CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901427

Acid-, Water- and High-Temperature-Stable Ruthenium Complexes for the Total Catalytic Deoxygenation of Glycerol to Propane

Deeb Taher,[a] Michelle E. Thibault,[b] Domenico Di Mondo,[b] Michael Jennings,[c] and Marcel Schlaf*[b]

Abstract: The ruthenium aqua complexes $[Ru(H_2O)_2(bipy)_2](OTf)_2$, $[cis\text{-}Ru(6,6'\text{-}Cl_2\text{-}bipy)_2(OH_2)_2](OTf)_2$, $[Ru(H_2O)_2(phen)_2](OTf)_2$, $[Ru(H_2O)_3(2,2':6',2''\text{-}terpy)](OTf)_2$ and $[Ru(H_2O)_3(Phterpy)](OTf)_2$ (bipy = 2,2′-bipyridine; OTf^- = triflate; phen = phenanthroline; terpy = terpyridine; Phterpy = 4′-phenyl-2,2′:6′,2′′-terpyridine) are water- and acid-stable catalysts for the hydrogenation of aldehydes and ketones in sulfolane solution. In the presence of $HOS(O)_2CF_3$ (triflic acid) as a dehydration co-catalyst they directly convert 1,2-hexanediol to *n*-hexanol and hexane. The terpyridine complexes are stable and active as catalysts at temperatures ≥250 °C and in either aqueous sulfolane solution or pure water convert glycerol into *n*-propanol and ultimately propane as the final reaction product in up to quantitative yield. For the terpy complexes the active catalyst is postulated to be a carbonyl species $[(4'\text{-}R\text{-}2,2':6',2''\text{-}terpy)Ru(CO)(H_2O)_2](OTf)_2$ (R = H, Ph) formed by the decarbonylation of aldehydes (hexanal for 1,2-hexanediol and 3-hydroxypropanal for glycerol) generated in the reaction mixture through acid-catalyzed dehydration. The structure of the dimeric complex $[\{(4'\text{-}phenyl\text{-}2,2':6',2''\text{-}terpy)Ru(CO)\}_2(\mu\text{-}OCH_3)_2](OTf)_2$ has been determined by single crystal X-ray crystallography (Space group $P\bar{1}$ ($a = 8.2532(17)$; $b = 12.858(3)$; $c = 14.363(3)$ Å; $\alpha = 64.38(3)$; $\beta = 77.26(3)$; $\gamma = 87.12(3)°$, $R = 4.36\,\%$).

Keywords: biomass · deoxygenation · glycerol · homogeneous catalysis · hydrogenation

Introduction

The exponential growth of the global bio-Diesel industry has lead to a large oversupply of glycerol with production estimated to reach 1.2 million tons p.a. by 2010. This in turn has triggered substantial efforts to find new and value added uses for glycerol, which have recently been expertly reviewed by several authors.[1–5] In this context, significant advances have been made into the deoxygenation of glycerol to 1,2-propanediol by using heterogeneous catalysts.[6–17] 1,2-Propanediol is an important anti-freeze agent and component of coating, lubricant and cosmetic formulations and Dow Chemical recently announced its intent to commercialize this process using a proprietary heterogeneous catalyst.[18] We recently discussed the possible origin of the typically observed selectivity for terminal glycerol deoxygenation to 1,2-propanediol with heterogeneous catalysts.[19]

A challenging, but potentially economically very attractive, alternative would be the metal-catalyzed deoxygenation of glycerol to 1,3-propanediol, a component of poly(propylene terephthalate) (PPT), marketed as Sorona™ and Corterra™ by DuPont and Shell, respectively. Such a process would compete with existing petrochemical and biotechnological routes to this material: The Degussa-DuPont process operates via hydration of acrolein to 3-hydroxypropion aldehyde (3-HPA), which cannot be isolated, followed by hydrogenation over a heterogeneous ruthenium catalyst, whereas Shell produces 1,3-propanediol by hydroformylation of ethylene oxide and in situ hydrogenation of the same

---

[a] Prof. Dr. D. Taher
Chemistry Department
Tafila Technical University
P. O. Box: 179, Tafila 66110 (Jordan)

[b] M. E. Thibault, D. Di Mondo, Prof. M. Schlaf
The Guelph-Waterloo Centre for Graduate Work
in Chemistry (GWC)^2, Department of Chemistry
University of Guelph
Guelph, Ontario, N1G 2W1 (Canada)

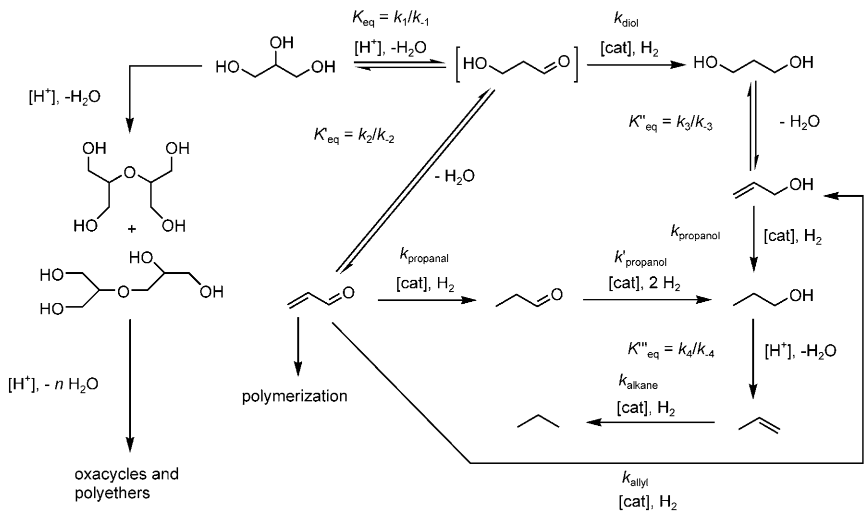
[c] M. Jennings
Chemistry Department
University of Western Ontario
London, Ontario, Canada, N6A 5B7 (UK)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901427 and contains ^{1}H and ^{13}C NMR spectra for all complexes synthesized and an image of the GC-MS trace and spectrum to establish the conversion of glycerol to propane.

intermediate by using a homogeneous Co/Ru catalyst system.[20,21] A new joint venture by DuPont and Tate & Lyle uses a fermentation process based on glucose.[22–24]

Hawley and co-workers have suggested a very selective and high-yielding glycerol dehydroxylation to 1,3-propanediol, but the reaction sequence requires the stoichiometric use of tosyl chloride.[25] Sasaki and co-workers recently reported the use of a mixed $Pt/WO_3/ZrO_2$ catalyst that yielded 24 % of 1,3-propanediol, 13 % 1,2-propanediol and 28 % 1-propanol at 170 °C and 8 MPa in 1,3-dimethyl-2-imidazolinidinone solvent, representing a benchmark result for the use of heterogeneous catalysts in the direct transformation of glycerol to 1,3-propanediol.[26]

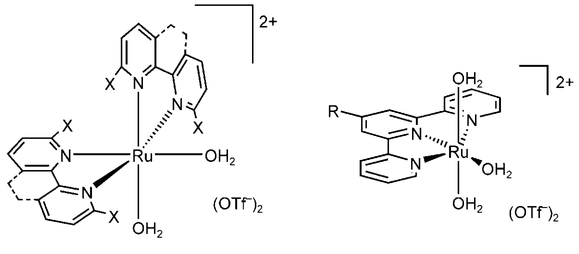
Motivated by the seminal work of Che,[27] that had shown that glycerol can be converted into mixtures of 1,2- and 1,3-propanediol in up to ≈20 % yield each using a combination of $H_2WO_4/[Rh(CO)_2(acac)]$ and by Braca et al.,[28] who reported the conversion of glycerol into 1-propanol by using $HI/[Ru(CO)_4I_2]$ as catalysts under synthesis gas (H_2/CO) in water or amide solvents at 200 °C, we postulated that the combination of an acid catalyzed dehydration with an in situ hydrogenation of 3-HPA by pyridine-type ligand supported homogeneous catalysts may be well suited to achieve a selective transformation of glycerol to 1,3- rather than 1,2-propanediol.[29] The desired reaction pathway along with its potential side reactions is shown in Scheme 1.



Scheme 1. Potential pathways and side reactions for the conversion of glycerol to 1,3-propanediol.

