

## Ir(triscarbene) Catalysts

## Highly Efficient Iridium-Catalyzed Production of Hydrogen and Lactate from Glycerol: Rapid Hydrogen Evolution by Bimetallic Iridium Catalysts

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**Abstract:** Mono- and bimetallic iridium complexes involving novel triscarbene ligands were synthesized and applied to the dehydrogenation of biomass-derived glycerol. This resulted in affording hydrogen and lactate with the excellent turnover number (TON; 3,240,000) and turnover frequency (TOF;

162,000 h<sup>-1</sup>). The triscarbene ligand in a single frame allowed the formation of bimetallic iridium complexes. This induced the cooperative effect of two iridium ions and rendered excellent TONs and TOFs in the production of hydrogen and lactate.

## Introduction

Hydrogen is considered a clean fuel that can be used for vehicles and heating facilities without emitting global warming gases; thus, a large production of hydrogen is urgently needed to fulfil the worldwide energy demand, as well as to reduce the consumption of fossil fuels. However, most of the hydrogen is generated from fossil fuels that simultaneously generate CO<sub>2</sub>.<sup>[1]</sup> Non-fossil fuel-based hydrogen production processes, such as water photolysis, has not yet been developed for commercial use.<sup>[2]</sup> Alternatively, transition-metal catalyzed dehydrogenation of biomass is a promising candidate to replace fossil fuel-based hydrogen production processes.<sup>[3,4]</sup> For large-scale hydrogen production, efficient dehydrogenation of glycerol is desirable because the production of glycerol from biodiesel has been drastically increasing. Furthermore, the co-production of bio-plastic raw materials (lactic acid) during dehydrogenation of glycerol would increase the economic value of this process.<sup>[5–7]</sup> Thus, investigating efficient catalytic systems for reforming glycerol to hydrogen and lactic acid are imperative.

Transition metal complexes involving monodentate or polydentate N-heterocyclic carbene (NHC) ligands have been extensively employed in homogeneous catalysis. This is because NHC ligands have unique electronic properties and the structural effect providing unexpected catalytic properties and stability during the catalytic reaction.<sup>[8–12]</sup> Compared to the monodentate NHC ligands, polydentate NHC ligands, such as tripodal NHCs, showed the ability to bind multiple metal ions in a homometallic<sup>[13–16]</sup> or a heterometallic manner.<sup>[17]</sup> There are a few types of tridentate NHC ligands, as illustrated in Figure 1. The scorpion-

ate-type and aromatic ring-bridged carbene ligands are commonly reported. They have a C<sub>3</sub>-symmetry around boron/carbon atoms or aromatic rings.<sup>[18]</sup> Another interesting class of tridentate carbene ligands is the Y-shaped tris-NHC.<sup>[11]</sup> In this study, we propose linear triscarbene ligands that can coordinate with iridium ions, resulting in the formation of new mono- and bimetallic iridium complexes.<sup>[19]</sup> These iridium complexes, including the linear triscarbene ligand, were employed for the catalytic transformation of glycerol to lactate and hydrogen.<sup>[20–26]</sup> Because the structural feature of the linear triscarbene ligands can induce multi-metal coordination, it is expected that the cooperative effect of metal ions increases the

