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Article

Electronic and steric factors for enhanced selective synthesis of 2-ethyl-1-hexanol in the Ir-complex-catalyzed Guerbet reaction of 1-butanol

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ABSTRACT

1-Butanol is a potential bio-based fermentation product obtained from cellulosic biomass. As a value-added chemical, 2-ethyl-1-hexanol (2-EH) can be produced by Guerbet conversion from 1-butanol. This work reports the enhanced catalytic Guerbet reaction of 1-butanol to 2-EH by a series of Cp*Ir complexes (Cp*: 1,2,3,4,5-pentamethylcyclopenta-1,3-diene) coordinated to bipyridine-type ligands bearing an *ortho*-hydroxypyridine group with an electron-donating group and a Cl[−] anion. The catalytic activity of the Cp*Ir complex increased by increasing the electron density of the bipyridine ligand when functionalized with the *para*-NMe₂ and *ortho*-hydroxypyridine groups. A record turnover number of 14047 was attained. A mechanistic study indicated that the steric effect of the ethyl group on the α-C of 2-ethylhexanal (2-EHA) and the conjugation effect of C=C=O in 2-ethylhex-2-enal (2-EEA) benefits the high selectivity of 2-EH from 1-butanol by inhibiting the cross-aldol reaction of 2-EHA and 2-EEA with butyraldehyde. Nuclear magnetic resonance study revealed the formation of a carbonyl group in the bipyridine-type ligand *via* the reaction of the Cp*Ir complex with KOH.

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1. Introduction

The development of renewable chemicals from biomass remains one of the most important objectives for attaining global sustainability. 2-Ethyl-1-hexanol (2-EH), one of the “plasticizer alcohols,” has been used in polyvinyl chloride manufacturing [1]. Moreover, 2-EH has been extensively applied in the production of soaps, surfactants, solvents, adhesives, diesel, and lube additives. The industrial three-step production of 2-EH involves the hydroformylation of propylene with CO and

hydrogen gas to butyraldehyde, and base-catalyzed aldol condensation of butyraldehyde to 2-ethyl-2-hexenal, followed by hydrogenation of 2-ethyl-2-hexenal with hydrogen gas (Scheme 1) [2–4]. Recent progress has been made to integrate the aldol condensation of butyraldehyde and hydrogenation of 2-ethyl-2-hexenal into a one-pot reaction [5,6]. However, industrial processes still depend on unsustainable fossil carbon resources, and external CO and hydrogen gas are required.

The abundance of cellulosic biomass provides an environmentally beneficial, renewable feedstock as an alternative to

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Scheme 1. Alternative route for the synthesis of 2-ethyl-1-hexanol.

fossil carbon resources to produce chemicals and fuels. The Guerbet reaction has been used for upgrading biomass-based light alcohols to value-added higher alcohols. For example, the Guerbet reaction of ethanol, a fermentation product of sugar-containing crops, has been studied to produce 1-butanol as an “advanced biofuel.” Heterogeneously and homogeneously catalyzed Guerbet reactions of ethanol to 1-butanol have been reported [7–20]. 1-Butanol is also a potential fermentation product obtained *via* the acetone-butanol-ethanol fermentation process [21–24].

The synthesis of 2-EH from the Guerbet reaction of 1-butanol is a green alternative process (Scheme 1). The hydrogen required for the Guerbet reaction is borrowed *in situ* from the dehydrogenation of 1-butanol and does not involve the typical H_2 dissociation step [15,25,26]. Compared with the conventional three-step process in the production of 2-EH from fossil resources, the synthesis of 2-EH through the Guerbet reaction offers technical and potentially economic advantages, as it is a one-step process that eliminates the need for operations under pressurized CO and H_2 . Heterogeneous catalysts, such as Ir on N-doped carbon and Pd on metal oxides, have been applied for the Guerbet reaction of 1-butanol to 2-EH under a high temperature ($> 170\text{ }^\circ\text{C}$) with byproducts including olefins, ethers, and higher alcohols [27–29]. Homogeneous catalysts, such as Ir complexes, have been reported to exhibit good catalytic dehydrogenation/hydrogenation functions involved in the Guerbet reaction of 1-butanol. Ishii *et al.* [30] reported that $[Cp^*IrCl_2]_2$ or $[IrCl(COD)]_2$ (Cp^* for 1,2,3,4,5-pentamethylcyclopenta-1,3-diene, and COD for cycloocta-1,5-diene) complex catalyzed the Guerbet reaction of 1-butanol to 2-EH in the presence of a $t\text{-BuOK}$ base catalyst in xylene at $120\text{ }^\circ\text{C}$. However, the performance of the Ir complex measured by the turnover number (TON) was less than 100. Xu *et al.* [31] reported that $IrCl_3$ combined with a functionalized 1,10-phenanthroline ligand in the presence of the required stoichiometric $KOH/NaOAc$ base-catalyzed Guerbet reaction of 1-butanol yielded a TON of approximately 250 in water at $150\text{ }^\circ\text{C}$. Given the current state of progress, developing an efficient catalyst with high activity and selectivity is an important but highly challenging research goal for enhanced productivity for the Guerbet reaction of 1-butanol to 2-EH. This work aims to identify the critical structural and functional factors of ligands in the catalyst design for enhanced performances of Ir complexes in the Guerbet reaction of 1-butanol to 2-EH.

