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## Selective hydrogenation of HMF to DHMF with Ru–PNP complexes in ionic liquids†

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The catalytic hydrogenation of 5-hydroxymethylfurfural (HMF) to 2,5-dihydroxymethylfuran (DHMF) represents a promising pathway for the valorisation of lignocellulosic-derived biomass feedstock. This study investigates the use of Ru–PNP complexes as (pre)catalysts to achieve efficient and highly selective hydrogenation of HMF in ionic liquids (ILs) as green reaction media under mild reaction conditions. Our results indicate that  $^{iPr}\text{Ru}$ -MACHO leads to excellent conversion and yield (up to 99%) of HMF to DHMF using 1-butyl-3-methylimidazolium acetate (BMIM OAc). The analogous cationic Ru–PNP complex bearing acetonitrile as ancillary ligand and hexafluorophosphate ( $\text{PF}_6^-$ ) as counterion also shows high catalytic activity (up to 99% conversion) in BMIM OAc under mild reaction conditions. Interestingly, the IL seems to prevent HMF polymerization to humins. Furthermore, the recyclability and reusability of the ionic liquid are systematically investigated.

## Introduction

Biomass valorisation plays a crucial role in aiding the global agenda of pursuing a carbon-neutral and waste-free society.<sup>1</sup> Biomass refers to a broad range of natural organic materials, either plant-based or animal-based, that are potential chemical and energy fuel sources.<sup>2</sup> Thus, the efficient utilization of renewable biomass has attracted growing interest in producing modern bio-based fuels and platform chemicals through advanced technologies and processes.<sup>3</sup> Non-catalytic thermochemical technologies have been developed as major strategies to transform biomass into chemicals, heat, electricity and materials.<sup>4</sup> A major drawback of these approaches is their lack of selectivity. Pyrolysis and gasification of biomass either produce ill-defined compositions or generate simple C1-based compounds and therefore require substantial further upgrading in the context of the synthesis of complex molecules. Hence, these methods fail to exploit the complex C–C connectivity already provided by nature. On the other hand, great effort has been devoted to the production and application of carbohydrate-derived building block chemicals such as 5-hydroxymethyl furfural (HMF).<sup>5</sup> HMF is an attractive platform chemical that can be easily converted into dimethylfuran, which has applications both as an alternative solvent and as a transportation fuel.<sup>6</sup> There are very few reports on the selective reduction of the aldehyde functionality to produce 2,5-bis(hydroxymethyl)furan (DHMF).<sup>7</sup> DHMF has garnered interest in

recent years for its potential as a valuable and renewable building block in the synthesis of polymers, pharmaceuticals, and agrochemicals.<sup>8</sup> It demonstrates versatile chemical properties, serving as an intermediate in synthesizing various chemicals (e.g., pharmaceuticals<sup>9</sup>) and materials (e.g., comonomer for furan-based polyisocyanurates, polyurethanes, polyacrylonitriles, and polyethers, which are components of foams and fibers<sup>10</sup>). Additionally, it acts as a polymer precursor (e.g., in producing poly(2,5-furandimethylene succinate) by polymerizing DHMF with succinic acid under basic conditions<sup>11</sup>) and as a fuel additive. Thus, HMF is suitable for various applications across different industries.

Catalysis extensively improves biomass valorisation processes with milder reaction conditions (*i.e.*, lower temperatures and pressures) and enhanced selectivity towards the desired product(s). Homogeneous<sup>6b,12</sup> and heterogeneous<sup>13</sup> catalysis have been investigated for the hydrogenation of HMF to DHMF. In particular, ruthenium-based catalysts have shown high efficiency in the hydrogenation of HMF.<sup>7,12</sup> A study by Bell demonstrated the use of  $\text{RuCl}_2(\text{PPh}_3)_3$  in 1-ethyl-3-methylimidazolium chloride (EMIM Cl) and acetonitrile, achieving high conversion and selectivity towards DHMF.<sup>12d</sup> The same reductive process was explored by Schaub and Hashmi using  $\text{Ru}(\text{methylallyl})_2\text{COD}$  (4.5 mol%) combined with an NHC-based ligand under 10 bar  $\text{H}_2$  and 120 °C. The reaction resulted in a 92% yield of DHMF after 16 hours.<sup>12e</sup> Our group showed that using  $^{iPr}\text{Ru}$ -MACHO in either EtOH or EtOH/H<sub>2</sub>O led to efficient HMF hydrogenation to DHMF already at 25 °C.<sup>7</sup>