From Scheme 1, a selective conversion of glycerol to 1,3-propanediol hinges on an acid-catalyzed preferential loss of the secondary rather than primary hydroxyl function of glycerol via a secondary rather than primary carbocation-like transition state leading to 3-HPA rather than acetol as the key intermediate. The reaction requires the adjustment of the three (*de*)hydration equilibria glycerol/3-HPA (K_{eq}), 3-HPA/acrolein (K'_{eq}) and 1,3-diol/allyl alcohol (K''_{eq}) in order to maximize the initial dehydration of glycerol, while minimizing the secondary dehydrations of either the 3-HPA intermediate or the desired product 1,3-propanediol. As demonstrated by Che this appears to be in principle possible through the right combination of a) the type of solvent and acid employed and b) the relative concentrations of acid, water and substrate (which in turn releases water) in the reaction mixture. However, to our knowledge the only quantitative experimental data on the relative positions of the three equilibria involved is given by Pressmann and Lucas,[30] who determined the equilibrium constant for the acid-catalyzed hydration of acrolein to 3-HPA in water, that is, K'_{eq}, over the temperature range 19.98 to 39.93 °C. From their data $\Delta H = -25\ kJ\,mol^{-1}$ and $\Delta S = -0.9\ J/(K \times mol)$, that is, the reverse dehydration of 3-HPA to acrolein is disfavored in aqueous solution at low temperature, but is likely entropically highly favored at the much higher temperatures required to overcome the activation barrier for the initial dehydration of glycerol. The determination of the optimum reaction conditions for the reaction cascade of Scheme 1 therefore depends on an empirical approach that varies the defining parameters, in particular the acid- and water-concentration in the reaction mixture as attempted in the work described here.

Catalyst selection and preparation: Following a set of explicitly formulated design criteria,[31] we have previously tested the catalysts $[\{(Cp^*)Ru(CO)_2\}_2(\mu\text{-}H)]OTf$,[32] [*cis*-Ru(6,6′-Cl_2-bipy)$_2(OH_2)_2](OTf)_2$[31] and $[(\eta^6\text{-arene})Ru(X)(N\cap N)](OTf)_n$, ($X = H_2O$, H; η^6-arene = *p*-Me-*i*Pr-C_6H_4, C_6Me_6; N∩N = bipy, phen, 6,6′-diamino-bipy, 2,9-diamino-phen, $n = 1,2$; (bipy = 2,2′-bipyridine; $OTf^- =$ triflate; phen = phenanthroline)[19] for activity in the deoxygenation of terminal diols and glycerol under aqueous acidic conditions. All three catalyst types convert terminal diols to the corresponding primary alcohols via acid-catalyzed dehydration to the corresponding aldehyde followed by its hydrogenation in situ. Under more forcing conditions further dehydration to the alkene and hydrogenation to the alkane can take place.[31] The first reaction serves as a model system that mimics the desired glycerol deoxygenation pathway shown at the top of Scheme 1 and catalyst activity for the hydrogenation of aldehydes and/or ketones (generated by dehydration of internal *vic*-diols) therefore constitutes a necessary, but not sufficient condition for the deoxygenation of glycerol and/or higher sugar alcohols by a given catalyst.[29] In contrast to the deoxygenation of terminal diols, which we found to proceed at temperatures as low as 110 °C, control experiments established that the Brønsted acid-catalyzed initial dehydration of glycerol requires temperatures in excess of 150 °C.[19] The catalysts tested by us to date thus fail to convert glycerol, because they decompose due to loss of their ligand support framework and reduction to ruthenium metal at temperatures above 125 °C as indicated by the formation of a black precipitate in the reaction mixtures. An example for this limitation is the complex [*cis*-Ru(6,6′-Cl_2-bipy)$_2$(OH_2)$_2$](OTf)$_2$ (**1Cl**), which had originally been developed as a water-soluble hydrogenation catalyst by Lau and co-workers.[33,34] They postulated that the *cis* configuration of the complex - locked in this configuration by the steric interactions between the *ortho* chloride substituents - would result in an active ionic hydrogenation catalyst[35] with two adjacent labile coordination sites. However, an examination of the extensive literature on the parent unsubstituted bipy [Ru(H_2O)$_2$(bipy)$_2$](OTf)$_2$ (**1**) and phen [Ru(H_2O)$_2$(phen)$_2$](OTf)$_2$ (**2**) complexes suggests that the *cis*-configuration represents the thermodynamically more stable isomer in these systems and that the isomerization to the *trans*-configuration requires photochemical activation.[36,37] We therefore hypothesized that the parent bipy and phen complexes **1** and **2** should also be active hydrogenation catalysts under aqueous acidic conditions. Remarkably, and in spite of being among best understood and most investigated ruthenium complexes known with hundreds of papers published, these complexes have, to our knowledge, never been tested as hydrogenation catalysts. Owing to the lower steric demand of the non-substituted ligands they should also be less susceptible to ligand loss at higher temperatures, that is, result in a thermally more robust catalyst system viable at $T \geq 150$ °C, while at the same time allowing easier access of the substrate to the metal centre. A further extension of this concept are the complexes [Ru(H_2O)$_3$(terpy)](OTf)$_2$ (**3**) and [Ru(H_2O)$_3$(Phterpy)](OTf)$_2$ (**4**), (terpy = terpyridine; Phterpy = 4′-phenyl-2,2′:6′,2″-terpy) in which the tris-chelating meridional coordination mode of the (4′-phenyl)-2,2′:6′,2″-terpy ligand[38,39] should result in a higher complex formation constant (vs. the bis-chelating bipy or phen ligands) and hence even higher temperature stability, while providing three adjacent labile *mer*-oriented aqua ligands that can easily be displaced by hydrogen and/or substrate leading to a potentially more active catalyst with sterically easily accessible coordination sites. The structures of these catalysts are shown in Figure 1. Common to all four complexes is their ease of preparation from commercially available components by (or for the new complex **4** analogous to) well established synthetic protocols,[40–43] their stability in air and their solubility and compatibility with water, which is intrinsic to the aquo complexes themselves rather than a function of the supporting ligand framework, as, for example, realized with sulfonated triphenyl phosphines.[44]



1, **1Cl**, **2**
X = H or Cl

3, **4**
R = H, Ph

Figure 1. Structures of the catalysts.

Results

Catalyst screening against carbonyl substrates: To establish the principle viability of complexes **1** to **4** as catalysts for the deoxygenation of polyalcohols they were first screened as hydrogenation catalysts for a series of 20 representative carbonyl compounds employing conditions similar to those anticipated in actual polyalcohol deoxygenation reactions and using a 24-well parallel reactor with 4 of the wells serving as controls for cross-contamination (none was observed). Reaction conditions were 9:1 sulfolane:water solvent at 175 °C for 3 h under 7.5 MPa hydrogen pressure and a substrate concentration of 500 mmolL^{-1} with 0.5 mol % catalyst load. Sulfolane was chosen as the solvent owing to its high boiling point (285 °C), high dielectric constant ($\varepsilon = 43$), miscibility with water, allowing it to dissolve both polyalcohols and the cationic catalysts, and its high chemical stability under the reducing as well as aqueous acidic conditions necessary for the deoxygenation of polyalcohols. All four catalysts are stable against decomposition under these conditions positioning them among of the most robust homogeneous hydrogenation catalysts ever reported. The catalysts give >90 % conversion of propanal and hexanal to 1-propanol and *n*-hexanol, respectively and also convert a variety of ketones to the corresponding secondary alcohols, albeit in lower yields that scale inversely with the steric accessibility of the carbonyl function in the substrate. Owing to secondary dehydrations and hydrogenations as well as aldol condensation, oligomerization or polymerization, which are driven by the high solvation energy of water in sulfolane, very complex reaction mixtures with poorly defined mass balances resulted for most of the ketones under these conditions.[45]

Terminal diol deoxygenation: Having established the principal activity of the catalysts **1**–**4** as carbonyl hydrogenation catalysts we tested them in the deoxygenation of the 1,2-hexanediol model system that mimics the desired deoxygenation of the terminal diol unit in a sugar polyalcohol (Scheme 1). 1,2-Hexanediol rather than 1,2-propanediol was chosen as the glycerol model, owing to the lower volatility of the potential deoxygenated products 1-hexanol, 1-hexene and *n*-hexane vs 1-propanol, propene and propane enhancing the reliability of the quantitative analysis of the reaction mixtures by GC against an internal standard. Table 1 summarizes the results of the deoxygenation reactions performed with this substrate comparing the observed product distribution for the four newly tested catalysts **1**–**4** with that

Table 1. Deoxygenation of 1,2-hexanediol by $[Ru(OH_2)_2(bipy)_2](OTf)_2$ (**1**), *cis*-$[Ru(6,6'\text{-}Cl_2\text{-}bipy)_2(OH_2)_2](OTf)_2$ (**1Cl**), $[Ru(OH_2)_2(phen)_2](OTf)_2$ (**2**), $[Ru(OH_2)_3(terpy)](OTf)_2$ (**3**) and $[Ru(OH_2)_3(4'\text{-}phenyl\text{-}2,2'{:}6',2''\text{-}terpy)](OTf)_2$ (**4**) as a function of temperature.[a]