The Guerbet reaction of 1-butanol involves the following catalytic sequence: (1) metal-catalyzed dehydrogenation of 1-butanol to butyraldehyde, (2) base-catalyzed aldol condensation of butyraldehyde, and (3) metal-catalyzed hydrogenation of the aldol condensation product [32–34]. Although Ir complexes exhibited the potential for Guerbet catalysis of

1-butanol, the reported catalytic performance measured by TON was less than 1000 [30,31]. Developing an efficient metal catalyst with superior performance for both dehydrogenation and hydrogenation is critical for enhanced performance in the Guerbet reaction of 1-butanol to 2-EH. The Cp^*Ir complexes coordinated by pyridine-type ligands bearing an *ortho*-hydroxypyridine group (a proton-response ligand) are a class of excellent catalysts for hydrogenation/dehydrogenation, such as the hydrogenation of CO_2 and 5-hydroxymethylfurfural (5-HMF), and the dehydrogenation of alcohol and formic acid [35–48]. We previously demonstrated the excellent performance of a series of Cp^*Ir complexes coordinated with bipyridine-type ligands bearing an *ortho*-hydroxypyridine group for the hydrogenation of 5-HMF to 1-hydroxyhexane-2,5-dione (HHD) with a turnover frequency (TOF) of 31560 h^{-1} [39,40]. The equilibrium reaction of *ortho*-hydroxypyridine to *ortho*-oxyanion was found to assist H_2 heterolytic dissociation. The strong electron-donating NMe_2 group on the bipyridine-type ligand was found to further enhance the high catalytic performance for hydrogenating aldehyde and olefin intermediates, resulting in the TOF of hydrogenating 5-HMF to HHD [40]. In this work, the *in situ* formed *ortho*-oxyanion as a base is expected to assist the deprotonation of 1-butanol, as well as to enhance the performance of the subsequent hydrogenation of the *in situ* generated aldol condensation intermediate, leading to an enhanced catalytic performance of the Guerbet reaction of 1-butanol catalyzed by the Cp^*Ir complex. Based on the above hypothesis, we synthesized Cp^*Ir complexes bearing an *ortho*-hydroxypyridine group, which are electron-donating groups targeted for Guerbet catalysis in this work (Scheme 2). The Cp^*Ir complex bearing an electron-donating group, *ortho*-hydroxypyridine, and a Cl^- anion, is favorable for the Guerbet reaction of 1-butanol to 2-EH under mild conditions. A mechanism for the Cp^*Ir complex-catalyzed Guerbet reaction of 1-butanol to 2-EH is proposed.

2. Experimental

All the reagents used were of analytical grade, purchased locally and used without any purification unless otherwise specified. NMR spectra were measured in $CDCl_3$, or CD_3OD on a 400 MHz instrument and recorded at the following frequencies: proton (1H , 400 MHz), carbon (^{13}C , 100 MHz).

Synthesis of $[Cp^*IrClL_4]Cl$: a mixture of Cp^*IrCl_2 (100 mg), L4 (64.3 mg) was stirred in methanol (20 mL) under N_2 at-

Scheme 2. Chemical structures of Cp^*Ir complexes in this work.

mosphere at room temperature for 12 h. The methanol solution was removed under vacuum to give the product as a yellow solid. The yellow solid was used for Guerbet catalysis without further purification. ^1H NMR (400 MHz, CD_3OD) δ 1.64 (s, 15H), 3.60–3.62 (m, 4H), 3.82–3.84 (m, 4H), 7.07–7.11 (m, 2H), 7.65 (d, $J = 2.8$, 1H), 7.88–7.99 (m, 2H), 8.36 (d, $J = 6.92$, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 8.0, 65.9, 88.5, 106.2, 110.6, 112.7, 114.4, 141.8, 150.1, 153.9, 155.9, 156.2, 164.0.

