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# COMMUNICATION

## Selective and High Yield Transformation of Glycerol to Lactic Acid Using NNN Pincer Ruthenium Catalysts

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Moumita Dutta,<sup>a</sup> Kanu Das,<sup>a</sup> Siriyara Jagannatha Prathapa,<sup>b</sup> Hemant Kumar Srivastava\*c and Akshai Kumar\*<sup>a,d</sup>

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## The conversion of glycerol selectively to lactic acid has been accomplished in high yields (ca. 90 %) by a NNN pincer-Ru catalyst. DFT explains the role of Ru–P bond and sterics in favoring catalysis.

Recent years have witnessed a surge in the utilization of biodiesel<sup>1</sup> which has significantly increased the formation of glycerol that is one of its major by-products.<sup>2</sup> Glycerol which is nontoxic and biodegradable<sup>3a</sup> is also generated as a waste from multiple processes that include hydrogenolysis of cellulose<sup>3b</sup> and fermentation processes involving microorganisms.<sup>3c</sup> While a small fraction of glycerol produced globally finds use as a green non-volatile solvent,<sup>3d-e</sup> as a fuel<sup>3f</sup> and as a source of hydrogen,<sup>3a,g-k</sup> it can potentially be employed as a versatile precursor to several synthetically useful transformations.<sup>31</sup>

One such useful transformation of glycerol involves the generation of hydrogen<sup>3h</sup> along with the production of lactic acid (LA). Lactic acid is valuable synthetic feedstock and finds wide application in food, pharmaceuticals, fine chemicals, cosmetics and also in the synthesis of poly lactic acid (PLA).<sup>4</sup> Lactic acid synthesis from glycerol via bioconversion<sup>3g</sup> involving traditional fermentation and heterogeneous catalysis<sup>3a, 5</sup> suffer from several limitations. On the other hand, homogeneous catalysis for glycerol to LA conversion have been reported to demonstrate very good reactivity and selectivity.<sup>2, 3i, 6</sup>

In his pioneering work, Crabtree reported the acceptorless dehydrogenation of glycerol using an Ir(I)-NHC complex which provided up to 30100 turnover numbers (TONs) in about 90% yield with a selectivity of 95% towards LA.<sup>6e</sup> In 2015, the Beller group demonstrated the exceptional activity of PNP-Ru that resulted in 270000 TONs with about 67% yield of LA at 140 °C using NMP as a solvent.<sup>6f</sup> Hazari and Crabtree have reported the

 <sup>b.</sup> Bruker India Scientific Pvt. Ltd., Bengaluru – 560092, Karnataka, India.
<sup>c</sup> Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research Guwahati, Guwahati – 781101, Assam, India. Email: hemantkrsri@gmail.com d. Centre for Nanotechnology, Indian Institute of Technology Guwahati

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synthesis of LA using pincer–Fe complexes.<sup>6g</sup> Tu and co-workers have shown the applicability of NHC-Ir based copolymers in the catalytic dehydrogenation of glycerol with good yield (98 % ca. 3266 TONs) and recyclability.<sup>6h</sup> In 2016, Williams achieved conditions that provide high TONs (1057172) as well as good yield (62%) of LA starting from glycerol using a Ir(I) complex at 145 °C.6i Very recently, Voutchkova-Kostal have utilized Ir(I), Ir(III) and Ru(II) NHC complexes for efficient transformation of glycerol to LA.<sup>6</sup> They have arrived at methods that provide high TONs at 150 °C and also under microwave conditions.

Recently, we have reported the synthesis<sup>7a</sup> of NNN pincer-Ru complexes and their activity towards N-alkylation which involved the dehydrogenation as the first step with 1a being more efficient than 1b.7b We envisaged the utility of these catalysts in other synthetically useful transformations that rely on dehydrogenation such as glycerol to LA formation. Herein, a systematic mechanistic insight has been obtained by comparing the activity of pincer-ruthenium complexes (1a-b) based on bis(imino)pyridine with corresponding sterically less hindered 2,6-bis(benzimidazole-2yl) pyridine based complexes (1c-d) towards synthesis of LA from glycerol (Figure 1).

