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Authors: Eduardo J. Garcia-Suarez, Dario Paolicchi, Hu Li, Jian He, Song Yang, Anders Riisager, Shunmugavel Saravanamurugan

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Pd-catalysed formation of ester products from cascade reaction of 5-hydroxymethylfurfural with 1-hexene

Eduardo J. Garcia-Suarez[a,b,c], Dario Paolicchi[a#], Hu Li[d#], Jian He[a,d#], Song Yang[d], Anders Riisager[a*], Shunmugavel Saravanamurugan[a,e*]

[a]Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.

E-mail: ar@kemi.dtu.dk

[b]Tecnalia, Energy and Environment Division, Parque Tecnológico de Álava, Leonardo Da Vinci 11, 01510 Miñano, Spain

[c]IKERBASQUE, Basque Foundation for Science, Maria Díaz de Haro 3, 48013 Bilbao, Spain.

[d]State-Local Joint Engineering Lab for Comprehensive Utilisation of Biomass, Center for R&D of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, China.

[e]Laboratory of Bioproduct Chemistry, Center of Innovative and Applied Bioprocessing (CIAB), Mohali-140306, Punjab, India.

Email: saravana@ciab.res.in

[#] These authors equally contributed

Graphical abstract

Valorisation with *in-situ* CO/H$_2$
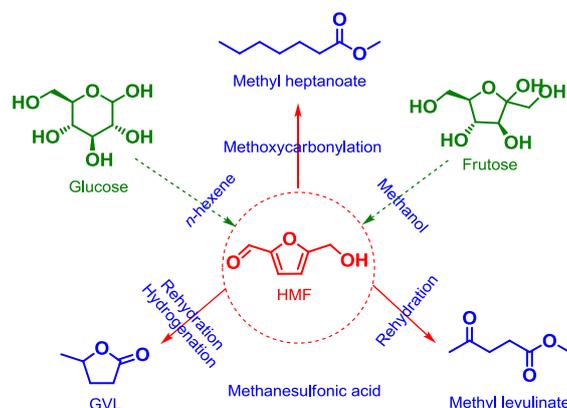
Highlights

- ❖ Methoxycarbonylation of 1-hexene to methyl hepatanoate using HMF as CO surrogate with Pd-complex is studied in methanol.
- ❖ Methyl levulinate and GVL are found to be other major ester products when changing the concentration of acid additive.
- ❖ The influence of phosphine ligand and Pd source on the yield of ester products is investigated.
- ❖ The direct conversion of sugars, such as glucose, fructose and xylose to ester products is studied in methanol with Pd-complex in the presence of 1-hexene and acid additive.

Abstract

A cascade reaction involving decarbonylation of 5-hydroxymethylfurfural (HMF) followed by methoxycarbonylation of 1-hexene produces methyl heptanoate (MH) using a catalytic system composed of a Pd-phosphine complex and methanesulfonic acid (MSA) co-catalyst at moderate reaction temperature. Concomitant hydration of HMF followed by hydrogenation of methyl levulinate (ML) to γ-valerolactone (GVL) occurs with the catalytic system under the same reaction

conditions using HMF and methanol as the source of CO and H_2, respectively. Under optimized reaction conditions, about 50% of MH along with 12% ML and 35% GVL is obtained from HMF using Pd(dba)2-(1,2-bis(di-tert-butylphosphinomethyl)benzene) (DTBPMB), MSA and 1-hexene in methanol at 120 °C. Interestingly, sugars, such as glucose, fructose and xylose, are able to be converted to MH, ML and GVL as well. Isotopic labeling studies with $^{13}C_1$-fructose in methanol-d_4 and ^{13}C-methanol-d_4 confirm that H_2 originates from methanol, while CO generates predominantly from the formyl group of the HMF formed by fructose dehydration.