Guerbet reaction of 1-butanol: As shown in Table 1, a mixture of Cp^*Ir complex, 1-butanol (2.0 g), and KOH was stirred under N_2 atmosphere. The final reaction mixture was diluted by CH_3CN , and dioxane was added as an internal standard for GC analysis. The TON was calculated based on converted 1-butanol in the products.

3. Results and discussion

We first tested the $[\text{Cp}^*\text{IrCl}_2]_2$ complex without a bipyridine-type ligand as the catalyst for the Guerbet reaction of 1-butanol with KOH as the base catalyst. The TON reached 411 in 6 h, and the desired 2-EH product was obtained with a selectivity of 74.3% (Table 1, entry 1). 2-Ethylhexanal (2-EHA), 2-ethylhex-2-enal (2-EEA), and 2-ethylhex-2-en-1-ol (2-EHE) were also detected with selectivities of 4.1%, 2.9%, and 18.7%, respectively. In comparison, the $[\text{Cp}^*\text{IrClL1}]\text{Cl}$ complex achieved a TON of 629, indicating that the bipyridine ligand L1 significantly enhanced the catalytic activity of the Cp^*Ir complex (Table 1, entry 2). To assess the effect of the *ortho*-hydroxypyridine group, the catalytic activity of $[\text{Cp}^*\text{IrClL2}]\text{Cl}$ with an *ortho*-hydroxypyridine group was tested for comparison (Table 1, entry 3). The TON of the $[\text{Cp}^*\text{IrClL2}]\text{Cl}$ complex nearly doubled that of the $[\text{Cp}^*\text{IrClL1}]\text{Cl}$ complex, indicating that the *ortho*-hydroxypyridine group of the bipyridine-type ligand played an important role in the formation of 2-EH, probably because the *ortho*-hydroxypyridine group assisted the dehydrogenation of 1-butanol and the subsequent hydrogenation step. The *ortho*-hydroxypyridine group is known to form an *ortho*-oxyanion that may serve as a base to trap the proton of 1-butanol to accelerate the dehydrogenation step [47]. The Cp^*Ir complex with a strong electron-donating *ortho*-oxyanion generated *in situ* may favor the hydrogenation step involved in the Guerbet reaction of 1-butanol [40].

Table 1

Guerbet reaction of 1-butanol to 2-EH by using a Cp^*Ir complex as catalyst.

Entry	Catalyst	T ($^\circ\text{C}$)	TON	Selectivity (%)			
				2-EHA	2-EEA	2-EHE	2-EH
1	$[\text{Cp}^*\text{IrCl}_2]_2$	120	411	4.1	2.9	18.7	74.3
2	$[\text{Cp}^*\text{IrClL1}]\text{Cl}$	120	629	3.8	7.6	26.6	62.0
3	$[\text{Cp}^*\text{IrClL2}]\text{Cl}$	120	1124	3.5	6.9	27.6	62.0
4	$[\text{Cp}^*\text{IrClL3}]\text{Cl}$	120	2900	1.1	6.1	15.0	77.8
5	$[\text{Cp}^*\text{IrClL4}]\text{Cl}$	120	2192	1.3	5.4	17.7	75.6
6	$[\text{Cp}^*\text{IrClL3}]\text{Cl}$	130	3492	0.7	4.5	8.4	86.4

Reaction conditions: Cp^*Ir complex (0.5 μmol), 1-butanol (2 g), and KOH (30 mg) under N_2 atmosphere (10 bar) for 6 h.

We previously reported that the hydrogenation performance of the Cp^*Ir complex was enhanced when ligand L2 was tuned to produce a more electron-rich variation [40]. Considering that the hydrogenation step is also involved in the Guerbet reaction, a Cp^*Ir complex bearing a stronger electron-donating group on ligand L2 may be expected to increase the activity of the Guerbet reaction of 1-butanol by enhancing the hydrogenation activity. Therefore, we studied the catalytic performance of the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ and $[\text{Cp}^*\text{IrClL4}]\text{Cl}$ complexes bearing the electron-donating groups, *para*-NMe₂, and *para*-morpholine, respectively (Table 1, entries 4 and 5). Compared with the $[\text{Cp}^*\text{IrClL2}]\text{Cl}$ complex (Table 1, entry 3), both the yield and selectivity of 2-EH were significantly increased. As a result, the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex bearing an electron-donating *para*-NMe₂ group exhibited higher catalytic activity (Table 1, entry 4). Upon further increasing the reaction temperature to 130 $^\circ\text{C}$, the TON of the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex reached a maximum of 3492 (Table 1, entry 6).

