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PAPER

Cyclopentadienyl and pentamethylcyclopentadienyl ruthenium complexes as catalysts for the total deoxygenation of 1,2-hexanediol and glycerol†

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The ruthenium aqua complexes [cp*Ru(OH_2)(N–N)](OTf) (cp* = η^5-pentamethylcyclopentadienyl, N–N = 2,2′-bipyridine, phen = 1,10-phenanthroline, OTf^- = trifluoromethanesulfonate) and the acetonitrile complex [cpRu(CH_3CN)(bipy)](OTf) (cp = η^5-cyclopentadienyl) are water-, acid-, and thermally stable (>200 °C) catalysts for the hydrogenation of aldehydes and ketones in sulfolane solution. In the presence of HOTf as a co-catalyst, they effect the deoxygenation of 1,2-hexanediol to 1-hexanol and hexane. Glycerol is deoxygenated to 1-propanol in up to 18% yield and under more forcing conditions completely deoxygenated to propene. The structure of the acetonitrile pro-catalyst [cpRu(CH_3CN)(bipy)]-(OTf) has been determined by X-ray crystallography (space group $P\bar{1}$ (a = 9.3778(10) Å; b = 10.7852(10) Å; c = 11.1818(13) Å; α = 101.718(5)°; β = 114.717(4)°; γ = 102.712(5)°; R = 3.95%).

Introduction

The transesterification of vegetable oils, and to a lesser degree animal fats, with methanol (or ethanol) gives bio-diesel, a fuel that can be used directly in diesel engines. By necessity glycerol is produced in stoichiometric amounts as a by-product of bio-diesel synthesis, decreasing the atom efficiency and economic feasibility of the process. The current world-wide oversupply of glycerol is estimated at more than 1×10^6 t/y and while there is some use for glycerol in the food and cosmetics industries, present supply far exceeds demand.[1] The conversion of glycerol into value-added products therefore has the potential to substantially enhance the overall economics of the process.[2–7] Solvay[8] has announced plans to build new epichlorohydrin (1-chloro-2,3-epoxypropane) plants that will use glycerol instead of propylene as the starting material while Dow and Archer Daniels Midland are also planning to use glycerol rather than propylene to produce propylene glycol (1,2-propanediol).[9]

Economically very attractive would be the selective deoxygenation of glycerol to 1,3-propanediol, a high value-added chemical used in the synthesis of the polyester poly(propylene) terephthalate (PPT), marketed as Sorona™ and Corterra™ by DuPont and Shell, respectively, and in the manufacture of Cerenol™ a new polyether developed by DuPont. Shell's process for the production of 1,3-propanediol involves hydroformylation of ethylene oxide to the intermediate 3-hydroxypropanal, followed by *in situ* hydrogenation to 1,3-propanediol using a homogeneous Co/Ru-based catalyst system.[10] The DuPont-Degussa process consists of the hydration of acrolein to 3-hydroxypropanal followed by *in situ* hydrogenation to 1,3-propanediol.[11–12] A more recent joint venture by DuPont and Tate & Lyle uses a fermentation process based on glucose.[13–15]

The use of heterogeneous catalysts for the deoxygenation of glycerol to both 1,2- and 1,3-propanediol has been widely investigated.[16–28] In general, 1,2-propanediol is the major product, with formation of little to no 1,3-propanediol observed. However, Kurosaka *et al.* reported a 13% yield of 1,2-propanediol, a 24% yield of 1,3-propanediol, and a 28% yield of 1-propanol from glycerol using a $Pt/WO_3/ZrO_2$ catalyst[29–30] and Tomishige reported the conversion of glycerol to 1,3-propanediol over rhenium-oxide modified iridium nanoparticles in 38% yield at 81% conversion of glycerol.[31] We recently proposed an acetol intermediate as the possible origin of the selectivity for glycerol deoxygenation to 1,2-propanediol

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† Electronic supplementary information (ESI) available: Details on the catalytic deoxygenation reactions of the 1,2-hexanediol model system. Images of ^{1}H and ^{13}C NMR spectra of the three catalysts **1–3** used. Image of the liquid/liquid extractor used in the optimized synthesis of the intermediate tris(acetonitrile)(η^5-cyclopentadienyl)ruthenium(II) triflate (**10**). CCDC reference number 782288. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0gc00255k

using heterogeneous catalysts,[32] whereas Liu and co-workers have proposed an alternative pathway *via* glyceraldehyde on a Cu–ZnO catalyst.[28] Ellman and Schüth and co-workers each reported an interesting alternative valuation of glycerol by converting it to allyl alcohol, using either formic acid or an iron-oxide catalyst.[33–34]

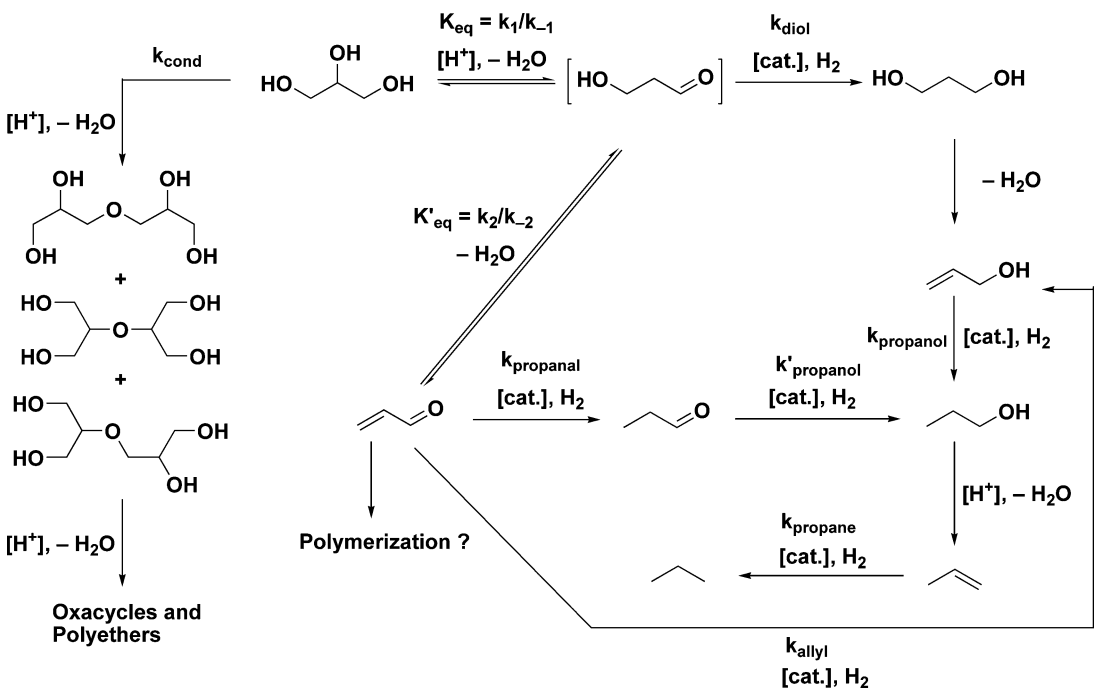
Comparatively few efforts have been directed towards a homogeneously catalyzed deoxygenation of glycerol. Shell has reported the synthesis of 1,3-propanediol from glycerol using a homogeneous phosphine-substituted palladium catalyst, acid, and syngas.[35] While this example illustrates proof-of-concept, the actual yield of the desired 1,3-propanediol was very low at only 2%, with the major product, acrolein, being formed in 41% yield. Braca reported the conversion of glycerol into 1-propanol using $HI/Ru(CO)_4I_2$ in water or amide solvents at 200 °C.[36]