The complex (1c) based on 2,6-bis(benzimidazole-2yl) pyridine was synthesised by improvising the procedure reported by us<sup>7a</sup> and others<sup>7c,d</sup> (see SI). Notably Zhang and Peng have reported similar complexes but with acetonitrile as ancillary ligands which were shown to be active for transformation of benzyl alcohols to corresponding acids.<sup>7e</sup> The <sup>31</sup>P NMR revealed that the major isomer in complex **1c** had the two PPh<sub>3</sub> groups *trans* to each other. Treatment of 1c with NaPF<sub>6</sub> in methanol resulted in **1d**<sup>‡</sup> which was characterized by single–crystal X–ray analysis (Figure 1d). We were fortunate to obtain the crystal structure of **1a**<sup>‡</sup> (Figure 1c) which was elusive in our previous attempts.<sup>7a</sup> In a typical experiment, to a flask containing 0.7 µmol of 1a in glycerol (2.56 mmol), KOH (1.48 mmol) was added followed by addition of 2 mL ethanol (bp=78°C) (entry 1, Table 1). The reaction mixture was then heated under open vessel conditions at 140 °C under an argon atmosphere. As glycerol is very viscous, ethanol is added to ensure proper homogeneity of the

<sup>&</sup>lt;sup>a.</sup> Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati – 781039, Assam, India. Email: <u>aks</u> ar@iitg.ac.ii

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Figure 1. NNN pincer-ruthenium complexes based on (a) bis(imino)pyridine ligands and (b) 2,6-bis(benzimidazole-2yl) pyridine ligands investigated in the current study. ORTEP diagram of (c) 1a and (d) 1d with ellipsoids drawn at 50% probability. The H atoms and Ph groups on P are omitted for sake of the clarity

reaction mixture. During the reaction, all the ethanol is lost within a few minutes of reaction. The NMR spectra (Figure S7-S24) of the crude product does not show any evidence either for presence of ethanol or its potential dehydrogenation products. The reactions catalyzed by 1a (entry 1, Table 1) gave moderate yield of LA. On the other hand, the performance of 1b was relatively poor (entry 2, Table 1). The catalyst 1c based on 2,6-bis(benzimidazole-2yl) pyridine ligand exhibited good activity towards the selective conversion of glycerol to LA (entry 3, Table 1). Its analog 1d with the PF<sub>6</sub> counterion gave yields of LA that was comparable with 1c. (entry 4, Table 1). This is attributable to the fact that both 1c and 1d give rise to the same active catalyst (See Scheme 1 and 2). Further optimization of reaction conditions was carried out with 1c (Table 2). Under the best reaction conditions, the observed high selectivity (Table 1 and 2) of LA clearly indicates that the decarbonylation of glycerol<sup>6</sup> and decarboxylation of lactic acid<sup>6</sup> leading to ethylene glycol and formic acid respectively are negligible.

Use of DMSO, DMF and benzonitrile leads to very low yield of LA in the **1c** catalyzed reactions (entries 2,3 and 5 Table 2). Moderate yields of LA were obtained with either *p*-xylene or water as solvent (entries 4 and 6, Table 2). Upon increasing the base loading, the **1c** catalysed reaction gave very good yield of LA (entry 8, Table 2). The yield however dropped to 59% (entry 9, Table 2) under solvent free conditions indicating the importance of thorough premixing of the contents. In particular, use of ethanol may assist in the easy generation of the catalytically active Ru-H species<sup>7b</sup>(**8a**-**c**) via  $\beta$ -hydride elimination from Ru(ethoxide). As dioxane offers no such possibility, not surprisingly, the yields are slightly lower in comparison (compare entries 7 vs. 1 and 10 vs. 8, Table 2) to the

