Postprint

# Selective, metal-catalyzed transfer of H₂ and CO from polyols to alkenes

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To reduce societal dependency on fossil fuels, we must develop practical methods for converting sugars and other renewable feedstocks into suitable starting materials for organic synthesis. The polyols that make up cellulosic biomass have a high O/C ratio and are thus very hydrophilic, contrary the petroleum products around which most chemical industries are built.[1] Hence, the transformation of the secondary alcohols, i.e. −CHOH functionalities, found in sugars to more lipophilic and synthetically useful compounds is a major challenge.

Among the most highly developed methods for transforming biomass is gasification at high temperature (typically 700-900 °C) to yield a gas-mixture rich in hydrogen and carbon monoxide, synthesis gas.[2] Synthesis gas is a versatile reagent that can be used in many reactions including alcohol or Fischer-Tropsch synthesis to produce fuels and chemicals.[3] In recent years, aqueous phase reforming has emerged as an attractive method to produce syngas from aqueous solutions of polyols and sugars.[4] Although this has allowed H₂−CO mixtures to be produced more selectively and under milder conditions,[5] the processes still requires high temperatures and pressures.

Recently, Olsen and Madsen reported the selective removal of mono-alcohols by iridium catalysts, presumably liberating hydrogen and carbon monoxide gas in a one-to-one ratio (Scheme 1).[6] Sadow and co-workers have also demonstrated the same overall metal-catalyzed reaction with photochemical activation.[7]
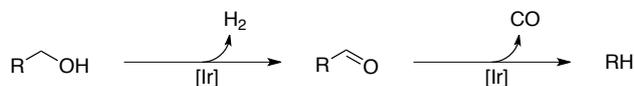
Scheme 1. The iridium-catalyzed tandem dehydrogenation-decarbonylation of an alcohol should liberate H₂ and CO in a 1:1 ratio.

We envisioned that this process could also be applied to polyols in order to produce highly pure syngas. C2−C6 polyols are frequently appointed as future platform chemicals[8] because they are inexpensive and readily available from polysaccharides.[9] As these chemicals contain C and O in a 1:1 ratio, the reaction should

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theoretically degrade them completely to CO and H₂, with the only byproduct being one equivalent of H₂ gas. Furthermore, if the H₂ and CO produced were used directly in the hydroformylation of alkenes, this would be an efficient method for incorporating biomass-derived −CHOH functionalities into high-value chemicals. Hydroformylation is one of the most commercially important homogeneous metal-catalyzed reactions,[10] and using it without the need to transport or store high-pressure cylinders of flammable and toxic gases would be an additional benefit of the degradation of polyols to syngas.

Here, we show that the hydroformylation of alkenes can indeed be performed using a low-pressure mixture of hydrogen and carbon monoxide that is produced *ex situ* by the selective iridium-catalyzed dehydrogenation-decarbonylation of polyols. A simple dual-reactor setup (Scheme 2) was used to convert olefins to aldehydes in high yields using inexpensive C3 to C6 polyols as syngas sources.
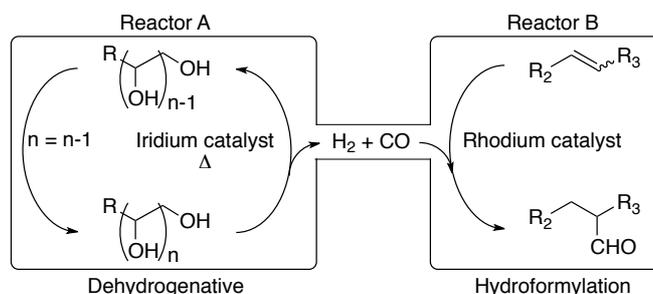
Scheme 2. Apparatus used to transfer CHOH from polyols, via iridium-catalyzed dehydrogenation-decarbonylation, to *ex situ* alkenes via rhodium-catalyzed hydroformylation.

For the hydroformylation reaction, we chose to use Wilkinson's hydroformylation catalyst, Rh(H)(CO)(PPh₃)₃, one of the few hydroformylation catalysts that have proven efficient even under very mild reaction conditions.[11] As hydroformylation is sensitive to steric bulk and also sometimes accompanied by undesired alkene isomerization,[12] we used styrene as the model alkene while developing this system.

