Homogeneous Catalysed Reactions of Levulinic Acid: To γ-Valerolactone and Beyond

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Abstract

Platform chemicals derived from lignocellulousic plant biomass are viewed as a sustainable replacement for crude oil based feed-stocks. Levulinic acid (LA) is one such biomass derived chemical that has been widely studied for further catalytic transformation to γ-valerolactone (GVL), an important 'green' fuel additive, solvent and fine chemical intermediate. Although the transformation of LA to GVL can be achieved using heterogeneous catalysis, homogeneous catalytic systems that operate under milder reactions, give high seletivities and can be recycled continue to attract much attention. A range of new homogeneous catalysts have now been demonstrated to efficiently convert LA to GVL, and to transform LA directly to other value added chemicals such as 1,4-pentanediol (1,4-PDO) and 2-methyltetrahydrofuran (2-MTHF). This mini review covers recent advances in the area of homogeneous catalysis for the conversion of levulinic acid and levulinic ester derivatives to GVL and chemicals beyond GVL.

1. Introduction

The rapid consumption of non-renewable resources, coal, gas and oil, over the past 100 years has resulted in an increase in atmospheric CO_2 levels and the irrefutable link to climate change. Whilst low carbon technologies for power generation such as wind, solar, hydroelectric, tidal and nuclear, can provide energy without emitting CO_2, the future production of transportation fuels and chemicals normally derived from crude oil will be a major issue as oil reserves decline.[1,2] Plant biomass is the most abundant and available source of biorenewable carbon on our planet, and is viewed as the main sustainable alternative to petrochemical derived chemicals and fuels.[1,3,4] Lignocellulosic plant material in particular has been specifically earmarked for conversion to higher value chemicals and fuels. The vast natural abundance of lignocellulosic material and potential for further functionalisation to generate industrially important chemicals could make them viable alternatives to crude oil derived products. In 2004, the United States Department of Energy (US DoE) identified 12 biomass derived molecules as 'top value-added chemicals', most are lignocellulose[†] based.[5] In contrast to petrochemical derived products, which are typically simple aliphatic or aromatic non-functionalized hydrocarbons, biomass derived molecules are much more complex and contain excess functionality such as alcohols, carboxylic acids, esters, ethers and amines. To enable their use as liquid fuels or fine chemicals they need to be de-functionalized and then re-functionalized, it is these chemical steps that provides significant synthetic challenges. In order to make these processes chemically and energetically viable, catalysis is playing a vital role and will continue to do so in the future.

Levulinic acid (LA) is one such biomass derived platform molecule highlighted in the US DoE report,[5] that has attracted considerable attention. LA can be efficiently obtained via the chemical degradation of cellulose[6][7] and transformed to a range of higher value molecules such as γ-valerolactone (GVL), 1,4-pentanediol (1,4-PDO), 2-methyltetrahydrofuran (2-MTHF), ethyl levulinate (EL), δ-amino levulinic acid (DALA), diphenolic acid (DPA), maleic anhydride (MA) and a series of other compounds (figure 1). A number of these

[†] It is estimated that over $1x10^{11}$ tonnes of cellulose are produced each year making it the most abundant renewable source of carbon on the planet.

compounds have commercial value, for example, DALA is used in the production of biodegradable pesticides and insecticides,[8] while DPA and diols such as 1,4-PDO can be used as monomers for the production of biodegradable polyesters.[7][9] GVL has applications in food and perfume industry, as a fuel component and green solvent,[10–13] while enantiomerically pure GVL has applications as a chiral building block for the synthesis of pharmaceutically active molecules.[14] 2-MTHF is a green alternative to THF that favourable physical and chemical characteristics such as higher boiling point (80.2 ^{o}C), water immiscibility, reactivity and biodegredation pathways.[15–19] 2-MTHF can be used a component of P-series fuel, a non-petroleum liquid fuel which can be substituted for or blended with gasoline.[7,16]

The transformation of LA to GVL and beyond typically involves a series of consecutive catalytic dehydration and reduction steps; although oxidative pathways are also possible.[20] The dehydration step is acid catalysed, while reduction is achieved using a transition metal catalyst with either molecular hydrogen or formic acid as hydrogen source. A number of heterogeneous and homogenous based catalytic systems have been reported for a range of biomass transformations; the area has been reviewed recently.[21,22] This mini review focuses on recent advances in the area of homogeneous catalysis for the conversion of levulinic acid and levulinic esters to GVL and other value added chemicals. The production and properties of LA are also briefly discussed.

2. Levulinic Acid

LA is a white crystalline solid that melts close to room temperature (~34 ^{o}C) but has a relatively high boiling point of 246 ^{o}C. It is soluble in both water and polar organic solvent which facilitates its reaction either in monophasic or biphasic systems. LA is typically prepared via the decomposition sugar monomers with acid. The dehydrated sugars intially form 5-hydroxylmethylfurfural (5-HMF), and following a second acid catalysed hydration step of 5-HMF, LA is formed along with equimolar amounts of formic acid (Scheme 1). The use of lignocellulose material and mineral acids has enabled larger scale and economically viable routes to LA.[23,24]

The presence of both ketone and carboxylic functional groups in LA greatly enhances its reactivity in comparison to straight chain alkyl carboxylic acids. The ketone carbonyl group is susceptible to nucleophilic attack, and can tautomerise to give reactive enol isomers following the abstraction of an adjacent α-proton. Additionally, the acidic proton on the carboxylic group is easily deprotonated forming a reactive carboxylate anion (scheme 2). It is the reactive functional groups of LA that enable its catalytic transformation via coordination to metal centres.

3. Hydrogenation of Levulinic Acid (LA) to γ-Valerolactone (GVL)

GVL is a non-hazardous, high boiling point liquid that has been identified as a green solvent, fuel additive, fine chemical intermediate and food additive.[10–14] Although it contains a chiral centre, it is usually produced and used in the racemic form. GVL is synthesised by the catalytic hydrogenation and dehydration of LA, either via hydrogenation of LA to give 4-hydroxyvaleric acid (4-HVA) followed by cyclization to give GVL; or via acid catalysed dehydration of LA to α-angelica lactone (α-ALA) and hydrogenation to GVL (Scheme 3). A number of heterogeneous catalysts have been successfully used for the transformation of LA to GVL, with processes typically employing high temperatures and pressures of hydrogen.[25–27] The ease of product recovery and catalyst recycling associated with heterogeneous system makes them both economical and practical for large scale processes. Although separation of catalyst from product is more challenging for homogeneous systems, high activities and selectivities can be achieved under milder reaction conditions. The properties of the homogenous catalyst can be tunned by tailoring the ligand structure which can have profound effects on reactivity, and direct enantioselectivity if chiral ligands are used. To date, the majority of homogenous catalysts for LA to GVL transformations are based on transition metal phosphine complexes. Recently, chelating tridentate phosphine complexes have been found to be excellent catalysts for these reactions.