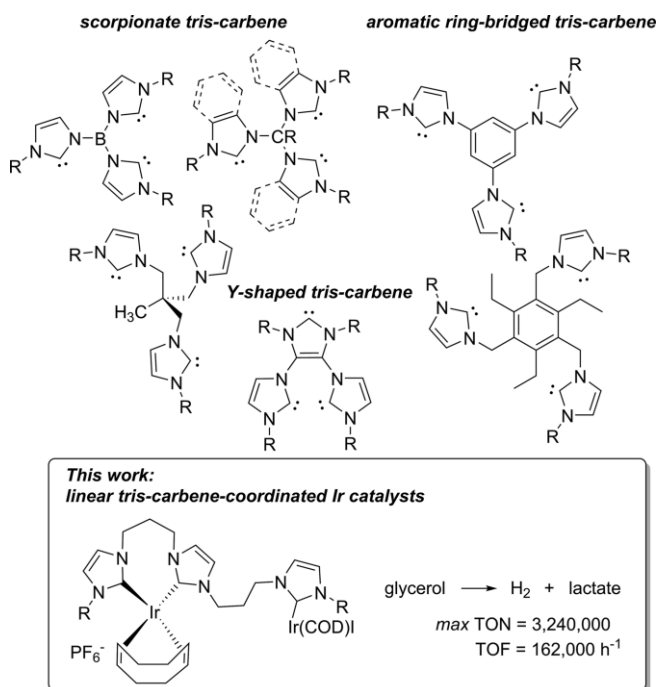


Figure 1. Examples of tridentate NHC ligands.

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rate of the dehydrogenation of glycerol. Herein, detailed synthetic procedures of these new iridium complexes and catalytic reaction results of hydrogen and lactate generation from glycerol [turnover number (TON); 3,240,000 and turnover frequency (TOF); 162,000 h<sup>-1</sup>] are presented.

## Results and Discussion

The synthesis of triscarbene ligands is illustrated in Scheme 1. Sodium imidazolate was di-alkylated with 1-bromo-3-chloropropane, followed by undergoing anion exchange to form compound **A**. The reaction of compound **A** and methyl and ethyl imidazole afforded tridentate NHC ligands **B** and **B'**, respectively. With tridentate NHC ligands **B** and **B'**, iridium complexation was carried out with [Ir(COD)Cl]<sub>2</sub> and NaH in EtOH. Methyl-substituted monometallic iridium **1** and bimetallic iridium **1'** were formed as a mixture. After separating the mixture, complexes **1** and **1'** were isolated with 23 % and 26 % yields, respectively. Ethyl-substituted monometallic iridium **2** and bimetallic iridium **2'** were synthesized with 11 % and 27 % yields, respectively. Complexes **2** and **2'** were further modified with CO to form **3** and **3'** with 93 % and 91 % yields, respectively. The structure of each complex is illustrated in Figure 2.

To examine optimal conditions for the conversion of glycerol, we examined the activity of catalyst **1** by measuring the TONs of lactate (Table 1). 24 mmol of a base was used with a slight excess of glycerol (28.9 mmol), assuming the formation of lactate is limited by the quantity of bases. The glycerol reactions involving NaOH, KOH, CsOH, Ba(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O (0.5 mL) at 180 °C showed modest to excellent TONs of lactate (Table 1, entries 1–6). The TONs of lactate were quantitated with <sup>1</sup>H NMR with an internal standard (see supporting