We began by using the primary mono-alcohol, 2-(naphthalen-2-yl)ethanol, **1** as the syngas source and reaction conditions similar to those previously reported for the dehydrogenative decarbonylation (Table 1, entry 1).[6] [Ir(cod)Cl]₂ (2.5 mol%) and (*S*)-BINAP (5.0 mol%) were used as pre-catalysts. In order to ensure complete conversion of styrene 1.5 equivalents of the alcohol (with respect to the alkene) were used. After sealing the system under an atmosphere of argon, reactor **A** was heated to 185 °C for 44 h. The pressure in the system was recorded during the reaction and the partial pressure of produced gases was approximately constant at ~130 mbar. ¹H NMR analysis of the hydroformylation solution showed complete conversion of styrene and 98% yield of aldehydes as a 3:2 ratio of the linear and branched products. Interestingly, the preference for the linear product is contrary to what is observed under a full

atmosphere of syngas[11b] where the branched aldehyde is the major product. Although selectively producing linear aldehydes from styrenes have been a challenge in hydroformylation chemistry, catalyst development has allowed the selective synthesis of both branched and linear products under a variety of reaction conditions.[13] Analysis of the residues in the syngas producing reactor **A** revealed that 93% of the alcohol had been consumed, giving β-methylnaphthalene in 85% yield. Small amounts of the corresponding aldehyde were also detected.
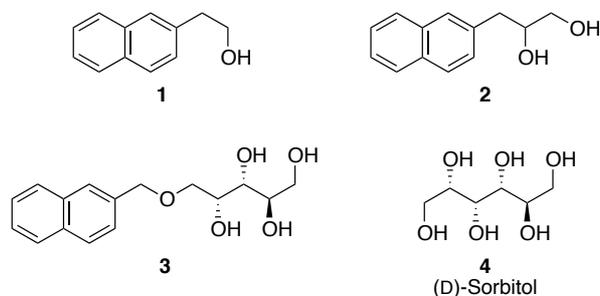

Figure 1. Substrates for dehydrogenative decarbonylation in reactor **A** (refer to Scheme 2).

Following the successful transfer of H_2 and CO from a mono-alcohol to styrene, we tested the structurally similar 1,2-diol **2** as syngas source (Table 1, entry 2). The catalyst loading and diol:alkene ratio, calculated based on the number of –CHOH groups, were maintained at 5 mol% and 1.5:1, respectively; thus these quantities were 10 mol% and 0.75:1 when calculated based on the moles of **2**. The alkene was again fully consumed over 44 h, but the yield of aldehydes dropped to 85% in favour of the hydrogenated product ethylbenzene which was obtained in 11% yield. This is likely due to formation of relatively inert ketoalcohol **5**, which was detected as a major reaction intermediate (Scheme 3). Hence, trapping of the intermediate α-hydroxy-aldehyde as ketoalcohol results in an initial buildup of an excess of H_2, resulting in some hydrogenated styrene.

Dehydrogenation of a secondary alcohol, 1-phenyl-2-propanol, was very slow under the reaction conditions, supporting the presumption that **5** is formed by tautomerization rather than from direct dehydrogenation of the secondary CHOH function. Furthermore, the twice dehydrogenated compound **6** could not be detected during the reaction. Decreasing the catalyst loading to 2.5 mol% with respect to the number of –CHOH groups resulted in incomplete conversion of the alkene but still 58% yield of aldehydes (Table 1, entry 3). Subsequently, we tested tetraol **3** as substrate, in mesitylene however, the solubility was low, resulting in poor yield of aldehydes (entry 5). In order to better solubilize polyols, we turned to diethylene glycol diethyl ether (DGDE) as solvent. Olsen and Madsen have showed that dehydrogenative decarbonylation proceeds slower in glymes, probably due to competing coordination of the ether to the catalyst.[6] However, the higher boiling point allowed higher working temperature and we hoped that would compensate for the inferiority of the ethereal solvent. Indeed, the diol **2** and tetraol **3** yielded 84% and 64% aldehydes respectively using 2.5 mol% catalyst with respect to the number of alcohol groups in the molecule (entries 4 and 6).