1. Introduction

The projection of limited fossil resources in the future has strived research to implement sustainable alternative feeds stocks, such as lignocellulosic biomass, in order to keep the value chain of chemicals [1-3]. In this context, a wide range of single reactions including aldol/retro-aldol, oxidation, reduction, hydrogenolysis, dehydration, decarbonylation, decarboxylation and dehydrogenation have been extensively studied in the past decade to valorize biomass-based substrates like glucose to added-value compounds that could potentially substitute the ones

derived from fossil resources [4-8]. Especially, the dehydration of glucose to 5-hydroxymethylfurfural (HMF) and its catalytic oxidation have been comprehensively investigated [10-17]. In addition, decarbonylation of furanics, such as HMF and furfural to furfural and furan, respectively, has also been thoroughly explored using metal-containing catalysts [18,19]. However, to the best of our knowledge, no study has been reported about the use of in-situ generated CO from furanics to generate other chemicals of potential interest in cascade, e.g. via alkoxycarbonylation of olefins.

Alkoxycarbonylation of olefins is an atom-efficient and important transformation for C-C bond formation in which alkenes are converted into esters/acids in the presence of CO, alcohol, a strong acid (typically sulfuric acid or methanesulfonic acid, MSA), and a metal-complex catalyst which usually is Pd-based. The reaction has already been widely studied to improve the catalytic system in terms of yield, recycling and easy product recovery as the products (esters/acids) have a wide spectrum of applications for production of fine and bulk chemicals [20-32]. Normally, fossil-derived CO gas supply in the processes is from pressurized external gas cylinders. Particularly, for smaller-scale applications this introduces some challenges and limitations, since CO gas is dangerous to handle and store due to its high toxicity and flammability and processing is not cost-efficient. To overcome these drawbacks, an alternative approach is to use biomass-based substrates, such as HMF and furfural, as CO surrogates. Regarding this, decarbonylation of furfural (FURAL) and HMF with Pd-based catalysts have separately been reported to achieve near quantitative yield of the corresponding products furan (98%) and furfuryl alcohol (96%), respectively [33, 34]. However, this study did not disclose to make use of in-situ produced CO to other chemicals.

This work presents a proof-of-concept study on the use of biomass-derived CO to produce methyl heptanoate (MH) with 1-hexene over a Pd-phosphine catalyst system in methanol at moderate reaction temperature. The applied phosphine ligand is diphoshine 1,2-bis(di-tert-butylphosphinomethyl)benzene (DTBPMB), which previously has shown excellent performance in Pd-catalyzed methoxycarbonylation [28,31,32]. Notably, the study not only focuses on the reaction cascade of decarbonylation followed by methoxycarbonylation, but also on the hydrogenation of methyl levulinate (ML) formed from HMF, to γ-valerolactone (GVL) (Scheme 1). Formation of GVL from HMF/fructose/glucose has previously been reported using various dual catalyst systems (acid plus metal catalyst) in

the presence of formic acid or under H_2 pressure in a two-step approach, affording overall yield of GVL about 50% [35-37]. However, the present study focuses on one-pot, one-step production of esters employing methanol as solvent as well as CO and H_2 source in the absence of external added H_2. The influence of the palladium source, the amount of acid additive, and various furanics such as, e.g. FURAL, furfuryl alcohol (FUROL), 5-methylfurfural and (5-methyl-2-furyl)methanol as CO source, on the yield of MH, ML and GVL are investigated.

Scheme 1. Pd-phosphine catalyzed cascade transformation of HMF to ester products.