Catalyst T [°C]	Recovery	**1**	**1Cl**	**2**	**3**	**4**
		Yield of identified products [%][b]				
125	1,2-hexanediol	48	68	94	>95[c]	>95[c]
	1-hexanol	3	23	1	0	0
	hexane	0	2	0	0	0
	hexane layer separates	no	no	no	no	no
150	1,2-hexanediol	0	n/d[d]	4	0	93[c]
	1-hexanol	17	n/d	14	26	0
	hexane	0	n/d	0	3	0
	hexane layer separates	no	no	no	no	no
175	1,2-hexanediol	0[d]	n/d	0	0	77
	1-hexanol	1	n/d	11	9	5
	hexane	0	n/d	0	5[e]	0
	hexane layer separates	no	n/d	no	yes	no
200	1,2-hexanediol	0[d]	n/d	0[d]	0[d]	0
	1-hexanol	0	n/d	4	0	21
	hexane	2.0	n/d	2	6[e]	5[e]
	hexane layer separates	no	n/d	no	yes	yes
225	1,2-hexanediol	n/d	n/d	0[d]	n/d	0
	1-hexanol	n/d	n/d	0	n/d	0
	hexane	n/d	n/d	3	n/d	5[e]
	hexane layer separates	n/d	n/d	no	n/d	yes
250	1,2-hexanediol	n/d	n/d	n/d	n/d	0
	1-hexanol	n/d	n/d	n/d	n/d	0
	hexane	n/d	n/d	n/d	n/d	5[e]
	hexane layer separates	n/d	n/d	n/d	n/d	yes

[a] Reaction conditions: 500 mmolL^{-1} substrate in sulfolane, 100 mmolL^{-1} dimethylsulfone as internal standard, 0.5 mol% catalyst, 4 equivalent of HOTf w.r.t. Ru, 4.82 MPa of $H_2(g)$, 24 h. [b] By quant. GC and GC-MS of the sulfolane reaction mixture. [c] No activity. [d] Catalyst decomposition observed, n/d = not determined. [e] Hexane content of the sulfolane phase. A hexane layer separates from the sulfolane solution, that is, 5% represents the solubility limit of hexane in sulfolane—not the total hexane yield—see main text.

of the previously reported Lau-system **1Cl**[31,33,34] and establishing the temperature limits of the catalysts. All reactions were performed in a 50 mL autoclave for 24 h under 4.82 MPa hydrogen pressure (at ambient temperature at $t=0$) with 500 mmolL^{-1} solutions of 1,2-hexanediol in sulfolane, 100 mmolL^{-1} dimethylsulfone as an internal GC standard, 0.5 mol% catalyst load and 4 equivalents of HOTf per ruthenium as the acid dehydration catalyst. HOTf was chosen as the acid, owing to its high hydrolytic stability, non-oxidizing nature and the low coordination tendency of the triflate counterion. The latter is essential to avoid coordinative inhibition of the catalytic cycle in which hydrogen competes with all other possible ligands (substrate, water, solvent, counterions) present. The yields given in Table 1 reflect the concentration of the sulfolane soluble components of the reaction mixture after 24 h and were determined by quantitative GC with multi-level calibration against authentic solutions of 1,2-hexanediol, 1-hexanol and the internal standard dimethylsulfone (100 mmolL^{-1}) in sulfolane. Control experiments without the addition of the homogeneous catalyst gave negligible conversions (<1%) of the diol substrate.

The data in Table 1 reveal the anticipated correlation of temperature stability of the catalysts with decreasing ligand steric demand and increasing chelation. The chloride-substituted catalyst **1Cl** decomposes at temperatures above 125 °C, the unsubstituted catalysts **1** and **2** show decomposition as evidenced by the formation of a black ruthenium metal precipitate in the reaction mixture at 150 and 175 °C, respectively, whereas the tris-chelate catalysts **3** and **4** are active at up to 250 °C—for catalyst **4** without any evidence of decomposition, that is, depending on the reaction temperature (see below) clear orange to deep purple-red solution are obtained at the end of the reaction. The relative temperature stability of the catalysts also directly scales with the minimum temperature at which they become active. Catalyst **1**, **1Cl** and **2** are active at 125 °C, whereas **3** and **4** require 150 or 175 °C to show conversion. The maximum yield of 1-hexanol at the 24 h time point was 26% observed with catalyst **3** at 150 °C and the maximum yields of the total deoxygenation product hexane quantifiable from the sulfolane solution is 5% with catalysts **3** and **4** at temperatures >175 °C. For catalysts **3** and **4** these numerical results however *systematically underestimate the actual catalyst activity*, as a hexane layer separates from the sulfolane phase above these concentrations, that is, ≈5% (here equivalent 25 mmolL)$^{-1}$ represents the solubility limit of hexane in sulfolane. The identity of the hexane was confirmed by GC and GC-MS analysis, and ^1H NMR spectroscopy. As the internal standard is not present in the hexane layer and some of the hexane is lost to the gas phase upon venting the cooled reactor upon completion of the reaction the amount of hexane formed cannot be quantified by GC. Attempts to cleanly separate the phases and determine the amount of hexane formed by weighing also proved to be unsatisfactory. However, the 1-hexanol concentration vs time profiles as a function of temperature obtained from reactions catalyzed by **4** illustrated in Figure 2 show a transient build-up of a much higher concentration of 1-hexanol (up to 40% yield) than that found after 24 h, which led us to conclude that catalysts **3** and **4** do in fact catalyze a quantitative deoxygenation of 1,2-hexanediol to hexane through the pathway 1,2-

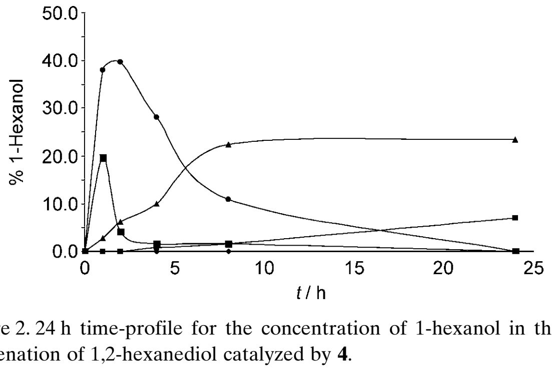


Figure 2. 24 h time-profile for the concentration of 1-hexanol in the deoxygenation of 1,2-hexanediol catalyzed by **4**.

hexanediol→hexanal→1-hexanol→hexene→hexane. This is also supported by the presence of traces of hexene in the reaction mixture, but complete absence of other GC identifiable condensation products (e.g. dihexyl ether, 1,3-dioxolanes or 1,4-dioxanes)[19] in the GC traces of these reactions. Control experiments under identical conditions but using 1-hexanol as the substrate yielded mixtures of hexane and hexene in the presence and mixture of dihexyl ethers and hexene in the absence of metal catalyst.

In contrast the equally low mass balances observed with the catalysts **1**, **1Cl** and **2** that can only operate at much lower temperatures are caused by the formation of higher molecular weight (poly)ether condensates that are not volatile enough for GC analysis. No hexane is formed with these catalysts and at low conversions the GC traces of these reaction show the presence of 2-pentyl-4-butyl-1,3-dioxolane and *cis/trans*-2,5- and *cis/trans*-2,6-1,4-dioxolane and 1,1-, 1,2- and 2,2-hexanediol ethers that were also identified in our earlier work, but not quantified in this study.[19,31]

From these experiments the terpy systems **3** and **4** emerge as some of the most robust homogeneous hydrogenation catalysts ever reported[46] and further investigations focused on these, in particular on the 4′-phenyl-2,2′:6′,2′′-terpy based catalyst **4**, as this ligand is substantially easier to prepare than the parent terpy ligand.[39] Initially, solutions of the triaqua complexes **3** and **4** in (aqueous) sulfolane are deep red-purple and air-stable. Samples taken during or after reaction at temperatures up to 200 °C appear yellow-orange, but reactions using **4** at temperatures >200 °C revert to a clear red-deep purple at the end of the reaction with no visible decomposition or formation of a precipitate. This catalyst solution can be reused without apparent loss of activity, that is, after reconstitution of the 1,2-hexanediol concentration to 500 mmolL^{-1} and heating to T>200 °C the recycled solution again achieves complete conversion of the substrate to hexane.