The majority of procedures discussed in the literature involve using additives along with organic solvents to enhance catalyst activation and stability in solution. While conventional bases are inexpensive, using these additives leads to reduced

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atom economy and increased costs due to material use and waste generation, which contradicts the fundamental principles of green chemistry guidelines. Our group recently established a Ru-PNP/ionic liquid (IL) system for versatile  $\text{CO}_2$  hydrogenation/dehydrogenation catalysis.<sup>14</sup> We rationalized that the basicity given by a suitable IL might promote HX elimination from the NH-RuX moiety (X = Cl in the case of Ru-MACHO complexes), avoiding the use of sacrificial bases, and demonstrated that acetate ILs effectively activate Ru-PNP. Herein, we envisioned to explore the same catalytic system to selectively hydrogenate HMF to DHMF. Performing the hydrogenation of HMF to DHMF in ILs *via* catalytic processes is an important research area in green chemistry and renewable energy.<sup>15</sup> ILs, known for their unique physicochemical properties, such as low volatility, high thermal stability, and tuneable solvation, offer an environmentally benign alternative to traditional organic solvents. Their ability to dissolve various compounds and stabilise catalytic species makes them ideal media for catalytic processes.<sup>16</sup> ILs are even capable of dissolving cellulose, and this property can be utilized for the one-pot conversion of this biopolymer into low-molecular-weight value-added chemicals through hydrogenation.<sup>17</sup> This research underscores the potential of using ILs in combination with homogeneous catalysts for the sustainable conversion of HMF (Fig. 1). The findings contribute to the broader goal of developing green chemical processes that minimise waste and energy consumption, thereby advancing the principles of green chemistry by integrating catalysis and advanced solvent systems.

## Results and discussion

In the preliminary screening, we investigated the catalytic activity of commercially available Ru-PNP complexes Ru-MACHO (**Ru-1**), the *p*-isopropyl congener (**Ru-2**), Ru-MACHO-BH (**Ru-3**), and Milstein's catalyst (**Ru-4**) (Fig. 2 and Table 1). We tested these (pre)catalysts for the hydrogenation of HMF at room temperature using 0.1 mol% of commercially available complexes, and 20 bar of  $\text{H}_2$  in EMIM OAc (2 mL) for 24 hours.

Catalysts **Ru-1**, **Ru-3**, and **Ru-4** showed low HMF conversion, observing the desired product only in traces or minor amounts (Table 1, entries 1, 3 and 4). Interestingly, a significantly higher conversion was detected under the same reaction conditions when using **Ru-2**, leading to the formation of DHMF in good yield (69%, Table 1, entry 2). Similarly, the analogous cationic

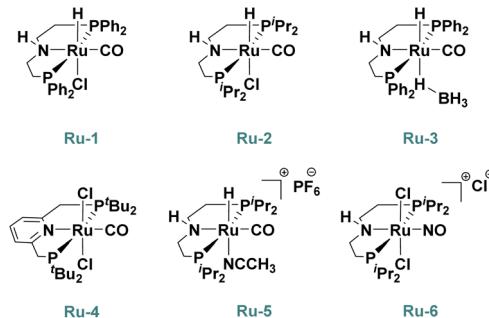


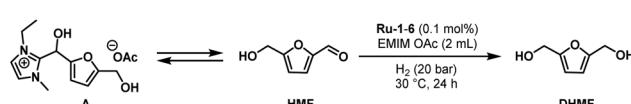
Fig. 2 Catalysts investigated in our preliminary screening for HMF hydrogenation in ILs.

Ru-PNP complex bearing acetonitrile as ancillary ligand and hexafluorophosphate ( $\text{PF}_6^-$ ) as counterion (**Ru-5**)<sup>18</sup> shows high catalytic activity (73% yield, Table 1, entry 5). The analogous cationic nitrosyl Ru-PNP complex bearing chloride ( $\text{Cl}^-$ ) as counterion (**Ru-6**)<sup>14d,19</sup> was also tested in the same conditions, but the desired product was observed only in traces (Table 1, entry 6). Independent of the catalyst, the reaction was exceedingly selective and provided the same yield of DHMF as a conversion of HMF.

