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## An improved catalytic system for the reduction of levulinic acid to $\gamma$ -valerolactone†

József M. Tukacs,<sup>a</sup> Márton Novák,<sup>b</sup> Gábor Dibó<sup>b</sup> and László T. Mika<sup>\*a</sup>

An improved bidentate phosphine-modified recyclable catalytic system was developed for the selective conversion of biomass-derived levulinic acid into  $\gamma$ -valerolactone with a TOF of 21 233 h<sup>-1</sup> in solvent-, chlorine- and additive-free reaction environments.

Currently, fossil resources provide more than 95% of our energy needs and feedstock in the chemical industry. Their replacement is one of the most challenging tasks faced by this generation. Especially, the production of carbon-based chemicals from sustainable resources has become a key issue for the chemical industry. Intensive research activities on biomass conversion have led to the identification of unique platform molecules such as 5-hydroxymethylfurfural (5-HMF)<sup>1</sup> and  $\gamma$ -valerolactone (GVL).<sup>2</sup> These small molecules can replace the currently used fossil-based chemicals or serve as renewable feedstock for their production. Due to its outstanding physical and chemical properties, GVL was suggested as a sustainable liquid by Horváth *et al.* in 2008.<sup>2,3</sup> Subsequently, GVL has been used for the production of transportation fuels,<sup>4</sup> butane isomers,<sup>4b</sup> octane boosters,<sup>2</sup> alkanes,<sup>5</sup> 2-methyltetrahydrofuran,<sup>5</sup> pentane-1,4-diol,<sup>5,15a</sup> ionic liquids,<sup>6</sup> adipic acid,<sup>7</sup> alkyl valerates,<sup>6a</sup> polymers,<sup>8</sup> and pentanoic acid<sup>9</sup> and as a solvent.<sup>10</sup>

Obviously, the most effective protocol to manufacture GVL is the selective hydrogenation of levulinic acid (LA).<sup>11</sup> LA is another platform molecule which can be obtained *via* 5-HMF by acid-catalysed dehydration of hexoses, a major component derived from biomass (Fig. 1). It is important to note that GVL can be used as a green solvent for the hydrolysis of fructose, the precursor of 5-HMF.<sup>12</sup> Although, heterogeneous catalysts can be easily removed from the reaction mixtures, their activities

are relatively low. Thus, high temperature and pressure as well as a co-catalyst and/or a suitable solvent are necessary to achieve a satisfactory conversion.<sup>13</sup> On the other hand, homogeneous catalysts exhibit higher activity and selectivity. Consequently, the development of a simple, highly efficient catalyst for the reduction of LA to GVL is of utmost importance.<sup>14</sup> Leitner and co-workers reported the application of Ru/triphos catalysts for the efficient and selective production of GVL, 1,4-pentanediol and methyltetrahydrofuran in the presence of additives such as NH<sub>4</sub>PF<sub>6</sub>.<sup>15</sup> The pincer ligand-modified iridium complexes were also found to be active catalysts (TOF = 1480 h<sup>-1</sup>) for the hydrogenation of LA in the presence of a base (*e.g.* NaOH or KOH) in alcohols (*e.g.* EtOH, *i*PrOH).<sup>16</sup>

Recently, similarly active (TOF = 2160 h<sup>-1</sup>) iridium complexes with 2,2'-bipyridine derivatives have been reported for the reduction of LA under mild reaction conditions in water using [LA] = 1 mol dm<sup>-3</sup> initial concentration;<sup>17</sup> *n.b.*: in spite of the high activity, the final product concentration was less than 1 M and the water-removal step resulted in low energy

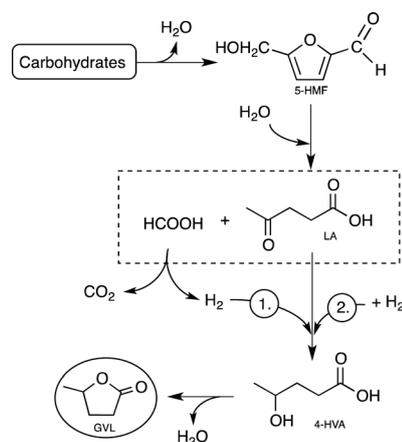


Fig. 1 Carbohydrate conversion.