Nature of the active catalyst: The distinct temperature dependent color changes of **4** observed in the course of the catalytic reactions prompted us to investigate this system in more detail. Starting with the hypothesis that a reaction of the pro-catalyst $[Ru(OH_2)_3(4'\text{-phenyl-}2,2':6',2''\text{-terpy})](OTf)_2$ (**4**) with the actual hydrogenation substrate hexanal (formed by the acid-catalyzed dehydration of 1,2-hexanediol[19]—see analogous reaction for glycerol in Scheme 1) causes the color change, the triaqua complex **4** was reacted with excess hexanal in deuterated methanol at 155 °C (sealed NMR tube) for three days and the reaction monitored by ^{1}H NMR. The same deep purple to orange–yellow color change as in the catalytic reactions in sulfolane along with a complete change of the appearance of the aromatic region of the NMR spectrum was observed.[47] Scale-up of this reaction followed by slow evaporation of the methanol solvent allowed the isolation of the methoxy-bridged centro-symmetric dimeric carbonyl complex $[\{(4'\text{-phenyl-}2,2':6',2''\text{-terpy})Ru(CO)\}_2(\mu\text{-}OCH_3)_2](OTf)_2$ (**5**) as an orange solid, which was fully characterized by ^{1}H, ^{13}C NMR, and IR spectroscopy, MALDI-TOF MS analysis, and single crystal X-ray crystallography. Figure 3 shows an ORTEP plot of the structure of the cation.[48] Complex **5** crystallizes in the triclinic space group $P\bar{1}$ (a=8.2532(17); b=12.858(3); c=14.363(3)°; α=64.38(3); β=77.26(3); γ = 87.12(3) Å, R=4.36 %). The characteristic bond length about the ruthenium centre are (in Å) Ru–N11=2.090, Ru–N22=1.972, Ru–N23=2.094, Ru–O1=2.131 and Ru–C3=1.835. The characteristic bond angles in the planar core of the dimer are (in deg) N11-Ru-N22=79.24, N22-Ru-N23=79.53, N11-Ru-N23=158.77, O1-Ru-O1^i=76.39, Ru-O1-Ru^i=103.81, C3-Ru-O1=173.81, O1-Ru-N22=166.77 and N22-Ru-C3=95.74 resulting in a distorted octahedral coordination environment for the ruthenium.

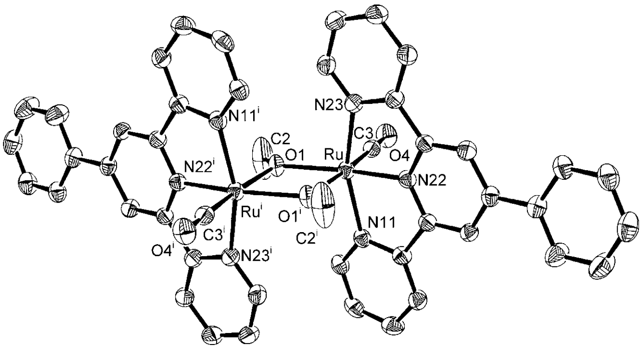
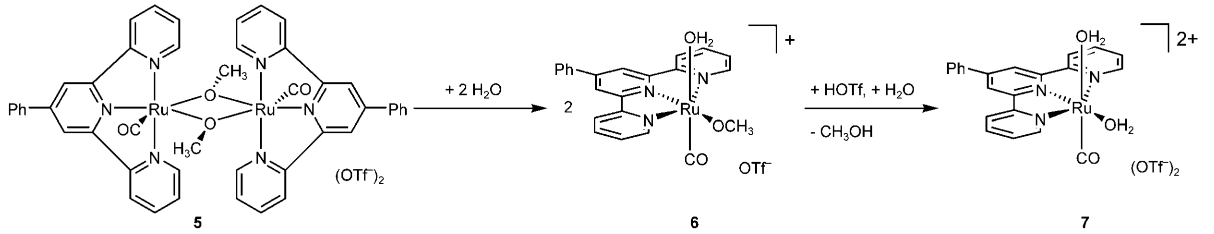


Figure 3. ORTEP plot of the cation of $[\{(4'\text{-phenyl-}2,2':6',2''\text{-terpy})Ru(CO)\}_2(\mu\text{-}OCH_3)_2](OTf)_2$ (**5**) as determined by single crystal X-ray crystallography. Ellipsoids are drawn at 50 % probability level. Hydrogen atoms, triflate counterions and methanol solvent contained in the unit cell are omitted for clarity.

The IR spectrum of the dimer **5** in the solid state (KBr) shows two ν(CO) bands at 1975 and 2079 cm^{-1} corresponding to the strong symmetry allowed B_u and the weak symmetry forbidden A_g band in the C_{2h} point group of the cation dimer, whereas in MeOH only a single ν(CO) band at 1967 cm^{-1} is observed, suggesting that in solution and with participation of traces of water present in the MeOH the dimer dissociates into a mononuclear complex $[(4'\text{-phenyl-}2,2':6',2''\text{-terpy})Ru(CO)(H_2O)(OCH_3)](OTf)$ (**6**) or in the presence of triflic acid and water as present in the actual reaction mixtures into $[(4'\text{-phenyl-}2,2':6',2''\text{-terpy})Ru(CO)(H_2O)_2](OTf)_2$ (**7**) as the actual catalyst resting state in aqueous solution. The dissociation reaction is illustrated in Scheme 2 showing one of several conceivable stereochemical arrangements of the aquo, methoxy and carbonyl ligands in **6** and **7**. For comparison the ν(CO) band in the related complexes $[(2,2':6',2''\text{-terpy})Ru(CO)(X)_2]$, X=Cl, Br, whose X-ray structure has also been determined, appear at 1948 and 1944 cm^{-1} (Nujol).[49]

When complex **5** is used as the pro-catalyst using the same reaction conditions (0.5 mol % ruthenium) as listed in the entries for 200–250 °C in Table 1 the same result as for complex **4** is observed, that is, complete conversion of 1,2-hexanediol to 1-hexanol and hexane with phase separation



Scheme 2. Dissociation of dimer complex **5** into monomeric complexes **6** and/or **7**.

of hexane from the sulfolane reaction mixture is observed. The color of the initially orange–yellow reaction mixture at the end of the reaction is purple, matching that of the reactions performed with **4** at these temperatures. When 1-hexanol is used as the hydrogenation substrate no color change to orange–yellow takes place, but slow hydrogenation to hexane is still observed along with the formation of di-*n*-hexylether, which is not present in reaction mixtures starting from 1,2-hexanediol.

From these observations we postulate, that in the orange–yellow solutions formed by using **3** or **4** as the procatalysts, the active hydrogenation catalysts are in fact the carbonyl complexes $[(L)Ru(CO)(H_2O)_2](OTf)_2$; L = terpy, 4′-Phenyl-2,2′:6′,2″-terpy or ultimately the corresponding transient hydride complexes $[(L)Ru(CO)(H_2O)(H)](OTf)$ or possibly $[(L)Ru(CO)(H)_2]$ resulting from the heterolytic activation of hydrogen gas.[50] The carbonyl complexes $[(L)Ru(CO)(H_2O)_2](OTf)_2$ are formed in situ through decarbonylation of the actual hydrogenation substrate hexanal. The (catalytic) decarbonylation of aldehydes at ruthenium centers has multiple precedents in the literature.[51–54] The color change back to purple after complete conversion of the substrate to 1-hexanol and hexanes at temperatures > 200 °C then points to a thermal loss of CO(g) from the complexes $[(L)Ru(CO)(H_2O)_2](OTf)_2$ regenerating the triaqua complexes $[(L)Ru(OH_2)_3](OTf)_2$ (**3** or **4**) in the aqueous acidic reaction medium.

Deoxygenation of glycerol:

In sulfolane solution: After establishing the tolerance of pro-catalysts **3** and **4** to the temperatures required for the initial dehydration of glycerol in acidic sulfolane solution we investigated the deoxygenation of glycerol by these catalysts as a function of acid and water content of the sulfolane reaction mixture at $t = 0$ h using a 24 × 2 mL well parallel reactor at the upper temperature limits of catalyst **3**, that is, 175 °C avoiding any decomposition (cf. Table 1) and the upper temperature limit of the reactor set-up, that is, 200 °C for catalyst **4**, well below the decomposition temperature of this catalyst. With four of the individually cooled wells containing sulfolane only and thus serving as controls for cross-contamination (none was observed), the reactor allows the simultaneous screening of a 4 × 5 array of reaction mixtures ranging in triflic acid content from 4, 8, 12 to 16 equivalents with respect to ruthenium catalyst (identical conditions as for 1,2-hexanediol, that is, 0.5 mol % in a 500 mmol L^{-1} solution of glycerol in sulfolane/water) and 10–50 % (v/v) of water content.

In no instance was 1,3-propanediol or 1,2-propanediol detected in these reactions at any time. Instead only the double deoxygenation product 1-propanol could be quantified, whose yields as a function of water (in % v/v) and acid (in mol equivalents with respect to ruthenium) content for catalysts **3** and **4** are graphically represented in Figure 4 and Figure 5, respectively. For catalyst **3** yields of up to ≈5 % of 1-propanol are present in the reaction mixture after 2 h at low water content (10 %), increasing to a maximum of ≈14 % at 24 h and 40 % water content with variable

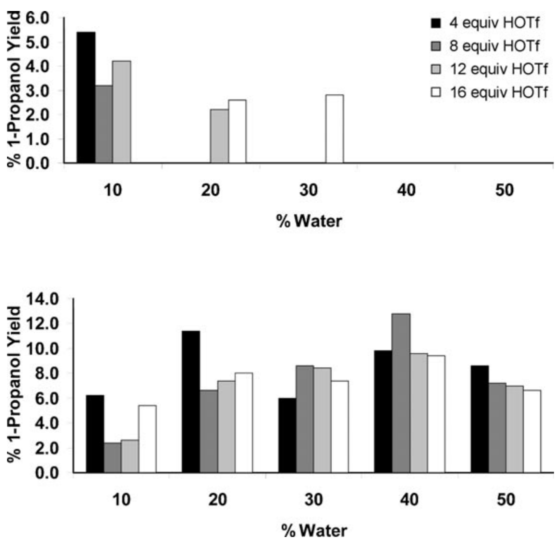


Figure 4. Yield of 1-propanol in the deoxygenation of glycerol with **3** in sulfolane at 175 °C, 7.58 MPa $H_2(g)$ and variable amount of water and HOTf added as indicated. Top: $t = 2$ h; bottom: $t = 24$ h.