Ru and Ir phosphine complexes have proven to be effective catalysts for C-O bond activation in carboxylic acids derivatives.[28–31] In early pioneering studies Osakada et al.,[32] showed the activation of C-O

bonds of five membered cyclic anhydride, aldehydic and keto acids using two different ruthenium(II) monodentate phosphine complexes $[RuCl_2(PPh_3)_3]$ and $[RuH_2(PPh_3)_4]$ as catalysts for the production of lactones. Performing the reduction of LA with $[RuCl_2(PPh_3)_3]$ catalyst, a high yield (99%) of GVL was obtained at 180 ^oC and 12 bar H_2 in 24 h reaction time (table 1, entry 1). Applying the same reaction conditions with the dihydride ruthenium catalyst $[RuH_2(PPh_3)_4]$ moderate yields of 58% GVL were reported (table 1, entry 2). Switching to the rhodium(I) catalyst $[RhCl(PPh_3)_3]$ resulted in low yields of 4% GVL. More recently Horváth and co-workers[10] demonstrated the use of an in situ generated Ru catalyst using a combination of $Ru(acac)_3$ and the strongly electron donating phosphine P^nBu_3 in the presence of NH_4PF_6 for LA hydrogenation to GVL (table 1, entry 3). The reaction demonstrated quantitative conversion of LA to GVL. Good conversions were also achieved with using the water soluble ligand triphenylphosphine-trisulfonic acid (TPPTS) (fig. 2) and $Ru(acac)_3$, giving yield of up 95% GVL under slightly lower pressures of H2 (table 1, entry 4). Following this study, Leitner et al.[33] reported the effect of the mondentate and chelating phosphines: trioctylphosphine (P^nOct_3), 1,4-diphenylphosphinobutane (DPPB) and triphos (fig. 2) and various acidic additives for the transformation of LA. The in situ generated catalyst with monodentate P^nOct_3 and $Ru(acac)_3$ in the presence of NH_4PF_6 gave GVL in 99% yield at 160 ^oC and 100 bar H_2 in neat LA. Applying the same reaction conditions using the bidentate DPPB and tridentate ligand triphos ligands gave yields of 89% and 8% of GVL respectively. Switching the acid additive from NH_4PF_6 to p-TsOH for the triphos system improved yield of GVL to 58% (table 1, entries 5-8). Interestingly the triphos ligand system showed significant conversions beyond GVL to both 1,4-PDO and 2-MTHF (see below). Using a related chelating triphosphine ligand, N-triphos (fig. 2) Miller et al.[34] were able to achieve high yields of GVL (77-95%) both in situ and with the preformed catalyst $[RuH_2(CO)(N\text{-triphos})]$ and NH_4PF_6 or *p*-TsOH additives under milder reaction conditions of 160 ^oC and 65 bar H_2 (table 1, entries 9-11). Beller and co-workers[35] recently screened a wide range of bidentate and tridentate phosphine ligands for methyl levulinate (MLA) to GVL conversions. Catalysts were generated in situ using $Ru(acac)_3$ and reactions run at 50 bar H_2, 140

^{o}C for 22 h in THF. The highest yields of GVL (95 %), TONs (up to 75,855) and TOFs (up to 1382 h^{-1}) were achieved using the triphos analogue TPP (fig. 2) (table 1, entry 12).

Iridium trihydride complexes generated *in situ* from [Ir(cyclooctene)$_2$Cl$_2$] and tridentate pincer type ligands: PNP, PNN, NNN and PCP (fig. 3) have recently been reported for the hydrogenation of LA to GVL under reaction conditions of 100 ^{o}C and 50 bar H_2 in the presence of a base.[36] The catalyst activity was found to be affected by the alkyl substituent attached to the phosphorus ligand. Electron donating ^{t}Bu and ^{i}Pr of the PNP ligand performed best giving high yields of 96% and 99% GVL. Following a series of in situ optimisation experiments the preformed catalysts [IrH$_3$(PNP^{t}Bu)] and [IrH$_2$(Cl)(PNP^{t}Bu)] using the PNP^{t}Bu ligand (fig. 3) were studied. The Ir-trihydride performed better than the Ir-chloride complex and achieved near quantitative yields and high TON of 71,000 when the catalyst loading was reduced (table 1, entry 13-15).

Iridium half-sandwich bipyridyl complexes (fig. 4) have also been used to convert LA into GVL in high yields and under mild temperatures of 120 ^{o}C and pressures of 10 bar H_2, and with some of the highest TON (78,000) reported to date.[37] A range of catalysts were investigated with various substituents on the bipyridyl ligand; stronger electron-donating substituents in sterically unhindered positions proving to give the best yields of GVL. The Ir-Bipy-OMe half-sandwich complex (fig. 4) gave the highest yield of 98% (table 1, entry 16) and was further studied under phase catalysis conditions using formic acid (FA) as the hydrogen source. Transfer hydrogenations are inherently safer since pressurised hydrogen gas is not required, hence this method can be used without specialised high pressure equipment. High activities for the Ir-Bipy-OMe half-sandwich complex for the generation of GVL from aqueous mixtures of LA and FA were achieved (table 1, entry 17). Simple phase separation could be used to isolate and reuse this water-soluble homogeneous catalyst, with a limited loss of activity. The high cost associated with these types of Ir catalysts may however preclude their industrial applications.

The transfer hydrogenation of LA to GVL using FA as hydrogen source and simple inexpensive $RuCl_3$/PPh_3 catalyst in the presence of a range of bases has been previously demonstrated by Guo and co-

workers.[38] High conversions to GVL (93%) were achieved under optimised conditions of 150 ^{o}C, 12 h using pyridine as base in a 1:1 aqueous mixture of LA and FA (table 1, entry 18). More recently Shvo's catalyst [2,5-Ph_2-3,4-$(Ph)_2(\eta^5$-$C_4CO)$]H}$Ru_2(CO)_4(\mu$-H)] (fig. 5) has been reported by Horváth *et al*. for the transfer hydrogenation of LA.[31] High yields of 99% GVL were selectively formed under mild reaction conditions of 100 ^{o}C for 5h. The effects of different reaction parameters (temperature, substrate/catalyst ratio, FA concentration) were investigated with highest the TON of 3400 being reported when and excess of FA was used at 100 ^{o}C (table 1, entry 19). Interestingly the catalyst could be recycled up to four times without loss of activity which could compensate for the high cost of this homogeneous catalyst.

A range of Pd-diphosphine complexes of the type [Pd(diphosphine)X_2] have recently been proven to be effective for LA to GVL conversion under both transfer hydrogenation using FA as hydrogen source and under low pressures of molecular hydrogen (5 bar, 80 ^{o}C).[39] The best performing catalyst was [Pd(DTBPE)Cl_2] (DTBPE = 1,2-(bis-di-tert-butylphosphino)ethane) (fig. 6) which displayed reasonably high TON of 2100 and TOF of 2100 h^{-1} (table 1, entries 20-21). The catalyst could be recycled several times but showed loss of activity catalytically due to the formation of an inactive Pd-carbonyl and Pd-hydride dimer complexes in situ (fig. 6). Nevertheless, this report demonstrates the first use of Pd complexes for these transformations under very mild reaction conditions.

The costs associated in the separation of homogenous catalysts from their products has often limited their commercial use, hence strategies to improve separations, catalyst recycling and catalyst longevity are key their commerical viability. Biphasic systems are viewed as one feasible route to improving such separations. Since LA is water soluble, a biphasic solvent system with a water soluble catalyst is reasonable approach to product separation and catalyst recycling. Water soluble phosphines bearing sulfonate groups have been employed for the transformation of LA to GVL, several examples of phase separations for isolating GVL have already been discussed above (*c.f*. Horváth, Garcia and Fu above). Horváth and co-workers were one of the first to employ the water soluble sulfonated triphenylphosphine ligand TPPTS (fig. 2) with $Ru(acac)_3$ for LA to

GVL conversions under pressures of 69 bar H_2 and 140^{o}C (table 1, entry 4).[10] GVL was extracted from the aqueous phase with ethyl acetate giving high isolated yields of 95%. Similarly, Heeres et al.[40] performed the hydrogenation of LA using in situ generated Ru catalyst from $RuCl_3.3H_2O$ and TPPTS ligand in CH_2Cl_2/H_2O biphasic system with molecular hydrogen (table 1, entry 22). The kinetics of the reaction was studied by varying the different parameters such as temperature, pH, substrate/catalyst ratio and hydrogen pressure. The reaction was found to be first order in LA, first order in hydrogen pressure below 15 bar and zero order above 15 bar pressure.