Table 1. Glycerol dehydrogenation to lactic acid catalysed by 1 under varying conditions									
но ( <b>3</b>	— он н )	Base (0.58 Equivalent H [Ru] (0.03 Mol %) Ethanol, 48 h, 140 °C, Open Vessel, Ar	$\xrightarrow{S}, HO \rightarrow $	но он <sup>+</sup> (5′)	+ HCO₂H + H₂ ( <b>5″</b> )				
Entry	1	3 Conversion <sup>a</sup>	5 Yield <sup>a</sup>	5'(5")	Selectivity <sup>b</sup>				
			(TONs)	Yield <sup>a</sup>	towards <b>5</b>				
1	1a	62%	53% (1767)	3%(2%)	85%				
2	1b	27%	26% (867)	1%(1%)	96%				
3	1c	71%	69±3°% (2300)	2%(1%)	97%				
4	1d	67%	66% (2200)	1%()	98%				

Reaction conditions: 0.7 µmol of **1**, 2.56 mmol of **3**, 1.48 mmol KOH, 2 mL solvent in an open vessel under Ar at 140 °C. <sup>a</sup>Determined from <sup>1</sup>H NMR using NaOAc as internal standard. <sup>b</sup>Selectivity = (yield of **5**/conversion of **3**)100. <sup>c</sup>Average of 2 runs.

но	) OH (3)	∽OH Base (X Equivalents), 1c (0.03 Mol %) Solvent, 48 h, 140 °C, Open Vessel, Ar	$\rightarrow \overset{HO}{\underset{(5)}{}_{OH}} \overset{+}{\underset{H}{}_{H}}$	O OH + H	HCO <sub>2</sub> H + H <sub>2</sub>
Entry		Base (Equiv.), Solvent	Yield <sup>a</sup>		3 Conversion
			5 (TONs)	5′(5 <b>″</b> )	(5 Selectivity)
1		KOH (0.58), Ethanol	69±3°% (2300)	2%(1%)	71% (97%)
2		KOH (0.58) <b>,</b> DMSO	9% (300)	5%(3%)	26% (35%)
3		KOH (0.58) <b>,</b> DMF	2% (67)	5%(25%)	34% (6%)
4		KOH (0.58) <b>,</b> <i>p</i> –Xylene	46% (1533)	2%()	73% (63%)
5		КОН (0.58) <b>,</b> PhCH₂CN	2% (67)	1%()	3% (67%)
6		KOH (0.58) <b>,</b> Water	40% (1344)	3%()	44% (98%)
7		KOH (0.58), Dioxane	68% (2267)	3%()	72% (94%)
8		KOH (1.0), Ethanol	90±2°% (3000)	1%()	92% (98%)
9		KOH (1.0), –	59% (1966)	2%()	61% (97%)
10		KOH (1.0) <b>,</b> Dioxane	76% (2557)	1%(1%)	78% (97%)
11		NaOH (1.0), Ethanol	37±1º% (1233)	4%(5%)	52% (71%)
12 <sup>d</sup>		KOH (1.0), Ethanol	5% (1667)	1%(1%)	6% (83%)
13 <sup>d,e</sup>	2	KOH (1.0), Ethanol	45% (15000)	1%(1%)	46% (98%)
14 <sup>d,e</sup>	e	КОН (1.0), —	44% (14666)	1%(1%)	46% (96%)

Table 2. Glycerol dehydrogenation to lactic acid catalysed by 1 under varying conditions

Reaction conditions:  $0.7 \mu$ mol (0.03 mol %) of **1c**, 2.56 mmol of **3**, 1.48 mmol KOH, 2 mL solvent in an open vessel under Ar at 140 °C. <sup>a</sup>Determined from <sup>1</sup>H NMR using sodium acetate as internal standard. <sup>b</sup>Selectivity = (yield of **5**/conversion of **3**)100. <sup>c</sup> Reported as an average of two runs. <sup>d</sup>0.3 µmol (0.003 mol %) of **1c**, 10.24 mmol of **3**, 10.24 mmol KOH, 2 mL solvent in an open vessel under Ar at 140 °C. <sup>e</sup> Performed in presence of 5.12 mmol of water.