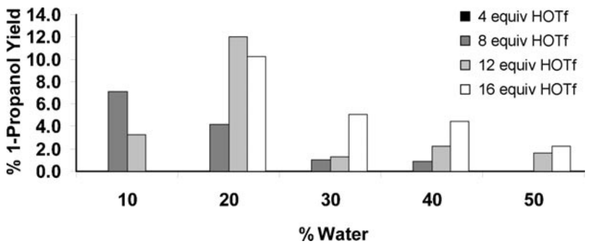


Figure 5. Yield of 1-propanol in the deoxygenation of glycerol with **4** in sulfolane at 200 °C, 7.58 MPa $H_2(g)$ after 2 h and variable amount of water and HOTf added as indicated.

amounts of glycerol remaining in the reaction mixture (0% glycerol at 10% water content to ≈50% glycerol at 50% water content). No clear trends or quantitative correlations emerge between the acid and water content of the reaction mixtures and the amount of propanol observed, reflecting the complexity of the interconnected (*de*)hydration equilibria discussed earlier (Scheme 1). Catalyst **4** shows similar behavior, that is, there is no simple correlation of the 1-propanol content with the acid or water content of the reaction mixture at the 2 h time point. After 24 h the GC traces of the reaction mixtures show only very small amounts of 1-propanol, acrolein and pairs of peaks assigned to traces of the isomeric mixtures of cis/trans-2-(2′-hydroxy-ethyl)-4-(hydroxymethyl)-1,3-dioxolane (by GC-MS) formed by acetalization of glycerol with 3-HPA. In total these amount to <25 mmol L,$^{-1}$ that is, <5% of the initial glycerol concentration. After 24 h no glycerol was detectable for the reactions containing 10 and 20 water% and 4, 8, 12 and 16 equivalents of HOTf acid, that is, complete conversion of glycerol had taken place. In light of our earlier result with the 1,2-hexanediol model substrate, we therefore postulated that the very low mass balances of these reactions as observed by quantitative GC of the liquid reaction mixtures are the consequence of the formation of the gaseous total deoxygenation product propane.

To be able to prove the production of propane by probing the gas headspace of these reactions (technically not possible nor meaningful with the parallel reactor) the reaction of catalyst **4** at a water content of 10% and with 8 equivalents of acid was repeated with 100 mL of reaction solution in a 600 mL Parr reactor at 200 °C and 7.58 MPa $H_2(g)$ pressure for 24 h. GC/GC-MS analysis of gas samples obtained from the 500 mL headspace volume of this reaction after ≈3 h showed a dominant peak of propane and traces of acrolein, propanal, propene and 1-propanol (identified by comparison with authentic gas/vapor samples).[55] Gas samples obtained after 24 h showed pure propane. GC analysis of the reaction solution after 24 h did not show any peaks other than those of the solvent sulfolane and internal standard dimethylsulfone (DMS) and MALDI-TOF MS analysis of the same reaction solution in both positive and negative ionization mode showed the presence of triflic acid and various fragments of the ruthenium catalyst, but equally did not reveal the presence of any non-volatile glycerol condensates or polyethers and no precipitate was observed in the reaction mixture. From this we conclude that under the reaction conditions employed, catalyst **4** quantitatively converts glycerol into propane.

In further control experiments using catalyst **4** and 1,3-propanediol instead of glycerol, but otherwise identical conditions, transient 1-propanol yields of up ≈8% are observed in samples drawn from the reactor at 3 h time intervals after 3, 6, and 9 h reaction time, but after 24 h the same result as glycerol is obtained, that is, any 1,3-propanediol that may have formed would under the reaction conditions required for the initial dehydration of glycerol also be converted into 1-propanol and ultimately propane.

In NMP solution: In an attempt to attenuate the overall acidity of the reaction solution the solvent was switched to the slightly basic N-methyl-pyrrolidin-2-one (NMP)[56] while keeping all other parameters for the glycerol deoxygenation reactions constant. Regardless of the acid/water content (4-16 equiv/10-50% using the parallel reactor as before) of the reaction solution no deoxygenation of glycerol was observed in this solvent at 200 °C and after 24 h the concentration of glycerol almost equaled the initial concentration. Black precipitate was observed in the reaction mixture indicating catalyst decomposition. Using a single well 50 mL reactor, which allows an increase of the reaction temperature to 250 °C, and with 4 equiv of HOTf and 4.82 MPa of $H_2(g)$ pressure (cold) the reaction yielded 4% 1-propanol, 12% of cis/trans-2-(2′-hydroxy-ethyl)-4-(hydroxymethyl)-1,3-dioxolane (equivalent to 24% glycerol) and 68% glycerol recovery along with catalyst decomposition for a total mass balance of 98%, that is, no higher molecular weight condensates or gaseous products were formed. As in the reactions carried out in sulfolane the reaction mixture underwent the color changes from purple to orange (sample taken after 1 h) and back to purple over the course of the 24 h reaction run again suggesting transient formation of a carbonyl complex $[(4'\text{-phenyl-}2,2'{:}6',2''\text{-terpy})Ru(CO)(H_2O)_2](OTf)_2$ as the active catalyst.

Also carried out were reactions designed to mimic the conditions and results reported in the patent by Che, which claims production of substantial amounts of both 1,2-propanediol and 1,3-propanediol in NMP solvent using a combined $[Rh(CO)_2(acac)]/H_2WO_4$ catalyst under 31.7 MPa of syn-gas atmosphere.[27] Deoxygenation reactions were carried out with catalyst **4** at 225 and 250 °C using 6.20 MPa of $H_2(g)$ pressure (cold) and at the same catalyst, substrate and acid concentrations that gave the optimum yields of 1,3-propanediol reported in the patent.[57] Samples were taken at 0, 1, 2, 4, 8, and 24 h. The reaction mixtures are initially purple with yellow suspended H_2WO_4 (that is, the tungstic acid is not soluble in NMP) and again turn orange after 1 h of heating under hydrogen. As in the other NMP reactions a black precipitate appears indicating catalyst decomposition. The samples taken at the 1, 2, 4 and 8 h time points showed no deoxygenation products. After 24 h in both reactions ≈5% of 1-propanol, ≈2.5% of 1,3-propanediol, ≈5% 1,2-propanediol and ≈5% cis/trans-2-(2′-hydroxy-ethyl)-4-(hydroxymethyl)-1,3-dioxolane had formed as verified by GC and GC-MS against authentic samples. 36% of the glycerol remained along with other condensation products that could not be identified by GC-MS. Running the reaction using our own standard concentrations[58] at 225 °C yielded ≈4% of 1-propanol with 95% of glycerol recovery. Again a black precipitate was formed indicating decomposition of the catalyst.

In water: The requirement for an acid-catalyzed dehydration of glycerol makes the use of pure water as the reaction medium counterintuitive, as the loss of water to 3-HPA or acrolein occurs against the equilibria (K_{eq} and K'_{eq} in Scheme 1). However, in terms of overall reaction medium acidity discussed above pure water falls in between sulfolane or sulfolane/water mixtures and the basic NMP solvent, which prompted us to also investigate pure water as the reaction solvent and again using complex **4** as the procatalyst. We also hypothesized that the use of pure water as the reaction medium may inhibit the secondary dehydration of 3-HPA to acrolein, thus favoring the formation of the desired 1,3-propanediol. As the results listed in Tables 2 and 3 show, glycerol is in fact efficiently deoxygenated in pure water using either HOTf or H_2WO_4 as the acid catalyst, where the latter is not soluble, but as in NMP forms a suspension, but again no 1,2- or 1,3-propanediol was formed.

All reactions listed in Tables 2 and 3 were carried out in a 50 mL Autoclave Engineers mini-reactor. In an attempt to directly quantify the amount propane formed in these reactions, the reactor was fitted with a pressure sensor allowing tracking of the total pressure as a function of the reaction chemistry occurring. Assuming ideal gas behavior for the H_2(g) consumed (2 mol equivalents/propanol and 3 mol equivalents/propane generated) and any propane formed the observed pressure drops measured after cooling the reactor back down to ambient temperature (295 K) give an approximate yield of propane. For the reactions where propane was formed, the observed pressure drops matched the expected theoretical value within ≈10% and the presence of propane was again verified by GC-MS of the gas headspace of the reactor. As with the reaction is sulfolane and NMP, MALDI-TOF MS analysis in both positive and negative ionization mode of the liquid phase did not show any non-volatile condensation products resulting in the quantitative mass balances listed in Tables 2 and 3 and further affirming the results obtained in sulfolane presented above.