A range of sulfonated phosphine ligands ($R_nP(C_6H_4\text{-}m\text{-}SO_3Na)_{3-n}$ n = 1 or 2, R = Me, Pr, ^{i}Pr, ^{n}Bu, Cp) with different electronic and steric parameters have been investigated by Mika and co-workers for the hydrogenation of LA to GVL.[41] Sulfonation of these ligands enhances both their solubility in polar solvents and also minimises their vapour pressure making them easier and safer to handle. Catalysts were generated in situ via reaction with $Ru(acac)_3$, and catalysis performed at 100 bar H_2, 140 ^{o}C. The steric and electronic properties of the phosphine ligands had significant influence on the activity of the catalysts. The linear butyl chain ligand ^{n}Bu-DPPDS (^{n}Bu-P(C_6H_4-m-$SO_3Na)_2$) ligand achieved highest yields of GVL (>99%) and TON of 6370. Ligands containing branched alkyl groups such as ^{i}Pr or Cp on the other hand gave much lower yields (<40%). Interestingly, the $Ru(acac)_3$/^{n}Bu-DPPDS system could be used for six consecutive LA reductions without a significant decrease in catalytic activity.

The activity of a range of bidentate diphosphine-Ru based catalysts, generated in situ form $Ru(acac)_3$, for LA to GVL conversion has been investigated by the same group[30] (fig. 5) and compared to the sulfonated monodenate phosphine ligand $Ru(acac)_3$/^{n}Bu-DPPDS system. Under optimised reaction conditions for the monodentate system (1.8 h, 100 bar and 140 ^{o}C), the $Ru(acac)_3$/DPPB system, with a *n*-butyl ligand backbone, was found to be the most effective bidentate ligand system giving comparable yields of >99% and TON (12,000) to the monodentate system (table 1, entry 23). The BINAP ligand also proved to be very effective giving comparable TON but was slightly lower yielding. Reducing the concentration of the Ru/DPPB system gave

higher TON and TOF without compromising yield of GVL (table 1, entry 24). Decreasing the length of the diphosphine ligand backbone (i.e. using DPPE or DPPP) gave reduced yields. Equally, increasing the diphosphine ligand backbone to five or six methylene groups (i.e. using DPPPe or DPPH) also give reduced GVL yields. This work demonstrates how small changes in ligand structure can have quite dramatic effects on the catalysis. This Ru/DPPB homogeneous catalyst system is very robust, and could be recycled for ten consecutive runs without loss of activity or GVL yield.

Until very recently all reported active homogeneous catalysts for the conversion of LA to GVL were based on more expensive row two and three transition metals such as Ru, Rh, Pd and Ir; with Ru catalysts appearing to be the most versatile. The cost of such complexes is a major concern for further industrial applications involving these catalysts. Recently, several iron catalysts have been reported for the converison of LA and EL to GVL under transfer hydrogenation conditions.[42–44] The iron catalysed transfer hydrogenation of EL to GVL using FA as hydrogen source was reported by Fu and co-workers.[42] A combination of $Fe(OTf)_2$ and tetraphos ligand (fig. 2) proved to be the most effective in situ catalyst generating GVL in 98% yield (table 1, entry 25). The cost of iron based catalysts make this method attractive however the high catalyst loadings required (5 mol%) and high associated cost of ligand are potential caveats. The same group also reported the use of Casey's catalyst (fig. 5) for the transfer hydrogenation of EL to GVL using isopropanol as the hydrogen source.[43] The reaction conditions this time were milder, 100 ^{o}C for 19 h under basic conditons, with lower catalyst loadings reported (1 mol%). Yields of up to 95% GVL were obtained under optimised conditions (table 1, entry 26). Lower catalyst loadings unfortunately resulted in greatly dimished yields and attempts to recycle and reuse this catalyst for subsequent catalytic runs were unsuccessful. The conversion of LA to GVL has been recently achieved using a simple and inexpensive iron carbonyl complex $[Fe_3(CO)_{12}]$ under transfer hydrogenation conditions.[44] The direct conversion of LA rather than EL is more promising via transfer hydrogenation since one equivalent of FA is produced during the synthesis of LA from 5-HMF (scheme 1) and which could therefore be utilised as the hydrogen source for LA reduction. Under optimised conditions, 180 ^{o}C,

15 h using ImN (imidazole) and excess FA, high yields of GVL (92%) were obtained (table 1, entry 27). High catalyst loadings (4 mol%) were, however, required for the reaction and four equivalents of base (ImN) and FA were required. Lowering catalyst loadings gave greatly diminished yields of GVL. The addition of triphenylphosphine the reaction to generate [$Fe(CO)_3(PPh_3)$] resulted low yields of GVL. Analysis of the reaction mixture after the reaction revealed that no [$Fe_3(CO)_{12}$] was present, however, particles of Fe_2O_3 were present, indicating that [$Fe_3(CO)_{12}$] is a precursor to the formation of Fe nanoparticles which may be the active catalytic species.

GVL is usually produced and used in the racemic form since major applications as fuels or solvents do not require one specific enantiomer. Enantiomeric purity is, however, important in the fragrance, flavouring and pharmaceutical industries were specific enantiomers can have very different properties. The enantioselective hydrogenation of different γ-ketoesters to chiral lactones has been investigated using a chrial Ru-BINAP complex as early as 1990 by Noyori and co-workers (table 1, entry 28).[45] The SEGPHOS ligand (fig. 2), which enforces a smaller dihedral angle at the Ru centre, was found to give higher activities and enantioselectivity for the hydrogenation of EL to the corresponding alcohol, 4-hydroxypentanoate (table 1, entry 29).[46] Ru-tetraMe-BITIOP (fig. 2) complexes were also discovered to give the high rates and stereoselectivities for the formation of enantiomerically pure γ-lactones from γ-ketoesters.[47] The more electron-rich nature, low dihedral angle and steric bulk of these BITIOP ligands were cited for the higher rates and ee compared to BINAP under their catalytic conditions (table 1, entries 30-31). The addition of bromoalkanes to this system was found to enhance the rate most likely due to partial hydrogenolysis giving the necessary acidity to transform the starting complex into the catalytically active species.

