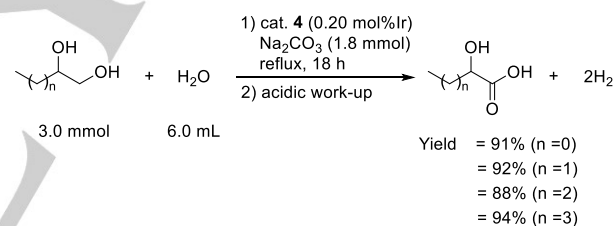
Entry	Substrate	Product	Isolated yield [%] <sup>[b]</sup>
1			98
2			97
3			97
4			97
5 <sup>[c]</sup>			95
6 <sup>[d]</sup>			94
7			97
8			96
9			90
10 <sup>[e]</sup>			93
11			92
12 <sup>[f]</sup>			88

[a] The reaction was performed with diol (3.0 mmol), iridium catalyst (0.20 mol%Ir), and NaOH (6.3 mmol) under reflux in water (6.0 mL) for 18 h. [b] Isolated after acidic work-up. [c] Reaction time was 44 h. [d] Cat. **4** (0.40 mol%Ir) was used. [e] Reaction time was 24 h. [f] Na<sub>2</sub>CO<sub>3</sub> (3.15 mmol) was used.

We next turned our attention to the dehydrogenative reactions of vicinal diols (Scheme 2), since these compounds are easily obtained through the dihydroxylation of alkenes, the hydration of

epoxides, and the fermentation of plant resources.<sup>[12,23-25]</sup> In the dehydrogenative reactions of vicinal diols, surprisingly, different results were obtained than for the distal diols, whereby  $\alpha$ -hydroxycarboxylic acid derivatives, important as building blocks prevalent in biologically active compounds,<sup>[26]</sup> were selectively afforded. More specifically, when a solution of 1,2-propanediol (3.0 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.8 mmol) in water (6.0 mL) was heated under reflux for 18 h in the presence of iridium catalyst **4** (0.20 mol%Ir), lactic acid was obtained in 91% yield after acidic work-up, accompanied by the evolution of two equivalents of hydrogen.<sup>[27]</sup> A series of linear  $\alpha$ -hydroxycarboxylic acids with carbon chain lengths ranging from C3 to C6 were synthesized in good to excellent yields. Among the results presented in Scheme 2, the high yield synthesis of  $\alpha$ -hydroxyhexanoic acid is of particular importance, since this compound is a synthetic precursor of Lipoxazolidinone A,<sup>[28]</sup> Prostaglandin analogues,<sup>[29]</sup> and a series of neutral thrombin inhibitors.<sup>[30]</sup>

To the best of our knowledge, selective oxidation of the primary alcoholic moiety in vicinal diols seems to be challenging due to a preference for oxidative cleavage or predominant oxidation of the secondary alcoholic moiety.<sup>[31,32]</sup> Although there are some precedent reports for the direct oxidation of vicinal diols to  $\alpha$ -hydroxycarboxylic acids, the employment of harmful oxidants<sup>[33]</sup> or strong bases<sup>[34]</sup> is necessary in most cases. It should therefore be noted using our protocol, the effective conversion of vicinal diols to  $\alpha$ -hydroxycarboxylic acids under weakly basic conditions in the absence of oxidant and with the co-production of hydrogen was accomplished.<sup>[35]</sup>



**Scheme 2.** Dehydrogenative oxidation of vicinal diols to  $\alpha$ -hydroxycarboxylic acid derivatives catalyzed by **4**.

In summary, we successfully developed a new catalytic system for the synthesis of dicarboxylic acids from aqueous solutions of diols accompanied by the evolution of hydrogen using an iridium catalyst bearing a functional bipyridonate ligand with *N,N*-dimethylamino substituents. Thus, the simultaneous production of industrially important dicarboxylic acids and hydrogen useful as an energy carrier was achieved. This result is of importance since previous routes to dicarboxylic acids from diols tend to be low yielding. Moreover, the present catalytic system was found to be applicable to the preparation of  $\alpha$ -hydroxycarboxylic acids from vicinal diols accompanied by the evolution of hydrogen.