Inspired by these results, the naturally occurring hexitol sorbitol was tested as substrate under the same reaction conditions, i.e. using only 0.25 equivalents of the hexitol with respect to the alkene, resulting in 53% yield of aldehydes (Table 1, entry 7). When

dropping the catalyst loading even further, to 1 mol% per CHOH unit, the yield dropped only slightly to 46% (entry 8).

Table 1. Optimization of reaction conditions in the dehydrogenative decarbonylation for hydroformylation of styrene.[a]

| Entry | Reactor A | | | | Reactor B |
	Substrate	Solvent [b]	Temp (°C)	Cat. Loading (mol%) [c]	Yield[d] (mol%) Aldeh.: EtPh
1	**1**	Mes.	185	5	98 : 0
2	**2**	Mes.	185	5	85 : 11
3	**2**	Mes.	185	2.5	58 : 16
4	**2**	DGDE	210	2.5	84 : 13
5	**3**	Mes.	185	5	26 : 10
6	**3**	DGDE	210	2.5	64 : 23
7	**4**	DGDE	210	2.5	53 : 21
8	**4**	DGDE	210	1	46 : 20

[a] Reaction conditions in reactor **A** (*cf*. Scheme 2): The molar amount of CHOH-units in the substrate corresponds to 1.5 equivalents of syngas with respect to the alkene in reactor **B**, (*S*)-BINAP was used as ligand to iridium, 44 h. See supporting information for details. [b] Mes. = Mesitylene, DGDE = diethyleneglycol diethyl ether. [c] Catalyst loading with respect to the number of CHOH functions. [d] Compound mixture in reactor **B** after the reaction. Yields were determined by ¹H NMR. See supporting information for details.

Increasing the amount of sorbitol to 33 mol% with respect to alkene (2.0 eq. potential syngas based on the number of CHOH functions) resulted in almost full conversion of styrene and 66% yield of aldehydes (Table 2 entry 1).

Although the yield of aldehydes was acceptable, 25% of the alkene was converted to the saturated alkane by hydrogenation. As indicated for the diol **2**, isomerization of initially formed aldehydes to ketones is a likely reason for hydrogen buildup, with the effect being more pronounced for longer polyols. Metal-catalyzed isomerization of α-hydroxy-aldehydes to hydroxyketones in water and ionic liquids has been reported by several groups and is frequently used for aldose-ketose transformations.[14]
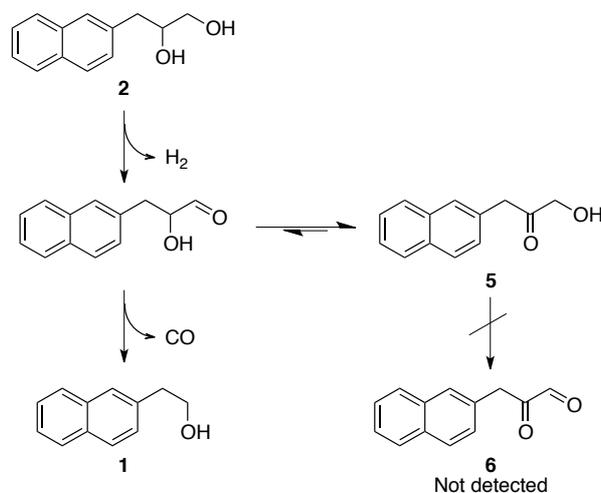
Scheme 3. Iridium-catalyzed transformations of diol **2**, 1,2-aldehyde-ketone tautomerization yields **5**.