In more recent studies by Vinogradov *et al.*[28][48] the conversion of LA, ethyl levulinate (EL) and other levuinate esters to enantiopure lactones was investigated using Ru-BINAP catalysts prepared in situ and activated with HCl. LA could be converted to S-GVL in moderate yields of 66% and with 98.5% ee at 60 ^{o}C, 60 bar H_2 in EtOH using a catalyst system generated in situ from [Ru(Me-allyl)$_2$(COD)], S-BINAP and HCl.[28] Higher

yields and ee where however achieved when EL was used as substrate, achieving 95% yields and 99% ee for S-GVL (table 1, entries 32-33). Using the cheaper $RuCl_3$ as precursor in combination R-BINAP and HCl gave high yields of R-GVL (96%, ee 99%) from methyl levulinate under the same catalytic conditions (table 1, entry 34). The ester substrate was demonstrated to influence on the rate of conversion, and is dictated by steric bulk of the alkoxyl moiety (^{i}Pr, ^{t}Bu, ethyl).[48] The same authors followed-up this study with a detailed kinetic study of the Ru-Cl_2-BINAP system yielding a greater mechanistic insight.[49] Other chiral diphosphines were explored: ^{i}Pr-DuPHOS, (S,S)-Me-BPE-HCl (Me-BPE = 1,2-[Bis(R,R)-trans-2,5-isopropyl-1-phospholano]ethane) and (R)-Prophos, but these were found to give lower activities.[28]

4. Hydrogenation of Levulinic Acid (LA) to 1,4-Pentanediol (1,4-PDO)

Short chain diols are valuable chemicals which are used on an industrial scale to form polymers, resins, platicizers, solvents and host of other chemical intermediates. Several sustainable routes to biogenic diols have been reported, notably the large scale production of 1,3-propanediol (1,3-PDO) can be achieved via fermentation methods from corn syrup or from glycerol obtained from sustainable sources using genetically modified strains of bacteria.[9] 1,2-propanediol (1,2-PDO) on the other hand can be produced from bio-glycerol via hydrogenolysis over a heterogeneous copper chromite catalyst at high temperatures and moderate pressures.[50] 1,4-PDO is a high value diol that can be directly synthesised from LA. Although 1,4-PDO is not as widely used as either 1,2-PDO or 1,3-PDO, it has potential applications for the production of biodegradable polymers, and importantly is an intermediate to 2-MTHF. In contrast to the synthesis of GVL from LA, which can be achieved using a wide range of both heterogeneous and homogeneous catalysts, as described above, the hydrogenation of LA beyond GVL to 1,4-PDO is much more challenging. The catalytic hydrogenation/dehydration of LA to GVL and then to 1,4-PDO involves the ring opening hydrogenation of GVL to give 4-hydroxylpentanal followed by further the reduction of the carbonyl functional group to generate 1,4-PDO (scheme 4).[33] The resistance of GVL to ring opening, due the stability of cyclic ester, hinders this process

and makes it more challenging to reduce GVL further. Therefore more forcing reaction conditions (higher temperature and pressure) are required to drive the hydrogenation beyond the lactone. Additionally, 1,4-PDO readily undergoes dehydration forming the cyclic ether (2-MTHF) making the selectivity of the desired product more challenging. Few homogeneous catalysts have been reported to effect the selective and direct transformation of LA to 1,4-PDO.

Horváth et al.[10] have performed the hydrogenation of LA to GVL and 1,4-PDO under hydrogen pressures (83 bar) with the in situ catalyst $Ru(acac)_3/P^nBu_3$ catalyst and also with the water soluble Ru catalyst $[(\eta^6\text{-}C_6Me_6)Ru(bpy)(H_2O)]SO_4$ (bpy = 2,2′-bipyridine) (fig. 8) under transfer hydrogenation conditions. Moderate yields and selectivities of 1,4-PDO (63%) were obtained using $Ru(acac)_3/P^nBu_3$ in neat levulinic under 83 bar of H_2 at 200 ^oC for 40 h (table 2, entry 1). Under their transfer hydrogenation conditions, sodium formate (HCOONa) was used as the hydrogen source and nitric acid was added to adjust to pH 4.0. Heating to 70^oC for 18 h resulted in a low yield of 1,4-PDO (25%) (table 2, entry 3). Leitner et al.[33,51] identified a ruthenium dihydride catalyst $[RuH_2(CO)(triphos)]$ (fig. 9) that could effectively hydrogenate both LA and itaconic acid beyond their corresponding lactones. The catalyst was generated in situ via the reaction of $Ru(acac)_3$ with the triphos ligand. The reaction temperature and additives, such as NH_4PF_4 and p-TsOH, were found to greatly affect the product selectivity. Under their standard reaction conditions (160^oC, 100 bar H_2) using in situ Ru/triphos complex 1,4-PDO could be formed in 95% yield (table 2, entry 4). When NH_4PF_4 was added 1,4-PDO was obtained in a diminished 35% yield since this proton source lead to the conversion of 1,4-PDO to 2-MTHF (table 2, entry 5). Increasing the reaction temperature did not improve the yield 1,4-PDO for the triphos system. When the additive was changed to p-TsOH, a stronger acid, 1,4-PDO was only formed in trace amounts and 2-MTHF was obtained in 39% (table 2, entry 6). The stronger acid is more able to protonate 1,4-PDO, better facilitating the dehydration step resulting in the cyclized ether product and lower amounts of 1,4-PDO. The effect of other phosphine ligands was also investigated; both the in situ $Ru(acac)_3/P^nOct_3$ and bidentate ligand system $Ru(acac)_3$/DPPB in the presence of NH_4PF_6 gave low yields of 1,4-PDO (6-30%). The preformed

catalyst [RuH_2CO(triphos)] was found to give appreciable yields of 1,4-PDO (73%) under the same catalytic conditions (table 2, entry 8),[51] although this was somewhat lower than yields compared to the best in situ generated triphos catalysts.

The ruthenium complex [Ru(triphos)(TMM)] (TMM = trimethylene methane) was discovered to be a highly effective precatalyst for the hydrogenation of a range of carbonyl substrates including carboxylic acids, esters, lactones, acid anhydrides, carboxamides, imides and ureas.[52] The TMM ligand appears to be very labile and readily decomplexes under reducing conditions generating the active catalyst. Near quantitative yields of 1,4-PDO were obtained from levulinic acid and methyl levulinate at 50 bar H_2 and 140 ^oC (table 2, entry 10).

More recently an Ru/N-triphos catalyst has proven to be effective for the conversion of LA beyond GVL.[34] In this study, a series of preformed Ru/N-triphos catalysts (fig. 8) were compared to in situ generated Ru/N-triphos catalysts for the transformation of LA to 1,4-PDO under 65 bar H_2 at 150 ^oC in THF. Using either the in situ generated Ru/N-triphos or the preformed [RuH_2(CO)(N-triphos)] catalysts only modest yields 36% of 1,4-PDO were obtained. However, when the carbonyl ligand on the preformed catalyst [RuH_2(CO)(N-triphos)] was replaced for a more labile triphenylphosphine ligand to generate [$RuH_2(PPh_3)$(N-triphos)] near quantitative yields of 1,4-PDO were obtained (table 2, entries 11-13). The more labile phosphine ligand is thought to readily generate the unsaturated active catalyst and thus facilitating the hydrogenation of GVL.

An air-stable Ru complex based on the tetradentate bipyridyl ligand PNNN (fig. 8, IV) has recently been reported to give high conversion of GVL to 1,4-PDO (99%), with very high TON (91,000) at room temperature and 50 bar H_2 under basic conditions (table 2, entries 17-18).[53] Key to this catalyst's activity is the appended diethyl amino group which is suspected to behave in a hemilable way. When the equivalent PNNP complex (i.e. with two *t*-butyl groups) much lower yields of 1,4-PDO (30%) were obtained over extended reactions times. NMR studies suggest that a *trans* dihydride complex is generated in the presence of H_2 and base. Dissociation of the hemilable NEt_2 group can then lead to the coordination of the substrate via the carbonyl oxygen. Hydride transfer to the carbonyl group is porposed to generate a Ru-hemiacetlaoxide intermediate.

Deprotonation of the benzylic group on the P^tBu_2 arm leads to geration of an alcohol group and a coordinated aldehyde. An equivalent of H_2 generates a dihydride that then reduces the aldehdye via another hydride transfer to give an alkoxide complex. Deprotonation of the benzylic group on the P^tBu_2 arm then leads to the formation of the a second alcohol group and regenateration of the catalyst with a second molecule of H_2.

