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Homogeneous Catalyzed Direct Conversion of Furfural to Gamma-Valerolactone

Sakhitha Koranchalil,^[a] Danielle Lobo Justo Pinheiro,^[a] Rosa Padilla,^[a] and Martin Nielsen^{*[a]}

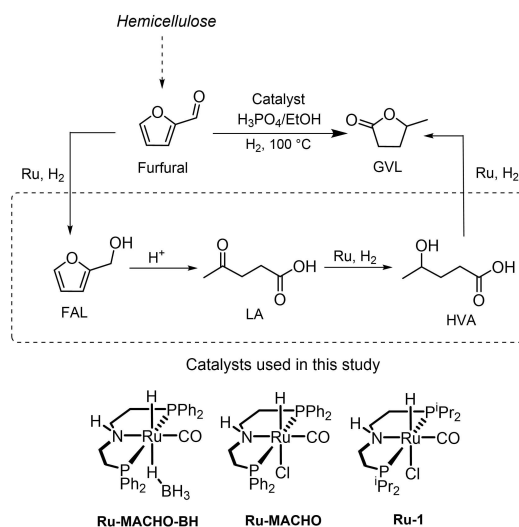
Herein, we report the direct conversion of biomass-derived furfural to γ -valerolactone (GVL) in a one-pot system, using the combination of Ru-MACHO-BH and a Brønsted acid (H_3PO_4). A

GVL yield of 84% is achieved under mild reaction conditions using 1 mol% of Ru-MACHO-BH and 3.8 M $\text{H}_3\text{PO}_4(\text{aq})$ at 100 °C for 7 hours.

Introduction

In the view of depleting fossil fuels and increasing environmental issues, modern society needs a sustainable production of fuels and chemicals.^[1] One solution is to develop new alternative methods utilizing renewable biomass, which has attracted recent interest.^[2] Lignocellulosic biomass is potentially an ideal carbon-neutral resource in a sustainable economy and is therefore highly attractive from environmental perspectives.^[3] In this scenario, furfural has recently been emphasized as one of the top value-added chemicals produced in the lignocellulosic biorefineries.^[4] Industrially, furfural is produced by acid-catalyzed dehydration of C5 sugars, such as xylose derived from hemicellulose depolymerization.^[5] As such, hemicellulose is first hydrolyzed to monosaccharides (mainly xylose), which are subsequently dehydrated to furfural.^[5] Moreover, many valuable chemicals can be synthesized as upgraded products from furan derivatives.^[6] Among them, γ -valerolactone (GVL) has a wide range of industrial applications and therefore constitutes an important target. For example, GVL is used as liquid fuel, additives in food, intermediate in fine chemical synthesis, green solvent, and building block for polymers.^[7]

The production of GVL from furfural involves a multistep process comprising hydrolysis and hydrogenation.^[8] First, furfural must undergo hydrogenation to furfuryl alcohol (FAL). FAL is subsequently transformed to levulinic acid (LA) in presence of aqueous acid media, and finally LA is converted to GVL through the formation of 4-hydroxyvaleric acid in a second hydrogenation step followed by a lactonization as the final step (Scheme 1).^[9] In the literature, each step has been separately studied and explored.^[8] In order to carry out this process in an



Scheme 1. Direct conversion of furfural to GVL using Ru-PNP complexes in presence of phosphoric acid ($\text{H}_3\text{PO}_4(\text{aq})$).

economically viable fashion, a direct production of GVL from furfural that does not involve any intermediate isolation and purification should be developed.^[10]

The direct conversion of furfural to GVL has been mainly achieved using heterogeneous catalysis. Jae reported a one-step process using a bifunctional Sn–Al-Beta zeolite (Si/Sn=63 and Si/Al=473), which possesses Lewis and Brønsted acid sites, in 2-butanol at 180 °C to obtain up to 60% of GVL.^[11] Melero utilized a Zr–Al-Beta (6.4) zeolite catalyst and 2-propanol as H-donor to reach a yield of 23% GVL after 24 hours at 170 °C.^[12] Employing 0.2 g of Au/ZrO₂ combined with ZSM-5 (Si/Al=100) and 2-propanol, Fan synthesized 80% GVL at 120 °C for 24 hours.^[13] Recently, Hu reported 91% yield of GVL with via consecutive hydrogenation and acid catalyzed reactions over CuAl and H-ZSM-5 with mass ratio of 2/2 wt% in ethanol. The reaction was conducted at 120 °C using a H₂ pressure of 50 bar for 4 hours.^[14]

Heterogeneous catalysts are interesting for their easy handling and operation, but drawbacks such as low selectivity, low activity, and typically the requirement of harsh reaction conditions challenge the development of environmentally viable processes.^[15] One of the solutions to address these issues

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is by homogeneous catalysis as it is generally highlighted for its high selectivity and mild reaction conditions.

