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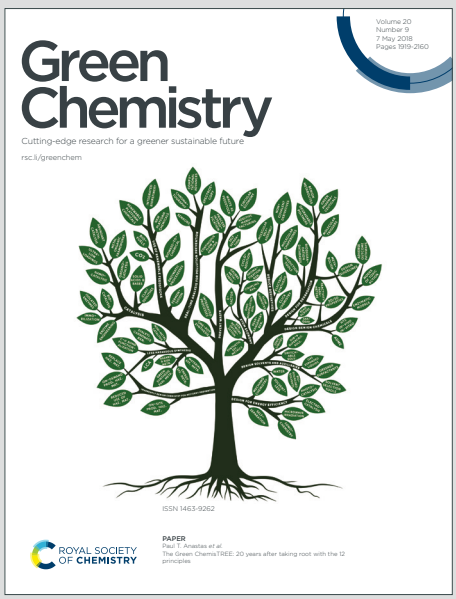

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COMMUNICATION

Efficient and Selective Catalytic Hydrogenation of Furanic Aldehydes using well defined Ru and Ir Pincer Complexes

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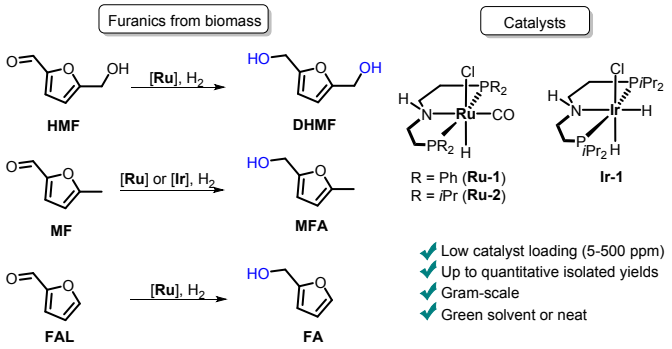
We report the homogeneous catalytic hydrogenation of biomass derived furanic aldehydes to furfuryl alcohols using low loadings of PNP metal complexes under mild conditions. Our strategy represents an efficient and selective approach to the direct hydrogenation of furan derivatives to promising platform chemicals.

Developing efficient processes for the valorizations of biomass-derived substrates is imperative for a future sustainable production of chemicals and fuels.[1] As such, particularly the last decade has witnessed the developments of a plethora of effective and selective biomass transformations using homogeneous organometallic catalysis under mild conditions.[2] One of the more recent additions to the list of substrates include furanic aldehydes, mainly represented by hydroxymethyl furfural (**HMF**),[3] which is derived from celullose.[1c,3b,4] However, the inherent difficulty of handling **HMF** induces considerable challenges for its selective synthetic modifications.[5] Thus, to access more suitable liquid biofuels, further chemical transformations of **HMF** are required. The majority of these synthetic modifications focus on transforming the furan ring itself.[3] Selective reduction of the aldehyde functionality to products such as 2,5-bis(hydroxymethyl)furan (**DHMF**) has been more scarcely reported. This product type is a highly important starting molecule for various polymerization or etherification processes.[3b,4,6] The selective conversion of **HMF** to **DHMF** has been mainly achieved by various hydrogenation methodologies, such as electrocatalytic hydrogenation,[7] transfer hydrogenation,[8] biocatalysis,[9] and heterogeneous catalysis.[10]

The gradual progress of selective homogeneous organometallic catalytic systems for **HMF** hydrogenation to **DHMF** is pioneered by Elsevier[11a] Mazzoni,[11b] Beller,[11c] and Hashmi.[3i] Mazzoni used 0.1 mol% of the dimeric Shvo's catalyst to reach a practically quantitative NMR yield of **DHMF** after 2 hours under 10 bar H_2 at 90 °C in a 29:1 mixture of toluene/H_2O. Beller used pure toluene and 1 mol% of an $^{i\text{Pr}}$PNP-Mn complex to afford 64% of isolated **DHMF** after 24 hours of reaction time under 30 bar H_2 at 100 °C (see SI).

Hence, the challenge remains to produce the desired product highly selectively under mild and sustainable conditions. This drawback is likely due to the labile nature of **HMF**, which significantly affects its potential in a bio-based industry.

Toward this end, the fructose derived 5-methyl furfural (**MF**) has been proposed as an alternative substrate for biofuels development due to its high stability, excellent synthetic utility and reduced oxygen content.[12,13] **MF** is industrially produced from biomass[13a] as an important intermediate for the production of pharmaceuticals,[14] food flavoring component[15] and agricultural chemicals.[16] Furthermore, 5-methyl furfuryl alcohol (**MFA**) is also interesting as an industrially important component and bio-diesel precursor.[4b,c,j] Moreover, to the best of our knowledge a homogeneous catalytic **MF** hydrogenation to **MFA** remains elusive in the literature.