A cobalt-triphos based catalyst has been recently reported to be effective the for the hydrogenation of a range carboxylic acid derivatives, including LA and GVL.[54] The catalyst was formed in situ from $Co(BF_4)_2.6H_20$ and triphos ligand, and catalysis performed in THF, at 80 bar H_2, 100 ^oC for 22 h (table 2, entry 19). Although high TONs were reported for several carboxylic acid substrates, high catalyst loadings (10 mol%) were required for the reactions of LA and GVL resulting in low TONs.[54] Although quantitative conversion of LA was achieved, modest yields of 1,4-PDO (47%) were obtained in addition to lower yields of 2-MTHF (14%). Using GVL as the substrate gave equally high conversions and higher yields of both 1,4-PDO (63%) and 2-MTHF (25%) (table 2, entry 20). The catalyst was formed in situ via the reaction of triphos and $Co(BF_4)_2.6H_2O$, and is thought to initially from the dimeric species $[Co_2(\mu\text{-}OH)_2(triphos)_2](BF_4)_2$ which subsequently splits when the hydroxyl ligands are substituted for a carboxyl group to give the active catalyst $[Co(triphos)(OOCR)]^+$. The authors propose that hydrogen coordinates and heterolytically splits across the Co-O bond, followed by the insertion of the hydride into the carbonyl carbon. A second hydrogenation and heterolytic splitting step then generates the complex $[Co(triphos)(H)(aldehyde)]^+$ and one equivalent of water. Hydride migration from the Co to the substrate and proton transfer from a new carboxylic acid substrate releases the alcohol and regenerates the active catalyst. Despite the low TONs for these reactions and modest yields of 1,4-PDO and 2-MTHF, this work sets a presedent for using cheap and abundant cobalt metal for carboxylic acid reductions under molecular hydrogen.

5. Hydrogenation of Levulinic Acid (LA) to 2-Methyltetrahydrofuran (2-MTHF)

2-MTHF is a cyclic ether that has several favourable characteristics over THF; these include higher boiling point, water immisciblity and much lower environmental impact due to its origins from sustainable resources and decomposition pathways.[15–19] The high energy density, lower flammablity, hydrophobic nature, low toxicity and high specific gravity of 2-MTHF make it suitable for use as fuel; thus 2-MTHF has been identified a non-petroleum liquid fuel which can be substituted for or blended with gasoline. 2-MTHF has also been reported to be a better blend with gasoline than methanol and can be more easily integrated into the distribution stream of a refinery.[7,55]

2-MTHF is typically produced via the sequential catalytic dehydrogenation-hydrogenation of levulinic acid (scheme 4) using either heterogeneous or homogenous catalysts. The reaction conditions employed and catalyst used for this process determines the product distribution of GVL, 1,4-PDO or 2-MTHF. The direct and selective formation of LA to 2-MTHF is a challenging process that requires forcing conditions. To date, there are only a few select homogenous catalysts that have been reported to effect this reaction efficiently. The first of these was reported by Horváth et al.,[10] on an NMR scale using a $Ru(acac)_3/P^nBu_3$ catalyst giving quantitative yields of 2-MTHF from neat LA under high pressure of H_2 and temperatures (80 bar, 200 ^oC) in the presence of the acidic additive NH_4PF_6 (table 2, entry 2). More recently, Leitner et al.,[33] reported the direct conversion of LA to 2-MTHF in moderate to high yields (39-92%) using a Ru/triphos catalyst in the presence of acidic additives (NH_4PF_6, p-TsOH and acidic ionic liquids), the highest yields being obtained using a mixture of NH_4PF_6 and ionic liquid additives (table 2, entries 5-7). In a mechanistic investigation of this process the same group conducted a detailed DFT study and a series NMR scale experiments on the catalytic hydrogenation of LA.[51] The active catalyst was proposed to be the unsaturated cationic complex $[Ru(triphos)H]^+$. The reduction of the carbonyl group of the LA substrate or intermediates (carboxylic acid, ester, ketone or aldehyde) was proposed to follow a common mechanistic pathway whereby the hydride from the catalyst is transferred to the carbonyl carbon

and then followed by protonation of the coordinated oxygen atom of the carbonyl via metathesis of a bound dihydrogen molecule.

The direct transformation of LA to 2-MTHF has also been achieved with a Ru/N-triphos catalyst, [$RuH_2(PPh_3)$(N-triphos)]. Only traces of 2-MTHF were found when the acidic additives NH_4PF_6 and p-TsOH were assessed, however, when $HN(Tf)_2$ was used yields of 2-MTHF greatly improved to 87% (table 2, entries 15-16). It was suspected that the reaction proceeds via a similar mechanism to that reported above, whereby an active catalyst of the type $[Ru(N\text{-triphos})H]^+$ is generated from [$RuH_2(PPh_3)$(N-triphos)] via the facile dissociation of PPh_3. The presence of acidic additives NH_4PF_6 and p-TsOH was detrimental to the reaction and is thought to remove a hydride ligand which is necessary for catalysis and may also compete with the LA substrate for binding to the metal centre. $HN(Tf)_2$ on the other hand produces a non-coordinating conjugate base which may explain why this acid was more effective leading to higher concentrations of 1,4-PDO that could then be acid catalysed to form 2-MTHF in the final transformation.[34]

6. Concluding Remarks

The catalytic transformation of biomass derived carboxylic acids such as levulinic acid provides numerous opportunities for the synthesis of a range of chemical feedstocks, solvents and fuel alternatives/additives that are of economic importance and environmentally beneficial. The use of homogeneous based catalysts for the transformation of LA is growing in academic interest and has the potential to offer excellent selectivity and high yields of GVL, 1,4-PDO and 2-MTHF. The range of homogenous catalysts that show excellent conversion of LA to GVL is increasing, and has extended beyond phosphine ligand sets and precious transition metals to include bipyidyl complexes and cheaper metals such as iron and cobalt. Going beyond GVL to 1,4-PDO and 2-MTHF presents challenges. Only a select number of homogenous catalysts have been reported to do this effectively, and all are based on phosphine ligands, tetradentate bipyridine/phosphine ligands or triphos-type ligands. These reactions are typically carried out at pressures and temperatures in excess of 50 bar of H_2 and

100 ^{o}C due to the inherent stability of GVL, although catalysis milder conditions is now proving to be successful.[53] The future direction of homogenous catalysis in this area may therefore lie in the discovery of catalysts that can effect this reaction under much milder reactions at lower pressures of H_2, at higher TOFs, with abundant first row transition metals and with cheaper ligands in order to encourage production of commercially valuable GVL and 2-MTHF. Catalyst separation also presents a challenge that is characteristic of homogeneous systems. The design of processes that more easily facilitate catalyst reuse and recovery from the product (e.g. biphasic systems or azeotroptic distillation) will go hand-in-hand with new milder and selective homogeneous processes for LA hydrogenation.

