Direct transformation of terminal *vic*-diols to primary alcohols and alkanes through hydrogenation catalyzed by [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ in acidic medium

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Abstract

Through a combination of consecutive acid catalyzed dehydration and metal catalyzed hydrogenation steps the system consisting of HOTf and [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ catalyzes a direct conversion of terminal diols to primary alcohols in a single reactor. Typical reaction conditions are 500 mmol/L diol, 0.5 mol% ruthenium and 6 mol% acid catalyst at 125 °C and 700 psi H$_2$(g) for 48 h resulting in primary alcohol yields of up to 63%. At higher acid concentrations total hydrogenation becomes the dominant reaction yielding corresponding alkane in up to 97% yield.
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1. Introduction and motivation

The direct transformation of *vic*-diols to the corresponding mono alcohols constitutes one of the key reactions required for the conversion of renewable sugar alcohols to α,ω-diols and other oxygen content reduced chemicals, which are actual or potential polymer components. By combining an acid catalyzed dehydration with a transition metal complex catalyzed hydrogenation of the resulting aldehyde or ketone, this transformation is in principle achievable by a two-step process in a single reactor (Fig. 1).

Applying this strategy, an economically and ecologically particularly attractive target would be the direct conversion of glycerol (the by-product of biodiesel production) to 1,3-propanediol (one of the components of Corterra^{TM}/Sorona^{TM}). Due to the high propensity for acrolein formation and other subsequent reactions (polymer-ization/decomposition or hydrogenation to *n*-propanol) under acidic conditions (Fig. 2), this conversion does however constitute a major challenge.[1]

To date only low yields of 1,3-propanediol at low turnover numbers and turnover frequencies have been achieved by this method using either (P–P)Pd(OAc)$_2$ (P–P = bulky chelating diphosphine ligand) [2], {[Cp*Ru(CO)$_2$]$_2$(μ-H)}$^+$OTf$^-$ (Cp* = η^5-C$_5$Me$_5$; OTf = OSO$_2$CF$_3$) [3] or Rh(CO)$_2$(acetylacetonato) [4] as the active metal component and either hydrochloric/methlysulfonic (MSA), trifluoromethylsulfonic acid (HOTf) or H$_2$WO$_4$, respectively, as the acid catalyst. The latter rhodium/tungsten catalyst system does in fact produce high yields of *n*-propanol through hydrogenation of the acrolein formed in the reaction, however the realization of higher yields of the desired 1,3-propanediol

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[1] Similar condensation reactions to carbonyl and ether compounds are observed with higher sugar polyol of the general composition HOCH$_2$(CHOH)$_n$CH$_2$OH, e.g. to 1,4-anhydroerythritol (for $n = 2$) or isosorbide (for $n = 4$), the discussion and implications of which for biomass conversion are beyond the scope of the present manuscript [1].

R = alkyl, (CHOH)$_n$CH$_2$OH; R' = H, alkyl
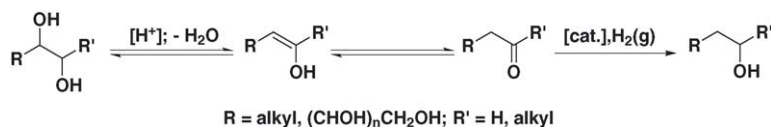
Fig. 1. Two step transformation of *vic*-diols to monools.

will require highly active catalysts that can compete effectively with the second dehydration step of the reactive 3-hydroxypropionaldehyde intermediate, i.e. with reference to Fig. 2 shows $k_{diol} \approx k_2$ or better $k_{diol} \gg k_2$ under reaction conditions amenable to the overall transformation. The identification of new types of catalysts that are capable of the generic diol transformation in Fig. 1 using terminal 1,2-diols as model substrates (i.e. R' = H in Fig. 1) is a first step towards this goal.

The combination of the complex {[Cp*Ru(CO)$_2$]$_2$(μ-H)}$^+$OTf$^-$ (Cp* = η^5-C$_5$Me$_5$; OTf = OSO$_2$CF$_3$) and HOTf provided an example of a catalyst system active in this type of reaction, achieving the conversion of 1,2-propanediol to *n*-propanol in good yields and very high selectivity [5]. The catalyst is believed to operate through a ionic hydrogenation mechanism [6] with the thermally unstable dihydrogen complex [Cp*Ru(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$ as the postulated active species effecting a heterolytic activation of hydrogen gas. This catalyst is however deactivated by water, the necessary by-product of the reaction [7]. At least in part this also explains its low reactivity with glycerol as the substrate [3], which through the unavoidable formation of acrolein generates more water in the reaction mixture than 1,2-propanediol.

