Biorefinery

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Selective and Flexible Transformation of Biomass-Derived Platform Chemicals by a Multifunctional Catalytic System**

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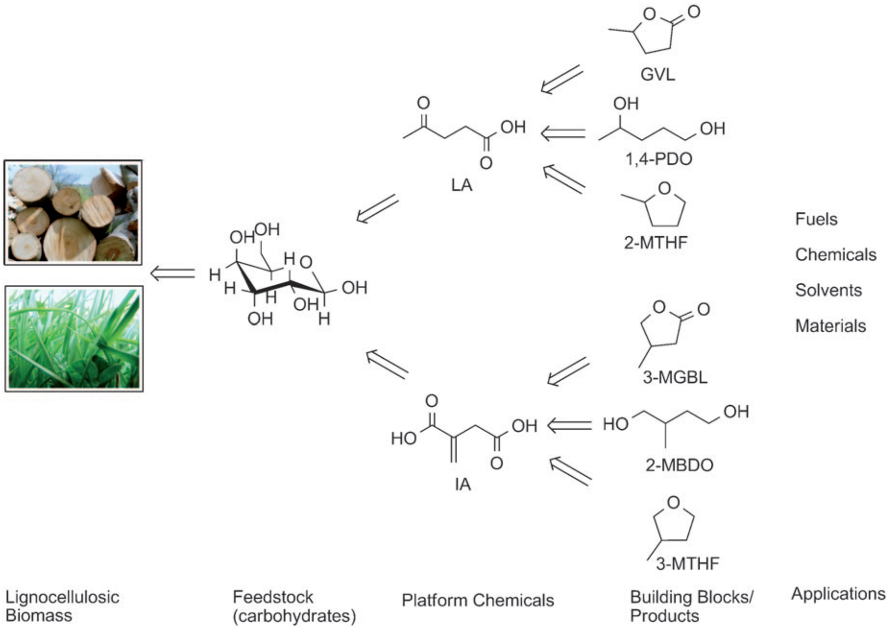
The limitation of fossil resources and the global efforts to reduce anthropogenic carbon dioxide emissions demand innovative strategies for the sustainable production of fuels and chemicals from renewable raw materials.[1] Carbohydrates derived from lignocellulosic biomass comprise the largest fraction of terrestrial biomass feedstocks. Their conversion into valuable products can be envisaged by subsequent selective transformations of a set of platform molecules (new building blocks) that constitute the key intermediates for molecular diversity.[2–4] The industrial implementation of such advanced biorefinery concepts faces a number of ecological, economic, and logistical challenges.[5] On the most fundamental level, it is essential to develop novel synthetic methods and catalytic processes for the selective de- and refunctionalization of biogenic substrates to yield a broad range of versatile chemical structures. Ultimately, this could allow the design of the optimum reaction pathway starting from the desired product structure, in analogy to a retrosynthetic analysis[6] in traditional organic synthesis.



Scheme 1. Analysis of reaction pathways for a variety of chemical structures formed from levulinic acid (LA) and itaconic acid (IA) as platform chemicals in a cellulose-based supply chain.

Whereas much effort currently focuses on production processes for platform molecules, their true potential for further conversion remains largely unexplored. Scheme 1 exemplifies how a diverse range of highly attractive products and building blocks could be derived from levulinic acid (LA), which is accessible from wood-based feedstocks, and itaconic acid (IA), which can be obtained from green biomass.[2,3] In particular, the cyclic ester γ-valerolactone (GVL) has been proposed as one of the key components in a biomass-derived economy.[7] Biogenic diols are interesting building blocks for biodegradable polyesters and other polymeric materials, as demonstrated by the commercialization of Sorona, a polyester which is made from glycerol-derived 1,3-propanediol.[8] Among the cyclic ethers, 2-methyltetrahydrofuran (2-MTHF) is advocated as an alternative solvent in the pharmaceutical industry and is also considered a fuel component.[3,9]