Acknowledgements

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Figures and Schemes

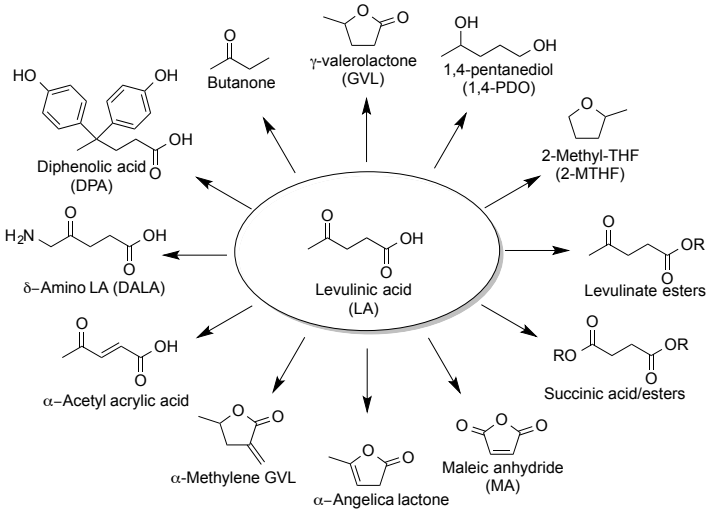


Figure 1. A selection of products that can be derived from levulinic acid (LA).

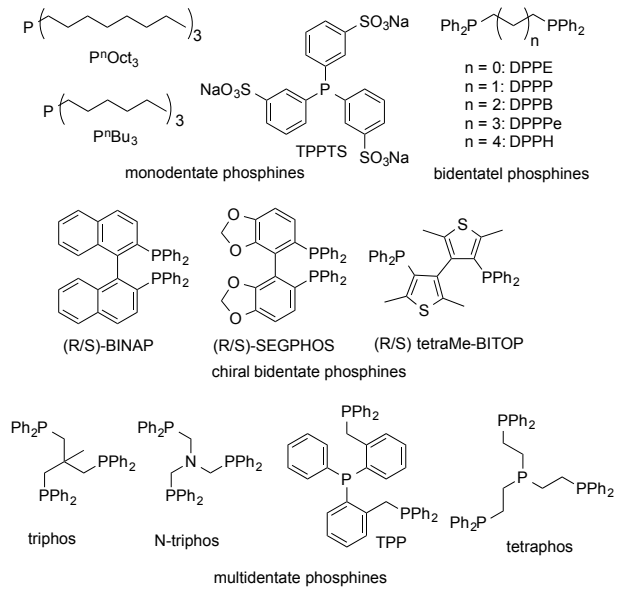


Figure 2. A range of mono-, bi- and multi-dentate phosphine ligands used for hydrogenation of LA.

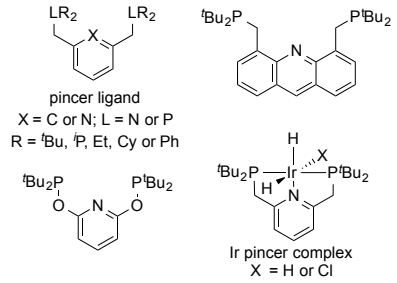


Figure 3. A range of pincer ligands and Ir pincer complexes studied for the hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL). [36]

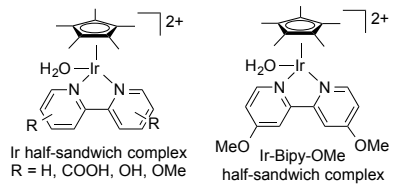


Figure 4. Iridium half-sandwich bipyridyl complexes studied for the hydrogenation of LA to GVL.[37]

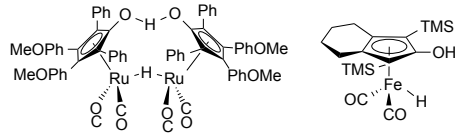


Figure 5. Shvo's catalyst and Casey's catalyst

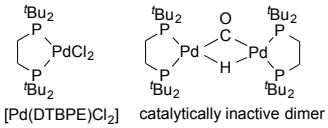


Figure 6. [Pd(DTBPE)Cl_2]preformed catalyst investigated for the hydrogenation of LA to GVL under gaseous and phase transfer conditions; and the catalytically inactive dimer that forms in situ. [39]

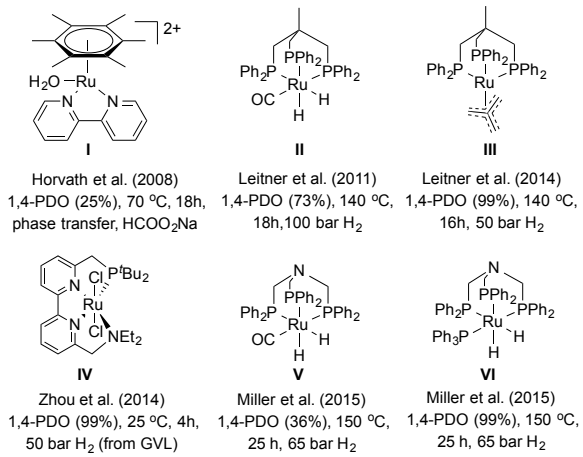
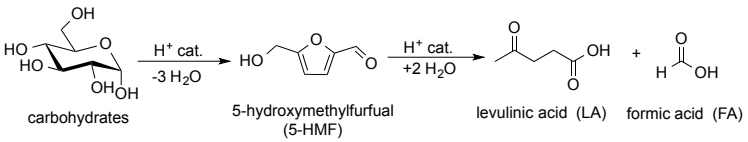
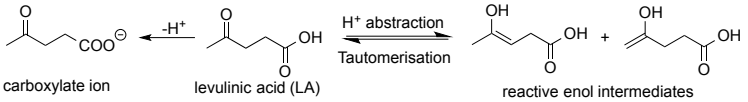


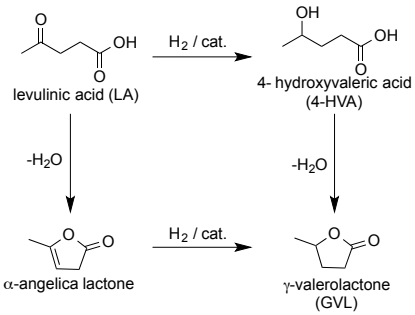
Figure 7. A range of preformed catalysts for the conversion of LA (or GVL) to 1,4-PDO.



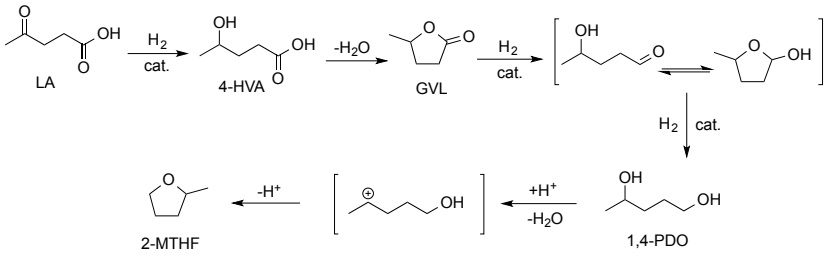
Scheme 1. Synthesis of levulinic acid from sugar monomers.



Scheme 2. Reactivity of levulinic acid.



Scheme 3. Synthesis of GVL from LA via either α-angelica lactone or 4-HVA.



Scheme 4. Catalytic route to 1,4-PDO and 2-MTHF from LA.[33]

Table 1. Homogenous catalysts used for the transformation of LA to GVL.

