Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Cadu, K. Sekine, J. Mormul, D. M. Ohlmann, T. Schaub and S. Hashmi, *Green Chem.*, 2018, DOI: 10.1039/C8GC01025K.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/green-chem

View Article Online
DOI: 10.1039/C8GC01025K

Homogeneous Catalysed Hydrogenation of HMF †

Alban Cadu,[a] Kohei Sekine [b], Jaroslaw Mormul,[c] Dominik M. Ohlmann,[c] Thomas Schaub,[a,c] A. Stephen K. Hashmi[a,b,d]

[a]Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 584, 69120 Heidelberg, Germany

[b]Institut für Organische Chemie, Universität Heidelberg, Im Neuenheimer Feld 270,

69120 Heidelberg, Germany.

[c]BASF SE, Synthesis and Homogeneous Catalysis, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany

[d]Heidelberg Center for the Environment (HCE), Universität Heidelberg, Im Neuenheimer Feld 229,

69120 Heidelberg, Germany. E-mail: hashmi@hashmi.de; Fax: +49-(0)6221-544205

†Electronic supplementary information (ESI) available: Full catalysts screening

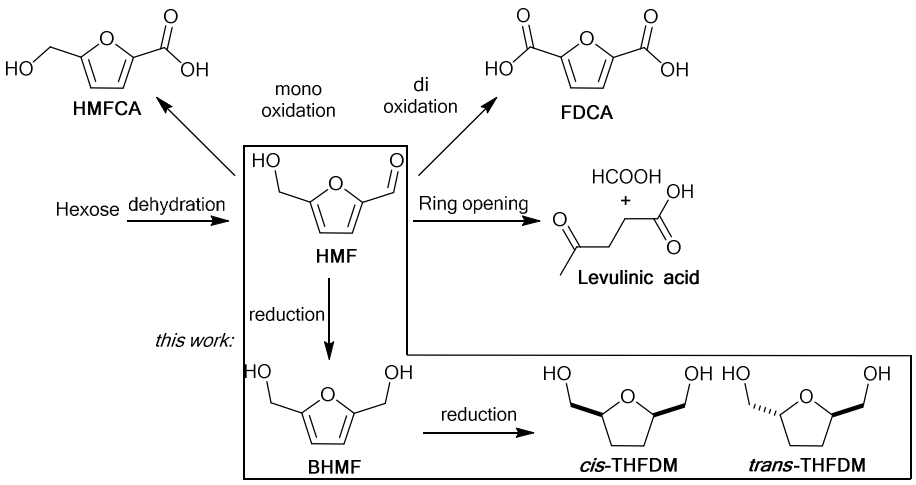
tables, detailed procedures and characterisation of the compounds.

Abstract

In this report, hydroxymethylfurfural (HMF) is used as a bio-based feedstock for homogeneous metal-catalysed hydrogenation. Several ligand classes and metals are employed to reduce the aldehyde and aromatic ring of HMF. The previously unknown homogeneous catalysed hydrogenation of HMF to tetrahydrofuran-dimethanol (THFDM) was investigated using different catalysts systems. NHCs and phosphites give higher *trans*/*cis* ratios (between 1:1.25 and 1:3.95) of the product THFDM, but low conversions of only up to 17% accompanied by up to 92% of bis(hydroxymethyl)furan at 10 bar H_2 and 120°C. Conversely di-phosphine ligated ruthenium catalysts in up to 87% yield lead to the highest overall conversion but only moderate *trans/cis* ratios of only 1:3.1-1:5.

Introduction

View Article Online
DOI: 10.1039/C8GC01025K



Scheme 1: HMF and related compounds

Hydroxymethylfurfural (HMF) is readily available from hexoses by catalytic dehydration of fructose, as such HMF stands to become a platform chemical, which has for over 10 years been hailed as one of the "*top value-added chemicals from biomass*".[1] The utilisation of HMF as a renewable feedstock has generated much academic interest,[2] with the hope of replacing petroleum-derived building-blocks with renewable plant-based ones. Moreover, it gives a straightforward access to molecules, such as FDCA, which are not readily available from petrochemical sources. Based on HMF, the diol tetrahydrofuran-dimethanol (THFDM) can be accessed, which is discussed as a bio-based monomer for polyesters or polyurethanes.[3] The reduction of HMF to bis(hydroxymethyl)furan (BHMF) has been reported using both homogeneous[4] and heterogeneous methodologies.[5] Further reduction to THFDM was observed, either as an over-reduced side product or as the target molecule. Of particular interest, in one report where THFDM was formed after Pd/Al_2O_3-catalysed hydrogenation of HMF under 70 bar of H_2. The ratio of *cis* to *trans*-THFDM was analysed,[6] this ratio was 9:1 in favour of the *cis* isomer, which can be explained by a preferential *syn*-facial hydrogenation, likely following the Horiuti-Polanyi mechanism.[7] Additionally, heterogeneous hydrogenation of bio-derived furans,[8] can in some cases lead to over-reduction and ring opening.[9] The mixture of *cis*/*trans*-THFDM has been used in patented bio-based polymers,[10] however the use of purely *trans*-THFDM is likely to show interesting properties as a bio-based monomer due to the possibility of a linear alignment of the monomeric *trans*-blocks compared to that of a corkscrew-like arrangement of the cusped *cis*-monomers. A recent report of the reduction of levoglucosenone yielded, amongst other products, THFDM in at best 2.5:1 *cis*:*trans* ratio,[3] which was, as the authors point out, the highest ratio of *trans*:*cis* obtained to date. However, this approach requires an elevated temperature (150 ºC) and yields a mixture of products (58 % combined yield of *cis*- and *trans*-THFDM). In order to achieve a more *trans*-selective reaction, we investigated homogeneous catalysis for the hydrogenation of HMF to THFDM, as this reduction had so far been limited to heterogeneous catalysis. Furans remain a difficult class of substrates with comparatively few examples of hydrogenation: mono-substituted furans were hydrogenated using bio-polymer heterogenised noble metals,[11] as well as homogeneous systems.[12] The Ru-catalysed homogeneous reduction of HMF and related furans was studied in one dissertation,[13] though it led only to the reduction and/or hydrogenolysis of the aldehyde group, but not to the formation of THFDM. The reduction of a few furans using homogeneous catalysts is known and the *cis*-diastereomer is normally favoured.[14] However, the combination of the aldehyde and alcohol groups of HMF (which can act as guiding groups) and through a choice of ligands (to modify the catalysts and its selectivity/activity) a preferred *trans*-hydrogenation could be envisaged.