Hydrogenation routes involving heterogeneous catalysts to produce GVL, 2-MTHF, or 3-MTHF have been proposed.[10–12] Organometallic catalysts based on ruthenium phosphine systems were reported to allow the conversion of succinic acid into γ-butyrolactone and LA into GVL.[7,13,14] In

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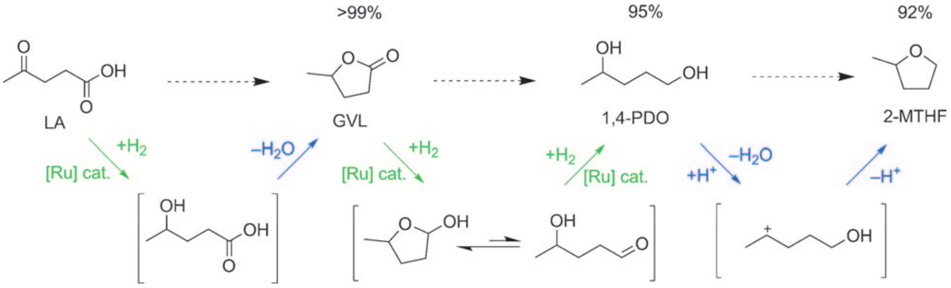


Scheme 2. Reaction sequence and maximum yields for the selective conversion of levulinic acid (LA) into γ-valerolactone (GVL), 1,4-pentanediol (1,4-PDO), and 2-methyltetrahydrofuran (2-MTHF).

the latter case, formation of 2-MTHF at temperatures around 200 °C and extended reaction times of 40 h could be inferred from NMR spectroscopy.[14] Ruthenium catalysts based on the specific tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) are particularly active for the reduction of carboxylic acid derivatives, and some reports include the hydrogenation of free acids to the corresponding alcohols.[15,16]

Inspired by these previous findings, we envisaged that molecular ruthenium phosphine catalysts might provide the basis for a multifunctional catalytic system that opens direct access to all lactones, diols, or ethers with high selectivity and flexibility starting from LA and IA. The molecular transformations of LA to GVL, 1,4-pentanediol (1,4-PDO), and 2-MTHF are shown in Scheme 2. The procedure consists of a consecutive series of hydrogenations (green) and dehydrations (blue) via well-defined but short-lived intermediates (in brackets). The metal-catalyzed addition of H_2 to the keto group of LA forms a hydroxy acid that undergoes intramolecular esterification to give γ-valerolactone (GVL). Further hydrogenation of the $C{=}O$ bond leads to the cyclic hemiacetal, which is in equilibrium with the open hydroxyaldehyde form. The remaining carbonyl group is hydrogenated to afford 1,4-PDO. Acid-catalyzed dehydration leads to cyclization of the diol by etherification to give 2-MTHF. A possible further reaction is the dehydration/hydrogenation of 1,4-PDO to the monoalcohols 1- or 2-pentanol (PAO, not shown). Most of the individual steps of the network are in principle reversible, which presents an additional challenge for control of the selectivity. Scheme 2 summarizes the optimum yields for the direct conversion of LA into the three main target products obtained in the present study, thus emphasizing the remarkable control and flexibility offered by the multifunctional molecular catalyst system.

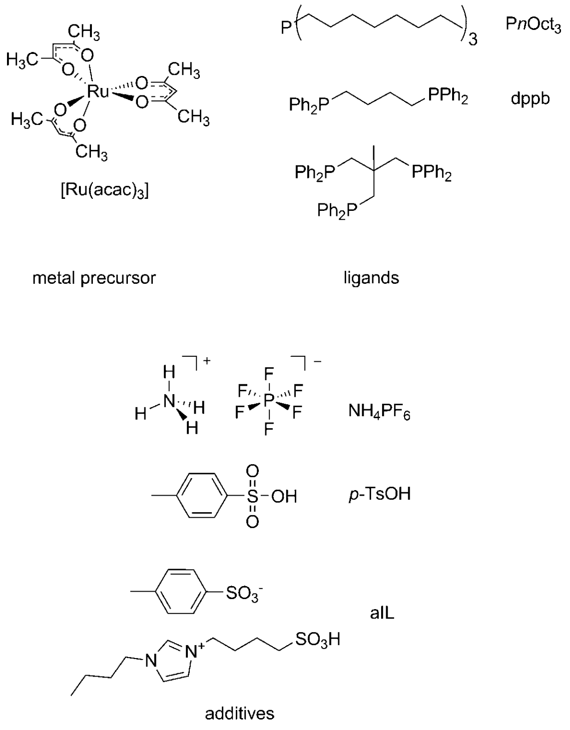
Analysis of the reaction network shows that the main features that will influence the formation of the target products are:

- the stereoelectronic properties at the metal center as defined by the ligand,
- the reactivity or stability of the active species as influenced by ionic additives,
- the acid strength of the reaction medium as influenced by acidic additives,
- reaction temperature and pressure.

On the basis of these considerations we set out to investigate a multifunctional catalyst system composed of a ruthenium-containing precursor complex, a set of mono-, bi-, and tridentate phosphine ligands, and ionic and/or acidic additives (Scheme 3).

In a first set of experiments the influence of the ligand structure and the reaction temperature in the hydrogenation of LA beyond the state of GVL was investigated. In accordance with previous reports, quantitative conversion into GVL was observed after 18 h at 160 °C with the monodentate ligand trioctylphosphine ($Pn\mathrm{Oct}_3$) and NH_4PF_6 as the additive (Table 1, entry 1).[14] Increasing the temperature to 200 °C resulted in moderate further conversion into 1,4-PDO, but monoalcohols (PAO, mainly 1-pentanol) were also formed in significant quantities (Table 1, entry 2). The use of the bidentate ligand 1,4-diphenylphosphinobutane (dppb) resulted in a considerably more active system, which already yielded detectable amounts of 1,4-PDO at 160 °C and a remarkable 51 % yield of 2-MTHF at 200 °C (Table 1, entries 3 and 4).

Finally, the most active catalyst was formed in the presence of the triphos ligand; LA was converted beyond the GVL level almost quantitatively already at 160 °C. Carrying out the reaction at 200 °C provides a mixture of 1,4-PDO and 2-MTHF as the main products in a combined



Scheme 3. Components for the generation of the multifunctional catalyst. aIL: acidic ionic liquid.

Table 1: Influence of the ligand, additive, and reaction temperature on the ruthenium-catalyzed conversion of levulinic acid.[a]

Entry	Ligand	T [°C]	Additive	Yield [%] GVL	1,4-PDO	2-MTHF	PAO
1	PnOct$_3$	160	NH_4PF_6	>99	0	0	0
2	PnOct$_3$	200	NH_4PF_6	56	30	3	11
3	dppb	160	NH_4PF_6	89	11	0	0
4	dppb	200	NH_4PF_6	39	6	51	4
5	triphos	160	NH_4PF_6	8	35	53	4
6	triphos	200	NH_4PF_6	7	31	59	3
7	triphos	160	–	3	95	0	2
8	triphos	160	p-TsOH	58	1	39	2
9	triphos	160	aIL	5	1	87	7
10	triphos	160	aIL + NH_4PF_6	1	0	92	7

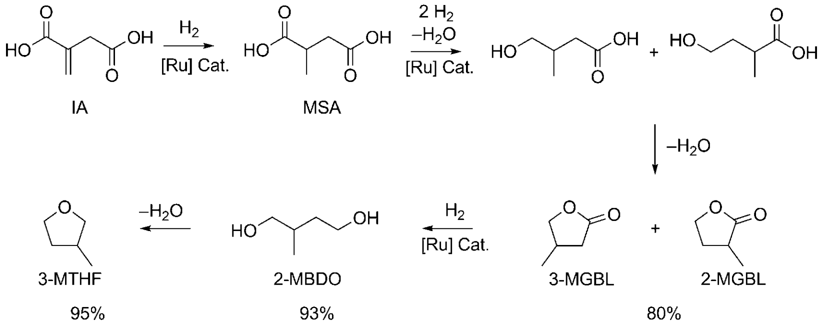
[a] Conditions: 10 mmol LA, 0.1 mol% [Ru(acac)$_3$], 1.0 mol% PnOct$_3$, 0.3 mol% dppb or 0.2 mol% triphos, 1 mol% additive, reaction time 18 h, hydrogen pressure $p(H_2) = 10$ MPa; Full conversion of LA was achieved in all cases.