Curious to see if we could counter this process, 1 equivalent (with respect to sorbitol) of methyl benzoyl formate **7** was added to reactor **A**. α-Keto-esters such as **7** are good hydrogen acceptors and have been used as substrates in transfer hydrogenation.[15] Our hope was to store a fraction of the initially formed hydrogen, allowing the carbon monoxide formation to catch up (Scheme 4). To our delight, a significantly smaller amount of ethylbenzene was detected after the reaction but, as expected, the conversion of styrene dropped significantly, most likely due to that a lesser fraction of the iridium catalyst is available for dehydrogenative decarbonylation (Table 2, entry 4).
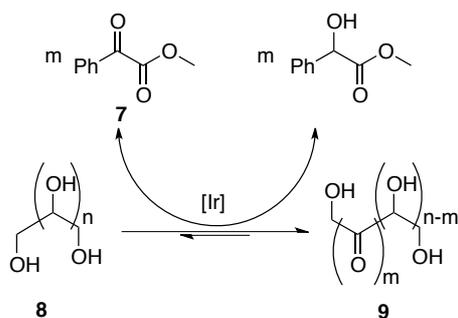
Scheme 4. Principle for H_2-storage by iridium-catalyzed transfer hydrogenation.

Being able to use (D)-sorbitol as a direct syn-gas source for hydroformylation, we wanted to see if the chirality of the catalyst affected the reaction outcome. Hence (*R*)-BINAP (Table 2, entry 2) was used, revealing that absolute configuration does not significantly affect the product distribution, possibly due to the fast tautomerization discussed (*vide supra*). Racemic BINAP however (entry 3), yielded less aldehyde product and lower conversion (see supporting information for details), but this effect is likely due to lower stability of the racemic complex.

Since the hydroformylation at ultra-low pressure clearly is very sensitive to the H_2:CO ratio, a screening of other polyol substrates was undertaken. Unsurprisingly, (D)-Mannitol gave similar results as sorbitol (Table 2, entry 8). The pentitol xylitol produced slightly lower yield of aldehydes and more ethylbenzene as compared to sorbitol (entry 9) and the tetraol erythritol gave even more hydrogenated product (entry 10).

Table 2. Screening of polyol substrates in dehydrogenative decarbonylation.[a]

| Entry | Reactor A | | | Reactor B |
	Substrate	Cat. Loading	Additive	Yield[b] (mol%) Aldeh.: EtPh
1	(D)-Sorbitol	1	-	66 : 28
2[c]	(D)-Sorbitol	1	-	65 : 30
3[d]	(D)-Sorbitol	1	-	50 : 30
4	(D)-Sorbitol	1	1.0 **7**	55 : 9
5	(D)-Sorbitol	1.5	1.5 **7**	X
6	(D)-Mannitol	1	-	60 : 32
7	Xylitol	1	-	54 : 34
8	(*meso*)-Erythritol	1	-	48 : 46
9	Glycerol	1	-	83 : 3

[a] Reaction conditions in reactor **A** (*cf.* Scheme 2): The molar amount of CHOH-units in the substrate corresponds to 2.0

equivalents of syngas with respect to the alkene in reactor **B**, (*S*)-BINAP was used as ligand to iridium, 44 h. See supporting information for details. [b] Compound mixture in reactor **B** after the reaction. Yields were determined by ^{1}H NMR. See supporting information for details. [c] Using (*R*)-BINAP as ligand for iridium. [d] Using racemic BINAP as ligand for iridium.

Glycerol is another naturally occurring polyol, which exists in a large world surplus since it is a by-product from biodiesel production and, at present, finds only limited use in production of bulk chemicals.[16] Under our conditions, glycerol degradation gave 83% yield of aldehydes and only 3% hydrogenated product (Table 2, entry 11). Since a mixture of glycerol and fatty alcohols can be obtained from triglycerides by carbonyl reduction,[17] we saw an opportunity to directly use this mixture to selectively produce syngas for hydroformylation along with hydrocarbon fuels. Dehydrogenative decarbonylation should theoretically produce six equivalents of syn-gas and three long chain hydrocarbons (Scheme 5). Hence, a 1:3 mixture of glycerol and 1-hexadecanol was subjected to dehydrogenative decarbonylation with *ex situ* hydroformylation of styrene. The mixture was able to hydroformylate four equivalents of styrene with our apparatus. A 1:1 isomeric mixture of aldehydes was obtained in 98% yield from reactor **B** and pentadecane was isolated in 89% yield from reactor **A**.
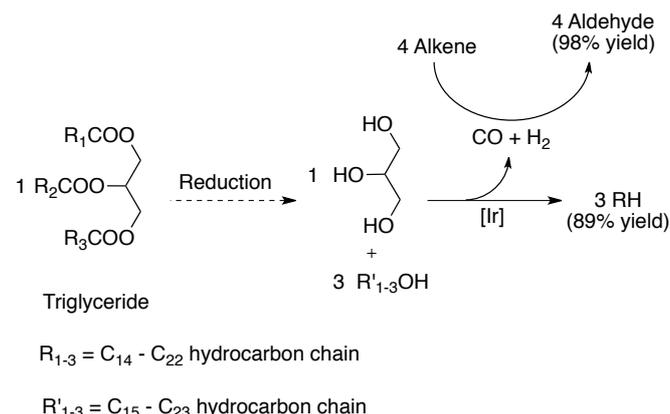
Scheme 5. Production of syngas and hydrocarbons from triglycerides.