View Article Online
DOI: 10.1039/C8GC01025K

Results and Discussions

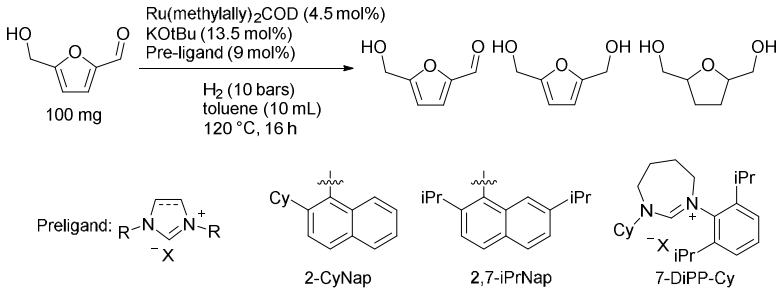
A key element in the study of reactions involving HMF is the variable quality of the starting material. Initial screenings were performed with a large supply of HMF synthesised by BASF (kept at 3 ºC, under air) which gradually showed a decrease in activity when reproducing experiments. Subsequently, different commercial sources of 99 % pure HMF were used, leading to irreproducible results due to variance from one batch of HMF to the next as well as exhibiting a gradual decrease in activity over time. The most consistent results were obtained by subliming the HMF (irrespective of the source) at 3 $\cdot 10^{-1}$ mbar at ca. 130 °C (see Supporting Information for more details on the sublimation).

As will be seen in the tables below, standard screenings and reaction optimisation are analysed by comparing the relative integration of the NMR peaks of the starting material, intermediate and product. Since all three compounds are known and characterised, it is not necessary to isolate each compound after every screening, this enables rapid identification of promising catalytic systems, which were in turn more thoroughly investigated. For ease of comparison, in each case the amount of BHMF was normalised and the amount of remaining HMF and formed THFDM expressed as a ratio to the amount of BHMF. In the tables, top entries were repeated with an internal standard, in order to determine an NMR yield, as in many cases dark precipitates were formed in the autoclave.[15] These insoluble precipitates were most likely humins which also occur in the synthesis of HMF.[16]

1. NHC as ligands

The use of NHC-ligated Ru complexes has been reported by Wysocki *et al*. to hydrogenate di-substituted furans.[14b] While the reaction led to *cis*-diastereomers being formed preferentially, this method was nonetheless investigated for its suitability to reduce HMF. As can be seen from Table 1, the unsaturated backbone proved to be more active compared to its saturated homologs (entries 1-2). Aromatic substitution on the carbene provided much more active catalysts than the alkyl substituted variants (entries 1-2, 6-7 vs 3-5), likely due to electronic effects. Interestingly, the recently reported mixed DiPP/cycloalkyl carbene[17] only gave trace amounts of THFDM (entry 8). Within the carbene family, IPr offered the highest *trans*:*cis* selectivity. However the highest conversions were observed for the bulky naphthyl containing substituents (entries 6-7).

Table 1: Ruthenium catalysed hydrogenation of HMF using NHC ligands



Entry	Ligand	HMF[a]	BHMF[a]	THFDM[a]	Cis:trans[b]
1	Unsaturated, R=di*iso*propylphenyl (IPr), X=Cl	0.03 (1%)	1 (43%)	0.37 (17%)	1.26:1
2	Saturated, R=di*iso*propylphenyl (SIPr), X=Cl	-	1 (92%)	0.08 (8%)	2.3:1

View Article Online
DOI: 10.1039/C8GC01025K

3	Saturated, R=*i*Pr,X=Cl	0.02	1	traces	-
4	Saturated, R= *t*Bu, X=Cl	0.01	1	0.18	3.3:1
5	Unsaturated, R= Ad, X=BF_4	0.05	1	traces	-
6	Saturated, R= 2-CyNap, X=BF_4	0.02	1	1.65	2.8:1
7	Saturated, R= 2,7-iPrNap, X=BF_4	-	1	3.2	3.95:1
8	7-DiPP-Cy, X=I	-	1	traces	-

[a]: ratio of products determined from normalised BHMF ^{1}H NMR peak, NMR yield in brackets as determined using hexamethylbenzene as internal standard, [b]: as determined by ratio of ^{13}C NMR peaks.