In spite of the limited viability of {[Cp*Ru(CO)$_2$]$_2$(μ-H)}$^+$OTf$^-$, several criteria that can serve as guidelines for the identification and/or rational design of other homogeneous catalysts for the reactions in Figs. 1 and 2 under acidic conditions emerge from the results obtained with this system:

(1) The complex should have a demonstrated ability to activate hydrogen gas in a heterolytic fashion. This criterion would be met by the formation of a highly reactive and acidic non-classical dihydrogen or a dihydride complex that serves as a source of active hydride and protons at the same time, i.e. acts as a *ionic hydrogenation catalyst* that tolerates and maintains the necessary acidic conditions. Fig. 3 illustrates this concept. (Note, however that the dihydride or dihydrogen complex does not have to be an isolable species, as long as it can be postulated to form in the catalytic cycle.)

(2) The complex must be compatible with acidic aqueous conditions, i.e. the catalytic centre must not be deactivated by the formation of inert metal–oxygen bonds (e.g. through formation of alkoxide, oxo complexes or in the extreme isopoly oxoacids). This behaviour is more typical for the earlier transition metals (up to group VII) that form a wide variety of metal alkoxides and through hydrolysis under aqueous acidic conditions potentially oxygen bridged or isopoly oxo species with relatively inert metal oxygen bonds [8]. By comparison, metal–oxygen bonds of the later transition metals, e.g. Ru, Rh, Ir, Pd, or Pt, are typically more reactive, both in homo- and heterolytic M–O bond cleavage reactions [9]. Thermochemical studies on Ru and Pt model systems [10] also indicate that exchange reactions between hydride and ligands with oxygen, nitrogen and carbon donor atoms on these later transition metals are close to thermoneutral suggesting that these metals are better candidates for hydrogenation catalysis in aqueous solutions involving oxygen rich substrates.

(3) The complex must not contain ligands that cannot withstand acidic aqueous and reducing conditions at elevated temperatures anticipated to be required for the reactions. This suggests robust nitrogen donor atom based ligands such as bipy and phenanthroline derivatives, while phosphites and most phosphines and carbenes are probably less suitable.

Applying these criteria in a systematic literature survey of known hydrogenation catalysts we identified the complex [*cis*-Ru(6,6'-Cl$_2$-bipy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (**1**) as a potential catalyst for the reaction in Fig. 1. Lau and co-workers established that **1** is an active catalyst for the hydrogenation of
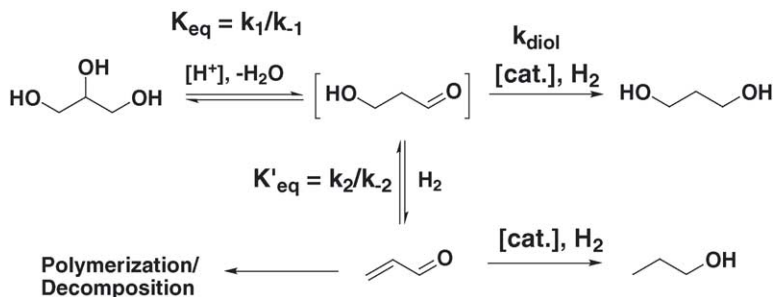

Fig. 2. Conversion of glycerol to 1,3-popanediol and acrolein.