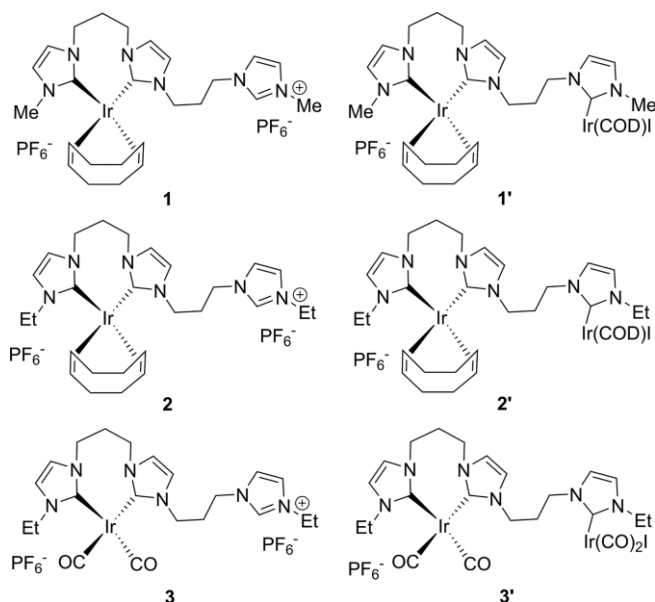
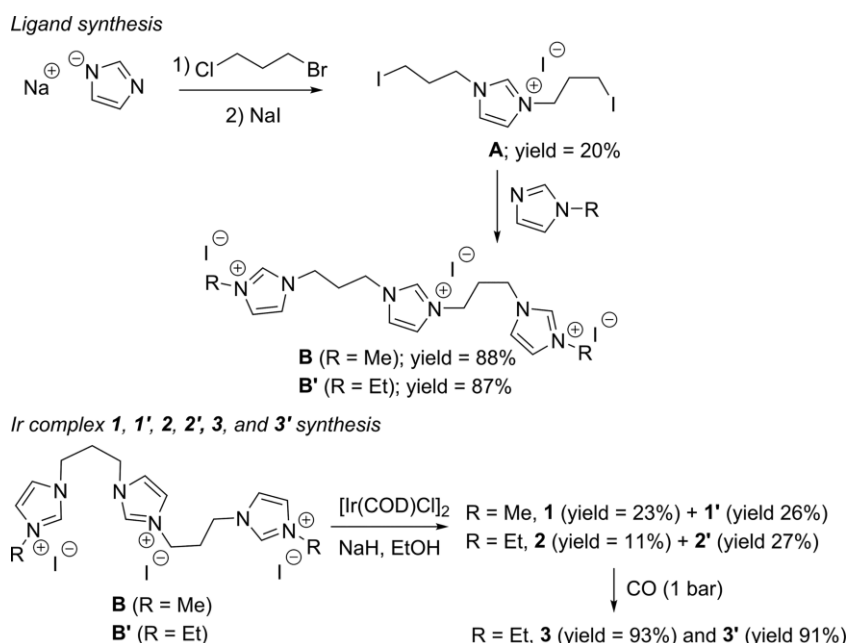


Figure 2. Examples of tridentate NHC ligands.

information). In the case of the reaction using K<sub>2</sub>CO<sub>3</sub>, formate was observed (TON 12,400), along with lactate. Among them, the combination of catalyst **1** and Ba(OH)<sub>2</sub> showed good catalytic activity (TON 123,000 and TOF 6,150 h<sup>-1</sup>, Table 1, entry 4). The high TON and TOF of entry 4 were accounted for by the combination of high catalytic activity of Ir complexes in the dehydrogenation of glycerol and the excellent activity of Ba(OH)<sub>2</sub> in the conversion of dihydroxyacetone to lactate.<sup>[27]</sup> TON increased to over 1 million with 70 % yield of lactate with 0.7 ppm of iridium ions (Table 1, entry 7). With the reaction conditions of entry 7, bimetallic Ir complexes **1'**, ethyl-substituted monometallic and bimetallic Ir complexes **2** and **2'**, and



Scheme 1. Synthesis of tris-NHC ligands and Ir complexes including tris-NHC ligands.

CO exchanged catalysts **3** and **3'** were examined to show similar high TONs and yields (Table 1, entries 7–12). The reaction using [Ir(COD)Cl]<sub>2</sub> or without catalysts provided lactate with 2 and 3 % yield, respectively (Table 1, entries 13 and 14). Using catalyst **1'**, the catalyst loadings were further decreased (Table 1, entries 15 and 16). As the amount of catalysts was decreased, TONs increased to over 3 million, corresponding to TOF = 162,000 h<sup>-1</sup>, albeit with slightly decreased yields of lactate (Table 1, entry 16). The catalytic activities of previously reported catalysts were illustrated, in which KOH was used at 115–150 °C (Figure 3).<sup>[22–25]</sup> Our catalyst **1'** (0.09 ppm) was subjected to the conditions using KOH at 150 °C, but lactate was not observed. Accordingly, we concluded that our catalyst combined with Ba(OH)<sub>2</sub> at 180 °C could provide the highest TOF of dehydrogenation of glycerol. The high reactivity and stability of our iridium catalysts even at 180 °C are attributed to the multidentate nature and linear geometry of the triscarbene ligand, preventing the catalytically inactive Ir complexes.<sup>[6,24]</sup>

Table 1. Optimization of glycerol dehydrogenation to afford lactate.