There are many examples for homogeneous catalytic production of GVL from the LA intermediate and its derivatives.^[16] Zhou employed a Nozaki type lutidine-based Ir-PNP catalyst^[17] (0.001 mol%) to obtain a TON of 71000 at 100 °C and a high H₂ pressure (100 bar) with the addition of 1.2 equivalent of base (KOH).^[18] Fu reported on Himeda-Ogo-Fukuzumi type half-sandwich iridium complexes^[19,20] to obtain a TON of 78000 with a catalyst loading of 0.001 mol% under additive free conditions at 120 °C and 10 bar H₂.^[21] As reported by Song, the Kirchner 2,6-diaminopyridine-based Fe-PNP complex^[22] catalyzes the hydrogenation of LA to GVL achieving a high TON as well (TON 23000).^[23] We reported the conversion of neat LA alkyl levulinates to GVL with low catalyst loadings (0.05–0.01 mol%) of either the Ru-MACHO Ru-PNP or the Abdur-Rashid Ir-PNP complexes.^[24–26] Recently, we demonstrated that neat or aqueous LA can be converted to GVL in a H₂ atmosphere using Ru-PNP sulfonate complexes.²⁷ Singh introduced an η₆-arene-Ru(II) complex for the ring opening of furfural, in which the reaction stops at LA with 42 % yield in the presence of formic acid (HCOOH) at 100 °C.^[28]

However, the direct and selective conversion of furfural to GVL is challenging due to undesired side reactions in presence of acid.^[29] Indeed, to the best of our knowledge there exist only two examples of homogeneous catalytic systems that convert furfural directly to GVL. Deng and Fu reported 55 % yield of GVL using 0.083 mol% of [Cp*Ir(4,4'-dihydroxyl-2,2'-bipyridine)(OH₂)]₂[SO₄] under 10 bar of H₂ at 120 °C and phosphate buffer solution (pH = 1.0).^[30] Recently, Li and Dai obtained 81.2 % yield of GVL using 8.0 mol% of Sc(OTf)₃ in isopropanol as H-donor at 143.9 °C and 400 W microwave irradiation for 8.1 hours.^[31]

Herein, we show the effective and direct conversion of furfural to GVL under mild reaction conditions using Ru-PNP pincer complexes. In fact, Ru-PNP complexes are known for

their robustness and efficacy in catalyzing both dehydrogenation as well as hydrogenation reactions.^[32] However, they are generally known to work under either basic^[33] or additive free conditions.^[34] Recently, we demonstrated that Ru-MACHO-BH is also an active hydrogenation catalyst under acidic conditions for the direct transformation of carbohydrates and raw biomass to GVL.^[35] Herein, we show the activity of PNP pincer complex in acidic medium (H₃PO₄) for the direct synthesis of GVL from furfural through a one-pot sequence of hydrogenation, hydrolysis, a second hydrogenation, and finally a lactonization (Scheme 1). Showing that furfural is a viable substrate for GVL production under acidic conditions using homogeneous catalysis demonstrates that hemicellulose is also a feasible substrate for this approach using similar conditions. This is important because there are only a handful of reported direct conversions of hemicellulose to GVL.^[36] Hence, disclosing the feasibility of utilizing homogeneous catalysis for converting a major polysaccharide component in lignocellulose to GVL is highly attractive. Furthermore, to realize the conversion of both hemicellulose and cellulose in lignocellulosic material in the same reaction pot, it is pertinent to study their individual transformation pathways as well as the intermediates in those pathways.