Table 2. Deoxygenation of glycerol by $[Ru(OH_2)_3(4'\text{-phenyl-}2,2':6',2''\text{-terpy})](OTf)_2$ (**4**) in pure water as a function of HOTf content and temperature.[a]

T [°C]	Mol equiv HOTf/Ru	Glycerol[b] [%]	1-Propanol[b] [%]	2-Propanol[b] [%]	*n*-Propane[c] [%]
200	16	92	8	0	0
200	32	82	12	0	6
200	64	76	14	0	10
200	100	49	19	0	32
225	16	59	19	0	22
225	32	26	28	0	46
225	64	12	35	0	53
225	100	5	35	0	60
250	4	0	35	0	65
250	8	0	22	0	78
250	12	0	17	2	81
250	16	0	23	3	74
250	32	0	2	0	98
250	64	0	6	1	93
250	100	0	0	0	100

[a] Reaction conditions: 500 mmol L^{-1} substrate in water, 100 mm L^{-1} dimethylsulfone as internal standard, 0.5 mol% catalyst, 4.82 MPa of H_2(g), 24 h. [b] By quant. GC and GC-MS. [c] By GC-MS, mass balance inferred and by pressure drop.

Table 3. Deoxygenation of glycerol by $[Ru(OH_2)_3(4'\text{-phenyl-}2,2':6',2''\text{-terpy})](OTf)_2$ (**4**) in pure water as a function of H_2WO_4 acid and temperature.[a]

T [°C]	Mol equiv H_2WO_4/Ru	Glycerol[c] [%]	1-Propanol[c] [%]	2-Propanol[c] [%]	*n*-Propane[c] [%]
250	0	36	35	0	29
250	1	7	39	2	52
250	4	0	30	5	65
250	8	0	24	0	76
250	8[d]	53	26	0	21

[a] Reaction conditions: 500 mmol L^{-1} substrate in water, 100 mm L^{-1} dimethylsulfone as internal standard, 0.5 mol% catalyst, 5.5 MPa of H_2(g), 24 h. [b] By quant. GC and GC-MS. [c] By GC-MS, mass balance inferred and by pressure drop. [d] 2 h.

With HOTf as the acid co-catalyst (Table 2) the reaction was carried out at 200, 225 and 250 °C. At the two lower temperatures both the conversion of glycerol and yields of 1-propanol and propane scale with the amount of acid added, whereas at 250 °C complete conversion of the substrate is achieved in 24 h in all cases. The amounts of 1-propanol detected in these reaction mixtures vary, but show a decreasing trend with increasing acid content. The small amounts of 2-propanol formed are attributed to Markovnikov rehydration of the intermediate propene. The solutions of the $[Ru(Phterpy)(OH_2)_3](OTf)_2$ (**4**) catalyst in water were initially purple, but became colorless after complete conversion of the substrate with formation of an orange-brown precipitate. The IR spectrum (KBr) of this solid shows one band at $\tilde{\nu} = 1612\ cm^{-1}$, its H^1 NMR spectrum in $[D_4]$MeOH only resonances assignable to the 4-Ph-terpy ligand and the MALDI-TOF mass spectrum only fragments assignable to $\{Ru_n(4\text{-Ph-terpy})_m\}$ (n, $m = 1$, 2) species, that is, the precipitate is not composed of polymeric organic species formed form the glycerol substrate, but originates from a reaction of the catalyst to a water insoluble ruthenium complex of unknown structure.

In light of the trace of 1,3-propanediol observed in the reactions using H_2WO_4 in NMP and recognizing the possibly unique properties of H_2WO_4 as a solid surface-active acid in a selective dehydration of glycerol,[26,27] we then carried out a second series of experiments using the combination of procatalyst **4** with H_2WO_4 in water, the results of which are summarized in Table 3. As with the reactions in NMP a black precipitate formed with use of H_2WO_4 as the acid and again no 1,2- or 1,3-propanediol was detected in any of the reaction mixtures and the yields of 1-propanol and propane are comparable to those obtained with the homogeneous acid HOTf. Notable is the build-up of 1-propanol and product distribution with 8 equivalent of H_2WO_4 observed after 2 h of reaction time that resembles the reaction profile obtained in the deoxygenation of the 1,2-hexanediol model system (Figure 2) and the fact that glycerol conversion occurs even without the addition of acid. This is due to the formation of free HOTf in the reaction mixture through the heterolytic activation of H_2(g) by the catalyst into protons and a hydride complex, a standard feature observed with ionic hydrogenation catalysts.[32,59,60]

Discussion

Regardless of the wide range of acid/water concentrations employed no 1,3-propanediol could be detected in any of the homogeneous sulfolane or water reaction mixtures. A marginal amount of both 1,2- and 1,3-propanediol along with 1-propanol was produced in the NMP/H_2WO_4 reaction mixtures, which, however, led to catalyst decomposition. In analogy to the known selectivity of heterogeneous catalyst systems for the conversion of glycerol to 1,2-propanediol through dehydration to acetol,[19] the appearance of 1,2-propanediol in the latter must be a function of the heterogeneous nature of the tungstic acid in NMP medium. The presence of 1,3-propanediol also suggests that the heterogeneous H_2WO_4 acid is less active in catalyzing the secondary dehydration reaction of 3-HPA to acrolein.

In contrast, in purely homogeneous phase with HOTf as the acid catalyst and under the reaction conditions employed (that is, $T \geq 175\,^{\circ}C$ in sulfolane or water solvent), the actual hydrogenation substrate is not 3-HPA, but likely acrolein formed by the rapid double dehydration of glycerol. With reference to Scheme 1 this means that the activation barrier for the initial dehydration of glycerol (associated with k_1) must be higher than that for the second dehydration to the α,β-unsaturated acrolein (associated with k_2) and - since control reactions in sulfolane solvent with 1,3-propanediol as the substrate yielded the same result as with glycerol - also higher than that for any other subsequent acid-catalyzed dehydration, that is, $\Delta G^{\neq}(k_1) \gg \Delta G^{\neq}(k_2)$, $\Delta G^{\neq}(k_3)$ and $\Delta G^{\neq}(k_4)$ and for our catalysts probably also $\Delta G^{\neq}(k_2) \ll \Delta G^{\neq}(k_{\text{diol}})$. As all metal catalyzed hydrogenations of the resulting aldehydes to alcohols or alkenes to alkanes are thermodynamically favored, this then explains the formation of 1-propanol and ultimately propane as the only detectable products under homogeneous acidic conditions. Figure 6 qualitatively summarizes the resulting reaction cascade, in which the initial glycerol dehydration is the rate determining step. Thus our results suggest that it may not be possible to realize an effective catalyzed synthesis of 1,3-propanediol from glycerol using catalyst systems in which both the acid and metal catalyst employed are homogeneous. In this scenario the relative hydrogenation activity of the metal catalyst has no impact on the product distribution, which is instead entirely governed by the selectivity of the dehydration reactions. The formation of 1,3-propanediol in the presence of H_2WO_4 as observed by Che and ourselves then logically suggests that the surface of this heterogeneous acid must have specific interactions with the glycerol substrate leading to the desired chemo- and regioselectivity of dehydration to 3-HPA rather than acetol as observed with other solid acids (see the results reported by Sasaki and coworkers, who also used H_2WO_4).[26]

In the hydrogenation reactions, hydride complexes must be formed from the aqua-complexes **1–4** under the reaction conditions in order to arrive at a catalytically active system. However our inability to synthesize and/or isolate any such complexes precluded any meaningful mechanistic studies. In analogy to the mechanism proposed by Lau and co-workers for **1Cl**[33,34] the mechanism of the catalytic hydrogenation of the aldehydes and alkenes formed in the reaction mixtures is very likely ionic in nature,[35] that is, relies on the heterolytic activation of hydrogen gas on the relatively electron poor ruthenium centre making the overall catalytic cycle compatible with the necessarily aqueous acidic reaction environment. The actual hydrogenation then occurs either by direct transfer of a hydride ligand from the ruthenium centre to a protonated substrate without actual coordination to the substrate to metal centre as observed for the related complex $[RuH(bipy)(terpy)]^+$ and CO_2 by Ishitani[61] and Creutz[62] or by insertion of the carbonyl or alkene substrate into a Ru−H bond followed by release of the substrate through protonation of the resulting Ru-O or Ru−C bond as proposed by Lau for **1Cl**. The latter could be considered a *reverse* ionic hydrogenation mechanism.