The most efficient homogeneous system for the synthesis of 1,3-propanediol from glycerol was patented by Celanese.[37] Glycerol was reacted with catalytic amounts of tungstic acid (H_2WO_4) and $[Rh(acac)(CO)_2]$ in a syngas atmosphere to yield approximately 20% each of 1,2- and 1,3-propanediol. In this catalyst the role of the CO is presumably to maintain the carbonyl ligands on metal centre, thus stabilizing the catalyst against reduction to Rh(0). This system has also not been commercialized, likely due to the cost of the rhodium catalyst and the still comparatively low yield of product. Motivated by the work of Braca and Che, we hypothesized that it may in principle be possible to design an effective homogeneous Brønsted acid/metal complex based catalyst system for the selective deoxygenation of glycerol to 1,3-propanediol, which then would potentially also be applicable to the deoxygenation of higher sugar alcohols.[38]

Scheme 1 outlines some of the principally conceivable deoxygenation and condensation pathways of glycerol. Initial dehydration of glycerol yields the highly reactive intermediate 3-hydroxypropanal, which could then be subsequently hydrogenated to the desired 1,3-propanediol, if the step labelled by k_{diol} is kinetically competent. However, 1,3-propanediol can itself also be further dehydrated and hydrogenated to 1-propanol and even propane. Whereas these secondary products are not nearly as valuable as 1,3-propanediol, their generation from a renewable resource in high yield could potentially be of interest.

Of concern is the second dehydration of 3-hydroxypropanal to acrolein, an undesirable product due to its tendency to polymerize or possibly react irreversibly with catalytically active metal centres. It is also apparent that a complex mixture of products will exist as a function of temperature and glycerol, acid and water concentrations. To our knowledge, the only published thermodynamic parameter for the dehydration of glycerol in the condensed phase known to us, is the reaction enthalpy for the dehydration of 3-hydroxypropanal to acrolein in acidic aqueous conditions, approximately 25 kJ mol^{-1} at 20 °C,[39–40] *i.e.*, at room temperature, the dehydration of 3-hydroxypropanal is unfavourable, but likely becomes favourable at higher temperature.[41] The condensation behaviour of glycerol in solvents such as sulfolane or NMP (*N*-methyl-pyrrolidin-2-one) as a function of temperature, acid, water, or substrate concentration is completely unknown. One of the challenges is to empirically establish whether reaction conditions can be identified that will favour the formation of 3-hydroxypropanal and to develop a highly efficient metal catalyst that will intercept 3-hydroxypropanal before the second dehydration, while at the same time limiting the reaction of glycerol or 1,3-propanediol to secondary products.

By definition any homogeneous metal catalyst capable of effecting the desired transformations in Scheme 1, must be acid- and water-stable. In an effort to design such

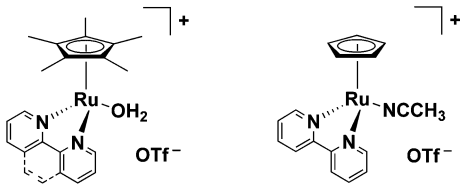


Scheme 1 Conceivable pathways for the deoxygenation of glycerol catalyzed by a homogeneous Brønsted acid/metal complex based system.

highly robust catalyst systems, we have previously tested the complexes $[(cp^*Ru(CO)_2)_2(\mu\text{-}H)](OTf)$,[42–43] *cis*-$[Ru(6,6'\text{-}Cl_2\text{-}bipy)_2(OH_2)_2](OTf)_2$,[44] and $[(\eta^6\text{-arene})Ru(OH_2)(N\text{–}N)](OTf)_2$ (η^6-arene = *p*-cymene, C_6Me_6; N–N = 2,2′-bipyridine = *bipy*, 1,10-phenanthroline = *phen*, 6,6′-diamino-2,2′-bipyridine = *dabipy*, 2,9-diamino-1,10-phenanthroline = *daphen*; OTf^- = trifluoromethanesulfonate = *triflate*)[32] for activity in the selective deoxygenation of terminal diols and glycerol under aqueous acidic conditions, *i.e.*, in aqueous sulfolane solution with HOTf added as the acid condensation catalyst.

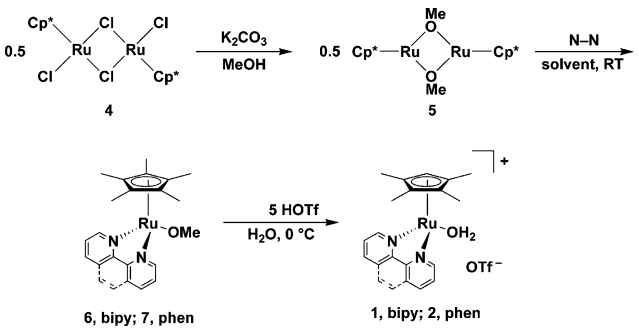
All these catalysts convert terminal diols to the corresponding *n*-alcohol by dehydration to the corresponding aldehyde and its *in situ* hydrogenation to the alcohol. Under more forcing conditions, dehydration to the alkene and hydrogenation to the alkane can occur. The deoxygenation of terminal diols serves as a model system for the desired glycerol deoxygenation pathway of glycerol to 1,3-propanediol *via* 3-hydoxypropanal and catalyst activity for the hydrogenation of aldehydes and ketones is therefore a necessary, but not sufficient, condition for the deoxygenation of glycerol and higher sugar polyols. Empirically we established that in sulfolane and sulfolane/water mixtures triflic acid-catalyzed terminal diol deoxygenation occurred at temperatures as low as 110 °C, while the initial dehydration of glycerol required temperatures of at least 150 °C. The above catalysts therefore failed to convert glycerol because they decompose by loss of the ligand framework and reduction to ruthenium metal at temperatures above 125 °C, as indicated by the formation of a black precipitate. Postulating that a tridentate pyridine-based ligand would result in a more temperature stable catalyst, we subsequently successfully tested the terpyridine complexes $[Ru(H_2O)_3(2,2':6',2''\text{-terpyridine})](OTf)_2$ and $[Ru(H_2O)_3(4'\text{-phenyl-}2,2':6',2''\text{-terpyridine})](OTf)_2$. These complexes are in fact stable in aqueous acidic medium at temperatures up to 250 °C, but also fail to generate any 1,3-propanediol. Instead they promote complete deoxygenation of glycerol.[45]