Entry	Catalyst (ppm)	Base (mmol)	Lactate TON, yield <sup>[a]</sup>
1	<b>1</b> (7.0)	NaOH (24)	110,000, 73 %
2	<b>1</b> (7.0)	KOH (24)	95,000, 62 %
3	<b>1</b> (7.0)	CsOH (24)	73,000, 48 %
4	<b>1</b> (7.0)	Ba(OH) <sub>2</sub> (12)	123,000, 81 %
5	<b>1</b> (7.0)	Ca(OH) <sub>2</sub> (12)	27,000, 18 %
6	<b>1</b> (7.0)	K <sub>2</sub> CO <sub>3</sub> (24)	41,000, 27 %
7	<b>1</b> (0.7)	Ba(OH) <sub>2</sub> (12)	1,010,000, 70 %
8	<b>1'</b> (0.35)	Ba(OH) <sub>2</sub> (12)	1,115,000, 77 %
9	<b>2</b> (0.7)	Ba(OH) <sub>2</sub> (12)	915,000, 63 %
10	<b>2'</b> (0.35)	Ba(OH) <sub>2</sub> (12)	995,000, 69 %
11	<b>3</b> (0.7)	Ba(OH) <sub>2</sub> (12)	851,000, 59 %
12	<b>3'</b> (0.35)	Ba(OH) <sub>2</sub> (12)	1,050,000, 72 %
13	[Ir(COD)Cl] <sub>2</sub> (0.35)	Ba(OH) <sub>2</sub> (12)	27,000, 2 %
14	–	Ba(OH) <sub>2</sub> (12)	–, 3 %
15	<b>1'</b> (0.18)	Ba(OH) <sub>2</sub> (12)	1,750,000, 61 %
16	<b>1'</b> (0.09)	Ba(OH) <sub>2</sub> (12)	3,240,000, 56 %

[a] The mixture of catalysts, base, and H<sub>2</sub>O (0.5 mL) in glycerol (28.9 mmol, 2.66 g) was heated at 180 °C for 20 h. The TONs of bimetallic Ir catalysts were calculated based on the amounts of iridium ions.

Based on the results of Table 1, hydrogen production by iridium catalysts **1**, **1'**, **2**, **2'**, **3**, and **3'** were measured with a gas burette after removing blank volumes. The amount of lactate could be used to evaluate the catalytic activity of iridium complexes at the end of the reaction. Still, the changes in catalytic activity over the reaction time could not be monitored by measuring the amount of lactate. Measuring the volume of hydrogen provides insights into the maximum catalytic activity during the reaction. Initially, measuring the volume of H<sub>2</sub> was attempted with catalyst loadings of 0.7 ppm (iridium ions), but this showed no H<sub>2</sub> evolution. The H<sub>2</sub> evolution was observed with an autoclave setup, showing ≈ 10 bar pressure increase. The catalytic activity may have been decreased because the gas burette setup and the low concentration-catalyst (0.7 ppm of iridium

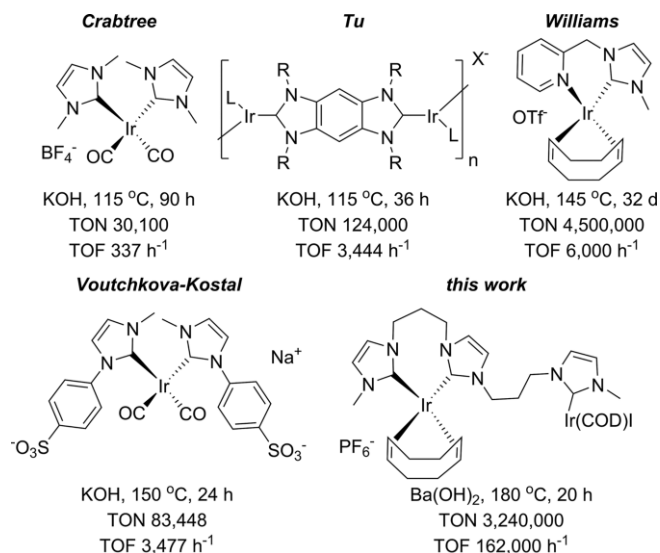


Figure 3. Comparison of the catalytic activities.