<sup>a</sup> Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Budapest, Hungary.  
E-mail: laszlo.t.mika@mail.bme.hu; Fax: +36 1 463 3197; Tel: +36 1 463 1263

<sup>b</sup> Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary

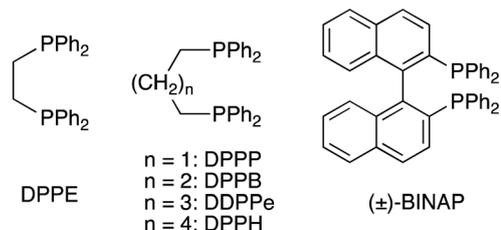
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efficiency of the process. We demonstrated that LA can be selectively and quantitatively reduced to GVL in the presence of a catalyst *in situ* generated from Ru(acac)<sub>3</sub> and 10 eq. of tertiary sulfonated phosphines without using any solvent or additive with TOF = 1440–3538 s<sup>-1</sup>.<sup>18</sup> It should be noted that this system was also found to be active under continuous conditions.<sup>19</sup>

During the decomposition of carbohydrates, LA and formic acid are formed in equimolar amounts. Thus, formic acid can be used as a hydrogen source for the reduction of LA and spontaneous lactone formation to GVL. Horváth and co-workers reported that LA was converted to GVL by using a complex catalyst [(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)Ru(bpy)(H<sub>2</sub>O)][SO<sub>4</sub>] at 70 °C.<sup>5</sup> Recently, GVL has been quantitatively prepared *via* transfer hydrogenation by using HCOOH in the presence of Shvo-type catalysts such as {[2,5-Ph<sub>2</sub>-3,4-Ar<sub>2</sub>-(η<sup>5</sup>-C<sub>5</sub>O)]<sub>2</sub>H}Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H) [Ar = *p*-MeOPh, *p*-MePh, and Ph] at 100 °C without any additive.<sup>20,21</sup> Deng *et al.* reported a RuCl<sub>3</sub>/PPh<sub>3</sub> catalytic system for the transfer hydrogenation of LA to GVL; however, this required the addition of a base (*e.g.* pyridine, LiOH, and NEt<sub>3</sub>), resulting in GVL with a yield of 16–95%.<sup>22</sup>

Here it is proposed that the activity of the Ru-based catalytic systems can be increased by the application of bidentate phosphine ligands, retaining the environmentally benign benefits of a solvent-free system.

Firstly, we attempted to reduce LA by Ru(III)-acetylacetonate in the absence of phosphine ligands. Expectedly, no conversion was detected after 2 h (Table 1, entry 1). Sulfonation of *n*BuP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, a malodorous, colorless liquid, resulted in the formation of the solid *n*BuP(C<sub>6</sub>H<sub>4</sub>-*m*-SO<sub>3</sub>Na)<sub>2</sub> (Bu-DPPDS) ligand with similar electronic and steric properties to *n*BuP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. For the selective conversion of LA to GVL, the highest activity of the Ru catalyst modified with a monodentate phosphine ligand was achieved by applying Bu-DPPDS under 100 bar H<sub>2</sub> at 140 °C (Table 1, entry 2).<sup>18</sup> It was revealed that



Scheme 1 Bidentate phosphine ligands.

the hydrogenation activity of the Ru catalysts can be significantly enhanced by the use of chelating-type bidentate Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (*n* = 1–3) ligands.<sup>23</sup>

Thus, we compared the activity of a Ru catalyst modified with Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub> (Scheme 1, DPPB), a Bu-DPPDS analogue, for the reduction of LA. Quantitative conversion of LA to GVL for 1 h (TOF = 6370 h<sup>-1</sup>) under identical conditions was achieved (Table 1, entry 3). It was shown that the catalytic activity was strongly influenced by the phosphine content of the reaction mixture. Furthermore, the activity was also influenced by the number of methylene spacers between the phosphorus atoms of the bidentate ligands, *i.e.* the size of the chelate ring of the active form of the catalyst. Consequently, hydrogenation was repeated at a lower catalyst concentration in the presence of various bidentate ligands (Table 1, entries 4–8). It was shown that the activity was negligible when DPPE was applied, whereas it was similar for the Bu-DPPDS- and DPPP-modified systems. In the case of DPPB, quantitative formation of GVL was detected within 1 h (Table 1, entry 6), exhibiting an outstanding activity (TOF = 7077 h<sup>-1</sup>). By increasing the number of methylene spacers in the ligand, *i.e.* the size of the chelate ring on the catalytically active species generated *in situ* from Ru(acac)<sub>3</sub> and ligands, the activity decreased. DPPPe showed a similar activity to Bu-DPPDS. The activity was below 2000 h<sup>-1</sup> in the case of