In a parallel effort to develop high-temperature, acid- and water-stable catalysts we also postulated that replacement of the η^6-arene ligand in the previously tested half-sandwich complexes[32] that decompose due to loss of their "lid" by an η^5-cyclopentadienyl (cp) or pentamethyl-cyclopentadienyl (cp*) ligand should result in a more temperature-stable system, as the bond between an anionic cyclopentadienyl ligand and the Ru^{2+} centre should be stronger than that between a neutral η^6-arene ligand and the metal. We also hypothesized that the anionic ligand would lead to higher electron density on the metal, resulting in a more *hydridic* metal hydride, possibly leading to a more active catalyst and that the cp-based catalyst should be more active than the cp*-based catalysts due to a decrease in steric bulk around the metal centre. Here we report the optimized synthesis of the ruthenium aquo complexes $[cp^*Ru(OH_2)(N\text{–}N)](OTf)$ (N–N = bipy (**1**), phen (**2**)) and the acetonitrile complex $[cpRu(CH_3CN)(bipy)](OTf)$ (**3**) (Chart 1) and their evaluation as catalysts for the deoxygenation of a terminal diol and glycerol.



1, bipy; 2, phen 3

Chart 1



4 5

6, bipy; 7, phen 1, bipy; 2, phen

Scheme 2 Preparation of $[cp^*Ru(OH_2)(N\text{–}N)](OTf)$ (**1** and **2**).

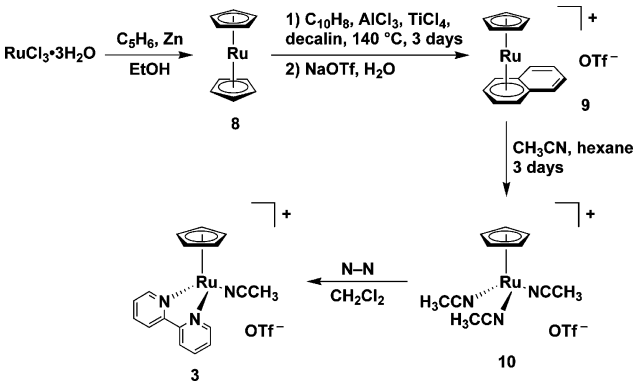
Results and discussion

Catalyst synthesis

The synthesis of **1** and **2** is outlined in Scheme 2. The common entry into cp*Ru chemistry is the dimer $[cp^*RuCl_2]_2$ (**4**), which is readily prepared from $RuCl_3 \cdot 3H_2O$ and pentamethylcyclopentadiene in refluxing EtOH.[46–48] Stirring **4** in MeOH for several hours (or refluxing for 1 h) with an excess of K_2CO_3 generated $[cp^*Ru(OMe)]_2$ (**5**). Dimer **5** is bright red in solution and as a solid. It is extremely air-sensitive and immediately turns brown upon exposure to oxygen or water.[48–49] However, it can be isolated in up to quantitative yield if care is taken. cp*Ru(OMe)(bipy), **6**, was prepared through direct reaction of $[cp^*Ru(OMe)]_2$ (**5**) with bipy;[49] cp*Ru(OMe)(phen), **7**, is prepared similarly.[50] The yield and purity of the cp*Ru(OMe)(N–N) complexes was higher if they were prepared from batches of **5** rather than *in situ* from **4**. The OMe complexes **6** and **7** are also highly oxygen-sensitive: a sample of solid **6** was observed to smoke upon exposure to air. The new aqua complexes $[cp^*Ru(OH_2)(N\text{–}N)](OTf)$, **1** and **2**, precipitated cleanly from deoxygenated water upon addition of excess HOTf.

In contrast to the corresponding dicationic η^6-arene complexes,[32] the cp* aqua complexes are also oxygen-sensitive; for example, an NMR sample of **1** in CD_3OD began to decompose within 15 min upon exposure to air, and had completely decomposed after 90 min. On the other hand, an NMR sample in dmso-d_6 exhibited no changes even after several days of exposure. No sign of DMSO coordination was observed in the ^1H NMR, ^{13}C NMR, or IR spectra. This proved to be extremely advantageous for catalysis, as given the similarities between DMSO and sulfolane, once the aqua complexes were dissolved in sulfolane they resisted oxidation, which made setup of the hydrogenation reactions in the pressure reactors straightforward.[51] The behaviour of **2** was comparable.

Scheme 3 illustrates the preparation of $[cpRu(CH_3CN)(bipy)](OTf)$, **3**, originally prepared as the hexafluoro phosphate salt by Lacour and co-workers.[52,53] The synthetic pathway begins with the formation of ruthenocene (**8**) through the reduction of $RuCl_3$ by zinc in the presence of excess



Scheme 3 Preparation of [cpRu(NCCH$_3$)(bipy)](OTf).

cyclopentadiene. Lewis acid mediated displacement of a cp ligand by naphthalene afforded [cpRu(naphthalene)](OTf) (**9**).[54] The reaction of **9** with bipy to directly generate **3** was unsuccessful in a variety of solvents. We therefore prepared complex **10**, [cpRu(CH$_3$CN)$_3$][OTf], which contains three labile acetonitrile ligands. Complex **10** was synthesized in high yield through an equilibrium reaction by stirring **9** in acetonitrile for three days. Optimizing the synthesis originally developed by Kundig and Monnier,[54] we found that a continuous extraction of hexane using a liquid/liquid extractor specifically designed for this purpose[55] allowed for dissolution and removal of the displaced naphthalene, pushing the reaction equilibrium towards the tris(acetonitrile) complex in excellent yields. Complex **10** was isolated as yellow oil upon removal of the solvent. Displacement of two acetonitrile ligands by bipy occurs readily at room temperature or with gentle heating in CH_2Cl_2 for 30 min to 1 h. Crystals of complex **3** suitable for X-ray diffraction were grown from a concentrated aqueous solution.

Shown in Fig. 1 is a view of [cpRu(NCCH$_3$)(bipy)][CF$_3$SO$_3$] (**3**) which crystallizes in the triclinic space group $P\bar{1}$ (a = 9.3778(10) Å; b = 10.7852(10) Å; c = 11.1818(13) Å; α = 101.718(5)°; β = 114.717(4)°; γ = 102.712(5)°; R = 3.95%). Characteristic bond lengths (Å) about the ruthenium centre are Ru–N6 = 2.071(3), Ru–N11 = 2.095(3), and Ru–N22 = 2.094(3). The distance from Ru to the centroid of the cp ring is 1.791(3) Å. Characteristic bond angles (°) about the ruthenium centre are N11–Ru–N22 = 76.36(10), N22–Ru–N6 = 85.76(11), N6–Ru–N11 = 87.39(10), C1–Ru–N22 = 108.88(13), C1–Ru–N11 = 110.33(12), and C1–Ru–N6 = 158.95(12), resulting in a piano stool coordination environment about the ruthenium centre.