ions) were exposed to outside air. Therefore, experiments measuring H<sub>2</sub> volume with a gas burette were conducted with the higher catalyst loadings (7.0 ppm of iridium ions). Interestingly, we observed that the different patterns of catalytic activity change between monometallic and bimetallic catalysts. In the case of monometallic catalysts, the TOFs of the catalyst continuously increased up to 7.5 h. In contrast, the highest TOFs of bimetallic catalysts were observed at the initial stage of the reaction. Accordingly, the volumes of hydrogen and TOFs at the indicated reaction time (1 h and 7.5 h) were compared (Table 2).

Table 2. Catalytic activities of monometallic and bimetallic catalysts on hydrogen production.

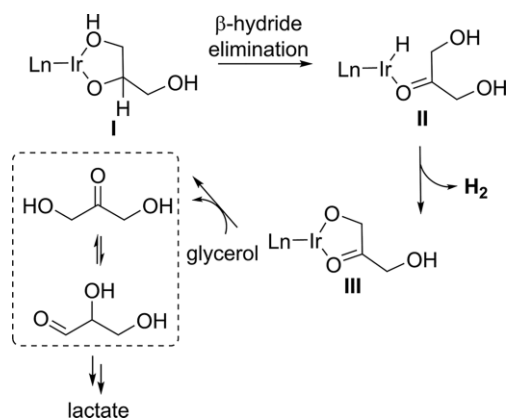
Entry	Catalyst (ppm)	1 h (volume, TOF) <sup>[a]</sup>	7.5 h (volume, TOF) <sup>[a]</sup>
1	<b>1</b> (7.0)	18 mL, 3,680 h <sup>-1</sup>	508 mL, 13,900 h <sup>-1</sup>
2	<b>1'</b> (3.5)	55 mL, 11,000 h <sup>-1</sup>	288 mL, 7,900 h <sup>-1</sup>
3	<b>2</b> (7.0)	5 mL, 1,080 h <sup>-1</sup>	296 mL, 8,500 h <sup>-1</sup>
4	<b>2'</b> (3.5)	83 mL, 17,900 h <sup>-1</sup>	380 mL, 10,910 h <sup>-1</sup>
5	<b>3</b> (7.0)	–	26 mL, 746 h <sup>-1</sup>
6	<b>3'</b> (3.5)	–	123 mL, 3530 h <sup>-1</sup>
7	catalyst mix (7.0)	6.5 mL, 1330 h <sup>-1</sup>	102 mL, 2,770 h <sup>-1</sup>

[a] The mixture of catalysts, Ba(OH)<sub>2</sub>, and H<sub>2</sub>O (0.5 mL) in glycerol (28.9 mmol, 2.66 g) was heated at 180 °C. The TOFs of bimetallic Ir catalysts were calculated based on the amounts of iridium ions.

With monometallic catalyst **1**, TOF of hydrogen generation was 3,680 h<sup>-1</sup> at 1 h and 13,900 h<sup>-1</sup> at 7.5 h, respectively (Table 2, entry 1). Catalyst **1'** showed a very different reaction pattern with the highest TOF at the beginning of the reaction; TOF at 1 h, 11,000 h<sup>-1</sup> and 7.5 h, 7,900 h<sup>-1</sup> (Table 2, entry 2). Over a 20 h reaction, lactates were formed with the yield 77 % (**1**) and 74 % (**1'**), respectively. The total amount of H<sub>2</sub> was lower than the amount of lactate due to the gas leak over a 20 h reaction (see Table S1 of Supporting Information). Ethyl-substituted catalysts **2** and **2'** also showed a similar reaction rate pattern with those of catalysts **1** and **1'** (Table 2, entries 3 and 4). The yields of lactate formed with catalysts **2** and **2'** were 81 % and 77 %, respectively. When catalysts **3** and **3'** including