2. Experimental Section

All reactions were performed in 15 mL Ace pressure tubes with appropriate amounts of 5-hydroxymethylfurfural, Pd(OAc)$_2$, DTBPMB ligand, n-hexene, methanesulfonic acid, and methanol, otherwise unless stated. The tube was inserted into a preheated oil bath and stirring started when the temperature set point was reached. After a desired reaction time, the tube was quenched in cold water, and aliquots of the reaction mixture withdrawn and analyzed in GC-FID (Agilent 6890N instrument, HP-5MS capillary column) and GC-MS (Agilent 6850GC system coupled with an Agilent 5975C mass detector) for quantification and identification of products. Substrate conversion and product yield were calculated using series of individual standards with naphthalene as internal standard. Yields of MH were calculated supposing that each mole of HMF gave one mole of CO, which eventually converted into MH during the methoxycarbonylation reaction. MH yield for the background experiment (Table 2, entry 7) was calculated by assuming a maximum of one mole of methanol being converted to MH. For the isotope labelling study, ^1H and $^{13}C\{H1\}$ NMR spectra of pure chemicals and mixtures

obtained from reactions performed under optimal conditions with isotope labeled $^{13}C_1$-fructose or normal fructose in MeOH-d_4 or ^{13}C-MeOH-d_4 were recorded on a JEOL-ECX 500 NMR spectrometer.

3. Results and Discussion

3.1 Influence of MSA

Initially, catalytic conversion of HMF with 1-hexene in methanol with Pd-DTBPMB catalyst was examined to optimize the addition of acid (MSA) on the yield of MH, as acid is required to form and stabilize catalytically active Pd species in the methoxycarbonylation reaction [38-40]. As shown in Table 1, no MH formed in the absence of MSA in the reaction mixture as expected (Table 1, entry 1). Upon addition of 15 µL of MSA, 29.3% of MH formed with a fair yield of 52.4% of ML and 2.2% of GVL after 20 h of reaction (entry 2). Interestingly, a further increase in acid amount (65 µL) enhanced the yield of MH to 41.2% along with 25.4 and 39.5% of ML and GVL, respectively (entry 4), whereas higher acid amount (80-100 µL) decreased the MH yield presumably due to protonation of the phosphine ligand and following lack of Pd complex stability. In contrast, both the yields of ML and GVL remained here largely unchanged. These initial results clearly indicated that the Pd-phosphine systems not only catalyzed the decarbonylation of HMF followed by methoxycarbonylation of 1-hexene with methanol and the CO liberated from HMF, but also the hydrogenation of ML formed from the hydration of HMF into GVL.

Table 1. Influence of MSA amount on product yields.[a]

Entry	MSA (µL)	HMF conv. (%)	Yield (%)		
			MH	ML	GVL
1	0	50.1[b]	0.0	0.0	0.0

2	15	>99	29.3	52.4	2.2
3	30	>99	35.7	27.7	27.6
4	65	>99	41.2	25.4	39.5
5	80	>99	31.7	25.9	33.1
6	100	>99	36.4	25.6	39.3

[a] Reaction conditions: $Pd(OAc)_2$ (0.025 mmol); HMF (1 mmol); DTBPMB ligand (0.125 mmol); 1-hexene (1.8 mmol); MeOH (5 mL), 120 °C, 20 h. [b] Mainly aldolization product.

3.2 Influence of furanic and other substrates

In order to substantiate the origin of CO and H_2 generated from the aldehyde and methyl hydroxy moieties of HMF, reference compounds as well as alternative furanic substrates were employed for the conversion to MH, ML and GVL (Table 2). Based on results from the investigations a plausible reaction pathway is proposed in Scheme 2. A reference experiment with ML in methanol under identical reaction conditions as the initial experiments, resulted in 49.6% conversion of ML into GVL, revealing that methanol was H-donor for the hydrogenation (Table 2, entry 6). Moreover, an experiments with methyl formate (MF), which formed along with ML from HMF during the reaction under similar conditions, yielded MH (18.1%) but neither ML nor GVL formed, implying that the CO for the methoxycarbonylation was partially generated from MF, possibly by decomposition of initially formed formaldehyde (entry 5)[41]. Moreover, H_2 might have generated from the decomposition of formate ions and participated in the methoxycarbonylation reaction to slightly enhance the yield of MH, as there was no transformation of ML to GVL. Other by-products, including methyl 2-methylhexanoate (5-7%, IMH), isomer of MH, was further observed by GC-MS analysis confirming that formation of the linear ester was predominant over the branched (Table S1). In addition, the hydrogenated byproduct 2,5-hexadione (HD) was also found as also reported previously for HMF hydrogenation [42] (Table S1).