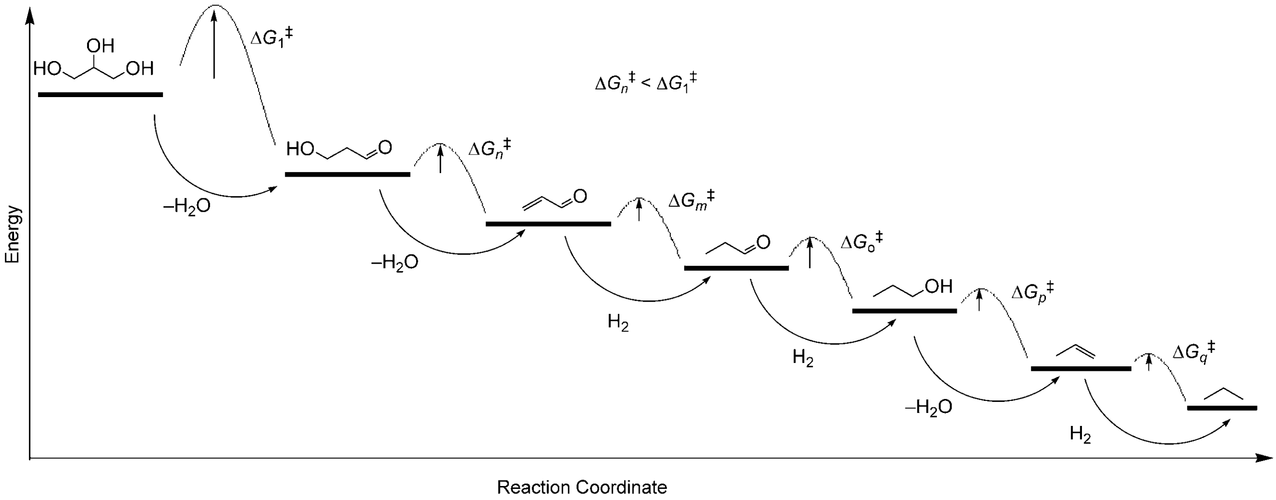


Figure 6. Reaction cascade for the deoxygenation of glycerol to propane under acidic conditions in homogeneous phase.

Conclusions

In combination with HOTf as a Brønsted acid co-catalyst the complexes $[Ru(H_2O)_3(terpy)](OTf)_2$ (**3**) and $[Ru(H_2O)_3(4'\text{-Phenyl-}2,2'{:}6',2''\text{-terpy})](OTf)_2$ (**4**) form an air-, water-, acid- and high-temperature (> 250 °C) stable catalyst system for the total deoxygenation of glycerol to propane in sulfolane or aqueous medium. Under these reaction conditions this is the result of the high propensity of the initial dehydration and hydrogenation products 3-hydroxy-propionaldehyde (3-HPA) and 1,3-propanediol to undergo secondary Brønstedt acid-catalyzed dehydration reactions to acrolein or allyl alcohols, both of which are hydrogenated to *n*-propanol, followed by a third dehydration to propene and hydrogenation to the final product propane, which under the reducing reaction conditions (hydrogen atmosphere) constitutes the thermodynamic sink of the system.

The high temperature stability of the 4′-phenyl-2,2′:6′,2″-terpy complexes suggests that these catalysts may also be applicable to deoxygenation reactions of higher sugars and sugar alcohols to high-value added products, for example, the conversion of erythritol to THF,[63,64] xylitol to hydroxymethyl tetrahydrofuran, D-fructose to 2-hydroxymethyl-6-methyl-tetrahydrofuran and sorbitol to other deoxygenated species. Experiments towards the realization of these goals using these catalysts are currently under way in our laboratories.

Experimental Section

General: All manipulations were performed under an atmosphere of argon employing standard Schlenk-line techniques or within a dry-box and using freshly distilled organic solvents or degassed water. Commercially obtained reagents were used as received. High-pressure hydrogenation reactions were conducted with 25 mL reaction solutions in an Autoclave Engineers (AE) Mini-Reactor with a 50 mL stainless steel (316 SS) reactor vessel or with 2 mL reaction solutions in a 24×4 mL well HEL CAT24 parallel reactor using standard 2 mL borosilicate glass tubes leaving four wells as blanks to check for cross-contamination (none was observed). All high-pressure experiments employed industrial grade hydrogen gas. GC analyses were carried out by using a Varian 3800 using either a 30 m DB-1701 column, for 1,2-hexanediol and carbonyls, or a 30 m polar WAX column, for glycerol and all other substrates. Quantification was achieved through a three-level calibration against authentic samples, employing dimethylsulfone (DMS) as an internal standard. GC-MS analysis were carried out by using a Varian Saturn 2000 GC/MS employing either a 30 m DB-1701 or a 30 m polar WAX column running in default EI mode. Sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (TSP) was used as a reference compound for NMR spectrum obtained in D_2O. All other NMR shifts were referenced to TMS using the residual solvent signals. IR spectra were recorded by using either a BOMEM or a NICOLET 4700 FT-IR employing solution cells with 0.1 mm CaF_2 or as KBr pellets Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. *cis*-$RuCl_2(bipy)_2$ and *cis*-$RuCl_2(phen)_2$ were prepared in 61 % and 81 % yield, respectively via ruthenium blue followed by reduction of the [*cis*-$RuCl_2(bipy)_2$]Cl and [*cis*-$RuCl_2(phen)_2$]Cl formed with $SnCl_2$.[41] $RuCl_3$(terpy) was prepared as reported by Sullivan et al.[42] $RuCl_3$(4′-phenyl-2,2′:6′,2″-terpy) was prepared as described by Constable and Cargill Thomson.[65] *cis*-$[Ru(6,6'\text{-}Cl_2\text{-}bipy)_2(OH_2)_2](OTf)_2$ (**1Cl**) was prepared as previously reported by Lau and co-workers[33,34] and ourselves.[31]

[*cis*-$Ru(bipy)_2(OH_2)_2](OTf)_2$ (1): [*cis*-$RuCl_2(bipy)_2$]·2 H_2O (0.522 g, 1.003 mmol) was stirred in degassed H_2O (50 mL) under Ar. AgOTf (0.527 g, 2.050 mmol) was added, and the mixture was stirred at 70 °C for 1 h to give an orange-brown solution with a white precipitate. Upon cooling, the mixture was filtered through a plug of Celite to remove the AgCl. The H_2O was removed at 50 °C on the vacuum line, and the red solid was vacuum-dried overnight. Yield: 0.6451 g (86 %). ^1H NMR (300 MHz, D_2O): $\delta=6.98$ (t, $J=6.5$ Hz, 1H), 7.65 (m, 2H), 7.78 (t, $J=6.5$ Hz, 1H), 8.14 (t, $J=7.5$ Hz, 1H), 8.26 (d, $J=8.1$ Hz, 1H), 8.47 (d, $J=8.4$ Hz, 1H), 9.26 ppm (d, $J=5.4$ Hz, 1H); ^{13}C NMR (75 MHz, D_2O): $\delta=123.2$ (*C*H), 123.4 (*C*H), 125.6 (*C*H), 126.8 (*C*H), 135.7 (*C*H), 137.4 (*C*H), 151.5 (*C*H), 154.4 (*C*H), 158.3 (*C*), 160.5 ppm (*C*); elemental analysis calcd (%) for $C_{22}H_{20}F_6N_4O_8RuS_2$: C 35.34; H 2.70; N 7.49; found: C 35.18; H 2.58; N 7.44.

$[Ru(CO_3)(phen)_2]$: The preparation of this intermediate follows the protocol given by Johnson et al. and Bonneson et al.[37,66] As no NMR or IR data has previously been reported for these complexes they are given here for completeness. [*cis*-$RuCl_2(phen)_2$]·2 H_2O (1.080 g, 1.899 mmol) was refluxed in degassed H_2O (30 mL) for 15 min, and then Na_2CO_3 (3.173 g, 0.0299 mol) was added. The mixture was refluxed for 2 h, cooled in the fridge, filtered, and the dark purple microcrystalline solid washed with H_2O and ether, then dried. Yield: 0.958 g (97 %). ^1H NMR (300 MHz, CD_3OD): $\delta=7.27$ (dd, $J=5.5$, 7.9 Hz, 4H), 7.77 (d, $J=5.1$ Hz, 2H), 8.10 (d, $J=8.7$ Hz, 2H), 8.22 (m, 8H), 8.71 (d, $J=8.1$ Hz, 2H), 9.69 ppm (d, $J=4.8$ Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): $\delta=125.5$ (*C*H), 126.7 (*C*H), 128.7 (*C*H), 128.8 (*C*H), 131.8 (*C*), 134.0 (*C*H), 135.6 (*C*H), 150.5 (*C*), 152.2 (*C*), 153.6 (*C*H), 155.2 ppm (*C*H); IR (KBr): $\nu(C{=}O)$ 1560 cm^{-1}.

