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Ir(triscarbene)-catalyzed sustainable transfer hydrogenation of levulinic acid to γ-valerolactone

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Funding information National Research Foundation of Korea, Grant/Award Numbers: 2015M3D3A1A01065436, 2019R1A2C1084021 Sustainable iridium-catalyzed transfer hydrogenation using glycerol as the hydride source was employed to convert levulinic acid to γ -valerolactone (GVL) with exceptionally high turnover numbers (TONs) (500,000) and turnover frequencies (TOFs) (170,000 h⁻¹). The highly efficient triscarbene-modified iridium catalysts demonstrated good catalytic activities with low catalyst loadings (0.7 ppm) and good recyclability with an accumulated TON of over two million in the fourth reaction. In addition to glycerol, propylene glycol (PG), ethylene glycol (EG), isopropanol (IPA), and ethanol (EtOH) successfully transferred hydrides to levulinic acid, producing GVL with TONs of 339,000 (PG), 242,000 (EG), 334,000 (IPA), and 208,000 (EtOH), respectively. Deuterium-labeling experiments were conducted to gain insight into the reaction mechanism.

K E Y W O R D S

iridium complex, sustainable reaction, transfer hydrogenation, triscarbene ligand, γ -valerolactone

1 | INTRODUCTION

Efficient catalytic systems to convert biomass to highvalue chemicals have been extensively investigated because sustainable, carbon-rich biomass has the potential to replace fossil fuels, thereby producing industrially important chemicals and fuels without further increasing the carbon concentration in the air. The synthesis of γ -valerolactone (GVL), a renewable biofuel and green solvent, is one of these important and useful biomass conversions.^[1-5] GVL is produced from biomass-derived levulinic acid^[6,7] by transition-metal-catalyzed hydrogenation or transfer hydrogenation.^[8-22] While hydrogenation systems for the synthesis of GVL from levulinic acid involving various ligand-modified Ru and Fe catalysts are being actively reported, transfer hydrogenation conditions are not intensively studied; a few phosphine and amine-modified Ir, Ru, and Pd catalysts have been utilized in the presence of formic acid as a hydride source.^[9,15,18,21] In addition to homogeneous catalysts,

heterogeneous core-shell and bimetallic catalysts were also reported for the transfer hydrogenation of levulinic acid using formic acid.^[23,24] In contrast to the transfer hydrogenation of levulinic acid using formic acid, only a few alcohol-mediated transfer hydrogenation reactions have been employed for the production of GVL.^[25–27]

Transfer hydrogenation has the benefits of avoiding the use of hydrogen at high pressures in favor of sustainable liquid hydrogen sources.^[28] Thus, it is valuable to study efficient and sustainable transfer hydrogenation conditions for the synthesis of GVL from levulinic acid. The judicious choice of a homogeneous catalyst, including consideration of the modifying ligands would allow efficient transfer hydrogenation to be conducted in the presence of various sustainable hydride sources. Glycerol has been employed in transition-metal-catalyzed transfer hydrogenation owing to the sustainability of glycerol derived from biomass and the usefulness of glycerol-derived products, such as dihydroxyacetone (DHA), propanediol, and lactic acid.^[29–31] Thereby, the ^{2 of 7} WILEY Organometallic

Voutchkova-Kostal group reported the Ir-catalyzed transfer hydrogenation of levulinic acid using glycerol under microwave heating conditions with a good turnover number (TON) and turnover frequency (TOF).^[26] Here, we report efficient Ir(triscarbene) catalysts for the transfer hydrogenation of levulinic acid to GVL in the presence of glycerol, propylene glycol (PG), ethylene glycol (EG), isopropanol (IPA), and ethanol (EtOH) with excellent TONs and TOFs. A TON of 500,000 (TOF of 170,000 h^{-1}) was observed when using glycerol as a hydride source under conventional heating conditions (Scheme 1). The efficiency and versatility of our catalysts, which can use various biomass-derived alcohols as hydride sources, increase the environmental benefit of this protocol for the transfer hydrogenation of levulinic acid.