Heterolytic H$_2$ Activation   **Ionic Hydrogenation**

L = ligands, B: = base (substrate, non-coordinating counterion, water, solvent),
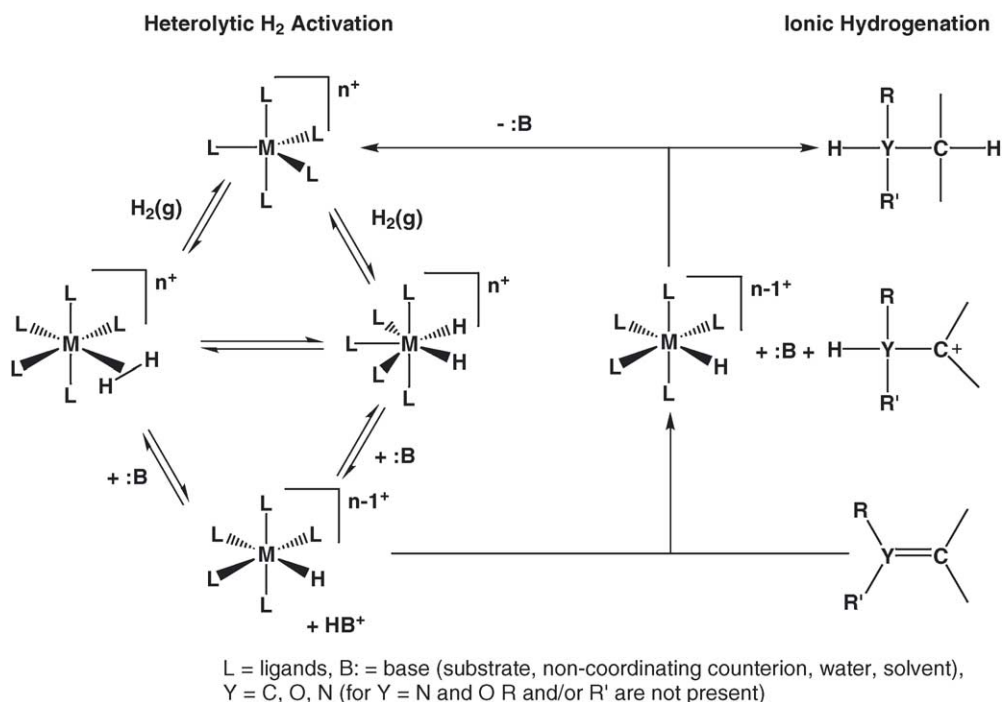Y = C, O, N (for Y = N and O R and/or R' are not present)

Fig. 3. Conceptual representation of heterolytic hydrogen gas activation and catalytic ionic hydrogenation.

ketones, aldehydes and alkenes in biphasic or purely aqueous phase. On the basis of isotope tracing studies with D$_2$O that showed deuterium incorporation into both hydrogen gas and product alcohols they also postulated a dihydrogen complex [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(η^2-H$_2$)X]$^{2+/+}$ (**1a**) as the intermediate that activates hydrogen heterolytically with the formation of H$_3$O$^+$ or HOTf as the proton and a hydride complex [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(H)(X)]$^{+/0}$ (X = H$_2$O, substrate, solvent, OTf$^-$) (**1b**) as the hydride source [11,12]. While presently no direct experimental or spectroscopic evidence for either **1a** or **1b** exists, these postulates appear reasonable, as other alternatives such as ligand loss and/or oxidative addition of hydrogen gas to give a Ru^{+IV} species are unlikely.

Complex **1** thus meets all the criteria listed above. Here we wish to report the evaluation of this system for the direct transformation of diols to monools and alkanes.

2. Experimental

General: All reagents and solvents were obtained from commercial sources and used as received. Trifluoromethanesulfonic acid was stored under argon. 6,6′-dichloro-2,2′-bipyridine [13], *cis*-Ru(6,6′-Cl$_2$-bipy)$_2$Cl$_2$ [14] and [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ [15] were prepared according to literature procedures (see Supplementary Material for an image of a ^{1}H NMR of the catalyst in CD$_3$CN). The catalyst is relatively air-stable only decomposing in air over the course of several days. *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane [16–20] and 2,5(6)-dimethyl-1,4-dioxane [21–24] have repeatedly been described previously and were synthe-

sized as isomeric mixtures according to the procedures given below. High-pressure hydrogenation reactions were carried out in a thermostated 900 mL Parr Reactor using industrial grade hydrogen gas. GC analysis were carried out on a Varian 3800 using a 30 m DB-1701 semipolar column. Quantitation was achieved through multi-level calibrations for starting materials, *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane and *cis/trans*-2,5(6)-dimethyl-1,4-dioxane (for 1,2-propanediol reactions) and product alcohols using authentic samples. GC–MS analysis were carried out on a Varian Saturn 2000 running in default EI mode.

Preparation of *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane: 73.5 mL 1,2-propanediol (76.1 g, 1.0 mol, 1.0 equiv.), 72.1 mL propanal (58.1 g, 1.0 mol, 1.0 equiv.) and 0.250 g (1.3 mmol, 0.13% equiv.) *m*-toluenesulfonic acid hydrate were combined in a 500 mL round bottom flask and a stir bar added. A Dean–Stark–Trap distillation apparatus with 75 mL benzene in the arm of the Dean–Stark–Trap flask was connected to the flask and the distillation carried out at 120 °C. After the volume of water in the arm of the Dean–Stark–Trap had reached 18 mL, the reaction was stopped by cooling to ambient temperature. The resulting clear reaction solutions was dried with sodium sulfate, filtered and subjected to fractional distillation obtaining the product *cis/trans*-2-ethyl-4-methyl-dioxolane (52.2 g, 0.45 mol, 45%) with a boiling point range of 110–115 °C. Compound identity was established by GC–MS, ^{1}H and ^{13}C NMR (see Supplementary Material for detailed spectral data and images).