Entry	Catalyst	T [°C]	H_2 [bar]	S/C	Time [h]	Additives	GVL yield [%]	Ref
1	$[RuCl_2(PPh_3)_3]$	180	12	180	24	-	99	[32]
2	$[RuH_2(PPh_3)_4]$	180	12	180	24	-	58	[32]
3	$Ru(acac)_3/P^nBu_3$	135	100	1660	8	NH_4PF_6	>99	[10]
4	$Ru(acac)_3$/TPPTS	140	69	600	12	-	95	[10]
5	$Ru(acac)_3/P^nOct_3$	160	100	1000	18	NH_4PF_6	99	[33]
6	$Ru(acac)_3$/DPPB	160	100	1000	18	NH_4PF_6	89	[33]
7	$Ru(acac)_3$/triphos	160	100	1000	18	*p*-TsOH	58	[33]
8	$[RuH_2(CO)(triphos)]$	160	100	1000	18	-	22	[51]
9	$[RuH_2(CO)(triphos)]$	150	65	200	25	-	85	[34]
10	$[RuH_2(CO)(N\text{-}triphos)]$	150	65	200	25	NH_4PF_6	95	[34]
11	$[RuH_2(PPh_3)(N\text{-}triphos)]$	150	65	200	25	*p*-TsOH	77	[34]
12	$Ru(acac)_3$/TPP[a]	140	50	53,333	22	*p*-TsOH	95	[35]
13	$[Ir(COE)_2Cl_2]_2/PNP^tBu$	100	50	1000	15	base	96	[36]
14	$[IrH_3(PNP^tBu)]$	100	50	10,000	24	base	98	[36]
15	$[IrH_3(PNP^tBu)]$	100	100	100,000	48	base	71	[36]
16	[Ir-Bipy-OMe]	120	10	1000	4	-	98	[37]
17	[Ir-Bipy-OMe][b]	25	-	1000	24	-	94	[37]
18	$RuCl_3/PPh_3$[b]	150	-	1000	12	Base	93	[38]
19	Shov's catalyst[b]	100	-	2400	8	-	>99	[31]
20	$[Pd(DTBPE)Cl_2]$	80	5	1000	5	-	>99	[39]
21	$[Pd(DTBPE)Cl_2]$[b]	100	-	1000	5	NEt_3	>99	[39]
22	$RuCl_3$/TPPTS	90	45	1000	1.33	-	>99	[40]
23	$Ru(acac)_3/^nBu$-DPPDS	140	100	6,370	1.8	-	>99	[41]
24	$Ru(acac)_3$/DPPB	140	100	12,740	1.8	-	>99	[30]
25	$Fe(OTf)_2$/tetraphos[b,c]	140	-	24	24	-	98	[42]
26	Casey's catalyst[b,d]	100	-	100	19	base	95	[43]
27	$[Fe_3(CO)_{12}]$[b]	180	-	25	15	ImN	92	[44]
28	$Ru(COOCH_3)_2$/S-BINAP	25	100	1000	110	-	96 (99 ee)	[45]
29	Ru/SEGPHOS[e]	50	50	1000	20	-	>99 (99 ee)	[46]
30	$[Ru\text{-}tetraMe\text{-}BITIOP](OTf)_2$	45	100	500	76	-	>99 (98 ee)	[47]
31	$[Ru\text{-}tetraMe\text{-}BITIOP](OTf)_2$	45	100	500	43	1-bromo-butane	>99 (98 ee)	[47]
32	$[Ru(Me\text{-}allyl)_2(COD)]$/S-BINAP	60	60	200	5	HCl	66 (98.5 ee)	[28]
33	$[Ru(Me\text{-}allyl)_2(COD)]$/S-BINAP [c]	60	60	200	5	HCl	95 (99 ee)	[28]
34	$RuCl_3/(R\text{-}BINAP)]$[b]	65	60	200	6	HCl	96 (99 ee)	[48]

[a] Methyl levulinate to GVL conversion. [b] Transfer hydrogenation catalysis conditions using formic acid as hydrogen source. [c] Ethyl levulinate to GVL conversion. [d] Transfer hydrogenation catalysis conditions using isopropanol as hydrogen source. [e] Ethyllevulinate to 4-hydroxypentanoate conversion. Notes: ImN = imidazole. ee = enantiomeric excess. S/C = substrate to catalyst ratio based on mols. of metal. Turn over number (TON) = (S/C) x yield. Turn over frequency (TOF) = TON/time.

Table 2. Summary of different catalysts used for the transformation of LA to 1,4-PDO and 2-MTHF

Entry	Catalyst	T [°C]	P [bar]	S/C	Time [h]	Additives	Yield[%]			Ref.
							GVL	1,4-PDO	2-MTHF	
1	$Ru(acac)_3/P^nBu_3$	200	83	400	40	-	37	63	-	[10]
2	$Ru(acac)_3/P^nBu_3$	200	83	400	40	NH_4PF_6	-	-	>99	[10]
3	$[Ru(\eta^6\text{-}C_6Me_6)(bpy)(H_2O)]SO_4$[a]	70	-	250	18	-	25	25	-	[10]
4	$Ru(acac)_3$/triphos	160	100	1000	18	-	3	95	-	[33]
5	$Ru(acac)_3$/triphos	160	100	1000	18	NH_4PF_6	8	35	53	[33]
6	$Ru(acac)_3$/triphos	160	100	1000	18	*p*-TsOH	58	1	39	[33]
7	$Ru(acac)_3$/triphos	160	100	1000	18	aIL/*p*-TsOH	1	-	92	[33]
8	$[RuH_2(CO)(triphos)]$	160	100	1000	18	-	22	73	3	[51]
9	$[RuH_2(CO)(triphos)]$[b]	160	100	1000	18	aIL/*p*-TsOH	1	-	96	[51]
10	[Ru(triphos)(TMM)]	140	50	100	18	-	-	99	-	[52]
11	$Ru(acac)_3$/triphos	150	65	200	25	-	9	83	-	[34]
12	$Ru(acac)_3$/N-triphos	150	65	200	25	-	60	37	2	[34]
13	$[RuH_2(CO)(N\text{-}triphos)]$	150	65	200	25	-	53	36	<1	[34]
14	$[RuH_2(PPh_3)(N\text{-}triphos)]$	150	65	200	25	-	1	99	-	[34]
15	$Ru(acac)_3$/N-triphos	150	65	200	25	$HN(Tf)_2$	54	-	45	[34]
16	$[RuH_2(PPh_3)(N\text{-}triphos)]$	150	65	200	25	$HN(Tf)_2$	10	<1	87	[34]
17	$[RuCl_2(PNNN)]$[b]	25	50	1000	4	NaOMe	-	99	-	[53]
18	$[RuCl_2(PNNN)]$[b]	25	100	100,000	48	NaOMe	-	91	-	[53]
19	$Co(BF_4)_2.6H_2O$/triphos	100	80	10	22	-	-	47	14	[54]
20	$Co(BF_4)_2.6H_2O$/triphos[b]	100	80	10	22	-	-	65	25	[54]

[a] Transfer hydrogenation catalysis conditions using sodium formate/HNO_3 as hydrogen source. [b] substrate is GVL. Notes: S/C = substrate to catalyst ratio based on mols. of metal. Turn over number (TON) = (S/C) x yield. Turn over frequency (TOF) = TON/time. aIL = acidic ionic liquid 1-butyl-2-(4-sulfobutyl)imaidazolium-*p*-toluenesulfonate.

References

[1] R. C. Saxena, D. K. Adhikari, H. B. Goyal, *Renew. Sustain. Energy Rev.* **2009**, *13*, 167–178.

[2] I. S. Nashawi, A. Malallah, M. Al-Bisharah, *Energy & Fuels* **2010**, *24*, 1788–1800.

[3] S. Raju, M. Moret, R. J. M. K. Gebbink, *ACS Catal.* **2015**, *5*, 281–300.

[4] C. Delhomme, L.-A. Schaper, M. Zhang-Preße, G. Raudaschl-Sieber, D. Weuster-Botz, F. E. Kühn, *J. Organomet. Chem.* **2013**, *724*, 297–299.