Table 2. Influence of substrate on product yields.[a]

Entry	Substrate	Conv. (%)	Yield (%)	

			MH	ML	GVL
1	Furfuryl alcohol	>99	19.3	21.4	19.5
2	Furfural	>99	25.0	24.6	23.2
3	5-methylfurfural	>99	16.6	2.5	0.0
4	5-methylfurfuryl alcohol	>99	17.6	0.0	0.0
5	Methyl formate	24.9	18.1	0.0	0.0
6	Methyl levulinate	63.2	0.0	36.8[b]	49.6
7	-	-	8.0	0.0	0.0

[a] Reaction conditions: $Pd(OAc)_2$ (0.025 mmol); Substrate (1 mmol); MSA (65 μL; 1 mmol); DTBPMB ligand (0.125 mmol); 1-hexene (1.8 mmol); MeOH (5 mL), 120 ° C, 20 h. [b] Unconverted ML.

The alternative furanic compound FUROL yielded 19.3% MH along with 21.4 and 19.5% of ML and GVL, respectively (Table 2, entry 1), inferring that FUROL could produce ML but not formic acid/MF under the applied reaction conditions. This demonstrated that CO and H_2 originated from the decomposition of the methyl hydroxy moiety of FUROL, as also suggested by the formation of formaldehyde dimethylacetal (found by GC-MS analysis). With FURAL as substrate the MH yield was improved ca. 30% (from 19.3 to 25%), exhibiting enhanced decarbonylation of FURAL followed by 1-hexene methoxycarbonylation (Table 2,
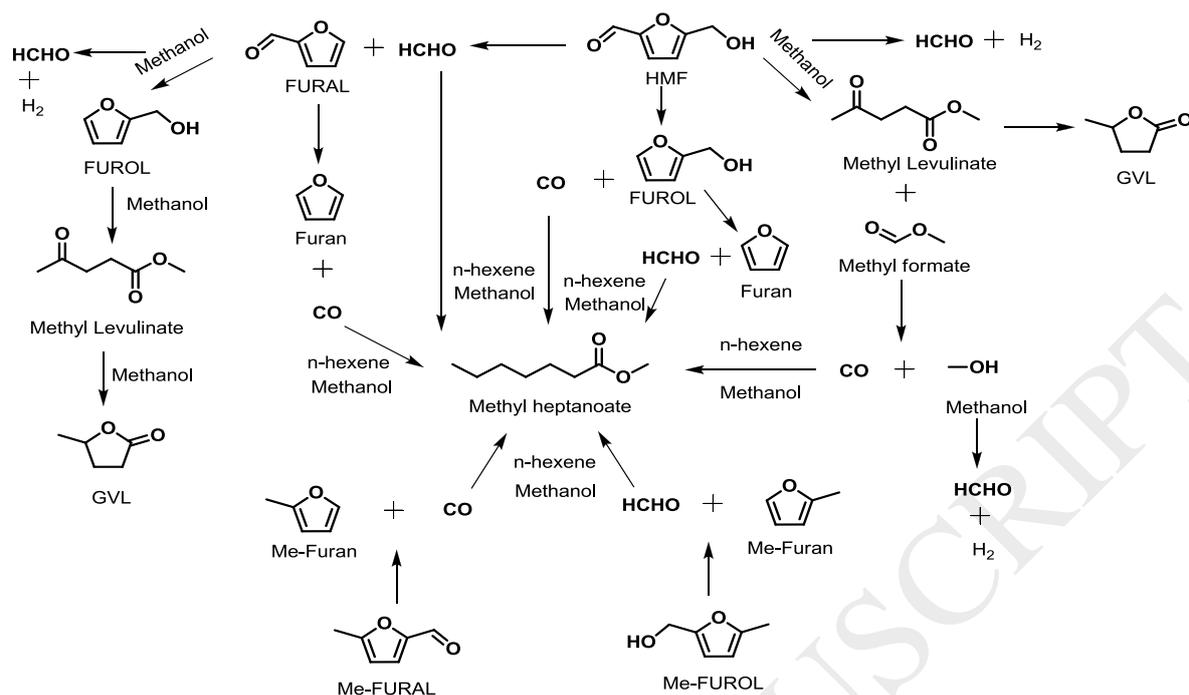
Scheme 2. Plausible reaction pathway for the formation MH, ML and GVL from furanic compounds under the applied reaction conditions.