Preparation of *cis/trans*-2, 5(6)-dimethyl-1,4-dioxane [24]: 131.16 mL di(propylene glycol) (134.18 g, 1.0 mol, 1.0 equiv.) and 15 g of acidic ion-exchange resin (Amberlite

IR-120, Dowex DR-2030 or similar) were combined in a 500 mL round bottom flask and a stir bar added. A Dean–Stark distillation was carried out as above. The reaction mixture turned black in the time (approximately 24 h) required to separate the expected amount of water (18 mL = 1 mol). The mixture was dried with sodium sulfate, filtered and products were obtained by fractionation at ambient pressure as a clear colourless liquid in the boiling point range 90–120 °C. By GC–MS all four isomers of the dioxane (2,6 and 2,5 with methyl groups *cis* or *trans*, respectively) as well as *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane were present in approximately 2:2:1:1:2:2 ratio (four dioxane isomers and two dioxolane isomers). This mixture was ideally suited for the identification of trace amount of the dioxanes by GC and GC-MS needed in the context of this study. Overall yield: 46.2 g, 0.4 mol, 40%. Compound identity was established by GC–MS and ^{13}C NMR (see Supplementary Material for detailed spectral data and images).

Hydrogenation reaction at ambient pressure: 1.903 g (25.0 mmol, 1000 mmol/L) 1,2-propanediol, 247 mg (2.5 mmol, 100 mmol/L) NMP were combined in a 25 ml graduated cylinder and filled up to a total volume of 25 mL with tetramethylene sulfone. The mixture was then placed into a 100 mL three-neck flask and 110.6 mg of *cis*-[Ru^{II}(6,6′-Cl$_2$-bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (0.125 mmol, 0.5 mol%) and 132 µL trifluoromethansulfonic acid (1.5 mmol, 15 mmol/L, 12 equiv. with respect to catalyst) were added. A continuous flow of hydrogen gas was introduced from one neck with a needle. A condenser and a T-joint adapter with one end connected to the hydrogen feed and the other end to a bubbler were placed on another neck. A stopper was placed on the centre neck allowing the withdrawal of samples. The flask was heated to 125 °C for 48 h with continuous hydrogen flow across the T-joint.

Typical hydrogenation reaction protocol under high pressure with NMP as the internal standard: 3.805 g (50.0 mmol, 500 mmol/L) 1,2-propanediol and 991.3 mg (10.0 mmol, 100 mmol/L) NMP were combined in a 100 mL graduated cylinder and the cylinder was filled up with tetramethylene sulfone to a total volume of 100 mL. The solution was transferred into the reactor. 221.2 mg *cis*-[Ru^{II}(6,6′-Cl$_2$-bpy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (0.25 mmol, 2.5 mmol/L, 0.5 mol%) was then added to the reactor. The solution was stirred to dissolve the catalyst. Then 265 µL trifluoromethansulfonic acid (3.0 mmol, 30 mmol/L, 12 equiv. of the catalyst) were added to the reactor. One sample (<1 mL) defining $T = 0$ was drawn from this solution, the reactor sealed and three times pressurized with hydrogen gas to 750 psi and vented in order to remove air from the vessel. Subsequently temperature and pressure adjusted to the desired values and reaction left stirring for 48 h.

Control reaction on the influence of the concentrations of the acid to NMP: In each of five 10 mL graduate cylinders A, B, C, D, E, were combined 190.3 mg (2.5 mmol, 500 mmol/L) 1,2-propanediol and 49.6 mg (0.5, 100 mmol/L) NMP. The following amounts of triflic acid were added to these five

graduate cylinders: A: 0 µL; B: 5.5 µl; C: 11.0 µL; D: 16.5 µL; E: 22.0 µL, equivalent to A: 0 equiv. (0 mmol/L); B: 5 equiv. (12.5 mmol/L); C: 10 equiv. (25 mmol/L); D: 15 equiv. (37.5 mmol/L); E: 20 equiv. (50 mmol/L) of the catalyst if there would be catalyst in the solution under the *standard conditions*. The cylinders were then filled up to 5 mL as the total volume with tetramethylene sulfone. These solutions were left for half an hour, and then analyzed by quantitative GC.