Table 1 Hydrogenation of levulinic acid in the presence of phosphine ligands

Entry	[Ru] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	Ligand	[Ligand] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	<i>T</i> (°C)	<i>P</i> (H <sub>2</sub> ) (bar)	Time (h)	Yield (%)	TON	TOF (h <sup>-1</sup> )
1	1.55	—	—	140	100	2.0	0	0	0
2 <sup>a</sup>	1.55	Bu-DPPDS	15.5	140	100	1.8	>99.9	6370	3538
3 <sup>a</sup>	1.55	DPPP	15.5	140	100	1.0	>99.9	6370	6370
4	0.775	DPPE	7.75	140	100	1.8	1.8	226	125
5	0.775	DPPPr	7.75	140	100	1.8	57.5	7325	4069
6	0.775	DPPB	7.75	140	100	1.8	>99.9	12 740	7077
7	0.775	DPPPe	7.75	140	100	1.8	51.2	6522	3623
8	0.775	DPPH	7.75	140	100	1.8	25.3	3223	1790
9	0.775	(±)-BINAP	7.75	140	100	1.8	98.6	12 561	6978
10	0.775	DPPB	7.75	140	75	1.8	>99.9	12 740	7077
11	0.775	DPPB	7.75	140	50	1.8	>99.9	12 740	7077
12	0.775	DPPB	7.75	140	25	1.8	50.6	6446	3581
13	0.775	DPPB	7.75	140	10	1.8	26.3	3350	1861
14	0.775	DPPB	7.75	140	10	4.5	70	8918	1981
15	0.775	DPPB	7.75	160	100	0.6	>99.9	12 740	21 233
16	0.775	DPPB	7.75	120	100	1.8	35.7	4548	2526
17	0.775	DPPB	7.75	100	100	1.8	6.4	815	453

<sup>a</sup> Conditions from ref. 18. Reaction conditions: 30 mL (293.02 mmol) of LA, Ru precursor: Ru(acac)<sub>3</sub>, ligand/Ru = 10. TON is defined as moles of substrate converted per mole of Ru.

DPPH. Due to the six CH<sub>2</sub> units, DPPH could act as a monodentate phosphine. To achieve further improvement in the TOF by optimizing the ligand concentration in the reaction mixture, we investigated the reduction of LA by using a Ru/DPPB catalyst in the concentration range of [DPPB] =  $0.77 \times 10^{-3}$ – $15.4 \times 10^{-3}$  at a constant Ru content of  $0.775 \times 10^{-3}$  mol dm<sup>-3</sup> ( $8 \times 10^{-3}$  mol%). Expectedly, the ligand content had a strong influence on the formation of GVL as shown in Fig. 2. When an equimolar amount or 2.5-fold excess of the ligand was used, 4.5 and 12% conversions were detected. A significant increase in the rate were achieved at DPPB/Ru ratios between 5 and 10 followed by a slight decrease at higher ratios. The concentration dependence curve shows a maximum at [DPPB] =  $7.75 \pm 1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, which corresponds to a ligand/Ru ratio of  $10 \pm 1.0$ . This is in good agreement with our previous report for Bu-DPPDS<sup>18</sup> and ligand excess favored reduction of carbonyl groups.<sup>24</sup> The ligand exchange equilibrium between the catalyst species and the free ligand—depending on the pressure, temperature, etc.—determines the optimal ligand concentration in the reaction mixture. Furthermore, due to the presence of a bidentate ligand, the reversible arm-off dissociation cannot be excluded.<sup>25</sup> The GC and NMR measurements of the conversion of 293.02 mmol of LA in the presence of the catalyst *in situ* formed from Ru(acac)<sub>3</sub> (0.023 mmol) and DPPB (0.23 mmol) proved that no by-product, including overhydrogenated products such as 2-methyltetrahydrofuran, could be detected. The <sup>31</sup>P-NMR spectrum of the final reaction mixture did not indicate the formation of phosphine oxide and any sign of decomposition of the ligand. These types of ligands are solid, thus no sulfonation was necessary. Finally, the binaphthyl derivative (±)-BINAP, which could also form a seven-member chelate ring with a Ru center similarly to DPPB, was also investigated. However, the activities were similar to those obtained using the less expensive DPPB (Table 1, entry 6).