entry 2). Furthermore, yields of 16.6 and 17.6% of MH were found when 5-methylfurfural (Me-FURAL) and 5-methylfurfuryl alcohol (Me-FUROL), respectively, were used as substrates (Table 2, entries 3 and 4). Aliquots of the reaction mixtures were subjected to GC-MS analysis and no decarbonylated product, i.e. 2-methylfuran, was found, implying that this product was highly unstable under the reaction conditions (Figure S1). In line with this, no unreacted furan or 2-methylfuran were found in the GC-MS chromatograms after reactions where the substrates were employed separately, substantiating that these products were indeed highly unstable during the reaction under this conditions (Figure S2). Notably, formation of MH (8%) also occurred when using only 1-hexene as substrate in methanol, evidencing that solvent reformed took place to a small extent (Table 2). Hence, overall the obtained results substantiated that the CO source when using HMF as substrate were predominantly the aldehyde and the methyl hydroxy moiety of HMF (product distributions from all experiments are compiled in Table S2). However, it cannot be ruled out that CO was not also generated from methanol and the generated CO might have partly reacted with n-hexene to form methyl heptanoate.
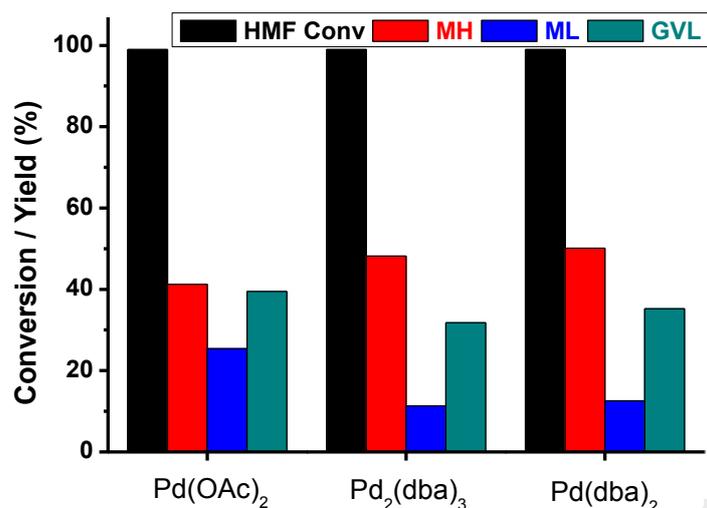
Figure 1. The influence of Pd source on the yield of MH. Reaction conditions: Pd (0.025 mmol); HMF (1 mmol); MSA (65 µL; 1 mmol); DTBPMB ligand (0.125 mmol); 1-hexene (1.8 mmol); MeOH (5 mL), 120 °C, 20 h.