2 | EXPERIMENTAL

2.1 | General

Levulinic acid (98%), glycerol (99%), ethylene glycol (99.8%), and EtOH (anhydrous, 99.5%) were purchased from Sigma-Aldrich. Ethyl levulinate (98%) was obtained from TCI, isopropyl alcohol (99.9%) was supplied from Samchun Chemicals, and PG (99%) was from Acros Organics. Catalysts **1**, **1**', **2**, and **2**' were prepared as described in the literature.^[32] The synthesis of catalysts **1**, **1**', **2**, and **2**' and the catalytic reactions were conducted with headspace N₂ without Schlenk techniques.

2.2 | General catalytic procedure for transfer hydrogenation of levulinic acid and ethyl levulinate using glycerol, EG, and PG

Levulinic acid (580.6 mg, 5 mmol), catalysts (0.0033 µmol for bimetallic catalysts, 0.0067 µmol for monometallic



SCHEME 1 Ir-catalyzed synthesis of γ -valerolactone (GVL) from levulinic acid

catalysts), bases (10 mmol based on moles of OH⁻), H₂O (0.5 ml), and alcohols (glycerol, EG, and PG; 10 mmol) were added into an autoclave. The mixture was heated at 150°C for 3 h under nitrogen atmosphere. The reaction mixture was then cooled down to ambient temperature, diluted with H₂O, and acidified with hydrochloric acid (1.0 ml). The TONs and yields of γ -hydroxyvaleric acid (GHV) and GVL were calculated by ¹H NMR spectroscopy in D₂O, using isonicotinic acid as an internal standard. For the transfer hydrogenation of ethyl levulinate, the experiment was performed the same as mentioned above with ethyl levulinate (5 mmol) instead.

2.3 | General catalytic procedure for transfer hydrogenation of levulinic acid using IPA and EtOH

Levulinic acid (580.6 mg, 5 mmol), catalysts (0.0033 µmol for bimetallic catalysts, 0.0067 µmol for monometallic catalysts), bases (10 mmol based on moles of OH⁻), H₂O (0.5 ml), and alcohols (IPA and EtOH; 5 ml) were added into an autoclave. The mixture was heated at 150°C for 3 h under nitrogen atmosphere. The reaction mixture was then cooled down to ambient temperature, diluted with H₂O, and acidified with hydrochloric acid (1.0 ml). The TONs and yields of GHV and GVL were calculated by ¹H NMR spectroscopy in D₂O, using isonicotinic acid as an internal standard.

2.4 | Experimental procedure for the recycling experiment

First cycle: Levulinic acid (580.6 mg, 5 mmol), catalyst 2 (0.0033 $\mu mol),$ Ba(OH)₂ (5 mmol), H₂O (0.5 ml), and glycerol (5 mmol) were added into an autoclave. The mixture was heated at 150°C for 3 h under nitrogen atmosphere. Then, the reaction mixture was cooled down to ambient temperature. Second cycle: Levulinic acid (580.6 mg, 5 mmol), Ba(OH)₂ (5 mmol), H₂O (0.5 ml), and glycerol (5 mmol) were added to the mixture of first cycle. The mixture was heated at 150°C for 3 h under nitrogen atmosphere. Then, the reaction mixture was cooled down to ambient temperature. Third cycle: Levulinic acid (580.6 mg, 5 mmol), Ba(OH)₂ (5 mmol), H₂O (0.5 ml), and glycerol (5 mmol) were added to the mixture of second cycle. The mixture was heated at 150°C for 3 h under nitrogen atmosphere. Then, the reaction mixture was cooled down to ambient temperature. Fourth cycle: Levulinic acid (580.6 mg, 5 mmol), Ba(OH)₂ (5 mmol), H₂O (0.5 ml), and glycerol (5 mmol) were added to the mixture of third cycle. The mixture

was heated at 150°C for 3 h under nitrogen atmosphere. Then, the reaction mixture was cooled down to ambient temperature.