CO were subjected to the reaction conditions, no gas was generated up to 3 h. The catalytic activity of the catalysts at 7.5 h was observed with TOFs of 746 h<sup>-1</sup> (catalyst **3**) and 3,530 h<sup>-1</sup> (catalyst **3'**), respectively (Table 2, entries 5 and 6). Bimetallic catalyst **3'** showed a much higher TOF than monometallic catalyst **3**. After 20 h, the yields of lactate formed with catalysts **3** and **3'** were 66 % and 69 %, respectively. The mixture of bidentate carbene-coordinated iridium catalysts and monodentate carbene-coordinated iridium catalysts [Figure S3(g) in the Supporting Information] was used for the hydrogen generation from glycerol, showing low TOFs and yields of lactate (46 %).

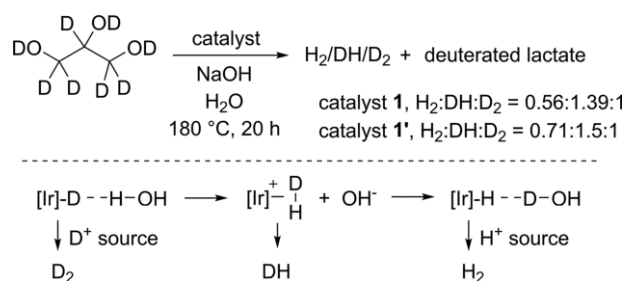
A generally accepted glycerol dehydrogenation mechanism involving iridium catalysts is presented in Scheme 2.<sup>[28,29]</sup> The reaction begins with the dissociation of cyclooctadiene of catalysts **1**, **1'**, **2**, and **2'**, and CO of catalysts **3**, and **3'**, followed by the coordination of an iridium complex with deprotonated glycerol to afford **I**. The dissociation of CO might not readily occur, resulting in no gas generation for three hours. Subsequent  $\beta$ -hydride elimination of **I** affords intermediate **II**. The Ir-H was protonated by the hydroxy of dihydroxyacetone to generate H<sub>2</sub> and intermediate **III**. An incoming glycerol replaces dihydroxyacetone in the iridium complex to close the catalytic cycle. Dihydroxyacetone undergoes equilibrium to form glyceraldehyde which is converted to lactate under basic conditions. Glyceraldehyde may form CO by decarbonylation, that can then be converted to CO<sub>2</sub> via a water gas shift reaction; however, the gas analysis showed that only hydrogen was formed without CO and CO<sub>2</sub> (see supporting information).<sup>[30]</sup> The fast rate of hydrogen production with bimetallic iridium catalysts is speculated by the proximity effect of two iridium ions in the catalyst. Although hydrogen production was illustrated by the protonation of iridium-hydride with dihydroxyacetone in the same iridium center (intermediate **II**), hydrogen may be formed by protonation with outer-sphere hydrogen sources, e.g. glycerol and water.<sup>[24]</sup> In the bimetallic catalysts, Ir-H can be protonated by glycerol or water coordinated to the neighbor iridium ion as well as dihydroxyacetone of Ir-H. Since there are more hydrogen sources near Ir-H, the hydrogen release of bimetallic catalysts is faster than monometallic catalysts.<sup>[31]</sup> The empirical results of entries 4 and 7 of Table 2 support this hypothesis.



Scheme 2. General catalytic cycle of glycerol dehydrogenation.