Scheme 1. This work: Selective catalytic hydrogenation of furanic aldehydes to their corresponding alcohols.

Likewise, only recent reports have emerged with furfural (**FAL**) as substrate.[17] **FAL**, derived from hemicellulose,[4b,h] is a key platform compound which can be widely converted to a variety of chemicals and biofuels.[18] However, selective hydrogenation

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of **FAL** to furfuryl alcohol (**FA**) is challenging due to undesired side reactions.[19] **FA** is the most significant derivative of **FAL** with high demand in the manufacture of foundry resins and feedstock for the production of levulinic acid.[20]

Transition metal pincer complexes are known for their robustness and efficacy in catalyzing both dehydrogenation as well as hydrogenation reactions.[21] In this regard, several concrete studies on mechanistic investigations for the hydrogenation of carbonyl functionalities are known. In particular, the outer-sphere stepwise mechanism of cooperating pincer ligands describes the catalyzed hydrogenation of aldehydes.[21f] Hence, we were prompted to study this type of complexes for the transformation of biomass-derived furanic aldehydes.

Herein, we show the effective and selective conversion of all three furanic aldehydes to their corresponding alcohols under mild conditions using low catalyst loadings (Scheme 1).

Our initial work concentrated on testing the conversion of **HMF** to **DHMF** using the PNP complexes Ru-MACHO (**Ru**-**1**),[22] its $^{i\text{Pr}}$PNP congener (**Ru**-**2**), and the Abdur-Rashid $^{i\text{Pr}}$PNP-Ir(H)$_2$Cl complex (**Ir**-**1**) [23] (SI, Table S1). Thus, with 0.1 mol% of **Ru**-**1** or **Ir**-**1** and 5 mol% of base under 10 bar of H_2 in EtOH, the conversion towards **DHMF** was highly selective, affording 76% and 93% conversion after 1.5h at 25 °C, respectively. Interestingly, **Ru**-**2** led to a significant increase in conversion, with 0.05 mol% affording >95% after 15 minutes and 2 mol% of NaOEt under 10 bar H_2 at 25 °C. Control experiments without any base additive led to no conversion, suggesting that the presence of a strong base seems to be necessary for the reaction to occur, which is in line with the typically necessary activation of the chlorido PNP complexes. Interestingly, the reaction rate seems to also be affected by the loading of the base. Thus, when lowering the NaOEt loading from 2.0% to 0.5% in the presence of 0.05 mol% **Ru**-**2**, the initial reaction rates dropped significantly. Nevertheless, both reactions reach full conversion after 20 min and 60 min, respectively (SI, Figure S2).

The effect of concentration of **HMF** in EtOH was investigated with 0.05 mol% of complex **Ru**-**2** by using 0.79 mmol of **HMF** and 10 bar H_2 at 25 °C in EtOH volumes ranging from 0.25-5.00 mL. The reaction afforded full conversion within 10 min in the solvent range 0.50-5.00 mL, but in 0.25 mL a minor drop to 91% conversion was observed (SI, Table S2), showing that a highly concentrated solution is slightly detrimental for catalytic activity. Moreover, the reaction is at all concentrations entirely selective (>99%), towards **DHMF** according to ^{1}H- and ^{13}C-NMR analysis as well as the absence of any humins by simple visual inspection.

Increasing the hydrogen pressure to 30 bar reduced the reaction time to 1 min before reaching >95% conversion of **HMF**, which corresponds to a turnover frequency (TOF) of >1900 min^{-1} (Table 1, Entry 1). To the best of our knowledge, this system constitutes the first example of homogeneous catalytic **HMF** hydrogenation to **DHMF** at room temperature. In addition, the catalytic rate is more than a 200 fold improvement to the previous state-of-the-art.[11b]

We then scaled up to 1 g of **HMF** using 0.01 mol% (100 ppm) of **Ru**-**2** at 25 °C and 30 bar H_2 (Entry 2). After 120 min, we isolated a quantitative yield of **DHMF** after a simple filtration through a silica gel. Further decreasing the catalyst loading to 50 ppm caused a sharp drop in conversion. Thus, 32% conversion was achieved after 6h, and practically no further conversion was observed after 24h, suggesting catalyst inhibition or even degradation.