Results and Discussion

We commenced the studies by testing the furfural conversion with the well-known PNP complexes Ru-MACHO-BH, Ru-MACHO, and its ^{ipr}PNP congener (Ru-1). The reductant formic acid (HCOOH)^[37] was initially used as the acid additive. As a note, using excess acid may lead to formation of humins from furan derivatives.^[38] Thus, with 0.2 mol% of Ru-MACHO or Ru-1 with 2 M formic acid under 20 bar of H₂ in 3:7 v/v EtOH/H₂O, the reaction afforded full conversion of furfural. However, the reaction stopped at LA even after 18 hours at 100 °C (Table 1,

Table 1. Furfural hydrogenation to GVL using formic acid.

Entry	Catalyst (mol%)	HCOOH [M]	EtOH/H ₂ O v/v ratio	GVL yield [%] ^[a]
1	Ru-MACHO (0.2)	2	3:7	0
2	Ru-1 (0.2)	2	3:7	0
3	Ru-MACHO-BH (0.2)	2	3:7	34
4	Ru-MACHO-BH (0.2)	4	3:7	46
5	Ru-MACHO-BH (0.2)	4	1:1	48
6	Ru-MACHO-BH (0.5)	4	1:1	48
7	Ru-MACHO-BH (1.0)	4	1:1	27
8	Ru-MACHO-BH (2.0)	4	1:1	10

Standard reaction conditions: Furfural (0.90 mmol), catalyst (0.2–2 mol%), 30 bar H₂ at 100 °C in 18 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.

Entries 1,2 and SI, Table S1, Entries 1–5). As a note, we employ EtOH and H₂O as solvents due to their green profiles.^[39] Increasing the H₂ pressure to 30 bar and using only water as solvent led to no significant changes (SI, Table S1, Entries 1,2, and 5 vs Entries 3, 4). Gratifyingly, employing **Ru-MACHO-BH** in 3:7 v/v EtOH/H₂O led to full conversion of furfural within 18 hours with 34% of GVL (Table 1, Entry 3). Some unreacted LA was still detected and increasing the amount of formic acid concentration to 4 M improved the GVL yield to 46% (Entry 4). Changing the EtOH/H₂O ratio to 1:1 resulted in no significant change in the yield (Entry 5). Moreover, the seemingly drastic and somewhat binary difference between **Ru-MACHO** or **Ru-1** leading to no GVL on one side and significant amount of GVL production with **Ru-MACHO-BH** on the other is difficult to explain with the current data available. The fact that **Ru-MACHO/Ru-1** succeeds in the first hydrogenation step of furfural to FAL (as part of the conversion to LA) only adds to obscuring the picture. We tentatively suggest that these observations can be explained by a significantly lower rate of thermal activation of **Ru-MACHO/Ru-1** than of **Ru-MACHO-BH** combined with a continuous deactivation **Ru-MACHO/Ru-1** by HCl or HCOOH, whereas **Ru-MACHO-BH** is deactivated only by HCOOH. The outcome could then be that whereas **Ru-MACHO/Ru-1** can hydrogenate the somewhat amenable substrate of furfural but not the more challenging LA, **Ru-MACHO-BH** is able to hydrogenate both compounds.

To probe for the effect of catalyst loading, we tested the reaction with catalyst loadings of **Ru-MACHO-BH** ranging from 0.2 to 2 mol% (Entries 5–8). Merely 10% yield was obtained with 2 mol% catalyst loading, while with 1 and 0.5 mol%, the yields were 27% and 48%, respectively (Entries 6, 7 vs 8). With the higher catalyst loading (2 mol%), FAL was observed as the major product with 47% yield, along with a formation of methanol (See SI, Table S2, Entry 6). These observations suggest that the formic acid itself is hydrogenated to methanol, which was confirmed by a blank reaction performed with **Ru-MACHO-BH** and formic acid under similar reaction conditions in the absence of furfural (SI, Table S2, Entry 1, Figure S9). We are currently studying this transformation more in depth and will report our findings in due time.

We then studied the effect of formic acid concentration. When increasing the acid concentration from 2 to 8 M in the presence of 0.2 mol% **Ru-MACHO-BH**, the initial reaction rates dropped significantly. Thus, the reaction yielded only LA with 8 M formic acid compared to the 34% of GVL when using 2 M formic acid (SI, Table S2, Entry 7 vs 3). This suggests that the higher acid concentration has a negative effect on the catalyst activity which might be due to the degradation or inactivation of catalyst.