The Guerbet reaction of 1-butanol to 2-EH was then carried out by prolonging the reaction time to 48 h at 130 $^\circ\text{C}$, resulting in a 2-EH yield of 23.9% and a 2-EH selectivity of 89.5% (Supporting Information). A TOF of 564 h^{-1} was achieved using the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex as the catalyst after half an hour. Significantly, the catalytic performance of the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex was further tested at a catalyst charge as low as 1.6×10^{-5} mol%, and a record TON of 14047 was reached (Supporting Information). The results indicate that the catalyst is highly active, while maintaining a high stability under the reaction conditions to achieve a high TON.

We studied the effect of the base amount on the Guerbet reaction of 1-butanol with the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex as a catalyst. As shown in Fig. 1(a), upon increasing the amount of KOH from approximately 1.0 to 6.6 mol%, the TON first increased to a maximum value of 2900 and then decreased steadily. As shown in Fig. 1(b), the selectivity of the desired product 2-EH followed a similar trend to the TON curve, suggesting that approximately 1.7 mol% of KOH is the optimum base amount for producing 2-EH from 1-butanol with the maximum TON and selectivity. The selectivity of 2-EHA and 2-EEA remained at a plateau of approximately 2% and 8%, respectively. The selectivity of 2-EHE followed a trend that first decreased and then increased, probably because the hydrogenation of 2-EHE to 2-EH was suppressed with increasing amounts of KOH.

We propose a Guerbet reaction pathway for 1-butanol to 2-EH, as shown in Scheme 3 [30–32]. 1-Butanol is dehydrogenated to butyraldehyde by $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ and KOH, followed by the KOH-catalyzed aldol condensation of butyraldehyde to an unsaturated aldehyde, 2-EEA. 2-EEA may first undergo hydrogenation of the C=O bond to 2-EHE (Scheme 3, path a) or hydrogenation of the C=C bond to 2-EHA (Scheme 3, path b). Further hydrogenation of 2-EHE or 2-EHA produces the final product 2-EH. The detection of 2-EHA, 2-EEA, and 2-EHE, as shown in Table 1, demonstrates that 2-EHA, 2-EEA, and 2-EHE are intermediates.

To understand the factors that determine the pathway and product selectivity involving the observed intermediates as shown in Scheme 3, the multiple potentially competing aldol

Fig. 1. (a) Effect of the amount of KOH on TON by using the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex as the catalyst (conditions: 0.5 μmol of $[\text{Cp}^*\text{IrClL3}]\text{Cl}$, and 2 g of 1-butanol under 10 bar of N_2 atmosphere at 120 $^\circ\text{C}$ for 6 h); (b) The effect of the amount of KOH on the selectivity by using $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ as the catalyst (conditions: 0.5 μmol of $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ and 2 g of 1-butanol under 10 bar of N_2 atmosphere at 120 $^\circ\text{C}$ for 6 h).

reactions of butyraldehyde, 2-EHA, and 2-EEA were studied (Scheme 4). The self-aldol reaction of butyraldehyde produced 2-EEA as a major product with a conversion of 73.7% and yield of 72.6%. In the presence of 2-EHA, the self-aldol product, 2-EEA, from butyraldehyde was still obtained with a yield of 68.7%, while the cross-aldol product, 2,4-diethyloct-2-enal, was only obtained with a yield of 3.2%. The reduced cross-aldol reaction of 2-EHA with butyraldehyde was probably due to the steric effect of the ethyl group on the α -C. In the presence of 2-EEA, the self-aldol reaction of butyraldehyde to 2-EEA was not influenced. The cross-aldol product, 2,4-diethyloct-2,4-dienal, was not detected, indicating that the $\text{C}=\text{C}-\text{C}=\text{O}$ conjugation effect suppressed the cross-aldol reaction of 2-EEA with butyraldehyde. As a result, for the Guerbet catalysis of 1-butanol, the conjugation effect and steric hindrance on the α -C of aldehyde intermediates enhanced the selectivity of the Guerbet alcohol, 2-EH, by suppressing the cross-aldol reaction of 2-EHA and 2-EEA with butyraldehyde.