## Acknowledgements

This work was supported by The Research Grant against Global Warming of the Ichimura Foundation for New Technology. This work was also financially supported by JSPS KAKENHI Grant Number JP18H04255, JP19H02715, and JP19H05053.

**Keywords:** dehydrogenation • dicarboxylic acid • diol •  $\alpha$ -hydroxycarboxylic acid • iridium

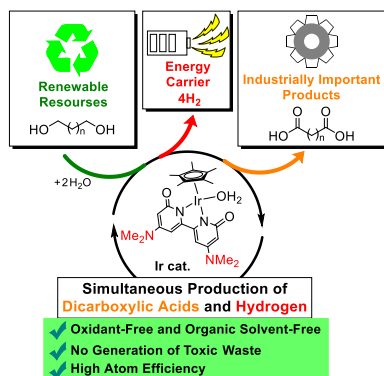
- [1] a) R. W. Johnson, C. M. Pollock, R. R. Cantrell, *Dicarboxylic Acids*, in Kirk-Othmer Encyclopedia of Chemical Technology, Wiley-VCH, Weinheim, **2010**. DOI: 10.1002/0471238961.0409030110150814.a01.pub2; b) B. Cornils, P. Lappe, *Dicarboxylic Acids, Aliphatic*, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2014**. DOI: 10.1002/14356007.a08\_523.pub3
- [2] a) K. Osowska-Pacewicz, H. Alper, *J. Org. Chem.* **1988**, *53*, 808-810; b) Y. Usui, K. Sato, *Green Chemistry* **2003**, *5*, 373-375; c) C.-M. Che, W.-P. Yip, W.-Y. Yu, *Chem. Asian J.* **2006**, *1*, 453-458; d) L. Rokhum, G. Bez, *Synth. Commun.* **2011**, *41*, 548-552; e) K. C. Hwang, A. Sagadevan, *Science* **2014**, *346*, 1495-1498; f) D. Lisicki, B. Orleńska, *Pol. J. Chem. Tech.* **2018**, *20*, 102-107.
- [3] BCC Research. (US), "Global Markets for Adipic Acid", can be found in <https://www.bccresearch.com/market-research/chemicals/adipic-acid.html>, **2019**.
- [4] a) M. T. Musser, *Adipic Acid*, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2000**. DOI: [https://doi.org/10.1002/14356007.a01\\_269](https://doi.org/10.1002/14356007.a01_269); b) S. V. Vyver, Y. Román-Leshkov, *Catal. Sci. Technol.* **2013**, *3*, 1465-1479.
- [5] a) S. Dunn, *Int. J. Hydrogen Energy* **2002**, *27*, 235-264; b) L. Barreto, A. Makihira, K. Riahi, *Int. J. Hydrogen Energy* **2003**, *28*, 267-284; c) G. Marbán, T. Valdés-Solis, *Int. J. Hydrogen Energy* **2007**, *32*, 1625-1637; d) A. Sartbaeva, V. L. Kuznetsov, S. A. Wells, P. P. Edwards, *Energy Environ. Sci.* **2008**, *1*, 79-85.
- [6] a) D.-Y. Lee, A. Elgowainy, Q. Dai, *Appl. Energy* **2018**, *217*, 467-479; b) H. Khasawneh, M. N. Saidan, M. Al-Addous, *Energy Explor. Exploit.* **2019**, *37*, 1053-1072.
- [7] a) W.-H. Chen, M.-R. Lin, T.-S. Leu, S.-W. Du, *Int. J. Hydrogen Energy* **2011**, *36*, 11727-11737; b) R. Razaq, C. Li, S. Zhang, *Fuel* **2013**, *113*, 287-299.
- [8] D.-Y. Lee, A. Elgowainy, *Int. J. Hydrogen Energy* **2018**, *43*, 20143-20160.
- [9] a) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, *114*, 1827-1870; b) S. H. Krishna, K. Huang, K. J. Barnett, J. He, C. T. Maravelias, J. A. Dumesic, G. W. Huber, M. De bruyn, B. M. Weckhuysen, *AIChE J.* **2018**, *64*, 1910-1922; c) S. Gupta, M. I. Alam, T. S. Khan, M. A. Haider, *ACS Sustainable Chem. Eng.* **2019**, *7*, 10165-10181.
- [10] J. He, K. Huang, K. J. Barnett, S. H. Krishna, D. M. Alonso, Z. J. Brentzel, S. P. Burt, T. Walker, W. F. Banholzer, C. T. Maravelias, I. Hermans, J. A. Dumesic, G. W. Huber, *Faraday Discuss.* **2017**, *202*, 247-267.
- [11] M. M. Ahsan, S. Sung, H. Jeon, M. D. Patil, T. Chung, H. Yun, *Catalysts* **2018**, *8*, 4.