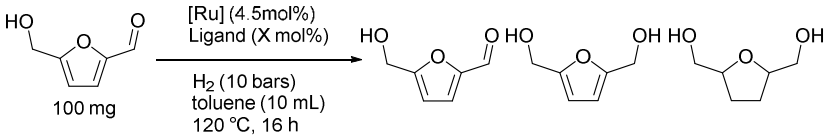
2. Phosphorus-based ligands

Since the NHC-based systems did not offer very high activity, further ligand screening was required. This was performed using a Chemspeed synthesis robot, with a series of rhodium, ruthenium and iridium hydrogenation (pre-) catalysts along with a selection of ligands (see SI for details). These three metals are known to form catalysts which can hydrogenate heterocyclic and hetero-aromatic compounds.[12,14,18] Of particular interest is the reduction of mono-substituted furans studied by Studer *et al.* using Rh-based catalysts, which led to high conversion but poor enantioselectivity,[18c] and then by the Pfaltz group using Ir-based catalysts (high enantioselectivity and conversion for monosubstituted furans but more mixed results for di-substituted substrates).[12c,14c] From this screening, Ru in combination with BINAP appeared to give the best results with a product distribution of 1:1 (BHMF: THFDM after 3.5 hours at 100 ºC and under 15 bars H_2). Starting with this result, a series of phosphines and phosphites was screened to improve the conversion and selectivity of the catalytic system. A solvent screening was performed which showed that while $PhCF_3$ led to higher conversion, but this came at the expense of *trans*:*cis* selectivity. Additionally more coordinating solvents affected the selectivity negatively (*cis* product only observed from THF as solvent and MeOH led to the formation of the acetal). Therefore, toluene was used as solvent of choice for the hydrogenation. The ratio of *cis*:*trans* isomers was determined in each case by ^{13}C NMR.[6]

As given in Table 2, an increase in bulk of the aromatic phosphine group increased both the selectivity and the conversion (entries 1 vs 2, 4 vs 5 and 6 vs 7). Similarly, the flexibility of the backbone as well as the preferred bite angle played a role in the activity of the catalyst, H_8-BINAP has a wider angle than BINAP and SEGPHOS the smallest bite angle (entries 1 vs 3 vs 5). A more flexible backbone was also probed, while the selectivity remained comparable, the conversion was lower (entries 5 vs 6). Further P-P ligands were screened with alternate backbones than the bi-phenyl based ones of the earlier attempts: chiraphos and M004-1 were both screened, however both led only to the formation of the *cis*-isomer (entries 8-9). TangPhos displayed a good balance of activity and selectivity (entry 10) and was the subject of further screening (see Table 5). Phosphites usually employed as ligands for the rhodium-catalysed hydroformylation gave comparatively good selectivity but suffered from poor activity (entries 11-12). A xylene-based backbone was tested, however while the selectivity was comparable to that of BINAPs the activity was lower (entry 13).

Table 2: Ruthenium-catalysed hydrogenation employing diphosphine and diphosphite ligands

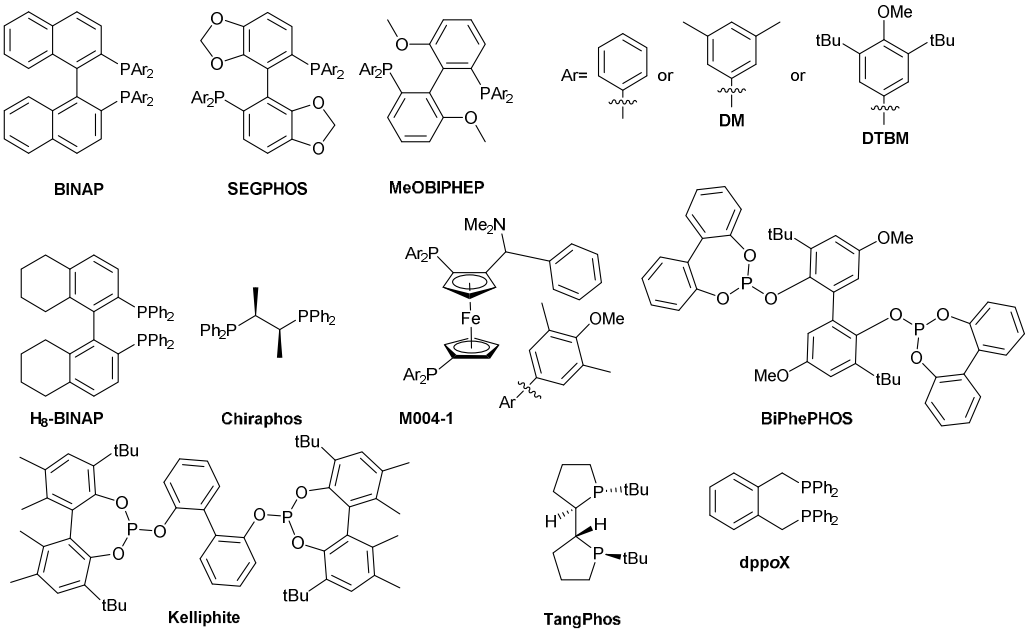
View Article Online
DOI: 10.1039/C8GC01025K



Entry	Metal/Ligand	HMF[a]	BHMF[a]	THFDM[a]	Cis:trans[b]
1	Ru-BINAP-OAc_2 (4.5%)	0.03	1 (71%)	0.34 (28%)	4-5:1 [c]
2	Ru-DM-BINAP-OAc_2 (4.5%)	0.03	1	1.5	4:1
3	Ru-H_8-BINAP-OAc_2 (4.5%)	0.27	1	0.05	-
4	Ru-DM-SEGPHOS-OAc_2 (4.5%)	0.2	1	0.58	4:1
5	DTBM-SEGPHOS-Ru-OAc_2 (4.5%)	0.2-1.2	1	21-26	3.1-3.6:1 [c]
6	DTBM-SEGPHOS (5%) Ru(methylallyl)$_2$COD (4.5%)	trace	1 (3%)	27 (87%)	4.7:1
7	DTBM-MeOBIPHEP (5%) Ru(methylallyl)$_2$COD (4.5%)	0.9	1	6.5-7.7	3.1-3.3:1 [c]
8	Chiraphos (5%) Ru(methylallyl)$_2$COD (4.5%)	0.25	1	1	Cis only
9	M004-1-Ru-acac-BF_4 (4.5%)	0.16	1	0.33	Cis only
10	TangPhos (5%) Ru(methylallyl)$_2$COD (4.5%)	0.02	1	0.65	2.2:1
11	BiPHEPHOS (5%) Ru(methylallyl)$_2$COD (4.5%)	0.28	1	0.27	4:1
12	Kelliphite (5%) Ru(methylallyl)$_2$COD (4.5%)	0.1	1	0.5	1.9-2:1 [c]
13	dppoX (5%) Ru(methylally)$_2$COD	0.03	1	0.1	3.4:1