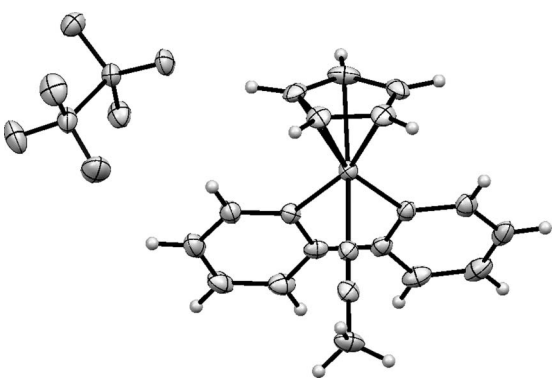
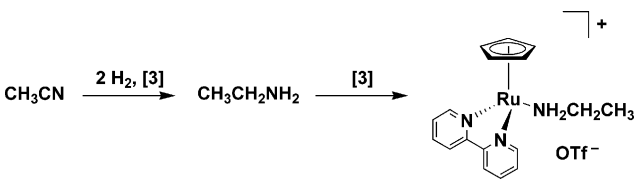


Fig. 1 A view of [cpRu(NCCH$_3$)(bipy)][CF$_3$SO$_3$] (3) as determined by single crystal X-ray crystallography. Displacement ellipsoids are drawn at the 50% probability level.

Catalyst screening against carbonyl substrates

Complexes **1–3** were initially screened against a series of aldehyde and ketone substrates to determine their principle viability as hydrogenation catalysts, as described in an earlier publication.[45] The [cp*Ru(OH$_2$)(N–N)](OTf) catalysts readily hydrogenated aldehydes to alcohols, while hydrogenation activity on ketones scaled inversely with substrate steric demand. No conversion of any of the substrates to their corresponding alcohols was observed with [cpRu(CH$_3$CN)(bipy)](OTf). This initial result was surprising, since at worst the catalyst should have been comparable to the cp* systems, but not entirely inactive. The only difference between the pro-catalyst complexes rests in their labile ligands, *i.e.*, H$_2$O *vs.* CH$_3$CN, which we postulate to be displaced by H$_2$(g) under the reaction conditions leading to a heterolytic activation of a transient η^2-H$_2$ ligand and a ionic hydrogenation mechanism in analogy to the previously investigated [(cp*Ru(CO)$_2$)$_2$(μ-H)](OTf) system.[42–43,56] The difference in place-holder ligands in the pro-catalysts must therefore be the origin of this effect. We hypothesized that once displaced during the reaction, the acetonitrile is hydrogenated to ethylamine and subsequently irreversibly coordinates to the complex's active site (Scheme 4). A control experiment in which two equivalents of triflic acid were added to protonate any ethylamine formed, thus preventing coordinative inhibition of the catalyst, did in fact render **3** active against carbonyl substrates, yielding results comparable to **1** and **2**. Furthermore, this means that **3** is also active for hydrogenation of nitriles, which was confirmed in a separate study.[57]



Scheme 4 Irreversible coordination of ethylamine to 3.

Catalytic deoxygenation of the 1,2-hexanediol model system

Having established the carbonyl hydrogenation activity of the catalysts **1–3**, they were evaluated for the deoxygenation of l,2-hexanediol, which serves as a model system for glycerol. 1,2-Hexanediol rather than 1,2-propanediol was chosen as the model system due to the lower volatility of the products (1-hexanol, hexene, and hexane *vs.* 1-propanol, propene and/or propane), resulting in improved quantification by GC. At temperatures ≥200 °C all three catalysts achieve complete conversion of the substrate to mixtures of 1-hexanol (up to 17% yield with catalyst **3**) and hexane (up to quantitative yield with catalyst **3**), which phase separates from the polar aqueous acidic reaction mixture. In these reactions all three catalysts give deep red reaction solutions. The solutions can be reused without loss of activity by adding more substrate to the reaction mixture upon complete conversion as determined by quantitative GC. For

catalyst **1** this results in formation of a layer of a mixture of hexene and hexane while for catalyst **3** hexane was obtained. The detailed results of the 1,2-hexanediol deoxygenation reactions are contained in the ESI†.

Glycerol deoxygenation

Having established catalytic activity and thermal stability of complexes **1–3**, parallel reactor studies as a function of acid and water concentration with glycerol as the substrate were conducted at 150, 175, and 200 °C using the same conditions as in the analogous 1,2-hexanediol study.[58] Using a 24-well parallel reactor allowed for an array of 20 samples, each with a different acid and water content, and 4 blanks containing only 100 mmol L^{-1} dimethyl sulfone in sulfolane. After 24 h at 150 °C, none of the systems showed any conversion of the glycerol substrate to identifiable products. In samples containing at least 20% H_2O, the initial glycerol concentrations essentially equalled the final concentrations, confirming that condensation reactions are suppressed, if the water content is sufficiently high. Upon increasing the temperature to 175 °C, up to 11% 1-propanol was produced after 24 h using catalyst **1** (Fig. 2). Glycerol conversion in these reactions varied from only 14% at 50% water content and 4 equivalents of acid to 100% at 10% water content at any acid concentrations, *i.e*, the conversions scale inversely with water and directly with acid content of the reaction mixture. Catalysts **2** and **3** produced up to 7% 1-propanol. Very small amounts of acrolein and *cis*/*trans*-2-(2-ethanol)-4-hydroxymethyl-1,3-dioxolane were identified by GC/GC-MS. As was observed with the 1,2-hexanediol model experiments, there was no 'best' acid/H_2O combination and the mass balance was incomplete. A small amount of a black precipitate was seen with **3** in samples containing 40–50% H_2O indicating catalyst decomposition at that high water concentration.

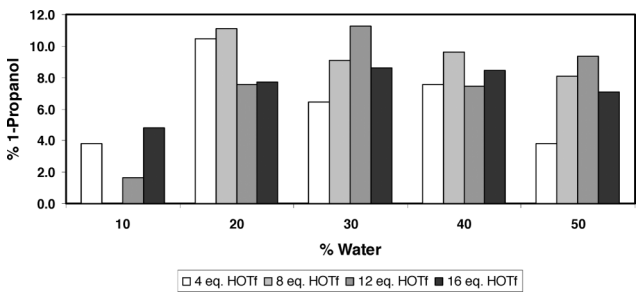


Fig. 2 Glycerol acid/water series, catalyst **1**, 175 °C, 24 h.