3. Results and discussion

1,2-Propanediol and its potential reaction products are volatile enough to be easily analyzed quantitatively by GC and it was therefore selected as the model substrate for a systematic study of the effectiveness of **1** as a catalyst for the reaction in Fig. 1 with R = CH$_3$. As in previous studies of the same type [2,5], sulfolane (tetramethylenesulfone) was chosen as the solvent. This solvent combines several properties that make it an ideal medium for the reaction in Fig. 1 and related transformations: it has a relatively low toxicity, is acid stable, fully miscible with water and alcohols, an extremely poor ligand, i.e. does not give rise to coordinative inhibition on metal centres, and has a very high boiling point (283 °C). The last point is of interest in the long term if an efficient catalyst system is identified, as it principally would allow for removal of the lower boiling oxygen content reduced product alcohols and water from the reaction mixture by simple distillation, with any unreacted higher boiling polyol substrates, acid and catalyst remaining in the reaction solution, which then could be directly recycled. The logical choice of the acid required for the dehydrogenation step is trifluoromethanesulfonic acid (HOTf) already present in its deprotonated form in **1**. It forms a very weakly coordinating counterion as evidenced by its displacement from the metal centre by water in **1** and is thermally and chemically robust.

Initial reaction parameters were selected to be similar to those established previously for **1** [12] and {[Cp*Ru(CO)$_2$]$_2$(µ-H)}$^+$OTf$^-$ [5] and set to 500 mmol/L 1,2-propanediol substrate, 125 °C, 2.5 mmol/L catalyst load (=0.5 mol% with respect to substrate) and 30 mmol/L HOTf (=12 equiv. with respect to catalyst). 100 mmol/L *N*-methyl-2-pyrrolidinone (NMP) or dimethylsulfone (DMS) were also added to the reaction mixture as an internal standard allowing for direct quantitative analysis by calibrated GC (vide infra for a discussion of the influence of the internal standard on the reaction). All reactions were run for a duration of 48 h.

Test runs with these reaction parameters revealed that – as with the only other catalyst system {[Cp*Ru(CO)$_2$]$_2$(µ-H)}$^+$OTf$^-$ investigated in this reaction – appreciable amounts (up to 10 mol% of the total amount of substrate) of propanal, di-*n*-propylether and of an isomeric mixture of *cis/trans*-2-ethyl-4-methyl-1,3-dioxolane were present, the latter two through condensation of *n*-propanol or the intermediate propanal with the starting material, respectively
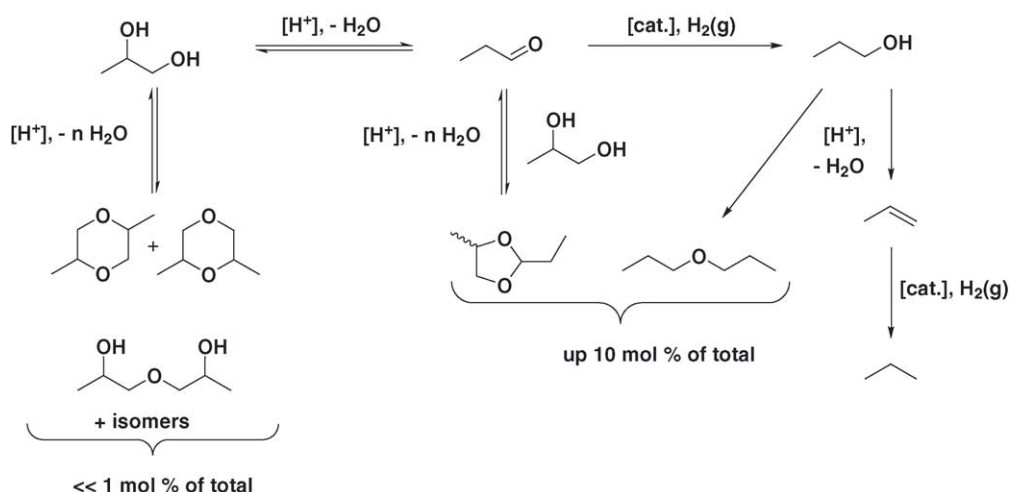
Fig. 4. Hydrogenation of 1,2-porpanediol to *n*-propanol and propane-pathway and intermediates.