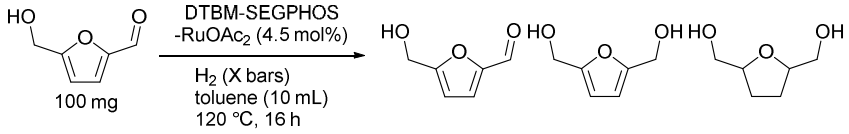
[a]: ratio of products determined from normalised BHMF ^{1}H NMR peak, NMR yield in brackets as determined using hexamethylbenzene as internal standard, [b]: as determined by ratio of ^{13}C NMR peaks, [c]: range of the ratios of *cis*:*trans* diastereomer obtained.

View Article Online
DOI: 10.1039/C8GC01025K



With DTBM-SEGPHOS showing itself to be the most efficient ligand in the early screening, its performance under different pressures of hydrogen was tested (see Table 3). An increase in pressure led to a slight increase in conversion, but at the expense of the desired *trans*-isomer (entries 1-2). Conversely, lowering the pressure to 5 bars led to an increase in *trans*-THFDM but with a sharp drop in the conversion (entry 3). A mercury drop test was performed, which had very minor effect on the reaction, which would indicate that the hydrogenation is performed by a homogeneous Ru-catalyst rather than a heterogeneous one (see Supporting information).

Table 3: Pressure dependence of the hydrogenation

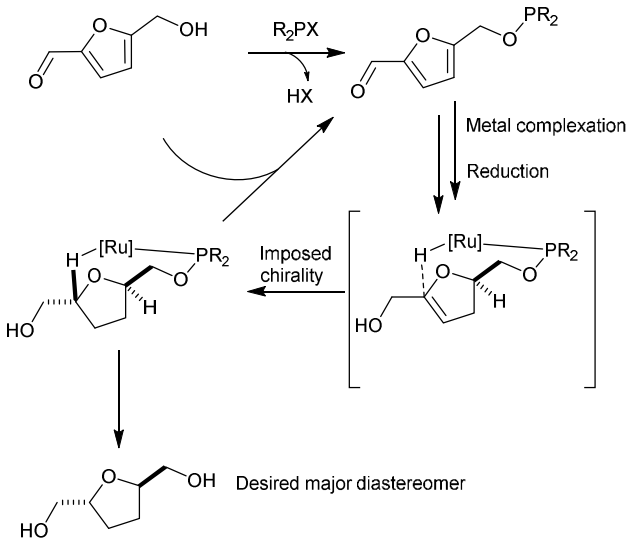


Entry	H_2 pressure ([bar)]	HMF[a]	BHMF[a]	THFDM[a]	Cis:trans[b]
1	70	-	1	23	6.8:1
2	10	0.2-1.2	1	21-26	3.1-3.6:1 [c]
3	5	0.01	1	0.12	1.7:1

[a]: ratio of products determined from normalised BHMF ^{1}H NMR peak, [b]: as determined by ratio of ^{13}C NMR peaks. [c]: range of the ratios of *cis*:*trans* diastereomer obtained.

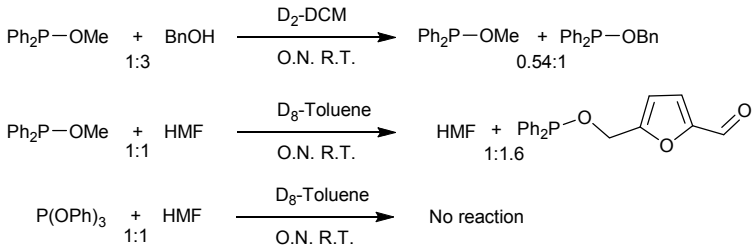
View Article Online
DOI: 10.1039/C8GC01025K

3. Auxiliary ligands



Scheme 2: Auxiliary ligand concept and sought outcome

As hydroformylation ligands proved themselves to have a desirable selectivity, the use of auxiliary ligands, which was pioneered in its field,[19] seemed a plausible solution. In an ideal case, the ruthenium metal centre would be coordinated to the HMF-bound auxiliary group, and after the reduction of one pro-chiral centre, the ligand would impose a preference for a hydrogenation of the remaining olefin leading to a



trans-product, as shown in Scheme 2.

Scheme 3: Phosphonite exchange experiments.

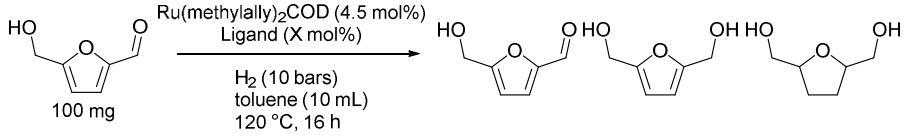
As a proof of this concept three exchange experiments were carried out. This showed that the method was viable, as the OH group from benzyl alcohol and the HMF would displace the methoxide, which by extension indicates that the saturated alcohol of the HMF would be able to replace the P-bound unsaturated alcohol of the product (Scheme 3). However, the phenoxide group proved to bind to the phosphorus preferentially over the HMF. These experiments were carried out at room temperature rather than at 120 ºC (as per reaction conditions) to avoid HMF decomposition which would muddle the results.