At room temperature, the ionic liquid (EMIM OAc) easily couples with HMF to form adduct **A**. This happens through a reversible reaction where the N-heterocyclic carbene (NHC) of EMIM, in equilibrium with EMIM OAc, attacks the electrophilic carbonyl group of HMF. Interestingly, we observe no uppolung coupling product as otherwise previously observed when treating HMF with a pro-NHC IL in the presence of a base.<sup>15c</sup> We speculate that the acetate is too weak a base to facilitate the formation of the Breslow intermediate. Moreover, after adding EMIM OAc to the reaction vial, the solution colour changes from light orange to light purple which may be due to the coupling of HMF with EMIM OAc.

With these promising results in hand, we evaluated the effect of time and temperature (Table 2). Our study focused on the

Table 1 Catalyst screening and identification of suitable conditions for the formation of DHMF from HMF in EMIM OAc at 30 °C for 24 h<sup>a</sup>



Entry	Catalyst	Conversion of HMF <sup>b</sup> (%)	Yield of DHMF <sup>b</sup> (%)
1	<b>Ru-1</b>	<5	<5
2	<b>Ru-2</b>	69	69
3	<b>Ru-3</b>	8	8
4	<b>Ru-4</b>	<5	<5
5	<b>Ru-5</b>	73	73
6	<b>Ru-6</b>	<5	<5

<sup>a</sup> Standard reaction conditions: 0.79 mmol of HMF (100 mg), **Ru-1-6** (0.1 mol%), EMIM OAc (2.0 mL),  $\text{H}_2$  (20 bar). <sup>b</sup> Conversion and yield were both determined by crude  $^1\text{H-NMR}$ . Dimethyl sulfone was used as internal standard.

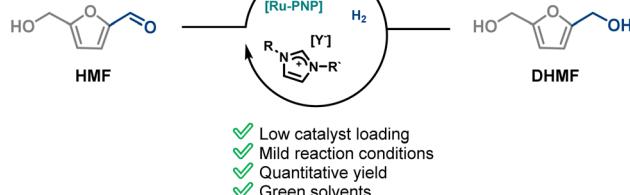


Fig. 1 Selective catalytic hydrogenation of HMF to DHMF with Ru-PNP catalysts in ILs.



Table 2 Time and temperature screening for the formation of DHMF from HMF in EMIM OAc<sup>a</sup>

Entry	Catalyst	<i>T</i> (°C)	<i>t</i> (h)	Conversion of HMF <sup>b</sup> (%)		Yield of DHMF <sup>b</sup> (%)
				Conversion of HMF <sup>b</sup> (%)	Yield of DHMF <sup>b</sup> (%)	
1	<b>Ru-2</b>	30	72	93	93	
2	<b>Ru-5</b>	30	72	74	74	
3	<b>Ru-2</b>	60	24	98	98	
4	<b>Ru-5</b>	60	24	98	98	
5	<b>Ru-2</b>	100	24	92	92	
6	<b>Ru-5</b>	100	24	98	98	

<sup>a</sup> Standard reaction conditions: 0.79 mmol of HMF (100 mg), **Ru-2** and **Ru-5** (0.1 mol%), EMIM OAc (2.0 mL), H<sub>2</sub> (20 bar). <sup>b</sup> Conversion and yield were both determined by crude <sup>1</sup>H-NMR. Dimethyl sulfone was used as internal standard.

best candidates **Ru-2** and **Ru-5**, which showed the best catalytic activity in the first catalyst screening at room temperature in EMIM OAc.