[5]. Authentic samples of both materials were therefore included in the multi-compound/multi-level GC calibration along with 1,2-propanediol and *n*-propanol. Propanal was calibrated with the same response factor as propanol. This introduced a small error, but was preferable to the use of propanal itself in calibration solutions, which tend to be unstable against autocondensation and disproportionation. Only negligible amounts ($\ll$1 mol% of total) of the other potential 1,2-propanediol condensates, 2,5/6-dimethyl-1,4-dioxolanes and di-1,2-propanediol ethers (both identified against authentic samples), were detected in the GC traces and therefore not included in the mass balance. Quantitative analysis of samples from the test runs did however show mass losses of up 88% against the total mass balance of GC analyzable liquid reaction mixture components defined as

$$[\text{total}]_t = [1, 2\text{-propanediol}]_t + [n\text{-propanal}]_t$$
$$+ [n\text{-propanol}]_t + 2[\text{di-}n\text{-propylether}]_t$$
$$+ 2[2\text{-ethyl-4-methyl-1, 3-dioxolane}]_t$$

where $[\ldots]_t$ is the concentration of the respective component at a given time *t*. Lau's earlier results [12] that showed that **1** is also an effective catalyst for the hydrogenation of alkenes to alkanes suggested that **1** – in contrast to $\{[Cp^*Ru(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ and other catalyst systems mentioned above – achieves a total hydrogenation of 1,2-propanediol to propane explaining the deficient mass balance obtained from liquid reaction mixture samples. GC–MS analysis of a gas sample captured from the reactor vent indeed confirmed the presence of propane as the dominant component in the headspace of the reaction mixture. In addition later experiments with higher terminal diols (vide infra, Table 2), showed the presence of the corresponding higher boiling alkanes in liquid reaction mixture samples.[2] Based on these

results the amount of propane formed in each reaction was indirectly determined from the mass loss according to

$$[\text{propane}]_t = [1, 2\text{-propanediol}]_{t=0} - [1, 2\text{-propanediol}]_t$$
$$- [n\text{-propanal}]_t - [n\text{-propanol}]_t$$
$$- 2[\text{di-}n\text{-propylether}]_t$$
$$- 2[2\text{-ethyl-4-methyl-1, 3-dioxolane}]_t$$

with the mass balance then defined as

$$[\text{total}]_t = [1, 2\text{-propanediol}]_t + [n\text{-propanal}]_t$$
$$+ [n\text{-propanol}]_t + 2[\text{di-}n\text{-propylether}]_t$$
$$+ 2[2\text{-ethyl-4-methyl-1, 3-dioxolane}]_t$$
$$+ [\text{propane}]_t$$

Fig. 4 gives an overview of all possible condensation and hydrogenation products obtainable from 1,2-propanediol under the reaction conditions.

Table 1 summarizes the performance of **1** as a catalyst in the direct conversion of 1,2-propanediol to *n*-propanol and propane as a function of variation of temperature, hydrogen pressure, acid and 1,2-propanediol concentration derived from the initial reaction parameters defined above. Yields reported for *n*-propanol include small amounts of di-*n*-propylether present.

The results from entries 1 to 4 in Table 1 show that the threshold temperature for catalyst activity was $\sim$75 °C and that a maximum yield of the desired product *n*-propanol was achieved at a the initially selected temperature of 125 °C, while the yield of the total hydrogenation product propane scaled with the temperature. At temperatures of 150 °C and above appreciable catalyst decomposition was observed as evidenced by a green colour and beginning deposition of a black precipitate from the otherwise red reaction solution. 125 °C was therefore selected as the standard temperature for all further runs.

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[2] Equipment limitations resulting from the formation of a gas (propane) as one of the major reaction products prevented us from conducting an initially intended kinetic study of the reaction with 1,2-propanediol.

Table 1
Performance of **1** as a function of temperature, pressure, internal standard, acid and 1,2-propanediol concentration[a]

Entry	T (°C)	H_2(g), p (psi)	HOTf/Ru (equiv.)	Internal standard[b]	1,2-diol (mmol/L)	Yield (%)		
						n-Propanol[c]	Propane[d]	Total
1	75	700	12	NMP	500	0	0	0
2	100	700	12	NMP	500	3	12	15
3	125	700	12	NMP	500	63	13	76
4	150	700	12	NMP	500	58	22	80
5	125	300	12	NMP	500	19	35	54
6	125	500	12	NMP	500	35	26	61
7	125	750	12	NMP	500	34	27	61
8	125	900	12	NMP	500	35	25	60
9	125	1200	12	NMP	500	53	11	64
10	125	700	0	NMP	500	0	0	0
11	125	700	1	NMP	500	0	0	0
12	125	700	4	NMP	500	28	9	37
13	125	700	8	NMP	500	60	10	70
14	125	700	16	NMP	500	56	29	85
15	125	700	12	DMS	500	9	88	97
16	125	700	12	DMS	2500	10	29	39
17	125	700	12	DMS	5000	3	3	6
18	125	700	12	DMS	10000	–	–	–
19	125	700	12	DMS	Neat	–	–	–

[a] 2.5 mmol/L catalyst (=0.5 mol%).
[b] Internal standard concentration 100 mmol/L; $t = 48$ h in all runs; NMP: 1-methyl-2-pyrrolidinone; DMS: dimethylsulfone.
[c] By quantitative GC of the sulfolane phase.
[d] Inferred from mass balance.