An initial screening of the same auxiliary ligand as used by the Breit group (Table 4, entry 1)[19] showed a good selectivity compared to phosphines, however suffered from poor conversion (see Table 2). Attempts to increase the conversion by increasing the pressure to 40 or 70 bar were unsuccessful, mostly decomposition of HMF was observed. One might suspect that a difference in reaction rates of the auxiliary ligand exchange and that of the hydrogenation might have altered the outcome of the reaction.

View Article Online
DOI: 10.1039/C8GC01025K

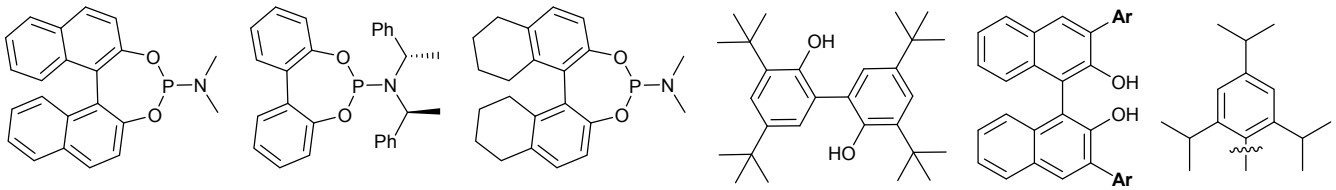
Additionally, replacing the homogeneous pre-catalyst with an equimolar amount of heterogeneous Ru/Al_2O_3 or Ru/C led to negligible conversion under the standard conditions. The analogous phosphinamide provided a higher conversion to THFDM, but at the expense of selectivity (entry 2). A series of three phosphoramidites were screened and while they showed higher stability, the selectivity remained unsatisfactory (entries 3-5). In order to probe the possibility of *in situ* assembly of ligands, $P(OMe)_3$ was employed as sole ligand (entry 6). The *in situ* formation of phosphites is plausible from the reaction of phenols with $P(OMe)_3$, and mixtures which would lead to phosphites were screened for the reduction of HMF. However, as can be seen from entries 7 and 8, the ligand system did not offer any tangible advantage over other screened ligands. Finally, an amino pyridine was screened, which while opening the possibility to N-ligation to the ruthenium, gave unremarkable results (entry 9). In the hope of increasing the auxiliary ligand exchange rate methyl sulfonic acid (5 mol %) was used as an additive but led to a rapid and abundant precipitation of black solid, neither HMF nor any of its reduction products were observed in the ensuing sample.

Table 4: Hydrogenation of HMF with ruthenium and auxiliary ligands



Entry	Ligand	HMF[a]	BHMF[a]	THFDM[a]	Cis:trans[b]
1	PPh_2OMe (10%)	0.02	1 (80%)	0.22 (16%)	1.3:1
2	PPh_2NMe_2 (10%)	0.08	1	0.3	4.7:1
3	MonoPHOS 1 (10%)	0.15	1	0.65	3.7:1
4	MonoPHOS 2 (10%)	0.06	1	0.41	2.3:1
5	MonoPHOS 3 (10%)	0.12	1	0.28	3:1
6	$P(OMe)_3$ (5%)	0.04	1	0.33	4:1
7	$P(OMe)_3$ (10%) + Diol 1 (10%)	0.17	1	0.38	2.5:1
8	$P(OMe)_3$ (10%) + Diol 2 (10%)	0.01	1	0.1	1.9:1
9	2-amino-pyridine (10%)	0.14	1	0.35	4.5:1

[a]: ratio of products determined from normalised BHMF H^1 NMR peak, NMR yield in brackets as determined using hexamethylbenzene as internal standard, [b]: as determined by ratio of C^{13} NMR peaks.

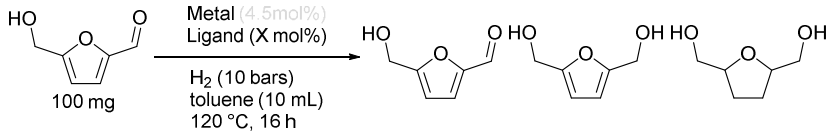


View Article Online
DOI: 10.1039/C8GC01025K

4. Other metals

As ruthenium is expensive and in the hope of obtaining more active catalysts, other metals than Ru were screened. As can be seen in Table 5, nickel proved a passable replacement for ruthenium in the case of a bidentate ligand (Table 2, entry 1 vs. Table 5, entry 1) but was unsuited to the auxiliary ligand methodology (entry 2). Similarly, the NHC-Ni catalyst gave some conversion to the BHMF intermediate, but large amounts of side products and humins were observed (entry 3). Re failed to provide any conversion, however it did not lead to much decomposition either (entry 4). As TangPhos had showed a moderately good combination of resilience and selectivity with ruthenium (see Table 2, entry 9), it was also screened in combination with Ir(COD)Cl and Rh(COD)Cl. However neither of these metal/ligand combinations yielded the desired reduction products, instead leading to heavy degradation of the starting material and sedimentation (entries 5-6).