3 | RESULTS AND DISCUSSION

The Ir catalysts used in transfer hydrogenation are illustrated in Figure 1. The catalysts 1, 1', 2, and 2' have been reported in our previous work in which the catalysts were used to dehydrogenate glycerol.^[32] During dehydrogenation, we observed that bimetallic catalysts 1 and 2 produced hydrogen faster than monometallic catalysts 1' and 2', implying that the Ir-H formation from bimetallic iridium catalysts and glycerol is facile. In our recent report on the iridium-catalyzed transfer hydrogenation of K₂CO₃ using glycerol,^[33] we noticed that the wing-tip substituent of the carbene ligand affected the reduction of CO₂ by Ir-H. Accordingly, methyl and ethyl substituents at the wing tip of the triscarbene ligand and the monometallic and bimetallic structure of Ir(triscarbene) catalysts might affect the catalytic activity of this reaction because this process also includes Ir-H generation from Ir(triscarbene) and glycerol and the reduction of levulinic acid by Ir-H. As a result, Ir(triscarbene)-catalyzed transfer hydrogenations of levulinic acid in glycerol are conducted as listed in Table 1. TONs of each reaction were determined by ¹H NMR analysis (see Figure S1). Optimization began with the reaction of bimetallic iridium catalyst 1 (0.1 µmol, 0.002 mol%), levulinic acid (5 mmol), and NaOH (10 mmol) in a mixture of glycerol (10 mmol) and H₂O (0.5 ml) to form GVL (TON, 6800) and GHV (TON, 520) after HCl treatment (Entry 1). Testing other bases (KOH, CsOH, Ca(OH)₂, and Ba(OH)₂) revealed that dicationic hydroxide bases $(Ca(OH)_2 \text{ and } Ba(OH)_2)$ showed much higher TONs for GVL and GHV (Entries 1-5).^[34] The significant effect of Ba(OH)₂ is presumed to be related with the consumption of DHA which is



FIGURE 1 Ir catalysts used in transfer hydrogenation

derived from the glycerol dehydrogenation. The reactions of DHA with Ba(OH)₂, Ca(OH)₂, and KOH were conducted, showing higher yields of lactate with $Ba(OH)_2$ (see Table S2). During the conversion of DHA to lactate, Ba²⁺ is reported to form a complex with reaction intermediates, resulting in improved yields of lactate.^[35] Without the consumption of DHA, DHA can function as an acceptor of the hydride, which can be a competing process of reducing levulinic acid by Ir-H. When a carbonate base (K_2CO_3) was used instead of a hydroxide base, there was no product (Entry 6). In our previous work with iridium-catalyzed transfer hydrogenation and dehydrogenation of glycerol, it was apparent that carbene-coordinated iridium catalysts were highly efficient for the reaction of glycerol even at low concentration.^[32,33] Accordingly, the reaction was attempted with lower iridium catalyst concentration; catalyst loadings of down to 0.0025 umol (0.00005 mol%, 0.5 ppm) showed consistently high TONs for GVL synthesis (Entries 7-10). Although a catalyst loading of 0.0025 µmol produced the highest TON, the yield of GVL began to decrease. Catalyst loadings of 0.0033 µmol for bimetallic catalysts and 0.0067 µmol for monometallic catalysts (0.00007 mol%, 0.7 ppm) showed (460,000-500,000)high TONS and TOFs $(150,000-170,000 h^{-1})$ (Entries 11-13). We did not observe the effect of wing-tip substituents; both catalysts 1 and 2 formed GVL with TON of 500,000 and GHV with TON of 33,000, and catalysts $\mathbf{1}'$ and $\mathbf{2}'$ formed products with similar TONs. Compared with CO₂ reduction, the ketone reduction of levulinic acid might occur readily, showing no catalytic activity difference induced by the ligand substituents. The bimetallic and monometallic structure of catalysts did not change TONs of GVL and GHV, dramatically. To compare catalytic activities of H₂ generation via Ir-H and the reduction of levulinic acid at the same temperature, the dehydrogenation reactions using catalysts 1 and 1' were attempted at 150°C, showing hydrogen generation with only catalyst 1 (TON = 860). Although bimetallic and monometallic catalysts showed different dehydrogenation reactivity at 150°C, TONs are low. We did not observe vigorous hydrogen generation at 150°C. Overall, the bimetallic and monometallic structure of catalysts does not result in different reactivities in the reduction of levulinic acid.