With catalysts **1** and **2** the yields of 1-propanol increased to a maximum of 18% at 200 °C (Fig. 3), but so did the amount of glycerol lost to unidentified products. Small amounts of the 1,3-dioxolane product and 2-propanol (from *Markovnikov* hydration of propene) were also observed. The combination of 50% H_2O and 8 equivalents of HOTf gave the best yield of 1-propanol for **1**. Yields of 1-propanol ranged from 4–14% for **2**, but again there was not a clear 'best' acid/H_2O combination. When using **3** at 200 °C (Fig. 4), increasing catalyst decomposition with increasing water concentration and hence lower 1-propanol yield was observed in all but the 10% H_2O samples. Thus, while the cp system is as thermally-stable as the analogous cp* systems, its water-tolerance decreases with

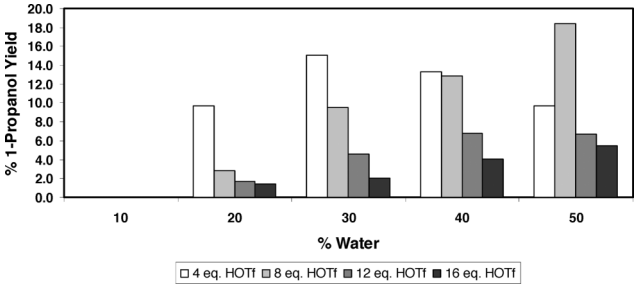


Fig. 3 Glycerol acid/water series, catalyst **1**, 200 °C, 24 h.

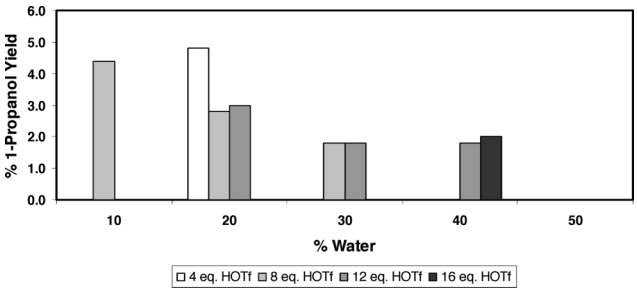


Fig. 4 Glycerol acid/water series, catalyst **3**, 200 °C, 24 h.

increasing temperature. However, with H_2O contents ranging from 0–8%, 1-propanol was produced in 6–8% yield with no signs of catalyst decomposition. The GC traces of the reactions carried out with **3** at low water concentrations showed no peaks other than those for 1-propanol, sulfolane and the internal standard DMS and no precipitate was present in the reaction solutions (clear red liquids).

Several experiments were conducted to better understand the possible reasons for the lack of mass balance in these reactions. ESI(–)-MS analysis of the reaction mixture did not show the presence of higher glycerol condensates, but ESI(+)-MS indicated the possible presence of a linear glycerol dimer. Column chromatography of several combined samples obtained from reactions carried out with **1** in the parallel reactor led to the isolation of a small amount of 2,2′-oxy-(dipropan-1,3-diol). Moreover, it had been observed that some samples obtained from reactions carried out with **1** or **2** in the acid/water series were cloudy or had formed a sticky residue at the end of the reaction. Several samples were combined, filtered, and a ^1H NMR spectrum in $CDCl_3$ obtained, which exhibited a broad peak from 0.5–3 ppm, indicating the formation of a polymer of unknown composition. Glycerol is readily dehydrated to acrolein, which is known to polymerize.[59] Glycerol oligomerization may account for the formation of the sticky residue and thus at least part of the deficient mass balances observed. Another possibility that would explain the mass balance issues is that the glycerol is being completely deoxygenated to propene or propane, which due to their low solubility in the polar reaction mixture resides in the gas phase and are lost upon venting the reactor.

Testing for the latter possibility, GC-MS analysis of gas samples obtained from the head space of acid/water series experiments carried out with catalyst **1–3** in the parallel reactor could however not unambiguously establish the presence of propene or propane, as the gas volumes available from the head space of this reactor are very small. However, when the reaction

Table 1 Product distribution from hydrogenation of glycerol in MeOH[a]

Compound[b]/catalyst	Yield [%]	
	1	**3**
Glycerol	38	52
1,3-PDO	0	0
1-Propanol	3	0
1,2,3-$(OMe)_3$-propane	8	0
1,3-$(OMe)_2$-2-propanol	12	5
2,3-$(OMe)_2$-1-propanol	39	6
3-OMe-1,2-propanediol	10	47

[a] Conditions: [Glycerol] = 500 mmol L^{-1}, 200 °C, 3.45 MPa H_2 (cold), 8 HOTf with respect to [Ru], 0.5 mol% catalyst, [dimethyl sulfone] = 100 mmol L^{-1} ISTD, in MeOH, 3.5 h. [b] Identified by GC-MS against authentic samples or by database match of fragmentation pattern.

was carried out at 200 °C in a 50 mL single well reactor in pure sulfolane, *i.e.*, with no added H_2O, analysis of gas samples obtained from the head-space of reactions carried out with catalysts **1** and **3** by micro-GC against authentic gas mixtures of C1–C6 alkanes and C2–C6 1-alkenes (1000 ppm each in helium) showed propene gas as the sole product. The solutions from these reactions are clear red with no precipitate polymer present and peaks in the GC and HPLC analysis of the remaining reaction solutions are limited to the internal standard DMS, the solvent sulfolane and (for HPLC) HOTf precluding the presence of soluble dimers or oligomers,[60] *i.e.*, under these conditions both catalysts achieve complete conversion of glycerol to propene.

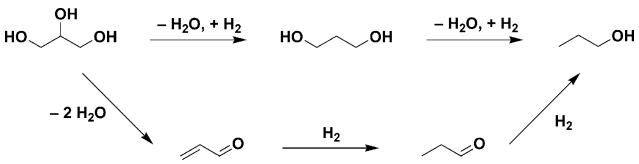
Glycerol hydrogenation in MeOH

As with 1,2-hexanediol†, glycerol was hydrogenated in MeOH in an attempt to trap the substrate and any intermediates and products as identifiable and quantifiable methyl ethers. The reaction pressure and time were reduced to 3.45 MPa H_2 (cold) and 3.5 h, as it was found that the volatile methyl ethers formed lead to a rapid increase in pressure.[61] The results of the MeOH experiment can be found in Table 1. Approximately 60–70% of the substrate was converted into methyl ethers.[62] This suggests that at 200 °C in aqueous acidic medium dimerization and oligomerization of glycerol is indeed an extremely facile process, which must however be reversible under these conditions leading to the formation of propene as discussed above. The fact that some polymer formation was observed in the reactions carried out in the parallel reactor may be a function of less efficient mixing and hydrogen dissolution in the small 2 mL glass-lined wells of the parallel reactor that in comparison to the impeller agitated reaction solution in the 50 mL reactor cannot be stirred as efficiently. This favours condensation/polymerization *vs.* hydrogenation, *i.e.*, in the parallel reactor the reactions may be hydrogen mass-transport limited and not operate in the kinetically competent regime.