[5] T. Werpy, G. Petersen, *Top Value Added Chemicals from Biomass Volume I; U.S. Department of Energy, Pacific Northwest National Laboratory, National Renewable Energy Laboratory, Office of Biomass Program*, **2004**.

[6] G. Centi, P. Lanzafame, S. Perathoner, *Catal. Today* **2011**, *167*, 14–30.

[7] J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenscwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, *Resour. Conserv. Recycl.* **2000**, *28*, 227–239.

[8] J. Wang, A. I. Scott, *Tetraherdon Lett.* **1997**, *38*, 739–740.

[9] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chemie - Int. Ed.* **2007**, *46*, 4434–4440.

[10] H. Mehdi, V. Fabos, T. Robert, A. Bodor, L. T. Mika, I. T. Horvath, *Top. Catal.* **2008**, *48*, 49–54.

[11] R. Weingarten, W. C. Conner, G. W. Huber, *Energy {&} Environ. Sci.* **2012**, *5*, 7559–7574.

[12] P. P. Upare, J. M. Lee, D. W. Hwang, S. B. Halligudi, Y. K. Hwang, J. S. Chang, *J. Ind. Eng. Chem.* **2011**, *17*, 287–292.

[13] V. Fabos, M. Y. Lui, Y. F. Mui, Y. Y. Wong, L. T. Mika, L. Qi, E. Csefalvay, V. Kovacs, T. Szucs, I. T. Horváth, *ACS Sustain. Chem. Eng.* **2015**, *3*, 1899–1904.

[14] J. M. Tukacs, B. Fridrich, G. Dibó, E. Székely, L. T. Mika, *Green Chem.* **2015**, *17*, 5189–5195.

[15] D. F. Aycock, *Org. Process Res. {&} Dev.* **2006**, *11*, 156–159.

[16] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.

[17] M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2014**, *16*, 516–547.

[18] M. G. Al-Shaal, A. Dzierbinski, R. Palkovits, *Green Chem.* **2014**, 1358–1364.

[19] V. Pace, P. Hoyos, L. Castoldi, P. Domínguez de Maria, A. R. Alcantara, *ChemSusChem* **2012**, *5*, 1369–1379.

[20] A. Chatzidimitriou, J. Q. Bond, *Green Chem.* **2015**, *17*, 4367–4376.

[21] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, *114*, 1827–1870.

[22] P. J. Deuss, K. Barta, J. G. de Vries, *Catal. Sci. Technol.* **2014**, *4*, 1174–11096.

[23] D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes, J. R. H. Ross, *Biorefineries-Industrial Process. Prod. Status Quo Futur. Dir.* **2008**, *1*, 139–164.

[24] D. M. Alonso, J. M. R. Gallo, M. a Mellmer, S. G. Wettstein, J. a Dumesic, *Catal. Sci. Technol.* **2013**, *3*, 927–931.

[25] D. J. Braden, C. A. Henao, J. Heltzel, C. C. Maravelias, J. A. Dumesic, *Green Chem.* **2011**, *13*, 1755.

[26] L. Deng, Y. Zhao, J. Li, Y. Fu, B. Liao, Q. X. Guo, *ChemSusChem* **2010**, *3*, 1172–1175.

[27] Y. Yang, X. Xu, W. Zou, H. Yue, G. Tian, S. Feng, *Catal. Commun.* **2016**, *76*, 50–53.

[28] E. V. Starodusteva, O. V. Turova, M. G. Vinogradov, L. S. Gorshkova, V. A. Ferpontov, *Russ. Chem. Bull.* **2005**, *54*, 2374–2378.

[29] T. P. Brewster, A. J. M. Miller, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2013**, *135*, 16022–16025.

[30] J. M. Tukacs, M. Novák, G. Dibó, L. T. Mika, *Catal. Sci. Technol.* **2014**, *4*, 2908–2912.

[31] V. Fábos, L. T. Mika, I. T. Horváth, *Organometallics* **2014**, *33*, 181–187.

[32] K. Osakada, T. Ikariya, S. Yoshikawa, *J. Organomet. Chem.* **1982**, *231*, 79–90.

[33] F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, *Angew. Chemie - Int. Ed.* **2010**, *49*, 5510–5514.

[34] A. Phanopoulos, A. J. P. White, N. J. Long, P. W. Miller, *ACS Catal.* **2015**, *5*, 2500–2512.

[35] A. D. Chowdhury, R. Jackstell, M. Beller, **2014**, 3360–3365.

[36] W. Li, J.-H. Xie, H. Lin, Q.-L. Zhou, *Green Chem.* **2012**, *14*, 2388.

[37] J. Deng, Y. Wang, T. Pan, Q. Xu, Q. Guo, Y. Fu, **2013**, 1163–1167.

[38] L. Deng, J. Li, D. M. Lai, Y. Fu, Q. X. Guo, *Angew. Chemie - Int. Ed.* **2009**, *48*, 6529–6532.

[39] C. Ortiz-Cervantes, M. Flores-Alamo, J. J. Garcia, *ACS Catal.* **2015**, *5*, 1424–1431.

[40] M. Chalid, A. A. Broekhuis, H. J. Heeres, *J. Mol. Catal. A Chem.* **2011**, *341*, 14–21.

[41] J. M. Tukacs, D. Király, A. Strádi, G. Novodarszki, Z. Eke, G. Dibó, T. Kégl, L. T. Mika, *Green Chem.* **2012**, *14*, 2057–2065.

[42] M. C. Fu, R. Shang, Z. Huang, Y. Fu, *Synlett* **2014**, *25*, 2748–2752.

[43] N. Dai, R. Shang, M. Fu, Y. Fu, **2015**, *3*, 405–408.

[44] G. Metzker, A. C. B. Burtoloso, *Chem. Commun.* **2015**, *51*, 14199–14202.

[45] T. Ohkuma, M. Kitamura, R. Noyori, *Tetraherdon Lett.* **1990**, *31*, 5509–5512.

[46] T. Saito, T. Yokozawa, T. Ishizaki, T. Moroi, N. Sayo, T. Miura, H. Kumobayashi, *Adv. Synth. Catal.* **2001**, *343*, 264–267.

[47] T. Benincori, S. Rizzo, T. Pilati, A. Ponti, M. Sada, E. Pagliarini, S. Ratti, C. Giuseppe, D. Ferra, F. Sannicolo, *Tetrahedron Asymmetry* **2004**, *15*, 2289–2297.

[48] E. V. Starodubtseva, O. V. Turova, M. G. Vinogradov, L. S. Gorshkova, V. A. Ferapontov, M. I. Struchkova, *Tetrahedron* **2008**, *64*, 11713–11717.

[49] O. V. Turova, E. V. Starodubtseva, M. G. Vinogradov, V. A. Ferapontov, *J. Mol. Catal. A Chem.* **2009**, *311*, 61–65.

[50] M. A. Dasari, P. Kiatsimkul, W. R. Sutterlin, G. J. Suppes, *Applies Catal.* **2005**, *281*, 225–231.

[51] F. M. A. Geilen, B. Engendahl, M. Holscher, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2011**, 14349–14358.

[52] T. Vom Stein, M. Meuresch, D. Limper, M. Schmitz, M. Holscher, J. Coetzee, D. J. Cole-Hamilton, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2014**, *136*, 13217–13225.

[53] W. Li, J. Xie, M. Yuan, Q. Zhou, *Green Chem.* **2014**, *16*, 4081–4085.

[54] T. J. Korstanje, J. I. Van Der Vlugt, C. J. Elsevier, B. De Bruin, *Science* **2015**, *350*, 298–302.

[55] M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2014**, *16*, 516.