Elongating the reaction time from 24 h to 72 h, **Ru-2** revealed an excellent NMR yield of 93% DHMF (Table 2, entry 1). **Ru-5** also revealed a good yield of 74% DHMF (Table 2, entry 2). Interestingly, when the temperature was raised to 60 °C for 24 h, promising results were observed as both **Ru-2** and **Ru-5** afforded the desired product with excellent yield (98%, Table 2, entries 3 and 4). We also tested the other Ru-PNP commercially available complexes (**Ru-1**, **Ru-3**, and **Ru-4**) under these conditions. The yields towards DHMF were moderate (77% with **Ru-1** and 72% with **Ru-3**) (ESI, Table S2, entries 7 and 8†), while the desired product was observed only in traces with **Ru-4** (ESI, Table S2, entry 9†). These findings showed that **Ru-2** and **Ru-5** have more activity towards the formation of DHMF from the hydrogenation of HMF in EMIM OAc. Increasing the temperature even more to 100 °C, the conversion of HMF towards DHMF was 92% and 98%, respectively, with **Ru-2** and **Ru-5** (entries 5 and 6). The selectivity towards DHMF remained practically quantitative even at this high reaction temperature.

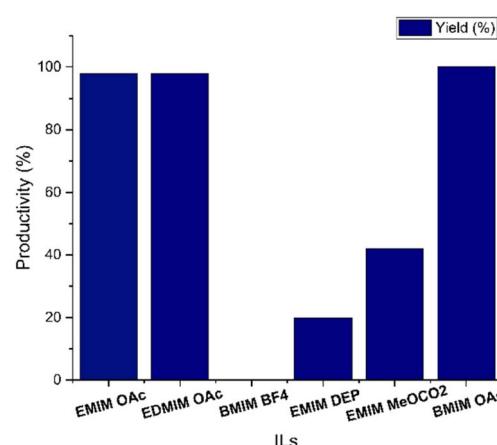
Table 3 Optimization of the reaction conditions employing EDMIM OAc as IL<sup>a</sup>

Entry	<i>T</i> (°C)	<i>t</i> (h)	Conversion of HMF <sup>b</sup> (%)		Yield of DHMF <sup>b</sup> (%)
			Conversion of HMF <sup>b</sup> (%)	Yield of DHMF <sup>b</sup> (%)	
1	60	24	98	98	
2	60	3	51	51	
3	30	24	28	28	
4	30	18	26	26	

<sup>a</sup> Standard reaction conditions: 0.79 mmol of HMF (100 mg), **Ru-2** (0.1 mol%), EDMIM OAc (2.0 mL), H<sub>2</sub> (20 bar). <sup>b</sup> Conversion and yield were both determined by crude <sup>1</sup>H-NMR. Dimethyl sulfone was used as internal standard.

We also screened different ILs (Table 3). To prevent the formation of adduct **A**, we tested the C2-methylated analogue of EMIM OAc, *i.e.*, 1-ethyl-2,3-dimethylimidazolium acetate (EDMIM OAc). **Ru-2** was chosen to continue our investigation since it is commercially available. We tested its activity at 60 °C under 20 bars of H<sub>2</sub> in 2.0 mL of EDMIM OAc for 24 h and it revealed 98% yield towards DHMF (Table 3, entry 1). When reducing the reaction time to 3 h at 60 °C, DHMF was afforded with moderate yield (51% yield, Table 3, entry 2). We speculate that EDMIM OAc is also able to form a reversible adduct with HMF akin to **A**. Moreover, based on NMR studies (ESI, Fig. S7†), it seems that the HMF generates a dimer adduct with itself when there is no better nucleophile present. Finally, when we reduced the temperature to 30 °C, the yield was drastically reduced (Table 3, entries 3 and 4), which could be due to EDMIM OAc higher viscosity at that temperature compared to other ionic liquids tested.

To further optimise the hydrogenation of HMF to DHMF, other ionic liquids were screened as reported in the Fig. 3.

Fig. 3 Solvents screening for the hydrogenation of HMF to DHMF in ILs. Standard reaction conditions: 0.79 mmol of the HMF (100 mg), **Ru-2** (0.1 mol%), ILs (2.0 mL), H<sub>2</sub> (20 bar), 60 °C, 24 h. <sup>a</sup>Conversion and NMR yield were both determined by crude <sup>1</sup>H-NMR. Dimethyl sulfone was used as internal standard.