yield of 90% in an approximate 1:2 ratio (Table 1, entries 5 and 6). Thus, all the hydrogenation steps could be catalyzed by the ruthenium/phosphine systems, and control of the dehydration reactions was now addressable through the acidity of the reaction medium.

Indeed, removing the slightly acidic additive NH_4PF_6 from the standard protocol increased the selectivity for 1,4-PDO, with yields approaching 95% (Table 1, entry 7).[17] On the other hand, the addition of the stronger p-toluenesulfonic acid (p-TsOH) shifted the hydrogenation beyond the lactone stage to the cyclic ether 2-MTHF, with only trace amounts of the diol remaining (Table 1, entry 8). These conditions, however, reduced the hydrogenation activity, which led to large amounts of the primary hydrogenation product GVL in the product mixture. In our search for an acid component that would combine both acidic and ionic features we turned to the recently introduced acidic ionic liquid (aIL) 1-butyl-2-(4-sulfobutyl)imidazolium-p-toluenesulfonate.[18] By using this functional ionic liquid as an additive, 2-MTHF was obtained in excellent yields approaching 90% (Table 1, entry 9). Combining the aIL and NH_4PF_6 gave a slight further improvement: 2-MTHF was obtained in a yield of 92% with almost no GVL and 1,4-DPO as side products (Table 1, entry 10). When the reaction temperature was increased to 200°C at 50 bar of hydrogen under otherwise identical conditions, this multifunctional catalyst system converted LA quantitatively with identical selectivity (92%) into 2-MTHF in less than 5 h.

Encouraged by the successful application in the conversion of LA, the scope of the multifunctional catalyst system was explored with itaconic acid (IA). The detailed transformation sequence is shown in Scheme 4. The hydrogenation of the C=C bond in IA to form methyl succinic acid (MSA) is straightforward with ruthenium phosphine catalysts, but the reduction of the free carboxylic acid function with molecular hydrogen to give the intermediate hydroxy acid is very challenging for an organometallic catalyst.[19,20] Once the lactone stage is reached, further conversion into 2-methylbutanediol (2-MBDO) and the tetrahydrofuran derivative 3-MTHF can proceed through analogous transformations as for LA.

Gratifyingly, the catalyst system could be readily adapted to IA as the substrate. The more challenging reduction of the carboxylic acid function as compared to LA was reflected only in a slightly higher reaction temperature being required for the formation of the lactones. A 1.2:1 mixture of the two regioisomers was obtained in a combined yield of about 80% at 195°C by using a ruthenium catalyst comprised of the bidentate ligand dppb in the absence of any additives (Table 2, entry 1). Again, the application of the triphos ligand led to a more active catalyst, which provided the diol 2-MBDO in excellent yields of up to 93% under otherwise identical conditions (Table 2, entry 2). The cyclization of the diol to 3-MTHF was initiated by the use of acidic additives in full analogy to the LA case (Table 2, entry 3). The use of the Ru/triphos catalyst with p-TsOH and NH_4PF_6 as additives led to the formation of 3-MTHF with a remarkable yield of 95% without any further optimization (Table 2, entry 4).



Scheme 4. Reaction sequence and maximum yields for the selective conversion of itaconic acid (IA) into lactones (MGBL), 2-methylbutanediol (2-MBDO), and 3-methyltetrahydrofuran (3-MTHF).