1,3-Propanediol control experiments

In order to establish whether any 1,3-propanediol that may have formed during the reaction according to the sequence shown at the top of Scheme 1 would under the reaction conditions have further reacted to 1-propanol or propene, the hydrogenation of 1,3-propanediol was carried out as a control experiment. After 24 h at 200 °C in 1 : 1 H_2O : sulfolane with 8 equivalents of HOTf (the optimum conditions from the glycerol deoxygenations) using catalyst **1**, only 1% of propanol had formed and 80% of the 1,3-propanediol remained, *i.e.*, 1,3-propanediol is only marginally reactive under these conditions.

The complete lack of 1,3-propanediol observed in the parallel reactions coupled with the presence of acrolein and propanal at the 2 h time point and the negligible production of 1-propanol in the control experiment with 1,3-propanediol logically demands the pathway involving double dehydration of glycerol to acrolein followed by hydrogenation of acrolein to propanal and then propanol as shown on the bottom of Scheme 5 below. It thus appears that – at least with the catalyst systems described here and as also observed with the previously described terpy system[45] – the desired pathway *via* 3-hydroxypropanal is not the operative pathway in the deoxygenation of glycerol under homogeneous acidic conditions.



Scheme 5 Proposed pathways from glycerol to 1-propanol.

Conclusions from the deoxygenation reactions of glycerol

The main insight reached from studies on the deoxygenation of glycerol is that the desired pathway of glycerol to 1,3-propanediol (and to further deoxygenation products such as 1-propanol or propene) is not the operative pathway. Instead, under homogeneous aqueous acidic conditions employed, glycerol is dehydrated to acrolein, which is subsequently hydrogenated to 1-propanol and eventually dehydrated propene. Illustrated in Fig. 5 is a likely reaction profile for the deoxygenation of glycerol.[45] In this scenario, the activation barrier for the initial dehydration of glycerol to 3-hydroxypropanal is the highest – all subsequent barriers are lower, *i.e.*, $\Delta G^{\ddagger}_1 >> \Delta G^{\ddagger}_n$. Thermodynamically, the reaction cascade is downhill and once the first dehydration occurs, there is nothing to stop the reaction from proceeding all the way to the totally deoxygenated product gaseous propene, which is not further hydrogenated, as it is no longer in contact with the active catalyst due to its low solubility in the polar reaction solution. Since the initial dehydration reaction is most likely catalyzed by the Brønsted

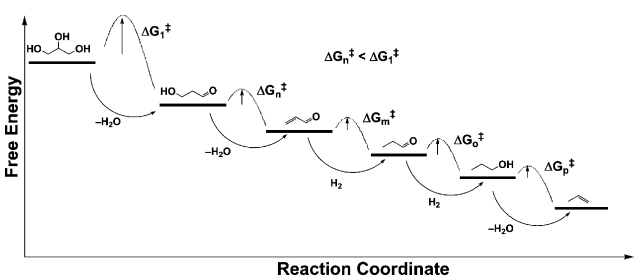


Fig. 5 Reaction profile for the catalytic deoxygenation of glycerol under homogeneous Brønsted acidic conditions.

acid present, its activation barrier is a function of the acid, the nature of the substrate and its solvation in the reaction medium (here water/sulfolane mixtures), but not of the metal hydrogenation catalyst present. This may be a general feature of homogeneously catalyzed sugar alcohol deoxygenations using a Brønsted acid/hydrogenating metal catalyst system – regardless of the carbon chain length.

Thus, we conclude that – regardless of the type of metal catalyst used – it is unlikely that 1,3-propanediol can be produced from glycerol under homogeneous Brønsted acidic conditions at the elevated temperatures (>150 °C) required for the initial dehydration of glycerol. This appears to contradict the earlier patent by Che,[37] but is in agreement with the report by Braca, who had obtained similar results using $HI/Ru(CO)_4I_2$ as the catalyst.[36] It also suggests that the generation of 1,3-propanediol from glycerol over heterogeneous catalysts must take place under kinetic rather than thermodynamic control, resulting in a product distribution that does not represent the thermodynamic sink of the reaction cascade shown in Fig. 5. We hypothesize that this is an effect of the glycerol interaction with the surface of a solid Lewis rather than a homogeneously dispersed Brønsted acid used by us. This would also explain the results claimed by Che, as we had previously noticed that in the H_2WO_4 used as the acid is in fact not soluble in the *N*-methyl-pyrolidin-2-one solvent used in this study.[37,45]

Furthermore, under homogeneous aqueous acidic conditions and depending on catalyst activity and reaction conditions (*i.e.*, the relative kinetic competency of the reactions associated with k_{diol} *vs* k_{cond} and k_2 in Scheme 1) the condensation chemistry of glycerol can dominate consuming the substrate before it can be deoxygenated.

In comparing the catalytic activity of [cp*Ru(OH_2)(N–N)](OTf) (N–N = bipy (**1**), phen (**2**)) and [cpRu($NCCH_3$)-(bipy)](OTf) (**3**), we found that **1** and **2** were very similar, with **3** being slightly more active for the deoxygenation of the substrates tested. All three catalysts are extremely thermally-stable (>200 °C), but **3** is less water-tolerant than **1** and **2**. Nevertheless, it appears to be the most active catalyst under conditions with little to no additional water (<10%) with the decrease in steric bulk around the metal centre resulting in increased catalytic activity, in particular with the larger 1,2-hexanediol substrate. The high thermal stability of these complexes suggests that they may be active for deoxygenation reactions of higher sugars and sugar alcohols, such as erythritol to THF or xylitol and sorbitol to a variety of other deoxygenated products.

Experimental

General

All manipulations were conducted under an atmosphere of argon using standard Schlenk-line techniques or in a glovebox, using freshly distilled solvents or degassed water saturated with argon. K_2CO_3 was vacuum-dried for several hours at 200 °C, then stored in the glovebox. All other reagents were available commercially and were used without further purification. NMR spectra were recorded on Bruker 300 MHz or 400 MHz spectrometers using sodium 2,2-dimethyl-2-silapentane-5-sulfonate as a reference for spectra obtained in D_2O; all other spectra were calibrated to the residual protonated solvent signal. IR spectra were recorded on a Nicolet 4700-FTIR spectrometer. Mass spectroscopic analyses of the metal complexes (MALDI-TOF) were performed by the WATSPEC Mass Spectrometry Facility, University of Waterloo, Waterloo, ON, Canada, the ThoMSon MS laboratory at the University of Campinas, Brazil and the Biological Mass Spectrometry Facility, University of Guelph, Guelph, ON, Canada (BMS/UofG). Di-μ-chloro-bis[(η^5-pentamethylcyclopentadienyl)chlororuthenium(III)] (**4**), di-μ-methoxo-bis(η^5-pentamethylcyclopentadienyl)diruthenium(II) (**5**), 2,2′-bipyridine(methoxo)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**6**), methoxo(η^5-pentamethylcyclopentadienyl) (1, 10 - phenanthroline) - ruthenium(II) (**7**), Bis(η^5-cyclopentadienyl)ruthenium(II) (Ruthenocene, **8**) and (η^5-Cyclopentadienyl)(η^6-naphthalene)ruthenium(II) triflate (**9**) were prepared according to the literature procedures cited in the main text. Tris(acetonitrile)(η^5-cyclopentadienyl)ruthenium(II) triflate (**10**) was prepared according to the modified optimized procedure given below.