- [12] a) W. Sabra, C. Groeger, A.-P. Zeng, *Adv. Biochem. Eng. Biotechnol.* **2016**, *155*, 165-197; b) Y. Zhang, D. Liu, Z. Chen, *Biotechnol. Biofuels* **2017**, *10*, 299.
- [13] a) T. Fujii, T. Narikawa, F. Sumisa, A. Arisawa, K. Takeda, J. Kato, *Biosci. Biotechnol. Biochem.* **2006**, *70*, 1379-1385; b) N. Fujita, F. Sumisa, K. Shindo, H. Kabumoto, A. Arisawa, H. Ikenaga, N. Misawa, *Biosci. Biotechnol. Biochem.* **2009**, *73*, 1825-1830.
- [14] a) Z.-L. Xiu, A.-P. Zeng, *Appl. Microbiol. Biotechnol.* **2008**, *78*, 917-926; b) A. Burgard, M. J. Burk, R. Osterhout, S. V. Dien, H. Yim, *Curr. Opin. Biotechnol.* **2016**, *42*, 118-125; c) A. Forte, A. Zucaro, R. Basosi, A. Fierro, *Materials* **2016**, *9*, 563.
- [15] a) E. Balaraman, E. Khaskin, G. Leitus, D. Milstein, *Nat. Chem.* **2013**, *5*, 122-125; b) Y. Sawama, K. Morita, T. Yamada, S. Nagata, Y. Yabe, Y. Monguchi, H. Sajiki, *Green Chem.* **2014**, *16*, 3439-3443; c) J.-H. Choi, L. E. Heim, M. Ahrens, M. H. G. Pechtl, *Dalton Trans.* **2014**, *43*, 17248-17254; d) J. Malineni, H. Keul, M. Möller, *Dalton Trans.* **2015**, *44*, 17409-17414; e) Y. Sawama, K. Morita, S. Asai, M. Kozawa, S. Tadokoro, J. Nakajima, Y. Monguchi, H. Sajiki, *Adv. Synth. Catal.* **2015**, *357*, 1205-1210; f) L. Zhang, D. H. Nguyen, G. Raffa, X. Trivelli, F. Capet, S. Desset, S. Paul, F. Dumeignil, R. M. Gauvin, *ChemSusChem* **2016**, *9*, 1413-1423; g) X. Wang, C. Wang, Y. Liu, J. Xiao, *Green Chem.* **2016**, *18*, 4605-4610; h) Z. Dai, Q. Luo, X. Meng, R. Li, J. Zhang, T. Peng, *J. Organomet. Chem.* **2017**, *830*, 11-18; i) A. Sarbajna, I. Dutta, P. Daw, S. Dinda, S. M. W. Rahaman, A. Sarkar, J. K. Bera, *ACS Catal.* **2017**, *7*, 2786-2790; j) Z. Dai, Q. Luo, H. Jiang, Q. Luo, H. Li, J. Zhang, T. Peng, *Catal. Sci. Technol.* **2017**, *7*, 2506-2511; k) Z. Shao, Y. Wang, Y. Liu, Q. Wang, X. Fu, Q. Liu, *Org. Chem. Front.* **2018**, *5*, 1248-1256.
- [16] With catalytic systems reported in references 15a, 15d, and 15i, the yields of dicarboxylic acids from diols were moderate to low, which was because of the formation of lactones as by-products.
- [17] Catalytic systems for the transformation of diols to lactones have been also reported: a) J. Zhao, J. F. Hartwig, *Organometallics* **2005**, *24*, 2441-2446; b) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem.* **2011**, *123*, 3595-3599; *Angew. Chem. Int. Ed.* **2011**, *50*, 3533-3537; c) J. Zhang, E. Balaraman, G. Leitus, D. Milstein, *Organometallics* **2011**, *30*, 5716-5724; d) K. Fujita, W. Ito, R. Yamaguchi, *ChemCatChem* **2014**, *6*, 109-112; e) A. Bhatia, M. Kannan, S. Muthaiah, *Synlett* **2019**, *30*, 721-725.
- [18] K. Fujita, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 344-351.
- [19] See also, K. Fujita, R. Tamura, Y. Tanaka, M. Yoshida, M. Onoda, R. Yamaguchi, *ACS Catal.* **2017**, *7*, 2226-7230.
- [20] M. Kuwahara, M. Nishioka, M. Yoshida, K. Fujita, *ChemCatChem* **2018**, *10*, 3636-3640.
- [21] This reaction gave a mixture of 2,4-diethylglutaric acid with *dl* and *meso* form in the ratio of 50:50, although the ratio of *dl* and *meso* form of starting diol was 44:56.