The molecular nature of the catalytically active metal species is strongly supported by the results of a mercury poisoning experiment: the performance of the catalyst was not affected by the addition of elemental mercury.[21] Furthermore, a uniform organometallic compound could be

Table 2: Influence of the ligand, additive, and reaction medium on the ruthenium-catalyzed conversion of itaconic acid.[a]

No.	Ligand	Solvent	Additive	Conv. [%]	Yield [%] MGBL	2-MBDO	3-MTHF
1	DPPB	THF	–	95	93	2	0
2[b]	triphos	dioxane	–	>99	6	93	0
3[b]	triphos	dioxane	p-TsOH	>99	53	0	38
4	triphos	dioxane	p-TsOH + NH_4PF_6	>99	2	0	97
5	triphos	2-MTHF	p-TsOH + NH_4PF_6	>99	0	0	96

[a] Conditions: 2.4 mmol IA, 0.5 mol% [Ru(acac)$_3$], 0.6 mol% triphos, 2 mol% additive, 2 mL dioxane, reaction time 18 h, initial hydrogen pressure $p(H_2) = 10$ MPa, 195°C; [b] 1 mL dioxane.

isolated from the hydrogenation of LA (160 °C, 10 MPa H_2, 18 h, no additives) in an amount corresponding to 80 % of the combined mass of the employed metal precursor and ligand. The $^{31}P\{^1H\}$ NMR spectroscopic data confirms the presence of the triphos ligand in the typical tripodal facial coordination mode at the ruthenium center ($^{31}P\{^1H\}$: triplet, $\delta = 34.6$ ppm, 1 P; doublet, $\delta = 27.0$ ppm, 2 P; $J_{PP} = 30$ Hz).

The formation of a ruthenium hydride species is proven by a singlet resonance at $\delta = -7.35$ ppm in the $^1H\{^{31}P\}$ NMR spectrum. The intensity of the signal indicates the presence of two terminal hydride ligands in the complex. It was possible to fully characterize the complex by multinuclear NMR spectroscopy as $[Ru(triphos)(CO)(H)_2]$.[22]

Although the homogeneous nature of the catalyst is advantageous for molecular control of the reaction pathway, it is often perceived as an inherent limitation for the implementation of a production process. This can be overcome, however, by integration of reaction and separation steps into a continuous process that allows for inherent recycling of the catalyst. The melting point of 31–33 °C and high thermal stability of LA results in it being suitable as a reaction medium for homogeneously catalyzed processes without addition of any solvent. The solvent-free conditions greatly facilitate the isolation and downstream processing of the individual products. This has been demonstrated for 2-MTHF, which forms a two-phase mixture with the water produced during the dehydration reactions if conversion and selectivity are high enough.

Conceptual process design methods were used to develop a flow sheet for a possible continuous production process based on the optimized reaction conditions (Figure 1).[23] The simulation of the separation was performed by using the RADFRAC model in the ASPEN PLUS flow sheet simulator.[24] Missing property data were estimated using group contribution methods and CosmoRS calculations.[25] In this concept, hydrogen and levulinic acid are heated, compressed to reaction conditions, and fed into a plug flow reactor. The homogeneous catalyst system is introduced with the liquid substrate in the starting phase of the process. Under continuous conditions the reactor effluent is partially vaporized and the remaining liquid stream, which contains the catalyst and additives as well as the high boiling compounds GVL and PDO, is recycled into the reactor. The potential recyclability of the catalyst system was demonstrated in repetitive batch mode on a laboratory scale. The yields of isolated 2-MTHF were 88, 79, 84, and 81 % in four consecutive batches with the same catalyst additive mixture, thus indicating that deactivation of the catalyst was negligible up to this point.