yields obtained with ethanol under otherwise identical conditions. Yields were drastically reduced either with use of NaOH as base (entry 11, Table 2) or upon decreasing the loading of **1c** (entry 12, Table 2). However, in the presence of 0.5 equivalents water,<sup>6e</sup> 45% LA (15000 TONs) was obtained with 0.003 mol % of **1c** (entries 13 and 14, Table 2). It is noteworthy that at this lower catalyst loading it is easy to homogenize the reaction mixture without the use of ethanol.

We have recently demonstrated the ability of catalysts (1a–b) to generate H<sub>2</sub> when treated with primary alcohols at 140 °C.<sup>7b</sup> The plausible mechanism involved in the reaction is provided in Scheme 1. The complexes (6a–c), (7a–c), (8a–c) and (9a–c) depicted in Scheme 1 are either the intermediates or the transition states (TSs) involved in the cycle catalyzed by the corresponding complexes (1a–d). For the sake of simplicity, only the NNN ligating section of the pincer framework is represented. While for (1a–b), the generation of active species (6a–b) is fairly straightforward (eq. 1, Scheme 2), one could anticipate, loss of two PPh<sub>3</sub> molecules in the corresponding

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Scheme 1. Plausible mechanism involved in the (1a-d) catalyzed transformation of glycerol to lactic acid

formation of the catalytically active species (6c) starting from both 1c and 1d (equation 2, Scheme 2).

A  $\beta$ -hydride elimination from (**6a**-c) results in the formation of (8a-c) and glyceraldehyde 4 via TS (7a-c) (Scheme 1). The active species (6a–c) is regenerated via a  $\sigma$ -bond metathesis of the O-H of **3** with the Ru-H of (**8a-c**) through TS (**9a-c**) (Scheme 1). Spontaneous dehydration of **4** gives  $\alpha, \beta$ -unsaturated aldehyde 4' and its tautomer 4". The Cannizzaro reaction of 4" leads to LA 5. It has been widely accepted that, in the transformation of glycerol to LA, only the dehydrogenation step is metal-catalyzed and the rest of the steps are spontaneous organic processes in basic solution.<sup>2</sup> The observed difference between various catalysts (Table 1) can be attributed to the variation in their relative dehydrogenation efficiencies. With an intent to understand the relative ease of dehydrogenation, the Ru–P interaction energy and the relative free energies at 140 °C  $(\Delta G_{140})$  for the species involved in the catalysis were computed. It has been shown<sup>7a,7f</sup> that the catalytic efficiency of Ru catalysts with phosphine as ancillary ligands is dependent on the ease of their release to generate the active catalyst (6 in this case). The phosphine release can be quantified as the interaction energy  $(-\Delta E_{int})$  of PPh<sub>3</sub> either with (<sup>R2</sup>NNN)RuCl<sub>2</sub> (R=<sup>t</sup>Bu, Ph) arising from **1a** and **1b** or with [(Bim2NNN)RuCl(PPh<sub>3</sub>)]<sup>+</sup> arising from both 1c and 1d (Table 3). The  $-\Delta E_{int}$  followed the trend; 1b (44.35 kcal/mol) > 1a (39.82 kcal/mol) > (1c or 1d) (39.00



Table 3. Interaction energy, free energy of formation and energy barriers, involved in the transformation of glycerol to glyceraldehyde catalysed by  $\Omega_{a} = 0.1039 / D0CC02884C$ 



aInteraction energy is calculated as the difference between the energy of the complex (1a-d) and the energy of the corresponding isolated PPh<sub>3</sub> and (R2NNN)RuCl<sub>2</sub> (R=<sup>t</sup>Bu, Ph) or [(Bim2NNN)RuCl]<sup>+</sup> in the geometry of the complex (1a**d**).<sup>b</sup>Free energy of formation at 140 °C for  $\beta$ -hydride elimination **6** $\rightarrow$ **8**. <sup>c</sup>Values obtained from Table 1. <sup>d</sup>As cation was computed, the values are same for 1c & 1d.