Scheme 3. Proposed pathways of the Guerbet reaction of 1-butanol to 2-EH.

Scheme 4. Steric and conjugation effects on product selectivity in the aldol reactions of butyraldehyde, 2-EHA, and 2-EEA. Reaction conditions: butyraldehyde (1 mmol), 2-EHA (0.5 mmol), 2-EEA (0.5 mmol), KOH (30 mg), 1-butanol (2 g), at 25 $^\circ\text{C}$ for 5 min.

To verify the rate-determining factor in the hydrogenation pathway of the unsaturated aldehyde, 2-EEA, the selective hydrogenation of 2-EEA catalyzed by the Cp^*Ir complex was studied as a model (Supporting Information). The hydrogenation products, 2-EHA, 2-EHE, and 2-EH were obtained with selectivities of 20.0%, 31.5%, and 39.7%, respectively. The results of hydrogenation of 2-EHA and 2-EHE to 2-EH are shown in Table 2. The blank reaction exhibited no Guerbet product generated from 1-butanol under the reaction conditions (Table 2, entry 1). The reaction rate measured by the TOF of 2-EHA hydrogenation to 2-EH (1409 h^{-1} , entry 2, Table 2) was much higher than that of 2-EHE hydrogenation to 2-EH (56 h^{-1} , entry 3, Table 2). The rates of TOF on 2-EHA and 2-EHE hydrogenations, as shown in Table 2, indicate that the hydrogenation of $-\text{C}=\text{O}$ is kinetically favored over that of $-\text{C}=\text{C}-$ by the $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ catalyst. The kinetics of the hydrogenation of these model compounds help to explain the intermediates observed in Fig. 1. As a result, for the Guerbet reaction of 1-butanol to 2-EH shown in Table 1, the selectivity of 2-EHE is generally higher than that of 2-EHA because the consumption rate of 2-EHE to 2-EH is much slower than that of 2-EHA to 2-EH.

The $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ complex is proposed to react with KOH, forming the $[\text{Cp}^*\text{IrClL3}']$ complex that bears an *ortho*-oxyanion group driven by the neutralization of HCl with a strong base, OH^- (Scheme 5) [36,49]. Further ligand exchange between OH^- and Cl^- in the $[\text{Cp}^*\text{IrClL3}']$ complex led to the formation of the $[\text{Cp}^*\text{Ir}(\text{OH})\text{L3}']$ complex [36]. As the $[\text{Cp}^*\text{Ir}(\text{OH})\text{L3}']$ complex

Table 2

Control experiments for the hydrogenation of 2-EHA and 2-EHE.

Entry	Substrate	TOF (h^{-1})	Selectivity (%)
1	—	—	—
2	2-EHA	1409	92.6
3	2-EHE	56	> 99

Reaction conditions: $[\text{Cp}^*\text{IrClL3}]\text{Cl}$ (0.4 μmol), 1-butanol (1 g), substrate (1 mmol), and KOH (1 mg) under H_2 atmosphere (10 bar) at 120 $^\circ\text{C}$ for 20 min.

Scheme 5. The proposed reaction of $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex with KOH.

could be rearranged to form a $[\text{Cp}^*\text{Ir}(\text{OH})\text{L}_3']$ complex that bears an *ortho*-carbonyl group, we studied the reaction of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex with KOH by ^1H NMR and ^{13}C NMR (Supporting Information). In Fig. 2(a), the peaks ($6.3 < \delta < 8.5$) are assigned to the bipyridine ring of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex. In the presence of KOH, a significant change in the ^1H NMR spectrum from that of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex was observed, indicating that a $[\text{Cp}^*\text{Ir}(\text{OH})\text{L}_3']$ complex with a carbonyl group on the bipyridine ring (Fig. 2(b)) is generated from the reaction of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex with KOH. For the corresponding ^{13}C NMR spectrum, as shown in Fig. 2(c), the peaks ($100 < \delta < 175$) are assigned to the bipyridine ring of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex, and the peak ($\delta = 164.0$, Fig. 2(c)) is assigned to C2 of the bipyridine ring [34,47]. In the presence of KOH, a significant change in the position of C2 in the ^{13}C NMR spectrum ($\delta = 171.6$, Fig. 2(d)) supported the formation of a carbonyl group in the $[\text{Cp}^*\text{Ir}(\text{OH})\text{L}_3']$ complex [36,49].