Table 5: Hydrogenation of HMF with other metals



Entry	Metal/Ligand	HMF[a]	BHMF[a]	THFDM[a]	Cis:trans[b]
1	$Ni(COD)_2$ (4.5%), BINAP (5%)	0.24	1	0.4	4.5:1
2	$Ni(COD)_2$ (4.5%), PPh_2OMe (10%)	0.8	1	-	-
3	$Ni(COD)_2$ (4.5%), IPr: (9%)	1.6	1	-	-
4	$Re(CO)_5$ (4.5%), BINAP (5%)	1	-	-	-
5	Ir (COD) Cl (4.5%), TangPhos (5%)	-	-	-	-
6	Rh (COD)Cl (4.5%), TangPhos (5%)	-	-	-	-

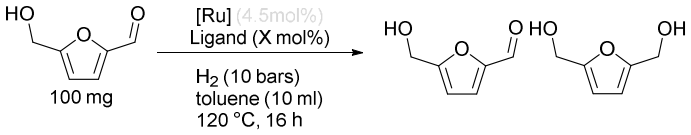
[a]: ratio of products determined from normalised BHMF H^1 NMR peak, [b]: as determined by ratio of C^{13} NMR peaks.

5. Selective reduction to BHMF

Based on the results of hydrogenation employing a pyridine (table 4, entry 9), it appeared that nitrogen containing ligands could be viable. As given in Table 6, only BHMF was observed as product albeit cleanly. Both ethylamine- and methanol-substituted diphenylphosphines provided almost exclusively BHMF as product (entries 1-2). The use of bispyridine as ligand gave the cleanest reduction, with the highest activity of the series (entries 3-4), with an NMR yield of 98% observed with only 1 mol% of Ru. As transient imine directing groups have been recently successfully employed as auxiliaries,[20] an electron rich di-amine, 2-dimethylamino-ethylamine (DMEN), was used (entry 5). Interestingly, DMEN appeared to inhibit the reduction of the aromatic ring by the usually resilient DTBM-SEGPHOS-$RuOAc_2$ catalyst (entry 6). As can be seen from entries 1 and 7, both flexible and highly rigid backbones had negligible effect on the chemo-selectivity of the reaction. The apparent poisoning of the ruthenium centre by the heteroatom, limiting its reactivity to the reduction of aldehydes echoes previous findings by the Janssen group.[4a]

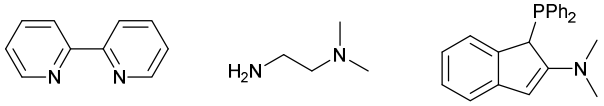
View Article Online
DOI: 10.1039/C8GC01025K

Table 6: Selective hydrogenation of HMF to BHMF



Entry	Ligand/metal source	HMF[a]	BHMF[a,b]	THFDM[a]
1	$PPh_2(C_2H_4)NH_2$ (5%) $Ru(methylallyl)_2COD$ (4.5%)	-	1	traces
2	PPh_2CH_2OH (5%) $Ru(methylallyl)_2COD$ (4.5%)	traces	1	traces
3	Bispyridine (10%) $Ru(methylallyl)_2COD$ (4.5%)	-	1 (94%)	-
4	Bispyridine (2%) $Ru(methylallyl)_2COD$ (1%)	-	1 (98%)	-
5	DMEN (10%) $Ru(methylallyl)_2COD$ (4.5%)	0.01	1	-
6	DMEN (10%) DTBM-SEGPHOS-$RuOAc_2$ (4.5%)	-	1	-
7	AP-Indene (5%) $Ru(methylallyl)_2COD$ (4.5%)	-	1	-

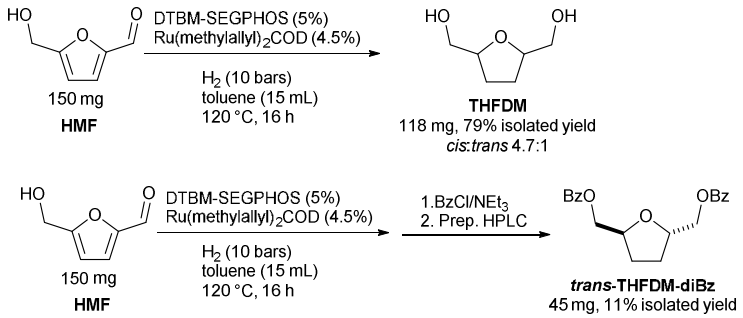
[a]: ratio of products determined from normalised BHMF H^1 NMR peak.; [b]:NMR yield in bracket,



Bispyridine **DMEN** **AP-Indene**

determined using hexamethylbenzene as internal standard.

Having determined that the catalytic system formed *in situ* by DTBM-SEGPHOS in conjunction with a ruthenium pre-catalyst would give the highest conversion (see Table 2), experiments were conducted to isolate the products from the reaction mixture. In keeping with green chemistry principles, the conversion and the purification of the product were conducted without the use of halogenated solvent, leading to an isolated yield of 79% (Scheme 5). These results mirror the results of the screening experiment, with identical *cis*:*trans* ratio observed and a small loss of material due to the purification process. The experiment was repeated but instead of isolating the diol, the corresponding di-benzoate was synthesised (as the presence of THFDM was not registered by the HPLC's UV-detector) and the desired trans-isomer was isolated through two sequential runs of preparative HPLC.