Aqua(2,2′-bipyridine)(η^5-pentamethylcyclopentadienyl)ruthenium(II) triflate (1). **6** (0.840 g, 1.98 mmol) was dissolved in 20 mL degassed H_2O at 0 °C to give a dark orange-brown solution. Concentrated HOTf (0.88 mL, 9.94 mmol) was added dropwise from a syringe; a precipitate formed immediately. The solution was stirred for 15 min at 0 °C, then warmed to room temperature. The solid was filtered, rinsed three times with 5 mL portions of H_2O, and vacuum-dried overnight. Yield: 0.819 g (74%) red-brown powder. ^{1}H NMR (300 MHz, CD_3OD): 1.60 (s, 15H), 7.69 (t, J = 5.7 Hz, 2H), 8.03 (t, J = 7.2 Hz, 2H), 8.37 (d, J = 7.5 Hz, 2 H), 9.45 (d, J = 4.2 Hz, 2H). ^{13}C NMR (75 MHz, CD_3OD): 9.6 (*C*H_3), 78.0 (*C*), 123.4 (*C*H), 127.5 (*C*H), 137.9 (*C*H), 154.0 (*C*H), 157.9 (*C*). MS (+ESI): m/z calc. for $C_{20}H_{23}N_2{}^{102}$Ru: 393.0937, found 393.0869 [(C_5Me_5)^{102}Ru(bipy)]+.

Aqua(η^5-pentamethylcyclopentadienyl)(1,10-phenanthroline)-ruthenium(II) triflate (2). **7** (0.430 g, 0.961 mmol) was dissolved in 10 mL degassed H_2O at 0 °C to give a yellow-brown solution. Concentrated HOTf (0.425 mL, 4.80 mmol) was added dropwise from a syringe; a precipitate formed immediately. The solution was stirred for 15 min at 0 °C, then poured onto a frit and allowed to settle for 15 min. A very gentle vacuum was applied as follows to prevent sucking the very fine precipitate through the frit along with the liquid: The hose connecting the Schlenk flask to the Schlenk line was evacuated and then isolated from the vacuum. The stopcock was very carefully opened to the evacuated hose until the filtrate began to slowly drip through the frit and then was closed. This procedure was repeated until the filtration was complete. The solid was rinsed three times with 3 mL portions of H_2O, then ether, and vacuum-dried overnight. Yield: 0.454 g (81%) dark yellow powder. ^{1}H NMR (300 MHz, dmso-d_6): 1.56 (s, 15H), 8.09 (dd, J = 5.1, 8.1 Hz, 2H), 8.25 (s, 2H), 8.79 (d, J = 7.8 Hz, 2 H), 9.38 (d, J = 5.1 Hz, 2H). ^{13}C NMR (75 MHz, dmso-d_6): 8.7 (*C*H_3), 86.5 (*C*), 126.1 (*C*H), 127.5 (*C*H), 129.8 (*C*), 136.5 (*C*H), 146.4 (*C*), 154.2 (*C*H). MS (+ESI) m/z calc. for $C_{22}H_{23}N_2{}^{102}$Ru: 417.0937, found 417.0879 [(C_5Me_5)^{102}Ru(phen)]+.

Tris(acetonitrile)(η^5-cyclopentadienyl)ruthenium(II) triflate (10). A 250 mL Schlenk flask was charged with 3.1 g (6.98 mmol) of **9** and dissolved in 80 mL of degassed acetonitrile. The clear brown solution was added under inert conditions using a cannula to a liquid/liquid extractor. The acetonitrile solution was continuously extracted using degassed hexane for 3 days. After 3 days the acetonitrile solution was orange in colour. It was transferred to a 100 mL Schlenk flask while maintaining an inert atmosphere. The solvent was then removed under dynamic vacuum to yield the product as a dark orange viscous oil, 80–90% yield. ^{1}H NMR (300 MHz, CD_3CN): 1.95 (s, 9H), 4.26 (s, 5H).

(Acetonitrile)(2,2′-bipyridine)(η^5-cyclopentadienyl)ruthenium(II) triflate (3). A 100 mL Schlenk flask was charged with 3.05 g (6.98 mmol) of the oil (**10**) and dissolved in 5 mL of degassed CH_2Cl_2. A separate 50 mL Schlenk flask was charged with 0.99 g (6.34 mmol) of 2,2′-bipyridine and dissolved in 20 mL of degassed CH_2Cl_2. This solution was added by syringe to the solution of **10**, which immediately turned clear dark red. The reaction was left to stir for 20 min at room temperature. Degassed ether (50 mL) was added to the solution and it was cooled to 0 °C for 3 h. Dark red crystals precipitated. The supernatant was removed by syringe and the crystals were washed with degassed ether (2 × 25 mL). The crystals were dried under dynamic vacuum. Yield 3 g (93%). ^{1}H NMR (300 MHz, CD_3CN): 1.95 (s, 3H), 4.41 (s, 5H), 7.49 (t, J = 6.6 Hz, 2H), 8.00 (t, J = 7.7 Hz, 2H), 8.29 (d, J = 8.1 Hz, 2H), 9.47 (d, J = 5.9 Hz, 2H). ^{13}C NMR (75 MHz, CD_3CN): 72.1 (*C*H), 123.8 (*C*H), 126.8 (*C*H), 138.0 (*C*H), 156.9 (*C*H), 157.1 (*C*). MS (MALDI) m/z calc. for $C_{15}H_{13}N_2{}^{102}$Ru: 323.1815, found 322.9991 [cp^{102}Ru(bipy)]+.