Fig. 2. The ^1H NMR and ^{13}C NMR spectra of the $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex with/without KOH. (a) The ^1H NMR spectrum of $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ without KOH; (b) The ^1H NMR spectrum of $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ with KOH; (c) The ^{13}C NMR spectrum of $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ without KOH; (d) The ^{13}C NMR spectrum of $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ with KOH.

Scheme 6. The proposed mechanism of the Guerbet reaction of 1-butanol to 2-EH.

Based on the above experimental results, we further propose a mechanism for the Cp^*Ir complex-catalyzed Guerbet reaction of 1-butanol to 2-EH (Scheme 6). The $[\text{Cp}^*\text{IrClL}_3]\text{Cl}$ complex may first react with KOH to form the active catalyst, $[\text{Cp}^*\text{Ir}(\text{OH})\text{L}_3']$ (Scheme 5) [36,49], followed by the dehydrogenation of 1-butanol to form the catalyst, Ir-H, and butyraldehyde [35]. The KOH-catalyzed aldol reaction of butyraldehyde produces an unsaturated aldehyde, 2-EEA. The aldehyde (2-EEA) is hydrogenated with the catalyst, Ir-H, to intermediate products, 2-EHA and 2-EHE, and further to 2-EH with the regenerated $[\text{Cp}^*\text{Ir}(\text{OH})\text{L}_3']$ -catalyst. The hydrogenation activity of the catalyst (Ir-H) was significantly enhanced with ligand L3, bearing a strong electron-rich *para*-NMe₂ group and an *ortho*-hydroxypyridine group. The ethyl group on the α -C and the conjugation effect of the C=C double bond inhibits the further cross-aldol reaction of 2-EHA and 2-EEA with butyraldehyde, resulting in an increase in selectivity in the Guerbet reaction of 1-butanol to produce 2-EH.

4. Conclusions

We have demonstrated an efficient homogeneous system for the catalytic Guerbet reaction of 1-butanol to produce 2-ethyl-1-hexanol. The catalytic activity of the Cp^*Ir complex increased when the electron density of the ligand was increased by introducing a *para*-NMe₂ group, an *ortho*-hydroxypyridine group, and a Cl[−] anion. A record TON of 14047 was attained. The ethyl group on the α -C of 2-EHA and the conjugation effect of the C=C double bond of 2-EEA are found to benefit the high selectivity of 2-EH from 1-butanol by inhibiting the cross-aldol reaction of 2-EHA and 2-EEA with butyraldehyde. The NMR study revealed the formation of a carbonyl group in the bipyridine-type ligand via the reaction of the Cp^*Ir complex with KOH. The new mechanistic understanding represents an important addition to the suite of Guerbet catalysis and hydrogen-borrowing chemistry. Further

improvement of the catalyst efficiency based on the mechanistic understanding and development of a homogeneous catalytic process for the economic production of higher alcohols from 1-butanol or ethanol is underway.

Electronic supporting information.

Supporting information is available in the online version of this article

Notes

The authors declare no competing financial interest.