Keeping the catalyst loading at 0.1 mol% and the temperature at 60 °C, a screening of ILs showed that BMIM OAc performs similarly to EMIM OAc and EDMIM OAc (98% conversion, 98% yield towards DHMF with a selectivity of practically 100%). Interestingly, BMIM OAc also forms an NHC adduct with HMF (**B**). On the contrary, the ILs containing other counterions such as tetrafluoroborate, carbonate and diethylphosphate afforded lower conversion of HMF and selectivity towards DHMF (ESI, Table S5, entries 3–6†). We also explored 1-ethyl-3-methylimidazolium hydrogen sulfate (EMIM HSO<sub>4</sub>) and 1,3-dimethylimidazolium methyl sulfate (DMIM MeSO<sub>4</sub>), but in both cases the reaction crudes showed the formation of a complicated mixture of products (ESI, Fig. S13 and S14†). These results indicate that the anion of the IL must be basic enough to promote catalyst activation and to facilitate either the formation of the NHC carbene, to generate the adducts **A** or **B**, or the formation of the HMF-dimer. Interestingly, it seems that all these reversible adducts in practice function as protecting the HMF from degrading to *e.g.* humins. This is a key advantage of this catalytic system, as HMF tends to polymerize into humins under similar reaction conditions when IL is replaced with water or other organic solvents.<sup>7,17,20</sup>

These promising results led us to further optimise the reaction conditions with BMIM OAc, which is also known for its ability to solubilize biomass.<sup>21</sup> We investigated the response of the catalytic system to several parameters such as time, temperature, overall pressure of H<sub>2</sub>, and concentration of the reaction mixture.

The catalytic system **Ru-2**/BMIM OAc was found to be highly responsive to the variation of the reaction parameters, as shown in Table 4. To evaluate the progress of the reaction over time, the hydrogenation reaction was monitored at different time points and the reaction showed practically full conversion already after 3 hours at 60 °C (entries 1–4). Lowering the temperature to 30 °C under 20 bars of H<sub>2</sub> for 24 h, afforded 45%

DHMF after 24 h (entry 5). We also evaluated the effect of the concentration of the reaction mixture. Comparing the hydrogenation reaction with 2.0 mL (0.40 M HMF), 1.0 mL (0.79 M HMF) and 0.5 mL (1.6 M HMF) of BMIM OAc, the reaction is faster when more dilute. As such, full conversion after 3 h at 60 °C in both 2.0 and 1.0 mL (entries 2 and 6), but after 1 h the 2.0 mL reaction gave 56% yield compared to 45% in 1.0 mL (entries 4 and 9). In 0.5 mL, merely 30% yield was reached after 3 h at 60 °C (entry 8). We also aimed at lowering the overall H<sub>2</sub> pressure but decreasing it to 10 bars yielded only 67% of DHMF (entry 9).

With the best reaction conditions for the hydrogenation of HMF in ILs in hand, we investigated how to isolate DHMF from the reaction mixture to recycle **Ru-2**/BMIM OAc for subsequent HMF hydrogenations. We tested three different methods for the isolation of the product: liquid–liquid extraction with organic solvents adding water to the IL, centrifugation and direct extraction with organic solvent without any additional water. Among the three purification methods and the organic solvents tested, the liquid–liquid extraction, ethyl acetate as the organic extracting solvent and an additional 4.0 mL of water to the system can extract >99% DHMF from the BMIM OAc (ESI, Fig. S17†). Both the centrifugation and direct liquid–liquid extraction without any additional water showed worse performance in the product isolation. Unfortunately, **Ru-2** was also transferred to the organic phase during the liquid–liquid extraction process.

Nevertheless, knowing that an additional amount of water is needed to fully extract DHMF from the IL, we explored the effect of the addition of different volumes of water (from 0.5 mL to 4.0 mL) on the selectivity of the HMF hydrogenation reaction (Fig. 4).