- [22] a) A. F. Sousa, C. Vilela, A. C. Fonseca, M. Matos, C. S. R. Freire, G.-J. M. Gruter, J. F. J. Coelho, A. J. D. Silvestre, *Polym. Chem.* **2015**, *6*, 5961-5983; b) S. Hameed, L. Lin, A. Wang, W. Luo, *Catalysts* **2020**, *10*, 120.
- [23] a) M. Schröder, *Chem. Rev.* **1980**, *80*, 187-213; b) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483-2547; c) C. J. R. Bataille, T. J. Donohoe, *Chem. Soc. Rev.* **2011**, *40*, 114-128.
- [24] a) S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315; b) S. Dey, D. R. Powell, C. Hu, D. B. Berkowitz, *Angew. Chem.* **2007**, *119*, 7140-7144; *Angew. Chem. Int. Ed.* **2007**, *46*, 7010-7014; c) Z. Wang, Y.-T. Cui, Z.-B. Xu, J. Qu, *J. Org. Chem.* **2008**, *73*, 2270-2274.
- [25] R. K. Saxena, P. Anand, S. Saran, J. Isar, L. Agarwal, *Indian J. Microbiol.* **2010**, *50*, 2-11.
- [26] a) H. Gröger, *Adv. Synth. Catal.* **2001**, *343*, 547-558; b) S. V. Ley, T. D. Sheppard, R. M. Myers, M. S. Chorghade, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1451-1472; c) L. Vieweg, S. Reichau, R. Schobert, P. F. Leadlay, R. D. Süßmuth, *Nat. Prod. Rep.* **2014**, *31*, 1554-1584.
- [27] Optimization of the reaction conditions for the dehydrogenative oxidation of 1,2-propanediol is shown in Table S2. The best result in terms of the yield of sodium lactate was obtained by using 0.6 equivalents of Na<sub>2</sub>CO<sub>3</sub> as a base. See the Supporting Information for details.
- [28] J. J. Mills, K. R. Robinson, T. E. Zehnder, J. G. Pierce, *Angew. Chem.* **2018**, *130*, 8818-8822; *Angew. Chem. Int. Ed.* **2018**, *57*, 8682-8686.
- [29] N. S. Barta, G. W. Endres, A. M. Kornilov, K. M. Maxey, A. Uzieblo (Cayman Chemical Company), US 20090124695A1, **2009**.
- [30] K. Abrahamsson, P. Andersson, J. Bergman, U. Bredberg, J. Brånalt, A.-C. Egnell, U. Eriksson, D. Gustafsson, K.-J. Hoffman, S. Nielsen, I. Nilsson, S. Pehrsson, M. O. Polla, T. Skjaeret, M. Strimfors, C. Wern, M. Öwegård-Halvarsson, Y. Örtengren, *Med. Chem. Commun.* **2016**, *7*, 272-281.
- [31] a) D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277-7287; b) K. C. Nicolaou, V. A. Adsool, C. R. H. Hale, *Org. Lett.* **2010**, *12*, 1552-1555; c) M. Shibuya, R. Doi, T. Shibuta, S.-i. Uesugi, Y. Iwabuchi, *Org. Lett.* **2012**, *14*, 5006-5009; d) M. Shibuya, T. Shibuta, H. Fukuda, Y. Iwabuchi, *Org. Lett.* **2012**, *14*, 5010-5013.
- [32] a) R. M. Painter, D. M. Pearson, R. M. Waymouth, *Angew. Chem.* **2010**, *49*, 9456-9459; *Angew. Chem. Int. Ed.* **2010**, *122*, 9646-9649; b) Y. Ryabenkova, P. J. Miedziak, D. W. Knight, S. H. Taylor, G. J. Hutchings, *Tetrahedron* **2014**, *70*, 6055-6058.
- [33] a) M. L. Testa, R. Ciriminna, C. Hajji, E. Z. Garcia, M. Ciclosi, J. S. Arques, M. Pagliaro, *Adv. Synth. Catal.* **2004**, *346*, 655-660; b) P. Gancitano, R. Ciriminna, M. L. Testa, A. Fidalgo, L. M. Ilharco, M. Pagliaro, *Org. Biomol. Chem.* **2005**, *3*, 2389-2392; c) K. Chinthapally, S. Baskaran, *Org. Biomol. Chem.* **2014**, *12*, 4305-4309; d) K. Furukawa, M. Shibuya, Y. Yamamoto, *Org. Lett.* **2015**, *17*, 2282-2285.