Next, the transfer hydrogenation of ethyl levulinate was examined under the optimized reaction conditions for levulinic acid (Table 2). As with the reactions of levulinic acid, ethyl levulinate was converted to GVL with excellent TONs and TOFs (Entries 1–4).

In addition to glycerol, PG, EG, IPA, and EtOH were evaluated as hydride sources (see the Table S1). As

TABLE 1Optimization of transferhydrogenation of levulinic acid

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Me OH -	catalyst Me base H [⊂] O, glycerol 50 °C, 3 h	GVL		
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Entry	Catalyst (µmol)	Base (mmol)	GVL (TON, yield ^a)	GHV (TON, yield ^a)
1	1 (0.1)	NaOH (10)	6800, 27%	530, 2.0%
2	1 (0.1)	KOH (10)	7500, 30%	530, 2.0%
3	1 (0.1)	CsOH (10)	1800, 7%	—
4	1 (0.1)	$Ca(OH)_2(5)$	11,000, 43%	720, 2.8%
5	1 (0.1)	$Ba(OH)_2(5)$	17,000, 67%	1100, 4.6%
6	1 (0.1)	$K_{2}CO_{3}(10)$	—	—
7	1 (0.01)	$Ba(OH)_2(5)$	150,000, 60%	8800, 3.6%
8	1 (0.005)	$Ba(OH)_2(5)$	330,000, 67%	21,000, 4.2%
9	1 (0.0033)	$Ba(OH)_2(5)$	510,000, 67%	34,000, 4.4%
10	1 (0.0025)	$Ba(OH)_2(5)$	580,000, 58%	36,000, 3.6%
11	1 ′ (0.0067)	$Ba(OH)_2(5)$	460,000, 62%	54,000, 7.2%
12	2 (0.0033)	$Ba(OH)_2(5)$	510,000, 67%	33,000, 4.4%
13	2 ′ (0.0067)	$Ba(OH)_2(5)$	480,000, 64%	32,000, 4.2%

Note: The mixture of catalysts, base, and levulinic acid (5 mmol) in glycerol (10 mmol) and H_2O (0.5 ml) was heated at 150°C for 3 h, and the resulting mixture was treated with HCl. The TONs of bimetallic Ir catalysts were calculated based on the amounts of iridium ions. The bold emphasis are the best TONs of this reaction using different catalysts.

Abbreviations: GHV, γ -hydroxyvaleric acid; GVL, γ -valerolactone; TOF, turnover frequency; TON, turnover number.

^aThe yields of GVL and GHV were quantitated with ¹H NMR with an internal standard (isonicotinic acid).



TABLE 2Transfer hydrogenationof ethyl levulinate to GVL

Note: The mixture of catalysts, base, and ethyl levulinate (5 mmol) in glycerol (10 mmol) and H_2O (0.5 ml) was heated at 150°C for 3 h, and the resulting mixture was treated with HCl. The TONs of bimetallic Ir catalysts were calculated based on the amounts of iridium ions.

Abbreviations: GHV, γ -hydroxyvaleric acid; GVL, γ -valerolactone; TOF, turnover frequency; TON, turnover number.

^aThe yields of GVL were quantitated with ¹H NMR with an internal standard (isonicotinic acid).

illustrated in Figure 2, the catalysts were most reactive in the presence of glycerol. The TONs were slightly lower with the secondary alcohols (PG and IPA) at \sim 300,000.