References

- [1] J. Ma, L. Xu, L. Xu, H. Wang, S. Xu, H. Li, S. Xie, H. Li, *ACS Catal.*, **2013**, 3, 985–992.
- [2] S. K. Sharma, R. V. Jasra, *Ind. Eng. Chem. Res.*, **2011**, 50, 2815–2821.
- [3] L. Zhao, Y. Wang, H. An, X. Zhao, Y. Wang, *Catal. Commun.*, **2018**, 103, 74–77.
- [4] G. M. Torres, R. Frauenlob, R. Franke, A. Börner, *Catal. Sci. Technol.*, **2015**, 5, 34–54.
- [5] Y. Li, X. Liu, H. An, X. Zhao, Y. Wang, *Ind. Eng. Chem. Res.*, **2016**, 55, 6293–6299.
- [6] N. Liang, X. Zhang, H. An, X. Zhao, Y. Wang, *Green Chem.*, **2015**, 17, 2959–2972.
- [7] R. L. Wingad, P. J. Gates, S. T. G. Street, D. F. Wass, *ACS Catal.*, **2015**, 5, 5822–5826.
- [8] R. Mazzoni, C. Cesari, V. Zanotti, C. Lucarelli, T. Tabanelli, F. Puzzo, F. Passarini, E. Neri, G. Marani, R. Prati, F. Viganò, A. Conversano, F. Cavani, *ACS Sustainable Chem. Eng.*, **2019**, 7, 224–237.
- [9] V. N. Panchenko, E. A. Paukshtis, D. Y. Murzin, I. L. Simakova, *Ind. Eng. Chem. Res.*, **2017**, 56, 13310–13321.
- [10] G. R. M. Dowson, M. F. Haddow, J. Lee, R. L. Wingad, D. F. Wass, *Angew. Chem. Int. Ed.*, **2013**, 52, 9005–9008.
- [11] R. L. Wingad, E. J. E. Bergström, M. Everett, K. J. Pellow, D. F. Wass, *Chem. Commun.*, **2016**, 52, 5202–5204.
- [12] T. Moteki, D. W. Flaherty, *ACS Catal.*, **2016**, 6, 4170–4183.
- [13] C. N. Neumann, S. J. Rozeveld, M. Yu, A. J. Rieth, M. Dincă, *J. Am. Chem. Soc.*, **2019**, 141, 17477–17481.
- [14] K.-N. T. Tseng, S. Lin, J. W. Kampf, N. K. Szymczak, *Chem. Commun.*, **2016**, 52, 2901–2904.
- [15] H. Aitchison, R. L. Wingad, D. F. Wass, *ACS Catal.*, **2016**, 6, 7125–7132.
- [16] Y. Xie, Y. Ben-David, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.*, **2016**, 138, 9077–9080.
- [17] H. Li, A. Riisager, S. Saravanamurugan, A. Pandey, R. S. Sangwan, S. Yang, R. Luque, *ACS Catal.*, **2018**, 8, 148–187.
- [18] Q. Liu, G. Xu, X. Wang, X. Liu, X. Mu, *ChemSusChem*, **2016**, 9, 3465–3472.
- [19] G. Xu, T. Lammens, Q. Liu, X. Wang, L. Dong, A. Caiazzo, N. Ashraf, J. Guana, X. Mu, *Green Chem.*, **2014**, 16, 3971–3977.
- [20] S. Chakraborty, P. E. Piszcz, C. E. Hayes, R. T. Baker, W. D. Jones, *J. Am. Chem. Soc.*, **2015**, 137, 14264–14267.
- [21] E. M. Green, *Curr. Opin. Biotechnol.*, **2011**, 22, 337–343.
- [22] C. Jin, M. Yao, H. Liu, C.-F. Lee, J. Ji, *Renew. Sust. Energy Rev.*, **2011**, 15, 4080–4106.
- [23] A. Prakash, R. Dhabhai, V. Sharma, *Curr. Biochem. Eng.*, **2015**, 3, 37–46.
- [24] J. C. Liao, L. Mi, S. Pontrelli, S. Luo, *Nat. Rev. Microbiol.*, **2016**, 14, 288–304.
- [25] M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.*, **2007**, 349, 1555–1575.
- [26] G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.*, **2010**, 110, 681–703.
- [27] D. Liu, X. Chen, G. Xu, J. Guan, Q. Cao, B. Dong, Y. Qi, C. Li, X. Mu, *Sci. Rep.*, **2016**, 6, 21365.
- [28] C. Carlini, A. Macinai, A. M. R. Galletti, G. Sbrana, *J. Mol. Catal. A*, **2017**, 349, 1555–1575.

Graphical Abstract

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Electronic and steric factors for enhanced selective synthesis of 2-ethyl-1-hexanol in the Ir-complex-catalyzed Guerbet reaction of 1-butanol

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An enhanced catalytic Guerbet reaction of 1-butanol to 2-ethyl-1-hexanol by a Cp*Ir complex was reported.