- [34] a) L. Prati, M. Rossi, *J. Catal.* **1998**, *176*, 552-560; b) Y. Ryabenkova, Q. He, P. J. Miedziak, N. F. Dummer, S. H. Taylor, A. F. Carley, D. J. Morgan, N. Dimitratos, D. J. Willock, D. Bethell, D. W. Knight, D. Chadwick, C. J. Kiely, G. J. Hutchings, *Catal. Today* **2013**, *203*, 139-145; c) D. J. Chadderdon, L. Xin, J. Qi, B. Brady, J. A. Miller, K. Sun, M. J. Janik, W. Li, *ACS Catal.* **2015**, *5*, 6926-6936; d) F. Du, H. Wnag, X. Jin, W. Deng, C. Li, Z. Ren, H. Yan, B. Yin, *Catal. Lett.* **2019**, *149*, 1037-1045; e) Y. Zhan, W. Hou, G. Li, Y. Shen, Y. Zhang, Y. Tang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 17559-17564.
- [35] A plausible catalytic mechanism is shown in Scheme S3 in the Supporting Information.

WILEY-VCH

Accepted Manuscript

## Entry for the Table of Contents



A catalytic system for the synthesis of dicarboxylic acids from aqueous solutions of diols accompanied by the evolution of hydrogen was developed. An iridium complex bearing a functional bipyridonate ligand exhibited a high catalytic performance for this reaction. Simultaneous production of industrially important dicarboxylic acids and hydrogen, which is useful as an energy carrier, was achieved. Selective dehydrogenative oxidation of vicinal diols to give  $\alpha$ -hydroxycarboxylic acids was also accomplished.