The deuterium labeling experiments using *d*<sup>8</sup>-glycerol, H<sub>2</sub>O, and NaOH were conducted in the presence of mono and bime-

talic iridium catalysts (Scheme 3). With catalysts **1** and **1'**, mixtures of D<sub>2</sub>, DH, and H<sub>2</sub> with ratios of 1:1.39:0.56 and 1:1.5:0.71 were observed by GC-MS, respectively. The formation of D<sub>2</sub> is explained by the mechanism of Scheme 2. Deuterated glycerol provided Ir-D via  $\beta$ -hydride elimination, which subsequently reacted with D<sup>+</sup> to form D<sub>2</sub>. The formation of DH and H<sub>2</sub> can be explained by the H<sup>+</sup>/D<sup>+</sup> exchange reaction of Ir-D.<sup>[32,33]</sup> Ir-D, formed from  $\beta$ -hydride elimination of *d*<sup>8</sup>-glycerol, underwent protonation by H<sub>2</sub>O or proton-exchanged *deuterio*-glycerol to afford a  $\eta^2$ -DH complex, resulting in DH. The iridium complex including  $\eta^2$ -DH underwent deprotonation by OH<sup>-</sup> (or alkoxy glycerol) to form Ir-H. Ir-H then reacted with a proton to provide H<sub>2</sub>. These results imply that protonation of Ir-D with external H<sub>2</sub>O or proton-exchanged *deuterio*-glycerol could be a possible route to produce hydrogen.



Scheme 3. Deuterium labeling experiments using *d*<sup>8</sup>-glycerol.

## Conclusion

We present structurally novel tris-NHC ligand-coordinated iridium complexes that show excellent catalytic activities for the conversion of glycerol to H<sub>2</sub> and lactate. The hydrogen production rates of monometallic and bimetallic iridium catalysts were monitored. The proximity of two iridium ions in the bimetallic catalyst rendered the cooperative effect to promote the fast evolution of H<sub>2</sub>. The unique structure of triscarbene ligands provided the most superior catalytic activity reported thus far in the hydrogen and lactate generation from glycerol (TON = 3,240,000 and TOF = 162,000 h<sup>-1</sup>). Our research results would contribute to the large production of hydrogen through non-fossil fuel sources.

## Experimental Section

**Synthetic Procedure for the Synthesis of A:** Imidazole sodium (2 g, 22.2 mmol) and 1-bromo-3-chloropropane (5.6 mL, 55.5 mmol) were dissolved in tetrahydrofuran (THF, 1 M) and stirred for 18 hours at room temperature. Then, the reaction mixture was refluxed for 8 hours. Sodium iodide (16.64 g, 111 mmol) and acetone (0.8 M, 27.8 mL) were added and the resulting solution was refluxed for 18 hours. The solid was filtered and washed with 10 % MeOH/CH<sub>2</sub>Cl<sub>2</sub> solution. The filtrate was dried under reduced pressure and the product was purified by column chromatography (MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 5:95) to afford **A** with 20 % yield.

**Synthetic Procedure for the Synthesis of B:** A mixture of **A** (2.4 g, 4.5 mmol) and 1-methylimidazole (1.4 mL, 17.8 mmol) was refluxed in MeCN (0.05 M, 89.2 mL) for 18 hours. After cooled down to ambi-



ent temperature, the reaction mixture was concentrated and washed with  $\text{CH}_2\text{Cl}_2$ /diethyl ether. The product **B** was afforded as a white solid in 88 % yield.

**Synthetic Procedure for the Synthesis of B':** A mixture of **A** (1.8 g, 3.4 mmol) and 1-ethylimidazole (1.3 mL, 13.4 mmol) was refluxed in MeCN (0.05 M, 67.2 mL) for 18 hours. After cooled down to ambient temperature, the reaction mixture was concentrated and washed with  $\text{CH}_2\text{Cl}_2$ /diethyl ether. The product **B'** was afforded as a white solid in 87 % yield.

**Synthetic Procedure for the Synthesis of 1 and 1':** Sodium hydride (35 mg, 0.875 mmol) was dissolved in ethanol (4.4 mL) and slowly added to a suspension of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (144 mg, 0.22 mmol) in ethanol (2.9 mL). The reaction mixture was stirred at room temperature for 1 h and **B** (348 mg, 0.5 mmol) was added and stirred at room temperature for 12 h. Then, the mixture was filtered, and the filtrate was evaporated in vacuo. Potassium hexafluorophosphate (158 mg, 0.9 mmol) in DCM/EtOH (v:v, 1:1) was added and stirred at room temperature for 1 h. The mixture was concentrated and purified by column chromatography. Complex **1'** was obtained as an orange solid with 26 % yield (eluent:  $\text{CH}_2\text{Cl}_2$  and acetone), and complex **1** was obtained with 23 % yield (eluent:  $\text{CH}_2\text{Cl}_2$  and MeOH).