Replacing formic acid with other acid additives such as HCl, H₂SO₄, KHSO₄, oxalic acid, and pTSA (*p*-toluenesulfonic acid) resulted in no conversion of furfural or in LA as the sole product for all except KHSO₄, which led to merely 17% GVL (SI, Table S2, Entries 9–13). Interestingly, with 3.8 M H₃PO₄(aq) the catalytic hydrogenation of furfural exhibited an excellent GVL yield of 72% with 0.5 mol% catalyst loading in 1:1 v/v EtOH/H₂O after 18 hours (Table 2, Entry 1). Increasing the catalyst loading to

2 mol% results in a decrease in the GVL to 63% (Entry 3). However, when using ethanol as the sole solvent, the reaction afforded 80% yield of GVL using 0.5 mol% of the **Ru-MACHO-BH** (Entry 6). The considerably lower yields observed in the presence of EtOH/H₂O mixtures compared to only EtOH might be due to humins formation, which is corroborated by the presence of black insoluble solids observed by visual inspection at the end of the reactions. Thus, further optimizations were carried out in EtOH. For the catalytic reactions with the combination of either lower catalyst loading (0.2 mol%) or lower concentrations of H₃PO₄(aq) (1.9 M), the hydrogenated intermediate LA was also observed along with the GVL (Entries 5 and 8) (SI, Figure S8). With higher catalyst loadings (0.5 or 1 mol%), full conversion of furfural was achieved with high yields of 80% and 83% of GVL, respectively, with 3.8 M H₃PO₄(aq) in ethanol under 30 bar of H₂ for 18 hours (Entries 6 and 7).

The catalytic system with **Ru-MACHO-BH** was also evaluated at shorter reaction times. Thus, using 1 mol% catalyst loading and 3.8 M of H₃PO₄(aq) the reaction afforded full conversion with 84% GVL after 7 hours (Entry 9). The discrepancy between conversion and yield is likely due to formation of humins, again observed by visual inspection. With 0.5 and 0.2 mol% catalyst loading and under identical reaction conditions, 64% and 9% yields, respectively, were obtained (SI, Table S3, Entries 3, 1). The low yield observed indicates an incomplete reaction, with LA observed as the major product (SI, Table S3, Entry 1). Further increase or decrease in acid concentration led to lower yields as well (SI, Table S3, Entries 2, 4, 5, 7, 8 vs 1, 3, 6). Additionally, lowering the reaction time to 5 hours results in a yield of 72% using 1 mol% catalyst loading and 3.8 M of H₃PO₄(aq) (Entry 10). The reaction still afforded 68% GVL yield with low acid concentration (1.9 M) after 5 hours (SI, Table S5, Entry 3). However, decreasing the catalyst loading to 0.2 and 0.5 mol%, low yields (19% and 5% respectively) with unreacted LA as the major product was observed (SI, Table S5, Entries 1, 2).

The effect of furfural concentration in the total solution comprising of EtOH volumes ranging from 0.5–2.0 mL and 3.8 M H₃PO₄(aq) was investigated with 1 mol% of **Ru-MACHO-BH** and 0.90 mmol of furfural using 30 bar H₂ at 100 °C. A drop in the yield of GVL was observed affording 64% and 54%, respectively, with 0.5 and 2 mL of EtOH (SI, Table S3, Entries 8, 7) when compared to 1 mL of EtOH, showing that a concentrated solution is slightly detrimental for catalytic activity. Finally, we tested the effect of temperature by performing the reaction at 80 °C and 120 °C, respectively. Thus, at 120 °C GVL was obtained in 80% yield using 1 mol% catalyst loading and 3.8 M H₃PO₄(aq) after 7 hours compared to 84% after 18 hours (Entries 11 and 12). At lower temperature (80 °C), we noticed no conversion of furfural, which suggests that **Ru-MACHO-BH** requires a minimum temperature to be catalytically active for hydrogenation (Entry 13).^[40] The performance of other Ru-PNP complexes, such as **Ru-MACHO** and its ^{iPr}PNP congener (**Ru-1**), was evaluated as well. Both catalysts work in presence of H₃PO₄(aq) towards hydrogenating furfural to GVL, but their activities are inferior to **Ru-MACHO-BH** (Entry 7 vs Entries 14 and 15). We tentatively suggest that the absence of HCOOH

Table 2. Furfural hydrogenation to GVL using phosphoric acid (H₃PO₄(aq)).