Next, we tested the tolerance of the catalytic protocol by performing the reaction in H_2O in the presence of various additives. A number of common bases were evaluated, and LiOH was found to be optimal (SI, Tables S6-S7). Thus, employing 2 mol% LiOH, 0.05 mol% of **Ru**-**2**, and 30 bar of H_2 afforded full conversion after 2 hours (Entry 3).

We also carried out the **HMF** hydrogenation in varying ratios of EtOH/H_2O mixtures. Thus, >95% conversion was achieved after 15 min in both 95:5 and 80:20 EtOH/H_2O ratios using 0.05 mol% **Ru**-**2** under 30 bar H_2 at 25 °C (Table 1, Entries 4-5), suggesting the feasibility of using bioethanol as solvent.

Finally, we attempted to reuse **Ru**-**2** for the hydrogenation of **HMF** through consecutive addition using 0.79 mmol of **HMF** per loading and an initial 0.05 mol% of catalyst (30 bar H_2, 25 °C, 2h per run, SI, Figure S26). The experiment shows a detrimental effect in the conversion after the third run, where the overall catalyst loading is 0.0125 mol%. As such, we observed 75% overall conversion in the last run, and we were unable to carry out the additions to the point where the overall catalyst loading goes below our best results with batch reactions.

To shed light on the fate and stability of the catalyst during the consecutive additions, we carried out some crude NMR studies for the characterization of the resting species. The catalytic hydrogenation of **HMF** in EtOH with 1 mol% of **Ru-2** at 25 °C and 30 bar of H_2 was monitored by ^{1}H-NMR (SI, Fig. S40). Based on the hydride region, we suggest the expected presence of an alkoxide complex, **Ru-OR**, overlapping with remnant **Ru-2** at -16.5 to -16.7 ppm. These **Ru**-**OR** species might correspond to coordinated **DHMF**. Interestingly, **Ru-OR** is still found after carrying out the first consecutive addition of **HMF** under similar reaction conditions, suggesting to some extent the stability of the catalyst.

As much as the result points to the feasibility for conducting consecutive addition reactions, we speculate whether a behavior similar to what was suggested by Mazzoni for their hydrogenation of **HMF**[11b] is occurring in our system as well, *i.e.* that the presence of two hydroxyl units in **DHMF** is particularly responsible for the catalyst inactivation.

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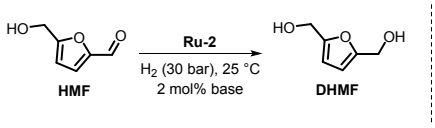
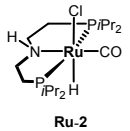
Table 1. Hydrogenation of **HMF** to **DHMF** using **Ru-2**.[a]



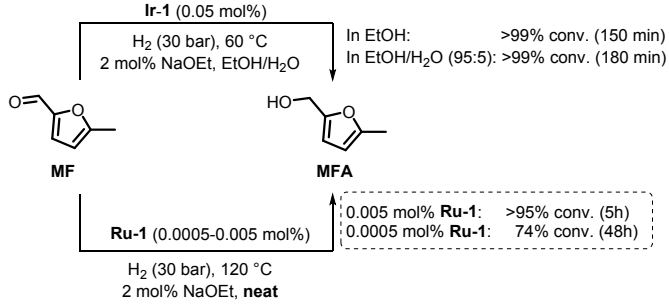


Ru-2

Entry	Ru-2 mol%	EtOH/H_2O ratio	Time min	Conv. %[b]	TON	TOF min^{-1}
1[c]	0.05	EtOH	1	>95	>1900	>1900
2[c,e]	0.01	EtOH	120	≥99	10000	83
3[d]	0.05	H_2O	120	≥99	2000	17
4[d]	0.05	95:5	15	>95	>1900	>127
5[d]	0.05	80:20	15	>95	>1900	>127

[a] Standard reaction conditions: 0.79 mmol HMF, **Ru-2**, 2 mol% base, 30 bar H_2, 25 °C. [b] Determined by ^{1}H-NMR. Selectivity ≥99%. [c] Base is NaOEt: 2.0 M/EtOH. [d] Base is LiOH. [e] 4.36 mmol HMF.