At hydrogen pressures above 500 psi and up to 1200 psi (the maximum pressure technically available to us in this study), the total yield of hydrogenated products did not change significantly (entries 5–9 in Table 1). The product distribution of hydrogenated products however did, shifting to the alcohol at higher pressures. The reason for this behaviour is unclear, but it is conceivable that η^2-alkene coordination to the metal centre forming $[(6,6'\text{-}Cl_2\text{-bipy})_2Ru(\eta^2\text{-}C_3H_6)X]^{2+/+}$ (X = H_2O, ROH, $RR'C=O$, solvent, OTf^-) is a prerequisite for the hydrogenation of propene and that this step is in effect inhibited by competition with hydrogen gas at higher pressures. This is congruent with the formation of an isostructural dihydrogen complex $[(cis\text{-}Ru(6,6'\text{-}Cl_2\text{-bipy})_2(\eta^2\text{-}H_2)X]^{2+/+}$ (**1a**) as the first step of the catalytic cycle as postulated by Lau on the basis of deuterium exchange studies (see also Schemes 2 and 3 of Ref. [12]). It also implies that the hydrogenation pathways for alkenes and carbonyls may be different. The lower conversion at 300 psi probably represents a rate limitation by the diffusion of hydrogen gas into the reaction solution. A control reaction at ambient hydrogen pressure showed no conversion to hydrogenated products.

The type and concentration of the acid co-catalyst added is arguably the most important variable in the reaction as it impacts the position of the dehydration equilibria (Figs. 1 and 4) and therefore the product distribution. As entries 3, 10–14 show, a minimum of 4 equiv. of acid were required for dehydration and hydrogenation to occur and the catalyst was active at concentrations up to 16 mol equivalents of HOTf with respect to ruthenium with no loss of activity within the 48 h

timespan investigated. The total yield of hydrogenated products increased with the amount of acid added. The amount of the total hydrogenation product propane scaled with the overall acidity of the reaction mixture. The yield of n-propanol reached a maximum at 12 equiv. of acid. Acid concentrations above 16 equiv. are not practical with NMP as the internal standard, as acid induced decomposition of the internal standard to unidentified products occurs, which was confirmed by control reactions at various acid concentrations in the absence of catalyst. Replacement of NMP with DMS, whose structure and properties are very similar to that of the sulfolane solvent had the unexpected effect of leading to catalyst decomposition indicated by a colour change to green at acid concentrations of 12 equiv. and completely changing the product distribution at acid concentrations as low as 4 equiv. (run 15, Table 1). HOTf has a pK_a of 3.4 in sulfolane [25], but is known to completely dissociate at H_2O:HOTf ratios as low as 1.6 [26]. The active acidic species in the reaction mixture should therefore be H_3O^+ or possibly ROH_2^+. While the pK_as of protonated amides $RC(OH)NR_2^+$, alcohols ROH_2^+ and H_3O^+ in sulfolane are unknown, the values for the first two in water are approximately −1 [27] and −2.2 [28], respectively. The results of entries 1–14 in Table 1 therefore represent a series of reactions in which the internal standard NMP acts as an auxiliary base explaining the shift in product distribution with DMS (compare entries 3 and 15).

The presence of water in the reaction mixture also precludes the use of other strong acids with non-coordinating but potentially hydrolyzable counterions such as HPF_6 and HBF_4, as **1** is deactivated by halogenides probably through

formation of *cis*-(6,6′-Cl$_2$-bipy)$_2$RuX$_2$ (X = halogenide), which is effectively the reverse reaction of the preparation of **1** from *cis*-(6,6′-Cl$_2$-bipy)$_2$RuCl$_2$ with AgOTf [15]. E.g. reactions with **1** and HBF$_4$ rather than HOTf with under otherwise identical reaction conditions gave no or only traces of hydrogenated products.