View Article Online
DOI: 10.1039/C8GC01025K

Scheme 5: Reduction and isolation of THFDM and *trans*-THFDM-dibenzoate

Conclusion

In summary, the homogeneous catalysed reduction of HMF to THFDM has been probed for the first time through the use of metal catalysed hydrogenation. Carbene ligands offered moderate activity and selectivity, with a preference for unsaturated backbones (for selectivity) and for bulky aromatic substitution pattern (for conversion). Di-phosphorus containing ligands offered the highest conversion, with DTBM-SEGPHOS leading to a good isolated yield of a mixture of THFDM. Auxiliary ligands were also screened, offering similar results as the phosphites, with comparatively higher selectivity but limited activity. Ruthenium showed itself to be the most active metal, although others were screened for comparison. Additionally, HMF was reduced to BHMF in high selectivity and yield through tactical use of nitrogen containing ligands. However, the current systems suffer from limitations: the need for comparatively high catalytic loading (for an industrial use) which often led to only moderate conversion past the reduction of the aldehyde. In conclusion, we report for the first time the homogeneous reduction of HMF selectively to THFDM, under comparatively mild conditions, with a higher *trans*:*cis* ratio of THFDM than the related heterogeneous systems.

Experimental

Typical reaction conditions: HMF (100 mg.0.79 mmol), the metal salt (4.5 mol%. 0.036 mmol) and the ligand (5 or 10 mol%. 0.040 or 0.079 mmol) were weighted in a microwave vial, dissolved in toluene (10 mL) under argon atmosphere, and sonicated or shaken at ca 250 rpm for up to an hour (until full dissolution of all solids). The solution was transferred into a (nitrogen purged) glass autoclave, purged a further three times with nitrogen (5-10 bars) and then with hydrogen (5-10 bars). The autoclave was pressurised to the desired pressure (typically 10 bars H_2) and heated to 120 ºC. The reaction was stirred overnight (ca 600 rpm), cooled down to room temperature at which point a sample was evaporated to dryness, dissolved in d_6-DMSO and analysed by ^{1}H and ^{13}C NMR spectroscopy.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

CaRLa (Catalysis Research Laboratory) is co-financed by Ruprecht-Karls-Universität Heidelberg (Heidelberg University) and BASF SE.

[1] (a) T. Werpy, G. Petersen, *Top Value Added Chemicals from Biomass. Volume I - Results of Screening for Potential candidates from Sugars and Synthesis Gas*, U. S. D. o. Energy, 2004; (b) J. J. Jozell, G. R. Petersen, *Green Chem.*, 2010, **12**, 539–554; (c) B. H. Shanks, P. L. Keeling, *Green Chem.*, DOI: 10.1039/c7gc00296c