3.3 Influence of Pd precursor and ligand

The influence of the Pd precursor on the MH formation from HMF was investigated after optimizing the reaction time and temperature (Table S3) under identical reaction conditions as previous experiments (Figure 1). The yield of MH improved to 48-50% from 41% with significant amount of GVL (30-35%) when changing $Pd(OAc)_2$ to $Pd_2(dba)_3$ or $Pd(dba)_2$, (dba: dibenzylideneacetone), signifying that the Pd source was indeed important for the reaction (Table S4). Similar enhancement in MH yield was also obtained with half or twice of Pd loading, whereas only ML (87%) and no GVL or MH formed in absence of Pd (Figure S3). Furthermore, to shed light on the role of the ligand the monophosphine ligand triphenylphosphine (TPP) was used instead of DTBPMB along with $Pd(OAc)_2$ but here no MH formed (Figure 2). Instead, the $Pd(OAc)_2$-TPP system rendered a fair yield of ML (61%) which was similar to the ML yield (77%) obtained without added ligand. Importantly, no MH nor GVL formed in these latter systems, clearly showing that the presence of DTBPMB ligand in the Pd catalyst system was indispensable to form MH and GVL by methoxycarbonylation and hydrogenation/cyclisation, respectively.
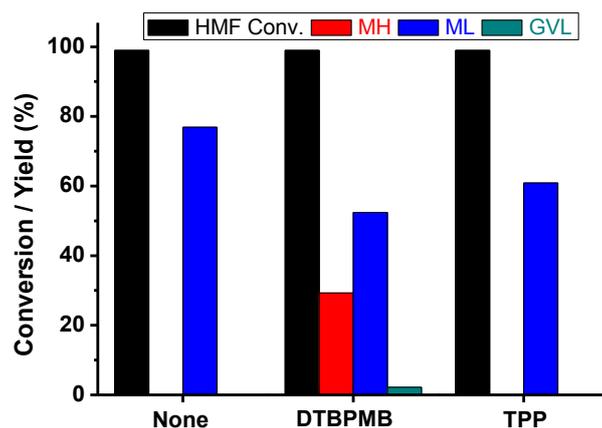
Figure 2. The influence of phosphine ligand on the yield of MH, ML and GVL. Reaction conditions: Pd (0.025 mmol); HMF (1 mmol); MSA (65 μL; 1mmol); ligand (0.125 mmol); 1-hexene (1.8 mmol); MeOH (5 mL); 120 °C, 20 h.

3.4 Influence of sugars as substrate

Attempts was also made to extend the reaction protocol with the Pd(OAc)$_2$-phosphine system to C6 and C5 sugars, such as glucose, fructose and xylose. Here, fructose and xylose yielded about 18% of MH along with significant amount of ML and GVL, whereas glucose yielded only 8.8% of MH under identical reaction conditions (Table 3). This suggested that fructose dehydrated in the presence of the strong mineral acid MSA to HMF followed by decarbonylation and/or rehydration to form ML and formic acid/MF as well as MH.

Table 3. Conversion of sugars to MH, ML and GVL.[a]

Entry	Substrate	Conv. (%)	Yield (%)		
			MH	ML	GVL
1	Glucose	>99	8.8	24.1	1.7
2	Fructose	>99	17.8	30.1	19.1
3	Xylose	>99	17.5	24.6	19.0

[a] Reaction conditions: Pd(OAc)$_2$ (0.025 mmol); substrate (1 mmol); MSA (65 μL; 1 mmol); DTBPMB (0.125 mmol); 1-hexene (1.8 mmol), MeOH (5 ml); 120 °C, 20 h.