The transfer hydrogenations using primary alcohols (EG and EtOH) had TONs of \sim 200,000. Overall, the secondary alcohol and multihydroxy alcohol hydride sources



FIGURE 2 Catalytic activities for γ -valerolactone (GVL) synthesis in various alcohols

promoted GVL synthesis with excellent TONs. Recently, Voutchkova–Kostal group reported the water-soluble iridium-catalyzed transfer hydrogenation of levulinic acid using glycerol and EtOH under microwave heating conditions to afford GHV with TON of 101,000 (glycerol) and 7580 (EtOH), respectively.^[26] Our catalytic conditions using Ir(triscarbene) catalysts and Ba(OH)₂ promoted these transformations with excellent TONs using various alcohols such as glycerol, PG, IPA, and EtOH.

A recycling test using the isolated iridium catalyst from the reaction mixture would be challenging because of the low catalyst concentration. Therefore, the reutilization of catalyst **2** was attempted by repeatedly adding levulinic acid, Ba(OH)₂, and glycerol to the reaction mixture (Figure 3 and Table S3). The acid treatment



for cyclization of GHV to GVL was not performed, resulting in the TONs of GHV being shown in Figure 3. As illustrated in Figure 3, the catalytic activity of the Ir(triscarbene) catalyst was maintained up to the third reaction, and in the fourth reaction, slightly decreased TON value was observed. Notably, the accumulated TONs for GHV increased from 519,000 in the first cycle to 2,040,000 in the fourth cycle.

A reaction mechanism is illustrated in Scheme 2. Based on the mechanism of the previously reported Ir-catalyzed transfer hydrogenation of glycerol,^[33] the glycerol-bound Ir(I) complex undergoes β -hydride elimination to afford **II**, which transfers a hydride to levulinic acid to form GHV. As we reported, iridium catalysts modified with bidentate ligands showed the higher catalytic activity in transfer hydrogenation using glycerol than monodentate ligands by inhibiting catalyst deactivation.^[33] The second iridium ion of catalyst **1** and the imidazolium of catalyst **1**' are speculated to pull levulinate into the reaction sphere as illustrated in



SCHEME 2 A plausible reaction mechanism and a deuterium-labeling study

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IV and IV'. As a result, a facile reduction of levulinate occurs to provide high TONs. When the reaction was conducted in deuterio-glycerol, deuterium was incorporated in ~92% of the GHV product at the α -position (see Figure S2). The 8% of nondeuterated GHV was attributed to hydrogen exchange between Ir-D and water.^[36,37]

4 | CONCLUSIONS

We have presented an Ir(triscarbene)-catalyzed transfer hydrogenation protocol for the sustainable conversion of levulinic acid to GVL. These robust and efficient Ir(triscarbene) catalysts promoted levulinic acid reduction with superb TONs and TOFs using sustainable hydrogen sources (glycerol, PG, EG, IPA, and EtOH). In addition to levulinic acid, ethyl levulinate was converted to GVL with high TONs and TOFs, like levulinic acid reactions. Recycling experiments showed that the catalyst could be recycled without losing catalytic activities up to the third reaction with high TONs. The structural difference of catalysts did not affect the catalytic activity, but multidentate carbene ligands might play an important role in promoting this reaction with good recyclability in the presence of extremely low catalyst loadings (0.7 ppm).

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AUTHOR CONTRIBUTIONS

Kihyuk Sung: Data curation; methodology. **Mi-hyun Lee:** Data curation; methodology. **Yeon-Joo Cheong:** Data curation; methodology; project administration.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in the Supporting Information.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article. How to cite this article: Sung K, Lee M, Cheong Y-J, Jang H-Y. Ir(triscarbene)-catalyzed sustainable transfer hydrogenation of levulinic acid to γ -valerolactone. *Appl Organomet Chem*. 2020; e6105. https://doi.org/10.1002/aoc.6105