The effect of hydrogen pressure on the GVL formation was also determined in the range of 10–100 bar using the

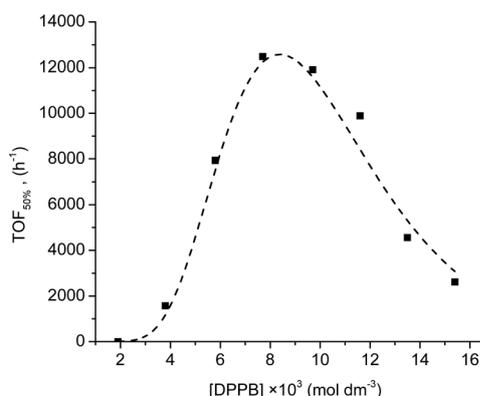


Fig. 2 Turnover frequencies (TOF<sub>50%</sub> = moles of LA per mole of Ru per hour at 50% conversion) at different DDPB concentrations. Reaction conditions: [Ru] =  $0.775 \times 10^{-3}$  mol dm<sup>-3</sup> ( $8 \times 10^{-3}$  mol%), 100 bar H<sub>2</sub>, 140 °C.

Ru/DPPB system (Table 1, entries 6, 10–14). As was shown for the Ru/DPPDS system,<sup>18</sup> the conversion rate was not affected by the reduction of the pressure to 50 bar for 1.8 h; however, upon further decreasing the pressure (25 and 10 bar), the reaction rates decreased significantly.

The investigation of the effect of reaction temperature (Fig. 3, Table 1, entries 6, 15–17) showed that the conversions were negligible at 100 °C and modest at 120 °C. By increasing the temperature to 160 °C, full conversion was achieved after 0.6 h, corresponding to TOF =  $21\,233$  h<sup>-1</sup>. To our best knowledge, so far it is the highest TOF value obtained for the selective homogeneous hydrogenation of LA to GVL.

The recyclability of the Ru(acac)<sub>3</sub>/DPPB catalyst was investigated under batch conditions using [Ru] =  $1.55 \times 10^{-3}$  mol dm<sup>-3</sup> (0.16 mol%) and [DPPB] =  $0.15$  mol dm<sup>-3</sup> under 100 bar of H<sub>2</sub> at 140 °C.<sup>18</sup> Full conversion of LA to GVL was detected in the first run resulting in a light orange solution after 30 min (ESI† Picture S1). The volatile compounds were removed by vacuum transfer (4–6 mmHg) using a 20 cm column resulting in a clear solution. The orange glue-like residue (ESI† Picture S2) was completely dissolved in 30 mL (293.02 mmol) of LA. Expectedly no phosphorus compounds were detected in the distillate. The <sup>1</sup>H-NMR and GC analysis proved that the distillate was pure GVL. The light orange solution (ESI† Picture S3) was transferred to the reactor and then pressurized to 100 bar H<sub>2</sub>. The reaction was started by increasing the temperature up to 140 °C. A significant pressure drop indicated the reduction process. After a similar work-up of the initial run, the second yield was >99.9% GVL and was unchanged in the next 8 runs (ESI† Fig. S1, Table S1, and Picture S4). The water content of the combined 10 distillates was removed by vacuum distillation (5 mmHg) using 10 cm of Sulzer EX-20 package at 40 °C, resulting in 247.5 g (2.47 mol) of colorless GVL with a water content of 98 ppm and 36.3 g of water. This result showed that the improved Ru/BDPP catalytic system was stable enough with the catalyst and ligand amounts and reaction conditions applied here for successful recycling including the low-

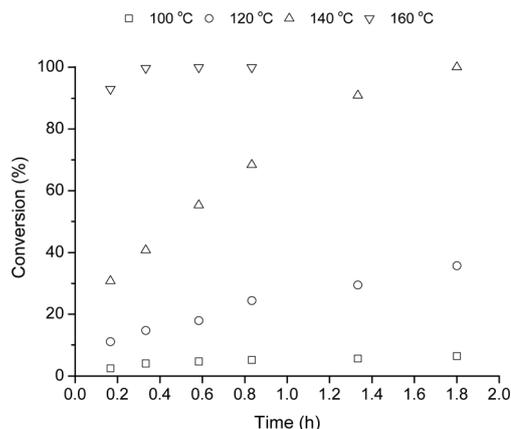


Fig. 3 Conversion of LA to GVL at different temperatures. Conditions: [Ru] =  $0.775 \times 10^{-3}$  mol dm<sup>-3</sup> ( $8 \times 10^{-3}$  mol%), [DPPB] =  $7.75 \times 10^{-3}$  mol dm<sup>-3</sup>, 100 bar H<sub>2</sub>.