Entry	Ru-PNP (mol%)	EtOH/H ₂ O v/v ratio	Time [h]	GVL yield [%] ^[a]
1	Ru-MACHO-BH (0.5)	1:1	18	72
2	Ru-MACHO-BH (1.0)	1:1	18	73
3	Ru-MACHO-BH (2.0)	1:1	18	63
4 ^[b]	Ru-MACHO-BH (1.0)	1:1	18	56
5	Ru-MACHO-BH (0.2)	EtOH	18	67
6	Ru-MACHO-BH (0.5)	EtOH	18	80
7	Ru-MACHO-BH (1.0)	EtOH	18	83
8 ^[b]	Ru-MACHO-BH (1.0)	EtOH	18	68
9	Ru-MACHO-BH (1.0)	EtOH	7	84
10	Ru-MACHO-BH (1.0)	EtOH	5	72
11 ^[c]	Ru-MACHO-BH (1.0)	EtOH	7	80
12 ^[c]	Ru-MACHO-BH (1.0)	EtOH	18	84
13 ^[d]	Ru-MACHO-BH (1.0)	EtOH	7	0
14	Ru-MACHO (1.0)	EtOH	18	58
15	Ru-1 (1.0)	EtOH	18	75
16 ^[e]	Ru-MACHO-BH (1.0)	EtOH	18	83

Standard reaction conditions: Furfural (0.90 mmol), Ru-PNP (0.2–2 mol%), 30 bar H₂, 100 °C. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.

^[b] 1.9 M H₃PO₄. ^[c] 120 °C. ^[d] 80 °C. ^[e] 10.2 mmol furfural in 10 mL EtOH.

leads to all the complexes being catalytically active for LA hydrogenation, leading to GVL production with any of them but still with **Ru-MACHO-BH** as the superior catalyst.

Thus, we then scaled up to 1 g of furfural using 1 mol% of **Ru-MACHO-BH** with 3.8 M H₃PO₄(aq) at 100 °C and 30 bar H₂ (Entry 16). The GC yield of 83 % GVL demonstrates the feasibility of conducting the reaction in large scale.

Conclusions

We demonstrate an efficient route for the conversion of biomass derived furfural to GVL under mild and sustainable reaction conditions. Using low loadings of **Ru-MACHO-BH** (0.5 mol%) in presence of H₃PO₄(aq) (3.8 M) allows the unprecedented homogeneously catalyzed transformation of furfural to GVL in 80% yield at 100 °C after 18 hours. The yield can be further improved to 84% by using 1.0 mol% **Ru-MACHO-BH** for 7 hours. The influence on GVL yield of various catalytic parameters besides catalyst loading and reaction time was also evaluated, such as hydrogen source, solvent composition, acid concentration, and reaction temperature. This process may find important applications within homogenous catalytic hydrogenation for the efficient production of GVL from biogenic furanics without intermediate purification and isolation.

Experimental Section

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Furfural (99%), H₃PO₄ (85 w/w%), Ru-MACHO-BH, Ru-MACHO, **Ru-1** are commercially available and used without further purification. H₂ gas (H₂O ≤ 3 ppm; O₂ ≤ 2 ppm) was purchased from a commercial supplier as well. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091 J 413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as internal standard. The ¹H NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer.

General Procedure for the Hydrogenation of Furfural to GVL

For the hydrogenation screening experiment, in a glove box, furfural (0.65 mmol) and Ru-PNP complex (0.2–1 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, the solids were dissolved in 1 mL of solvent (H₂O/EtOH) followed by the addition of H₃PO₄(aq). Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally hydrogen pressure (30 bar) was loaded into the autoclave and desired temperature was applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis. The liquid sample was prepared for GC analysis by adding 100 μL of 1,4-dioxane (internal standard) followed by dilution of the mixture with 3.75 mL of

dichloromethane (DCM). The yield of GVL in the mixture is calculated by using calibration curve. To generate a calibration curve, standard GVL samples of various known concentrations along with 1,4-dioxane (100 μ l) with total volume made up to 10 mL with DCM and are injected into the GC.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: furfural · catalysis · GVL · biomass · sustainable

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