We then explored the catalytic activity for the transformation of **MF**. Interestingly, **Ir-1** is more active than **Ru-2** for hydrogenating **MF** in EtOH as well as in EtOH/H_2O mixtures (SI, Tables S9-S10). A slight increase in reaction temperature was found necessary to reach effective catalytic turnover rates. In fact, under identical reaction conditions (0.1 mol% catalyst, 30 bar H_2, 60 °C, 2 mol% NaOEt, EtOH as solvent, 10 min reaction time), both **Ru-1** and **Ru-2** facilitates <10% conversion whereas **Ir-1** leads to ≥99% conversion (TOF = 100 min^{-1}). Moreover, further lowering the **Ir-1** loading to 0.05 mol% requires 150 min until full conversion is observed (Scheme 2, upper reaction). In 95:5 and 80:20 EtOH/H_2O mixtures, excellent conversion rates were obtained as well.



Scheme 2. Hydrogenation of **MF** to **MFA**.

At this stage, we performed a benchmark reaction employing **MF** under neat conditions (Scheme 2, lower reaction). Surprisingly, **Ru-1** showed superior catalytic activity over **Ir-1**, whereas **Ru-2** merely reached 21% conversion (SI, Table S11). From these observations, we speculate whether the diminished activity and low conversion is a result of catalyst deactivation or a detrimental change in solubility of **Ru-2** in the neat conditions. Thus, employing 0.005 mol% of **Ru-1** or **Ir-1** led to high conversions (≥95% and 91%, respectively) with TONs of 19000 and 18200 after 5h. Decreasing the catalyst loading to 0.0005 mol% gratifyingly led to 17% conversion after 5h when using **Ru-1**, corresponding to a TON of 34000 and TOF of 113 min^{-1} (SI, Table S12). On the contrary, **Ir-1** exhibited a somewhat inferior TOF of 40 min^{-1}. Extending the reaction time to 48h resulted in 74% conversion in the **Ru-1** system, corresponding to a TON of 148000 and an overall TOF of 51 min^{-1}. Under identical conditions, **Ir-1** provided 56% conversion. Scaling up the reaction to 7.9 mmol of **MF** with 0.01% **Ir-1** under 30 bar and 120 °C for 2h allowed to isolate the product **MFA** in 97% yield.

Finally, we turned our attention to hydrogenating **FAL** to **FA**. In the literature, impressive results have been achieved by several research groups (see SI).[17] For example, Kirchner, Hoffmann, and Bica demonstrated that the 2,6-diaminopyridine based PNP complexes of the base metals Fe[17c-f] and Mn[17h] are highly competent catalysts for **FA** production, with catalyst loadings as low as 0.005 mol% still affording quantitative NMR yields under relatively mild conditions (EtOH as solvent, 1.0 mol% DBU additive, 30 bar H_2, 40 °C, 16h, TOF = 21 min^{-1}).[17c]

Interestingly, whereas **Ir-1** was superior for hydrogenating **MF** to **MFA** when a solvent is present, **Ru-2** is again the most competent catalyst for the transformation of **FAL** to **FA**. Thus, full conversion is achieved after 30 min with 0.05-0.1 mol% **Ru-2** in solvent mixtures ranging from 100:0 to 80:20 of EtOH/H_2O under 30 bar H_2 at 25 °C (Table 2, Entries 1-3). These results corresponds to TONs ranging from 1000-2000 and TOFs ranging from 33-67 min^{-1}. Next, the isolation of the product was carried out under similar reaction conditions using 0.90 mmol of **FAL** and 0.1 mol% **Ru-2** in EtOH. Then, the reaction mixture was filtered over silica gel affording 61% yield.

On the other hand, when the catalyst **Ru-1** (0.1 mol%) was evaluated in the presence of EtOH (30 bar H_2 at 25 °C), the reaction lead to low conversion (24%, SI, Table S13).

Finally, the reaction in water afforded full conversion in 10 min (Table 2, entry 4) albeit along with a clearly observable formation of an insoluble brown solid (humins).

Furthermore, we carried out a consecutive addition experiment under standard reaction conditions (25 bar H_2, 25 °C, 10 min) using 0.90 mmol of **FAL** per loading and an initial 0.1 mol% of **Ru-2** in water. The conversion dropped from ≥99% to 56% already after the second addition. This observation suggests the inhibition of **Ru-2** due to the presence of humins (SI, Figure S26). In fact, humins formation are frequently observed from **FAL** in aqueous conditions.[24]

Moreover, comparing with the mentioned literature precedence, our method allows to combine the use of relatively low catalyst loading with effective catalytic conversion rates of **FAL** to **FA** while still employing mild conditions and green solvents.