- 2004**, 212, 65–70.
- [29] V. N. Panchenko, E. A. Paukshtis, D. Yu. Murzin, I. L. Simakova, *Ind. Eng. Chem. Res.*, **2017**, 56, 13310–13321.
- [30] T. Matsu-ura, S. Sakaguchi, Y. Obora, Y. Ishii, *J. Org. Chem.*, **2006**, 71, 8306–8308.
- [31] G. Xu, T. Lammens, Q. Liu, X. Wang, L. Dong, A. Caiazzo, N. Ashraf, J. Guana, X. Mu, *Green Chem.*, **2014**, 16, 3971–3977.
- [32] S. Hanspal, Z. D. Young, J. T. Prillaman, R. J. Davis, *J. Catal.*, **2017**, 352, 182–190.
- [33] A. V. Chistyakov, P. A. Zharova, S. A. Nikolaev, M. V. Tsodikov, *Catal. Today*, **2017**, 279, 124–132;
- [34] W. Y. Hernández, K. De Vlieger, S. Clerick, P. Van Der Voort, A. Verberckmoes, *Catal. Commun.*, **2017**, 98, 94–97.
- [35] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.*, **2018**, 118, 372–433.
- [36] K. Fujita, R. Kawahara, T. Aikawa, R. Yamaguchi, *Angew. Chem. Int. Ed.*, **2015**, 54, 9057–9060.
- [37] K. Fujita, Y. Tanaka, M. Kobayashi, R. Yamaguchi, *J. Am. Chem. Soc.*, **2014**, 136, 4829–4832.
- [38] W. P. Wu, Y. J. Xu, R. Zhu, M. S. Cui, X. L. Li, J. Deng, Y. Fu, *ChemSusChem*, **2016**, 9, 1209–1215.
- [39] Z. Xu, P. Yan, W. Xu, X. Liu, Z. Xia, B. Chung, S. Jia, Z. C. Zhang, *ACS Catal.*, **2015**, 5, 788–792.
- [40] Z. Xu, P. Yan, H. Li, K. Liu, X. Liu, S. Jia, Z. C. Zhang, *ACS Catal.*, **2016**, 6, 3784–3788.
- [41] N. Onishi, S. Xu, Y. Manaka, Y. Suna, W.-H. Wang, J. T. Muckerman, E. Fujita, Y. Himeda, *Inorg. Chem.*, **2015**, 54, 5114–5123.
- [42] J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.*, **2012**, 4, 383–388.
- [43] W.-H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ChemSusChem*, **2014**, 7, 1976–1983.
- [44] W.-H. Wang, J. F. Hull, J. T. Muckerman, E. Fujita, Y. Himeda, *Energy Environ. Sci.*, **2012**, 5, 7923–7926.
- [45] Y. Suna, M. Z. Ertem, W.-H. Wang, H. Kambayashi, Y. Manaka, J. T. Muckerman, E. Fujita, Y. Himeda, *Organometallics*, **2014**, 33, 6519–6530.
- [46] W.-H. Wang, M. Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.*, **2015**, 5, 5496–5504.
- [47] W.-H. Wang, J. T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.*, **2013**, 3, 856–860.
- [48] W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, E. Fujita, *Chem. Rev.*, **2015**, 115, 12936–12973.
- [49] K.-I. Fujita, N. Tanino, R. Yamaguchi, *Org. Lett.*, **2007**, 9, 109–111.

电子和空间位阻效应促进铱配合物催化1-丁醇经Guerbet反应选择制备2-乙基己醇

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摘要: 2-乙基己醇是一种增塑剂醇, 可用于合成增塑剂、表面活性剂和溶剂等诸多化工领域。目前工业上2-乙基己醇的合成是以化石资源丙烯为原料, 与氢气和一氧化碳通过氢甲酰化反应制备1-丁醛, 后者经羟醛缩合和催化加氢反应生成2-乙基己醇。由生物质发酵产生的1-丁醇为原料, 只需要经Guerbet反应可一步直接生成2-乙基己醇。比较而言, Guerbet反应路线步骤更少, 且1-丁醇原位脱氢产生的氢为氢源, 无需额外氢, 因此比化石资源丙烯路线对环境友好。目前, 文献报道的非均相催化1-丁醇Guerbet反应条件苛刻(如温度 > 170 °C), 副产物多(如烯烃、醚和高碳醇等), 且均相催化剂的活性低。

本文报道了一类Cp*Ir(Cp*为1,2,3,4,5-五甲基环戊二烯基)配合物用于该Guerbet反应。当Cp*Ir配合物的配体上修饰给电子基N,N-二甲基氨基和邻羟基时, Cp*Ir配合物的催化活性增强, 催化剂的转化数最高达到了14047。当氢氧化钾和Cp*Ir配合物(配体上修饰了N,N-二甲基氨基和邻羟基官能团)在1-丁醇中的浓度分别为1.7 mol%和0.04 wt%时, 在130 °C反应48 h, 产物2-乙基己醇收率为23.9%, 选择性为89.5%。核磁(NMR)研究结果表明, Cp*Ir配合物配体上的邻羟基与氢氧化钾反应脱除质子, 生成了羰基结构配体配位的Cp*Ir配合物, 继续催化1-丁醇脱氢反应。机理研究表明, 中间产物2-乙基己醛 α -碳上乙基的位阻效应和2-乙基己烯醛本身的共轭效应抑制了其继续发生羟醛反应, 从而提高了目标产物的选择性。

关键词: 2-乙基己醇; Guerbet反应; 1-丁醇; 铱; 加氢

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