3.5 Validating origin of CO and H_2 with NMR studies

In order to corroborate the origin of CO and H_2 from the employed sugar substrates leading to the formation of MH and GVL, respectively, NMR studies were performed with normal and $^{13}C_1$-fructose in deuterated methanol-d4. In the ^1H NMR spectrum of the reaction mixture (Figure S4), the c3 (2.3 ppm) and b3 (4.6 ppm) GVL protons were absent probably due to the incorporation of deuterium. Especially, the formation of deuterium-labelled b3 suggested that methanol was the source for H_2 during the reaction. This was further substantiated by performing the experiment with $^{13}C_1$-fructose in normal methanol, where a peak appeared for the respective proton in GVL (δ 4.5 ppm, b3 proton of GVL) which originated from methanol as H_2-donor. (Figure S5) On the other hand, the protons in e2 (1.6 ppm), f2 (2.3 ppm), and g2 (3.6 ppm) positions of the formed MH disappeared due to either introduction of $-OCD_3$ by reaction with methanol (for g2), or fast ion exchange between hydrogens in the double bond of 1-hexene and deuterium in the hydroxyl group of methanol-d4 (for e2 and f2). The appearance of the g2 peak (Figure S5) of MH from the experiment with normal methanol confirmed that $-OCH_3$ was generated from methanol. The absence of proton signals from e1 (5.8 ppm) and f1 (5.0 ppm, partially overlapped with the solvent methanol-d4) of 1-hexene supported the occurrence of H/D exchange. In case of ML, the addition of $-OCD_3$ from methanol-d4 cause disappearance of the d4 (3.6 ppm) protons, and the incorporation of deuterium in the b4 (2.7 ppm) position of ML resulted possibly due to H/D exchange between the furan-ring of the upstream intermediate (e.g., HMF) and deuterium in the $-OD$ group of methanol-d4. Figure S5 revealed the d4 peak of ML due to the introduction of $-OCH_3$ from methanol, evidencing the role of the methanol. It is worth noting that a small singlet resonance at 4.5 ppm in the spectrum of reaction mixture indicated presence of H species assigned to H_2, thus implying formation of Pd hydride species during the reaction [43].

Comparison of the ^{13}C NMR spectra of $^{13}C_1$-fructose with the reaction mixture with $^{13}C_1$-fructose in methanol-d4 (Figure S6) and normal fructose in ^{13}C-methanol-d4 (Figure S7) indicated almost complete conversion of $^{13}C_1$-fructose. Moreover, a new peak appeared at around 173.1 ppm (Figure S6) assigned to $^{13}C=O$ in the ester of MH, while no corresponding peak was found when using normal fructose as substrate even in the presence of ^{13}C-methanol-d4 (Figure S7). However, MH was formed as confirmed by GC-MS (vide supra) when the experiment was performed with 1-hexene as substrate (Table S2). Combined, the NMR results corroborate that the formyl group of HMF, which formed in-situ from fructose by dehydration

during the reaction, was the predominant source for CO species for the methoxycarbonylation of 1-hexene.

4. Conclusions

In summary, this work demonstrates a novel and alternative approach where furanic compounds, such as HMF and furfural, are CO surrogates for the conversion of 1-hexene to MH by methoxycarbonylation with a Pd-catalyst system based on the diphosphine DTBPMB and MSA. The catalytic system yielded not only the methoxycarbonylated product MH (up to 50%) but also ML and its hydrogenated product GVL, revealing that methanol acted as source of H_2 in the system. This was confirmed by complementary experiments with ML in methanol, where up to 50% GVL formed. Supporting experiments with other furanic and reference compounds as substrates revealed that both aldehyde and methyl hydroxy moieties were potential sources of CO in the reaction system. Isotopic labeling studies with normal fructose or $^{13}C_1$-fructose in methanol-d_4 or ^{13}C-methanol-d_4 further corroborated that H_2 and CO originated from methanol and the formyl group of HMF formed by fructose dehydration, respectively. However, CO might also have originated from formaldehyde derived from methanol and reacted partly with n-hexene to form methyl heptanoate. Finally, the substrate scope of the reaction protocol was extended to the direct transformation of C5 and C6 sugars. Here, results clearly showed that the catalyst system was indeed able to convert the sugars into high valuable products such as MH, ML and GVL in significant amounts paving the way for upgrading biomass-containing hexoses and pentoses. However, further improvement to the catalytic system is required to enhance the yields of the respective products to close the carbon balance.

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