pressure separation step. Since 100% conversion was achieved, it cannot be stated whether the catalyst lost any activity or not during the course of the reactions.<sup>26</sup>

In order to investigate the applicability of the catalyst to the conversion of LA derived directly from the dehydration of carbohydrates, 4 g (22.2 mmol) of D-fructose was dissolved in 80 mL of 2 M H<sub>2</sub>SO<sub>4</sub> and heated at 170 °C for 8 h.<sup>27</sup> After our published work-up procedure was performed,<sup>26</sup> ca. 1.3 mL (1.57 g) of LA was obtained as a dark brownish-yellow solution (ESI,† Picture S5). This represents a slightly higher yield of LA than that obtained from the microwave-assisted dehydration of fructose (400 mg).<sup>26</sup> However, humin formation cannot be excluded from the acid-catalysed dehydration process as described by Horváth *et al.*<sup>12</sup> In 1 mL of this solution, 6.2 mg of Ru(acac)<sub>3</sub> and 66.5 mg of DPPB was dissolved, after which the solution was transferred to a 10 mL Parr HP reactor. The mixture was pressurized to 100 bar of H<sub>2</sub> and heated to 140 °C. By using <sup>1</sup>H NMR and GC monitoring, it was found that complete conversion was achieved after 1 h (ESI,† Fig. S2 and S3). To summarize, an improved catalytic system was developed and successfully used for the hydrogenation of “real” bio-derived levulinic acid.

## Experimental

Levulinic acid, 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB), 1,5-bis(diphenylphosphino)pentane (DPPPe), 1,6-bis(diphenylphosphino)hexane (DPPH), D-fructose, and (±)-BINAP were purchased from Sigma-Aldrich and used as received. GC analyses were performed on an Agilent 6890N instrument with an HP-INNOWax capillary column (15 m × 0.25 mm × 0.25 μm) using H<sub>2</sub> as a carrier gas. For the analysis, 10 μL of the reaction mixture was added to 1 mL of methylene chloride followed by the addition of 10 μL of toluene as an internal standard.

In a typical hydrogenation experiment, the 120 mL Parr HP reactor was charged with 34.02 g (30 mL, 293.02 mmol) of levulinic acid followed by the addition of Ru(acac)<sub>3</sub> and the corresponding phosphine ligand, resulting in a light red solution. The reaction mixture was pressurized to the desired values and heated up to 140 °C. Samples were taken for off-line GC analysis *via* a dip-leg into a sample holder. After the given reaction time, the autoclave was cooled to ambient temperature and stirring was stopped.

To prepare “real” bio-based levulinic acid, 4 g of D-fructose was dissolved in 80 mL of 2 M H<sub>2</sub>SO<sub>4</sub>. The solution was transferred to a 120 mL Parr HP HC reactor equipped with a PID temperature controller (Parr 4843), safety relief valve, sampling line and manometer. When the temperature reached 170 °C, the pressure increased to 18 bar. After 8 h, the mixture was cooled and the dark brownish-black reaction mixture was filtered through a glass filter. The black solid was washed with 3 × 30 mL of distilled water and with 3 × 30 mL of ethyl acetate. The aqueous phase was separated and extracted with 4 × 100 mL of ethyl acetate. The combined

straw-yellow organic phase was dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure at 60 °C resulting in ca. 1.3 mL (1.57 g) of a dark brown liquid as the product. Yield: 51%.

## Conclusions

We have demonstrated that the catalyst *in situ* generated from Ru(III)-acetylacetonate and 1,4-bis(diphenylphosphino)butane (DPPB) can be used for the efficient conversion of biomass-derived levulinic acid to gamma-valerolactone with a representative TOF of 21 233 h<sup>-1</sup>. The catalyst can be recycled for ten consecutive runs while full conversion of LA was achieved. The maximum hydrogenation rate was achieved by applying a 10-fold excess of the DPPB ligand to the Ru precursor.

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