It is in principle desirable to optimize a homogeneous catalytic reaction by running it at an as high as possible substrate concentration without negatively impacting the metal catalyst, e.g. through coordinative inhibition of the catalytic centre by the substrate. In the present reaction the situation is however complicated by the acid catalyzed dehydration reactions required for the in situ generation of the unsaturated actual hydrogenation substrates (Fig. 4) and associated side reactions. A change in diol concentration at equal acid and metal catalyst load also results in a change of the overall water concentration and acidity of the reaction mixture and can make undesirable condensates the main products. Therefore, a compromise between substrate concentration and catalyst activity has to be struck. In order to obtain a more accurate picture of how the increasing water content that necessarily results from an increase in diol concentration affects the reaction outcome, DMS was used as the internal standard for this series. The results from entries 15 to 19, Table 1 illustrates this point, which will have a major impact in future studies on the deoxygenation of glycerol or other polyols by combined acid/metal catalysis (Fig. 1). The results show that an increase of the substrate concentration in the model reaction with 1,2-propanediol is in fact detrimental to the overall reaction outcome. At a five-fold increase of 1,2-propanediol concentration to 2500 mmol/L absolute *n*-propanol yields similar to those obtained at 500 mmol/L were achieved,[3] but higher concentrations were counterproductive. In addition concentrations of 5000 mmol/L and higher resulted in catalyst decomposition to black ruthenium metal and increasingly viscous solutions of polyethers that were no longer analyzable by GC. Catalyst reduction to ruthenium metal is possibly the result of metal chelation by the diol that becomes feasible at higher concentration followed by β-hydride elimination, reductive elimination and ligand loss.

The results listed in Table 2 extend the model reaction to higher diols. As with 1,2-propanediol appreciable amounts of the analogous oxygen heterocycle condensates were observed, which in theses cases were quantified approximately by using the same FID response factor as for the starting diol. Beginning with 1,2-pentanediol emulsions of the corresponding alkanes in sulfolane result from the reaction that prevent their direct quantitative analysis.[4] The presence of the

Table 2
Hydrogenation of higher diols[a]

Entry	1,2-Diol	Yield (%)		
		n-Alcohol[b]	Alkane[c]	Total
20	Butanediol	24	21	45
21	Pentanediol	40	25	65
22	Hexanediol	29	33	62
23	Octanediol	27	34	61
24	Decanediol	34	31	65

[a] *T* = 125 °C; 700 psi H$_2$(g), 500 mmol/L 1,2-diol, 2.5 mmol/L catalyst (=0.5 mol%). 30 mmol/L HOTf (=12 equiv. with respect to catalyst). Internal standard 100 mmol/L NMP; *t* = 48 h in all runs.
[b] By quantitative GC of the sulfolane phase.
[c] Inferred from mass balance.

alkanes was confirmed against authentic samples, but yields reported are inferred as defined previously.

Finally attempts to hydrogenate glycerol under various conditions as listed in the tables above gave only traces of *n*-propanol (<10 mmol/L) and no detectable amounts of 1,3-diol. In all reactions a substantial consumption of glycerol (by GC) and formation of highly viscous solutions accompanied by catalyst reduction occurred leading in some cases to the deposition of metallic mirrors on the glass insert used in the pressure reactor. The latter phenomenon was not observed with diol substrates and may be a consequence of the presence of acrolein in the reaction mixtures.

4. Conclusions

A set of qualitative design and selection criteria for (ionic) hydrogenation catalysts that can withstand both acidic and aqueous conditions has been devised. The ruthenium complex [*cis*-Ru(6,6′-Cl$_2$-bipy)$_2$(OH$_2$)$_2$](CF$_3$SO$_3$)$_2$ (**1**) was identified on the basis of these rules and is an example of a type of homogeneous catalyst capable of effecting the direct transformation of terminal diols to primary alcohols in the presence of HOTf. Depending on the overall acidity of the reaction mixture the catalyst produces primary alcohols or the corresponding alkane as the main product with high selectivity, but the catalyst is not active enough to be effective for the conversion of glycerol to 1,3-propanediol or other hydrogenated products in principle obtainable from renewable sugar polyols.

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[3] 50% yield at 500 mmol/L = 10% yield at 2500 mmol/L.
[4] Since an internal standard is present, diluting the samples with an inert solvent capable of breaking the emulsions should in principle allow for a direct calibration of the alkanes. Due the large polarity difference of the emulsion components we did however fail to identify a suitable co-solvent from a variety of candidates (nitriles, aromatics, esters, etc.).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2004.11.018.

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