In summary, we have developed a catalytic method for direct transfer of CO and H_2 from polyols to alkenes using a dual-reactor system. Homogeneous iridium-catalyzed dehydrogenative decarbonylation of alcohols at 185-210 °C produces a low (<0.5 atm) pressure of H_2 and CO, which is sufficient to feed an *ex situ* hydroformylation reaction. Catalyst loadings of 1 mol% with respect to the number of CHOH functions were effective in the tandem dehydrogenation-decarbonylation reaction.

Although the degree of CHOH transfer from polyols ranges between 25 and 75 mol% in our system, further development could increase the efficiency. The formation of volatile C1-C2 alcohols and aldehydes is clearly a problem that remains to be solved. Studies are in progress to further develop the concept of direct H_2:CO-transfer from biomass polyols to synthesis intermediates.

Experimental Section

General procedure for dehydrogenative-decarbonylation with *ex situ* hydroformylation: [Ir(cod)Cl]$_2$ (6.05 mg, 9 µmol), (*S*)-BINAP (11.21 mg, 18 µmol) and polyol (300 µmol) were weighed into reactor vessel A and Rh(H)(CO)(PPh$_3$)$_3$ (8.30 mg, 9 µmol) was weighed into reactor vessel B. To reactor A was attached a cold-finger reflux condenser and to reactor B a 1-2000 mbar pressure reader. The system was then purged with argon and benzene (1.0 ml) and styrene (103µl, 900 µmol) were added to reactor B via canula. Solvent (3.5 ml) was added to reactor A and the system pressure was equalized with the surroundings. The solutions were stirred for 10 min at room temperature where after reactor A was immersed in a thermo-stated silicon oil bath. Upon complete reaction, the system was cooled to room temperature and vented. The hydroformylation reaction was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. See supporting information for detailed experimental.

[1]   ((Reference 1, **Example for Journals**: a) A. Author, B. Coauthor, *Angew. Chem.* **2006**, *118*, 1-5; *Angew. Chem. Int. Ed.* **2006**, *45*, 1-5; b) A. Author, B. Coauthor, *ChemBioChem* **2006**, *7*, 1-10.))

[2]   ((Reference 2: **Example for Books**: J. W. Grate, G. C. Frye, in *Sensors Update*, Vol. 2 (Eds: H. Baltes, W. Göpel, J. Hesse), WILEY-VCH, Weinheim, **1996**, pp. 10-20.))

[3]   …

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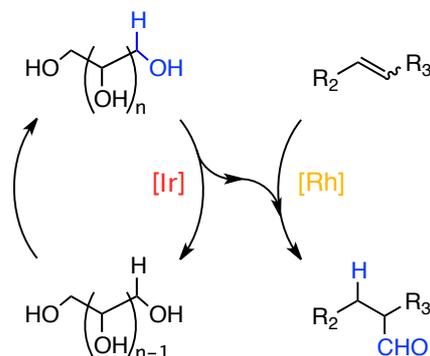
A method for direct transfer of the CHOH function of simple polyols to alkenes has been developed. In a dual-reactor system, iridium-catalyzed successive dehydrogenations and decarbonylations of polyols such as glycerol and sorbitol generates a low pressure of syn-gas, which is directly used in *ex situ* alkene hydroformylation.

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