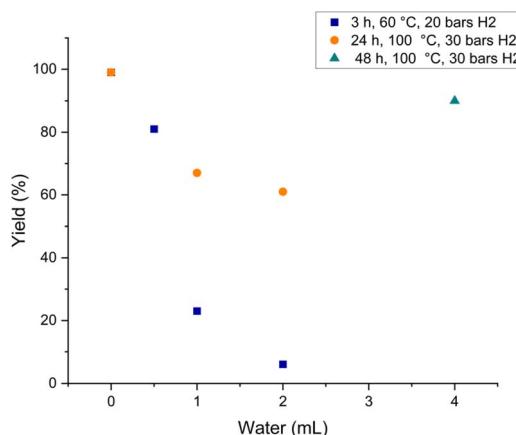
We started adding an increasing amount of water in the best reaction conditions previously found (0.1 mol% of **Ru-2** in 2.0 mL of BMIM OAc under 20 bars of H<sub>2</sub> at 60 °C for 3 h). Good

Table 4 Optimization of the reaction conditions employing BMIM OAc as solvent<sup>a</sup>

Entry	BMIM OAc (mL)	H <sub>2</sub> (bar)	T (°C)	t (h)	Conversion of HMF <sup>b</sup> (%)		Yield of DHMF <sup>b</sup> (%)
1	2.0	20	60	24	>99		>99
2	2.0	20	60	3	>99		>99
3	2.0	20	60	2	65		65
4	2.0	20	60	1	56		56
5	2.0	20	30	24	45		45
6	1.0	20	60	3	>99		>99
7	1.0	20	60	1	45		45
8	0.5	20	60	3	30		30
9	1.0	10	60	3	67		67

<sup>a</sup> Standard reaction conditions: 0.79 mmol of HMF (100 mg), **Ru-2** (0.1 mol%), BMIM OAc. <sup>b</sup> Conversion and yield were both determined by crude <sup>1</sup>H-NMR. Dimethyl sulfone was used as internal standard.





**Fig. 4** Water amount screening for the hydrogenation of HMF to DHMF in BMIM OAc. Standard reaction conditions. Blue squares: 0.79 mmol of HMF (100 mg), Ru-2 (0.1 mol%), BMIM OAc (2.0 mL), H<sub>2</sub> (20 bar), 60 °C, 3 h. Orange circles: 0.79 mmol of HMF (100 mg), Ru-2 (0.1 mol%), BMIM OAc (2.0 mL), H<sub>2</sub> (30 bar), 100 °C, 24 h. Green triangle: black squares: 0.79 mmol of HMF (100 mg), Ru-2 (0.1 mol%), BMIM OAc (2.0 mL), H<sub>2</sub> (30 bar), 100 °C, 48 h. <sup>a</sup>Conversion and yield were both determined by crude <sup>1</sup>H-NMR. Dimethyl sulfone was used as internal standard.

yield of DHMF from the hydrogenation of HMF in BMIM OAc in the presence of water can only be achieved by adding a low amount of water to the system (81% yield after adding 0.5 mL of water) as reported in Fig. 4, blue squares. For this reason, we briefly explored the effect of water in harsher reaction conditions. Increasing the temperature to 100 °C, the time to 48 hours and the H<sub>2</sub> pressure to 30 bars, we reprise a high yield of DHMF even when 4.0 mL of water was added to our system (90% yield of DHMF, Fig. 4, green triangle). This result proves the possibility of efficiently generating DHMF using a [Ru-PNP]/IL system in the presence of water to subsequently extract the desired product and recycle the IL for further catalytic transformations of HMF.

## Conclusions

In conclusion, we demonstrate a highly effective and selective hydrogenation of HMF under mild reaction conditions, leading to DHMF, catalysed by Ru-PNP pincer complexes in ionic liquids. Both the commercially available **Ru-2** and the recently developed **Ru-5** demonstrated high efficiency towards the selective hydrogenation of HMF to DHMF in EMIM OAc, EDMIM OAc or BMIM OAc under relatively mild reaction conditions (60 °C, 20 bar H<sub>2</sub>). Our methodology represents an efficient and highly selective approach for the catalytic hydrogenation of furanic compounds avoiding the formation of byproducts and the use of organic solvents. The ILs successfully mediating DHMF formation seem to generate a protective adduct of HMF that suppresses the formation of *e.g.* humins.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

MN conceptualized the project. MN and VN conceived and designed the project. VN and HAS carried out the experiments. VN and HAS carried out the data curation. VN and HAS did the formal analysis. VN wrote the original manuscript. All authors revised the manuscript. MN did project administration and funding acquisition.

## Conflicts of interest

There are no conflicts of interest to declare.

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