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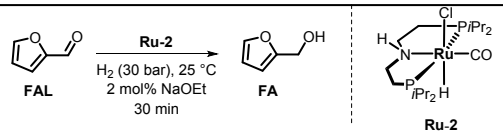
Table 2. Hydrogenation of **FAL** to **FA** using **Ru-2**.[a]

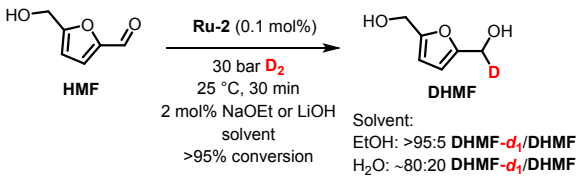


Entry	**Ru-2** mol%	EtOH/H_2O ratio	Conversion %[b]	TON	TOF min^{-1}
1	0.05	EtOH	>99	2000	67
2	0.1	95:5	≥99	1000	33
3	0.05	80:20	≥99	2000	67
4	0.1[c]	H_2O	≥99	1000	100
5	0.05[c]	H_2O	93	1860	186

[a] Standard reaction conditions: 0.90 mmol **FAL**, **Ru-2**, 2 mol% base (NaOEt: 2.0 M/EtOH), 30 bar H_2, at 25 °C, 30 min. [b] Determined by ^{1}H-NMR. Selectivity ≥99%. [c] Formation of an insoluble dark solid in the reaction (humins) observed by visual inspection.

Further insight into the formation of **DHMF** was obtained from deuterium-labeling experiments using the catalyst system **Ru-2** in presence of 30 bar of D_2 (Scheme 3).[22b,25] In EtOH, practically exclusively d_1 labeled product, **DHMF-*d*$_1$**, was formed. When changing the solvent to H_2O, the D-incorporation is diminished to approximately 80%, the remainder being simply **DHMF**. The observation might be explained by the fact that the reaction is significantly faster in EtOH than in H_2O. Thus, for the reaction in EtOH, we suggest that when the active catalyst is loaded with deuterium, it is delivered to **HMF** before any scrambling with the protic proton on the EtOH alcohol unit occurs. This scenario is corroborated by previous results we have obtained for the hydrogenation of ethyl levulinate.[22b] In this case, 24 hours under 30 bar D_2 at 60 °C led to a ~2:1 mixture of labeled/unlabeled products.

When conducted in H_2O, both the higher acidity of the solvent compared to EtOH as well as the different catalytic rate might contribute to the lower degree of deuterium labeling. Previous work by Dumeignil and Gauvin strongly suggest that for the same catalyst family, temperatures significantly higher than 25 °C are needed to facilitate hydride/deuteride exchange.[25b] However, those studies were conducted with ~10 equivalents D_2O in toluene, and not in an all-aqueous solvent, which might explain the somewhat diverging observations. Finally, a Cannizaro type reaction could explain the presence of non-labeled **DHMF**. However, no conversion was observed in the absence of the catalyst, strongly suggesting that this option can be ruled out.



Scheme 3. Deuterium-labeling experiments.

Conclusions

In conclusion, we demonstrate the highly effective and selective hydrogenation of the furanic aldehydes **HMF**, **MF**, and **FAL** under mild reaction conditions toward the corresponding alcohols catalyzed by PNP-Ru and PNP-Ir complexes. Moreover, our method allows to achieve a TOF >1900 min^{-1} or a TON = 10000, as well as isolating a quantitative yield of **DHMF** and **MFA**. Unfortunately, the yield is somewhat diminished for **FA** due to humins formation. Furthermore, we show for the first time the homogeneously organometallic catalyzed hydrogenation of neat **MF** to **MFA** with a TOF = 100 min^{-1} or a TON = 148000. In addition, our method allows for converting **FAL** to **FA** under mild conditions using low catalyst loading with a TOF = 67 min^{-1}. Importantly, we demonstrate the feasibility of employing "green" solvents or even neat conditions. Finally, we shed light on the involvement of the solvent in the hydrogenation process via deuterium-labeling experiments.

Conflicts of interest

There are no conflicts to declare

Acknowledgments

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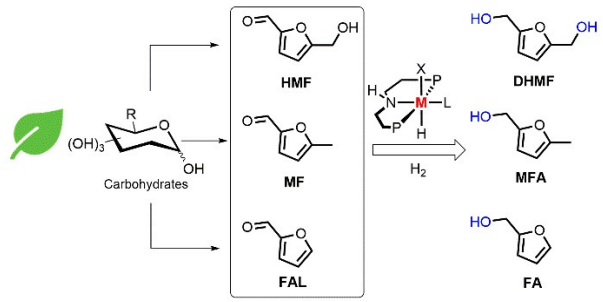

Homogeneous catalyzed hydrogenation of furanic aldehydes to their corresponding alcohols using PNP complexes