kcal/mol). Clearly, the complex 1b where the PPh<sub>3</sub> is the hardest to remove in comparison with 1a, 1c and 1d exhibited the lowest activity (867 TONs). However, among 1a and 1c or 1d with comparable Ru-P bond energy, 1a exhibited much lower activity (1767 TONs) than 1c (2300 TONs) and 1d (2200 TONs). This can be satisfactorily explained if one considers the energetics of  $\beta$ -hydride elimination and H<sub>2</sub> evolution (Figure 2). The overall uphill reaction  $(6+3\rightarrow 6+4+H_2;$  Figure 2) justifies the need of high operating temperature (140 °C). While for the reactions catalyzed by **1a**,  $\beta$ -hydride elimination is the RDS, H<sub>2</sub> evolution is the RDS for corresponding reactions catalyzed by 1b and 1c/1d (Table 3, Figure S25). The barrier for the RDS followed the trend; **1a** (TS **7a**;  $\Delta G_{140}^{*} = 31.78 \text{ kcal/mol} > 1b$  (TS **9b**;  $\Delta G_{140}^{*}$ = 23.90 kcal/mol) > (1c or 1d) (TS 9c; ΔG<sup>+</sup><sub>140</sub> = 21.39 kcal/mol) (Table 3, Figure 2, Figure S25). Though the energetics of the 1b catalyzed reactions are more favourable than 1a (Table 3, Figure S25), the reluctance of 1b to easily release the PPh<sub>3</sub> (entry 2, Table 3) contributes to its lower reactivity. On the other hand, the reaction with catalyst 1c or 1d proceeds very efficiently not only because the barrier for the  $\beta$ -hydride elimination





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(TS **7c**;  $\Delta G_{140}^{\dagger} = 16.17$  kcal/mol) is about 1.96 folds (TS **7** barrier in entries 1 and 3 Table 3) lower but also because the  $\beta$ -hydride elimination is downhill by 6.54 kcal/mol ( $\Delta G_{140}$  for entries 1 and 3 Table 3) in comparison with 1a (Figure 2). This results in a significant build-up of glyceraldehyde in reactions catalyzed by 1c/1d in stark contrast to 1a where the equilibrium is more towards the left (6a + 3). The open vessel conditions ensure that the equilibrium for the subsequent step (8c +3  $\rightarrow$ **6c**+H<sub>2</sub>) is more towards the right. Furthermore, among **1c/1d** and 1a, the barrier for the RDS with 1c/1d is lower by about 10.39 kcal/mol (Ts:9c, TS:7a, Table 3). Despite the fact that the generation of the active catalyst 6 starting from 1c and 1d is comparable to 1a (Table 3), the favourable energetics that is attributable to lower steric encumbrance (Figure 3) around the Ru centre makes the catalysis with 1c/1d more conducive. It is interesting to note that the inclusion of higher basis set or dispersion corrections has minimal affect on the overall energetics and no affect on the trend of the results (Table S3).

The utility of NNN pincer–ruthenium complexes (**1a–d**) towards synthesis of LA from glycerol has been demonstrated. Catalysts based on 2,6–bis(benzimidazole–2yl) pyridine ligands not only have optimal Ru–P bond energy that facilitates easy generation of active catalyst, but also enjoys less steric crowding around the Ru center that leads to favorable energetics making them highly efficient catalysts.

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### **Conflicts of interest**

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There are no conflicts to declare

## Notes and references

**‡** CCDC 1998012 and CCDC 2009680 contains the supplementary crystallographic data for this paper and can be obtained free of charge via <u>http://www.ccdc..cam.ac.uk/structures</u>.

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A sterically less hindered 2,6-bis(benzimidazole-2yl) pyridine based pincercomplex has ruthenium been employed to accomplish the catalytic conversion of glycerol selectively to lactic acid in high yield.

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