**Synthetic Procedure for the Synthesis of 2 and 2':** Sodium hydride (35 mg, 0.875 mmol) was dissolved in ethanol (4.4 mL) and added dropwise to a suspension of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (144 mg, 0.22 mmol) in ethanol (2.9 mL). The reaction mixture was stirred at room temperature for 1 h and **B'** (375 mg, 0.5 mmol) was added and stirred at room temperature for 12 h. Then, the mixture was filtered, and the filtrate was evaporated in vacuo. Potassium hexafluorophosphate (158 mg, 0.9 mmol) in DCM/EtOH (v:v, 1:1) was added and stirred at room temperature for 1 h. The mixture was concentrated and purified by column chromatography. Complex **2'** was obtained as an orange solid with 27 % yield (eluent:  $\text{CH}_2\text{Cl}_2$  and acetone), and complex **2** was obtained with 11 % yield (eluent:  $\text{CH}_2\text{Cl}_2$  and MeOH).

**Synthetic Procedure for 3:** Complex **2** (40 mg, 0.043 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (1.4 mL) under CO (1 atm) and stirred for 24 h at room temperature. The solvent was removed in vacuo. The yellow solid was washed with diethyl ether to afford **3** with 93 % yield.

**Synthetic Procedure for 3':** Complex **2'** (41 mg, 0.033 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (1.4 mL) under CO (1 atm) and stirred for 24 h at room temperature. The solvent was removed in vacuo. The yellow solid was washed with diethyl ether to afford **3'** with 91 % yield.

**Catalytic Procedure for Dehydrogenation of Glycerol:** The catalyst (for monometallic complexes 0.02  $\mu\text{mol}$ , for bimetallic complexes 0.01  $\mu\text{mol}$ ), base (12 mmol),  $\text{H}_2\text{O}$  (0.5 mL), and glycerol (2.66 g, 28.9 mmol) were added into an autoclave. The mixture was heated at 180 °C for 20 h. Then, the reaction mixture was cooled down to ambient temperature, and diluted with  $\text{H}_2\text{O}$ . The TONs of lactates were calculated by  $^1\text{H}$  NMR spectroscopy in  $\text{D}_2\text{O}$  using isonicotinic acid as an internal standard.

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**Keywords:** Carbene ligands · Iridium · Homogeneous catalysis · Hydrogen · Lactate · Glycerol

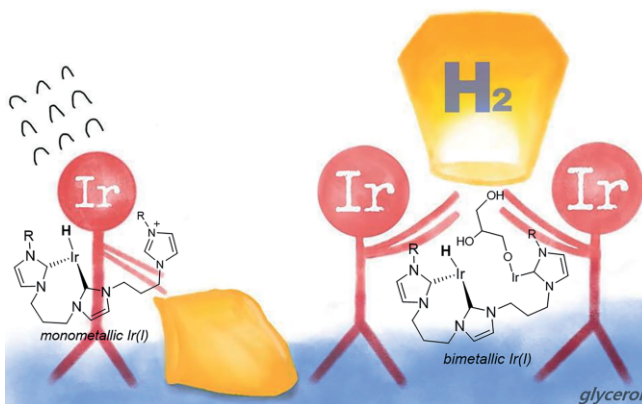
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## Ir(triscarbene) Catalysts

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 **Highly Efficient Iridium-Catalyzed Production of Hydrogen and Lactate from Glycerol: Rapid Hydrogen Evolution by Bimetallic Iridium Catalysts**



Highly efficient iridium catalysts modified with triscarbene ligands showed excellent TONs and TOFs for hydrogen generation from glycerol. The initial

rate of hydrogen generation by bimetallic iridium catalysts was much faster than monometallic catalysts.

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