View Article Online
DOI: 10.1039/C8GC01025K

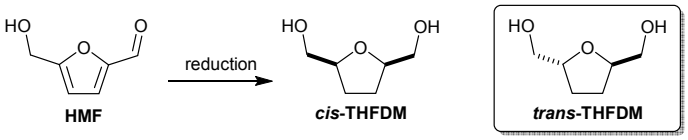
[2] (a) A. S. K. Hashmi, M. Wölfle, J. H. Teles, W. Frey, *Synlett*, 2007, 1747–1752 ; (b) H. A. Rass, N. Essayem, M. Besson, *Green Chem.*, 2013, **15**, 2240–2251; (c) J. Cai, H. Ma, J. Zhang, Q. Song, Z. Du, Y. Huang, J. Xu, *Chem. Eur. J.*, 2013, **19**, 14215–14223; (d) S. Tsupova, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Green Chem.*, 2016, **18**, 5800–5805; (e) X.-Y. Zhang, M.-H. Zong, N. Li, *Green Chem.*, 2017, DOI: 10.1039/c7gc01751k ; (f) P. Domínguez de María, N. Guajardo, *ChemSusChem*, DOI:10.1002/cssc.201701583.
[3] S. H. Krishna, D. J. McClelland, Q. A. Rashke, J. A. Dumesic, G. W. Huber, *Green Chem.*, 2017, **19**, 1278–1285.
[4] (a) E. Jansen, L. S. Jongbloed, D. S. Tromp, M. Lutz, B. de Bruin, C. J. Elsevier, *ChemSusChem*, 2013, **6**, 1737–1744; (b) T. Pasini, G. Solinas, V. Zanotti, S. Albonetti, F. Cavani, A. Vaccari, A. Mazzanti, S. Ranieri, R. Mazzoni, *Dalton Trans.*, 2014, **43**,10224–10234.
[5] (a) J. Ohyama, A. Esaki, Y. Yamamoto, S. Arai, A. Satsuma, *RSC Adv.*, 2013, **3**, 1033–1036 ; (b) A. J. Kumalaputri, G. Bottari, P. M. Erne, H. J. Heeres, K. Barta, *ChemSusChem*, 2014, **7**, 2266–2275; (c) H. Jeong, C. Kim, S. Yang, H. Lee, *J. Catal.*, 2016, **344**, 609–615; (d) N. Perret, A. Grigoropoulos, M. Zanella, T. D. Manning, J. B. Claridge, M. J. Rosseinsky, *ChemSusChem*, 2016, **9**, 521–531.
[6] G. Bottari, A. J. Kumalaputri, K. K. Krawczyk, B. L. Feringa, H. J. Heeres, K. Barta, *ChemSusChem*, 2015, **8**, 1323–1327.
[7] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164–1172.
[8] (a) F.-A. Khan, A. Vallat, G. Süss-Fink, *Catal. Comm.*, 2011, **12**, 1428–1431; (b) Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, *ChemCatChem*, 2012, **4**, 1791–1797; (c)P. Panagiotopoulou, D. G. Vlachos, *App. Catal. A*, 2014, **480**, 17–24; (d) C. Li, G. Xu, X. Liu, Y. Zhang, Y. Fu, *Ind. Eng. Chem. Res.*, 2017, **56**, 8843−8849; (e) S. Sang1, Y. Wang, W. Zhu, G. Xiao, *Res Chem Intermed*, 2017, **43**, 1179–1195; (f) Z. Zhang, J. Song, Z. Jiang, Q. Meng, P. Zhang, B. Han, *ChemCatChem*, 2017, **9**, 2448 –2452.
[9] X. Hu, R. J. M. Westerhof, L. Wu, D. Dong, C.-Z. Li *Green Chem.*, 2015, **17**, 219–224.
[10] (a) E. Hagsberg, S. J. Howard, K. Stensrud, Oligomerizations of FDCA and glycols in a one-pot esterification-transesterification process catalyzed by homogeneous organometallic lewis acids, **2017**, WO2017091435 A1; (b) S. J. Howard, K. Stensrud, Oligomers of FDCA and glycols from a one-pot esterification-transesterification process using water-tolerant metal triflate catalyst, **2017**, WO2017091412 A1
[11] (a) M. He, D.-Q. Zhou, H.-L. Ge, M.-Y. Huan g, Y.-Y.Jiang, *Polym. Adv. Technol.*, 2003, **14**, 273–277; (b) W.-L. Wei, H.-Y. Zhu, C.-L. Zhao, M.-Y.Huang, Y.-Y. Jiang, *React. Funct. Polym.*, 2004, **59**, 33–39.
[12] (a) T.Ohta, T. Miyake, N. Seido, H. Kumobayashi, H. Takaya, *J. Org. Chem.*, 1995, **60**, 357–363; (b) M. Studer, C. Wedemeyer-Exl, F. Spindler, H.-U. Blaser, *Monatsch Chem*., 2000, **131**, 1335–1343; (c) S. Kaiser, S. P. Smidt, A. Pfaltz, *Angew. Chem. Int. Ed.*, 2006, **45**, 5194–5197.
[13] A. S. Gowda, doctoral dissertation, *University of Kentucky*, 2013, Hydrogenation and hydrogenolysis of furan derivatives using bipyridine-based electrophilic ruthenium(II) catalysis.
[14] (a) P. Feiertag, M. Albert, U. Nettekoven, F. Spindler, *Org. Lett.*, 2006, **8**, 4133–4135; (b) J. Wysocki, N. Ortega, F. Glorius, *Angew. Chem. Int. Ed.*, 2014, **53**, 8751–8755; (c) L. Pauli, R. Tannert, R. Scheil, A. Pfaltz, *Chem. Eur. J.*, 2015, **21**, 1482–1487.
[15] The dark precipitate formed was best removed from the glass autoclave by soaking for several days in a KOH/iPrOH solution, followed by a night in a dilute aqueous HCl bath.
[16] For a recent review on the synthesis of HMF, which also touches upon the formation of humins, see: R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499–1597.
[17] T. Wurm, doctoral dissertation, *Ruprecht-Karls-Universität Heidelberg*, **2017**, Vinyl- und Arylkationintermediate in der Goldkatalyse sowie neue Ligandenkonzepte für Goldkatalysatoren.
[18] (a) K. Satoh, M. Inenaga, K. Kanai, *Tetrahedron: Asymmetry*, 1998, **9**, 2657–2662; (b) C. Y. Legault, A. B. Charette, *J. Am. Chem. Soc.*, 2005, **127**, 8966–8967 (c) W.J. Tang, J.Tan, L.J. Xu, K.H. Lam, G.H. Fan, A.S.C. Chan, *Adv. Synth. Catal.*, 2010, **352**, 1055–1062; (d) W. Tang, Y. Sun, L. Xu, T. Wang, Q. Fan, K.-H. Lam, A, S. C. Chan *Org. Biomol. Chem.*, 2010, **8**, 3464–3471 (e) S. Urban, N. Ortega, F. Glorius, *Angew. Chem. Int. Ed.*, 2011, **50**, 3803–3806; (f) Z.-S. Ye, M.-W. Chen, Q.-A. Chen, L. Shi, Y. Duan, Y.-G. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10181–10184; (g) A. Cadu, P. K. Upadhyay, P. G. Andersson, *Asian J. Org. Chem.*, 2013, **2**, 1061–1065; (h) Y. Kita, K. Yamaji, K. Higashida, K. Sathaiah, A. Iimuro, K. Mashima, *Chem. Eur. J.*, 2015, **21**, 1915–1927; (i) A. Iimuro, K. Higashida, Y. Kita, K. Mashima, *Adv. Synth. Catal.*, 2016, **358**, 1929–1933.
[19] (a) C. U. Grünanger, B. Breit, *Angew. Chem. Int. Ed.*, 2008, **47**, 7346–7349; (b) T. E. Lightburn, M. T. Dombrowski, K. L. Tan, *J. Am. Chem. Soc.*, 2008, **130**, 9210–9211; (c) A. D. Worthy, M. M. Gagnon, M. T. Dombrowski, K. L. Tan, *Org. Lett.*, 2009, **11**, 2764–2767; (d) C. U. Grünanger, B. Breit, *Angew. Chem. Int. Ed.*,

View Article Online
DOI: 10.1039/C8GC01025K

2010, **49**, 967–970; (e) Candice L. Joe, Thomas P. Blaisdell, Allison F. Geoghan, and Kian L. Tan, *J. Am. Chem. Soc.*, 2014, **136**, 8556−8559; (f) K. Yang, Q. Li, Y. Liu, G. Li, H. Ge, *J. Am. Chem. Soc*., 2016, **138**, 12775−12778.
[20] S. St John-Campbell, A. J. P. White, J. A. Bull, *Chem. Sci.*, 2017, DOI 10.1039/C7SC01218G.

View Article Online
DOI: 10.1039/C8GC01025K

table of contents entry



Homogeneous Ru-catalyzed hydrogenation of HMF delivers a high percentage of *trans*-THFDM rather than only *cis*-THFDM known from heterogeneous hydrogenation.