Catalysis

All reagents and solvents were obtained from commercial sources and used without further purification. Catalysts **1–3** were stored under argon atmosphere in the glovebox after preparation. Trifluoromethanesulfonic acid (HOTf) was stored under argon in a Rotaflo Schlenk tube. Industrial grade hydrogen gas was used for all hydrogenation experiments. An Autoclave Engineers (AE) Minireactor with a 50 mL stainless steel (316SS) reactor vessel was employed for the 1,2-hexanediol temperature profiles, 1,3-propanediol control experiment, all hydrogenations in MeOH and for the hydrogenation of glycerol yielding gas phase analysis samples. A HEL™ Cat-24 reactor containing 2 mL borosilicate glass test tubes was utilized for all acid/H_2O parallel experiments and the carbonyl screen. GC analyses were performed on a Varian 3800 using either a 30 m × 0.25 mm × 0.025 μm medium polarity DB-1701 column (carbonyls, 1,2-hexanediol) or a 30 m × 0.25 mm × 0.025 μm high polarity WAX column (glycerol). Quantitative analysis of the 1,2-hexanediol and glycerol experiments was performed through a three-level calibration against authentic samples using dimethyl sulfone (100 mmol L^{-1}) as an internal standard for 1,2-hexanediol, 1-hexanol, glycerol, 1,3-propanediol, and 1-propanol. Quantification for all other substrates from 1,2-hexanediol and glycerol experiments was approximated using the GC-FID response factor for 1-hexanol or 1,3-propanediol, respectively, corrected for the effective carbon number.[63] GC-MS analyses of the reaction solutions were conducted using a Varian 3800 GC/Saturn 2000 MS using either a DB-1701 or WAX column. ESI-MS analyses for glycerol dimers/oligomers were performed at (BMS/UofG) and the ThoMSon Laboratory for Mass Spectrometry, Institute of Chemistry, State University of Campinas, Brazil (Instituto de Química, Universidade Estadual de Campinas, Brasil). Analysis of gas samples obtained from the head space of the reactors was carried out by GC-MS using the Varian Saturn 2000 and by GC using a SRI-8610 micro-GC. With the latter, propene was identified against two authentic gas mixtures containing methane, ethane, propane, butane, pentane and hexane or ethylene, propene, 1-butene, 1-pentene and 1-hexene (1000 ppm each, balance helium). HPLC analysis was carried out according to Varian Application Note 1534 (00.1 N H_2SO_4 on Metacarb 87H) using an RI Detector. Stock solutions were prepared in 250.0 or 500.0 mL volumetric flasks of 1,2-hexanediol (500 mmol L^{-1} 1,2-hexanediol, 100 mmol L^{-1} dimethyl sulfone, in sulfolane) and glycerol (500 or 1000 mmol L^{-1} glycerol, 100 or 200 mmol L^{-1} dimethyl sulfone, in sulfolane). A stock solution of 100 mmol L^{-1} dimethyl sulfone in sulfolane was prepared in a 100.0 mL volumetric flask. Control reactions carried out in sulfolane solutions with up 50% water content in the absence of catalysts **1–3** gave no hydrogenated products in either reactor type.

Representative procedure for a glycerol deoxygenation in the 50 mL mini-reactor

Glycerol stock solution was dispensed into a 25.0 mL volumetric flask, HOTf (22 μL, 4 mol equivalents with respect to catalyst) was added, and the solution mixed well. The catalyst (2.5 mmol L^{-1}, 0.5 mol% of substrate concentration) was weighed into a small vial. The stock solution and catalyst were combined in the mini-reactor vessel and stirred in the sealed reactor for several minutes before opening the reactor, removing 0.5 mL for initial GC analysis, and resealing the reactor. The reactor was evacuated for 2 min using a water aspirator, pressurized to 4.83 MPa with H_2 gas, and allowed to equilibrate for 2 min. The evacuation/pressurization cycle was repeated twice more. Stirring was set at about 200 rpm and the reactor was heated to the reaction temperature. Samples were taken at 1, 2, 4, and 8 h from reaching the set operating temperature *via* the sample tube, which was first flushed with 0.5 mL of the reaction mixture to ensure cross-contamination from an earlier sample did not occur. After 24 h the reactor heating was turned off and the reactor placed in an ice bath for 30 min to condense any volatile products. The reactor was vented, opened, and a final sample taken for GC.

Representative procedure for a glycerol parallel hydrogenation experiment

The catalyst (5 mmol L^{-1}, 0.5 mol% of substrate concentration) was weighed into a 50.0 mL volumetric flask. The flask was filled to the mark with glycerol stock solution and the solution mixed well. Acid stock solutions were prepared by adding the desired volume of HOTf (18, 35, 53, 71 μL for 4, 8, 12, 16 equivalents with respect to catalyst) to 10.0 mL of the catalyst solution in a volumetric flask and mixing well. Water (0.15, 0.30, 0.45, 0.60, 0.75 mL for 10, 20, 30, 40, 50% H_2O) and sulfolane (0.60, 0.45, 0.30, 0.15, 0.00 mL for 10, 20, 30, 40, 50% H_2O) were

measured into 2 mL glass test tubes, followed by 0.75 mL of the acid stock solution. Final [glycerol] = 500 mmol L^{-1}, [dimethyl sulfone] = 100 mmol L^{-1}, [catalyst] = 2.5 mmol L^{-1}, [HOTf] = 10, 20, 30, 40 mmol L^{-1} in the sample test tubes. Dimethyl sulfone stock solution (1.0 mL) was added to the four blank test tubes. A 2 × 2 mm stir bar was added to each test tube, but to ensure complete homogeneity each tube was thoroughly mixed using a vortex mixer. A 0.5 mL sample was taken for initial GC analysis from all but the blank samples. The tubes were loaded into the parallel reactor and the reactor sealed. The reactor was evacuated for 2 min using a water aspirator, pressurized to 7.58 MPa with H_2 gas, and allowed to equilibrate for 2 min. The evacuation/pressurization cycle was repeated twice more. The reactor was placed in a glass wool-lined aluminium heating block on a hotplate, magnetic stirring was set to the maximum, and the reactor was heated to the reaction temperature. Timing started once the reactor reached the set operating temperature. At the end of the reaction, heating was stopped and the reactor placed in an ice bath for 30 min, followed by a dry ice/acetone bath for 5 min to condense and freeze any volatile products. The reactor was vented, warmed to room temperature, opened, and the remainder of the solutions in the test tubes transferred to GC vials for analysis.

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GC standard), in sulfolane. Water concentrations ranged from 10 to 50 v/v %, while acid equivalents with respect to catalyst ranged from 4 to 16 [10 to 40 mmol L^{-1}].
59 An attempt to carry out a control reaction using acrolein directly as the substrate failed due to its high reactivity with acid in water/sulfolane mixtures resulting in the instantaneous formation of brown solutions upon addition of HOTf indicating decomposition of the substrate.
60 With these HPLC analysis conditions (Varian Application Note 1534 ñ Analysis of trace polyglycerols in glycerol by HPLC; 00.1 N H2SO4 on Metacarb 87H) separation of components in solution occurs through a combination of ion exclusion, ion exchange, ligand exchange and size exclusion with the lowest molecular weight conceivable liquid or liquid soluble product *n*-propanol having the highest retention time.
61 In several instances during these experiments very high pressures (>12 MPa) caused by the formation of dimethyl ether in the reaction mixtures were observed, which resulted in the bursting of the rupture disk in the safety valve of the reactor. The authors thus advise caution when running reactions in either MeOH or EtOH solvent in the presence of acid. The use of a fail-safe pressure limiting device is essential in these cases. The same precautions should apply to any other polyalcohol reactions carried out in acidic MeOH.
62 The yield percentage total in this experiment adds up to 110% due to errors introduced by using approximate response factors for the methyl ethers calculated through the use of effective carbon numbers - see reference 63.
63 J. T. Scanlon and D. E. Willis, *J. Chromatogr. Sci.*, 1985, **23**, 333–340.