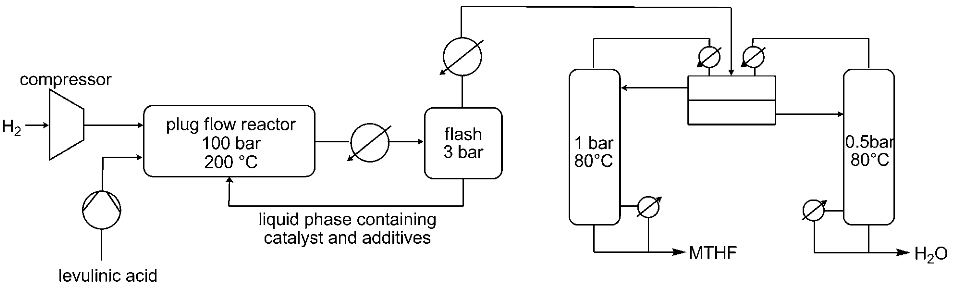


Figure 1. Flow sheet for a possible LA to 2-MTHF process. The flexible design can be readily adapted to the production of 3-MTHF from IA as described in the text.

The vapor stream from the flash distillation, which consists of the products water, 2-MTHF, and the side product pentanol, is condensed and fed into the decanter of a heteroazeotropic distillation system. The 2-MTHF, which is recovered in high purity at the bottom of the respective column, contains pentanol as a side product and can be used directly if the alcohol impurities can be tolerated in the application. A single additional rectification column is sufficient to obtain pure 2-MTHF, if needed. Exploiting the same heat source for catalyst recycling and product recovery can significantly reduce the energy demand of the process, which is on the order of 3 % of the energy content of the recovered 2-MTHF. A preliminary economic evaluation revealed that the production costs are dominated mainly by the costs of the raw materials and catalyst.

This finding indicates that aspects of economy of scale are not as important as for example in biomass-to-liquids (BTL) concepts. Thus, relatively small production units could be envisaged to address infrastructure limitations with biorenewable feedstocks.

In contrast to LA, IA has a high melting point of 183 °C and tends to polymerize rapidly at higher reaction temperatures. As a consequence, the use of a suitable solvent is necessary to carry out the selective transformation of this substrate. In an initial screening of various types of reaction media, cyclic ethers were found to be suited best for the reaction sequence. This opens the possibility to use biomass-derived ethers and, indeed, the application of 2-MTHF in the reduction of IA in the presence of p-TsOH and NH_4PF_6 resulted in the exclusive formation of 3-MTHF (Table 2, entry 5). Thus, a process for the production of 3-MTHF can be readily envisaged, where the reaction medium is provided by the product itself. Only minor changes involving a feedback loop, which recycles part of the MTHF product back into the substrate stream, would be necessary to adjust the process of Figure 1 for such a "self-breeding" production of 3-MTHF from IA. Hence, the scope of the molecular pathways is matched by the flexibility of the process engineering approach.

In summary, the results of the present study demonstrate that the two biogenic platform chemicals levulinic acid (LA) and itaconic acid (IA) can be converted into a diverse set of isomeric lactones, diols, and cyclic ethers with high to excellent yields by using a multifunctional catalyst system comprised of a ruthenium/phosphine complex in combination with ionic and/or acidic additives. The catalyst system was developed by rational mechanistic analysis of the individual steps in the complex reaction network. As the control of hydrogenation and dehydration sequences is a very general issue in the conversion of biogenic substrates, the concept used here is expected to be of broad applicability in the utilization of biomass. The possibility to implement this approach in an efficient and flexible process design was exemplified for the production of 2-MTHF and 3-MTHF by an integrated reaction and separation concept.

In this context it is important to note that the platform chemicals and intermediates of a biomass-derived supply chain are not yet fixed as firmly as in petrochemistry. Therefore, the selection of a desired pathway is not predetermined by the availability of the intermediates, but still can be defined on the basis of the desired product range.[26] The development of highly selective and flexible catalytic conversions at all stages is a necessary prerequisite to establish the corresponding transformation lines, and the full exploitation of these opportunities will require additional efforts in pathway, process, and product design. Interdisciplinary collaboration between synthetic chemists, chemical engineers, and the product users are essential in this endeavor.

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