[*cis*-$Ru(OH_2)_2(phen)_2](OTf)_2$ (2):[37] $[Ru(CO_3)(phen)_2]$ (0.503 g, 0.964 mmol) was suspended in degassed H_2O (10 mL)in a foil-wrapped flask. HOTf (32 mL, 1.5 M in H_2O) was added. Bubbles were seen, the solution turned red, the solid dissolved, and then reprecipitated. The mixture was stirred for 0.5 h at room temperature, then the volume was reduced by half. The solid was filtered, rinsed 3 times with 1 mL portions of H_2O, then 3 times with 5 mL portions of ether, and vacuum dried. Yield: 0.632 g (82 %) dark red-orange powder. ^1H NMR (300 MHz, D_2O): $\delta=7.18$ (dd, $J=5.4$ and 8.1 Hz, 2H), 7.77 (d, $J=5.1$ Hz, 2H), 8.00 (d, $J=9.0$ Hz, 2H), 8.17 (m, 6H), 8.72 (d, $J=7.8$ Hz, 2H), 9.68 ppm (d, $J=4.8$ Hz, 2H); ^{13}C NMR (75 MHz, D_2O): $\delta=119.6$ (q, $J_{CF}=315$ Hz, $CF_3SO_3^-$), 124.2 (*C*H), 125.6 (*C*H), 127.6 (*C*H), 127.7 (*C*H), 130.3 (*C*), 130.5 (*C*), 134.9 (*C*H), 136.5 (*C*H), 149.2 (*C*), 151.1 (*C*), 152.8 (*C*H), 155.3 ppm (*C*H); elemental analysis calcd (%) for $C_{26}H_{22}F_6N_4O_8RuS_2$: C 39.15; H 2.78, N 7.03; found: C 39.30; H 2.75; N 7.08.

$[Ru(OH_2)_3(terpy)](OTf)_2$ (3): (1.112 g, 2.523 mmol) was suspended in degassed H_2O (25 mL). AgOTf (2.044 g, 7.955 mmol) was dissolved in degassed H_2O (10 mL) and added to the $[RuCl_3(terpy)]$ suspension. The flask was covered in foil and stirred 1 h at 50 °C. The green solution was cooled and filtered through a plug of Celite to remove the AgCl. Zn dust (4.12 g, 0.063 mol) was added to the filtrate, which instantly changed to a maroon color. The solution was stirred 15 min at room temperature, then filtered through a plug of Celite. The H_2O was removed using the vacuum line and the solid vacuum dried overnight. Yield: 1.225 g (71 %) dark purple powder. ^1H NMR (300 MHz, D_2O): $\delta=7.72$ (t, $J=6.3$ Hz, 3H), 8.02 (t, $J=7.8$ Hz, 2H), 8.31 (d, $J=7.8$ Hz, 2H), 8.38 (d, $J=7.8$ Hz, 2H), 9.12 ppm (d, $J=4.5$ Hz, 2H); ^{13}C NMR (75 MHz, D_2O): $\delta=119.6$ (q, $J_{CF}=315$ Hz, $CF_3SO_3^-$), 121.8 (*C*H), 122.9 (*C*H), 127.5 (*C*H), 131.9 (*C*H), 137.9 (*C*H), 153.0 (*C*H), 160.3 (*C*), 163.9 ppm (*C*); UV/vis (H_2O): $\lambda_{max}(\varepsilon)=533$ (1350), 483 (1260), 363 nm (1430 $L\,mol^{-1}\,cm^{-1}$). This procedure follows the one given by Adeyemi et al., who prepared the corresponding perchlorate complex, but could not isolate this salt as a solid.[43] As the $Zn(OTf)_2$ formed cannot be separated from the highly soluble complex we were unable to obtain meaningful elemental analysis for this material. Instead MALDI-TOF mass spectrometry analysis was performed. m/z calcd for $C_{15}H_{17}N_3O_3{}^{102}Ru$: 389.03, found 567.23 $[Ru(terpy)_2]^+$, 370.09 $[Ru(OH_2)_2(terpy)]^+$, 351.16 $[Ru(OH_2)(terpy)]^+$, 334.13 $[Ru(terpy)]^+$.

$[RuCl_3(4'\text{-phenyl-}2,2'{:}6',2''\text{-terpy})]$: $RuCl_3$·3 H_2O (0.5 g, 1.91 mmol) and 4′-phenyl-2,2′:6′,2″-terpy (0.68 g, 2.19 mmol) were refluxed in EtOH

(75 mL) for 16 h. The red solution was cooled and filtered. The solid was rinsed three times with EtOH (10 mL), then ether, and vacuum-dried. Yield: 0.980 g (98 %) dark red-brown powder. This paramagnetic material was used in the next step without further purification or characterization.

[Ru(OH$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpy)](OTf)$_2$ (4): [RuCl$_3$(4′-phenyl-2,2′:6′,2″-terpy)] (0.880 g, 1.703 mmol) was suspended in degassed H_2O (30 mL). AgOTf (1.320 g, 5.14 mmol) was dissolved in degassed H_2O (15 mL) and added to the Ru suspension. The flask was covered in foil and stirred for 1 h at 80 °C. The dark green solution was filtered through a plug of Celite and Zn dust (2.7 g, 24.5 mmol) was added to the filtrate. The instantly purple solution was stirred for 15 min and then filtered through Celite. The H_2O was removed in vacuo. Yield: 0.800 g (68 %) dark purple powder. ^{1}H NMR (300 MHz, D_2O): $\delta = 7.41$ (d, $J = 7.2$ Hz, 1 H), 7.52 (t, $J = 7.5$ Hz, 2 H), 7.67 (t, $J = 6.6$ Hz, 2 H), 7.86 (d, $J = 7.5$ Hz, 2 H), 7.96 (t, $J = 7.7$ Hz, 2 H), 8.39 (d, $J = 8.1$ Hz, 2 H), 8.51 (s, 2 H), 9.06 ppm (d, $J = 5.1$ Hz, 2 H); ^{13}C NMR (75 MHz, D_2O): $\delta = 118.7$ (*C*H), 119.6 (q, $J_{CF} = 315$ Hz, $CF_3SO_3^-$), 122.8 (*C*H), 126.7 (*C*H), 127.5 (*C*H), 129.3 (*C*H), 129.8 (*C*H), 135.8 (*C*), 137.8 (*C*H), 143.2 (*C*), 153.1 (*C*H), 160.0 (*C*), 163.5 ppm (*C*); UV/vis(H_2O): $\lambda_{max}(\varepsilon) = 533$ nm (1151 L mol^{-1} cm^{-1}). This is analogous to the one given by Adeyemi et al., who prepared the corresponding terpy perchlorate complex, but also could not isolate this salt as a solid.[43] As the Zn(OTf)$_2$ formed cannot be separated from the highly soluble complex we were unable to obtain meaningful elemental analysis for this material. Instead MALDI-TOF mass spectrometry analysis was performed. *m*/*z* calc′d for $C_{21}H_{15}N_3O_3{}^{102}Ru$: 465.42, found 719.21 [Ru(4′-phenyl-2,2′:6′,2″-terpy)$_2$Ru]$^+$, 464.08 [Ru(OH$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpy)]$^+$, 446.09 [Ru(OH$_2$)$_2$(4′-phenyl-2,2′:6′,2″-terpy)]$^+$ 427.12 [Ru(OH$_2$)(4′-phenyl-2,2′:6′,2″-terpy)]$^+$, 411.13 [Ru(4′-phenyl-2,2′:6′,2″-terpy)]$^+$.

[(4′-phenyl-2,2′:6′,2″-terpy)Ru(CO)(μ-OCH$_3$]$_2$(OTf)$_2$ (5): [Ru(OH$_2$)$_3$(4′-phenyl-2,2′:6′,2″-terpy)](OTf)$_2$ (25 mg) was dissolved in deuterated methanol (0.5 mL) and hexanal (100 μL) was added to that solution. Three freeze-pump-thaw cycles were performed on the NMR tube to remove the air and prior to charging the NMR tube with Ar gas. The NMR tube was heated for 3 days at 155 °C, leading to a change in color from purple to orange and the formation of a small quantity of black solid. After filtration, crystals suitable for single-crystal X-ray analysis were obtained from this solution by slow evaporation. Scale-up of this procedure in normal methanol and precipitation with diethylether yields the complex as an orange–yellow powder in 75 % yield. ^{1}H NMR (300 MHz, CD_3OD): $\delta = 7.59$ (m, 3 H), 7.79 (m, 2 H), 8.03 (dd, $J_1 = 7.9$ Hz, $J_2 = 8.4$ Hz, 2 H), 8.27 (dt, $J_1 = 8.0$ Hz, $J_2 = 7.75$ Hz, $J_3 = 1.74$ Hz, 2 H), 8.82 (s, 2 H), 8.70 (d, $J = 8.0$ Hz, 2 H), 8.98 ppm (d, $J = 5.72$ Hz, 2 H); ^{13}C NMR (75 MHz, CD_3OD): $\delta = 122.8$ (*C*H), 126.0 (*C*H), 128.9 (*C*H), 129.6 (*C*H), 130.7 (*C*H), 132.0 (*C*H), 137.5 (*C*), 141.6 (*C*H), 153.7 (*C*), 154.9 (*C*H), 159.4 (*C*), 160.17 ppm (*C*); IR(KBr): $\tilde{\nu} = 1975$, 2079 cm^{-1}; IR(MeOD): $\nu(CO) = 1967$ cm^{-1}; UV/vis (H_2O): $\lambda_{max}(\varepsilon) = 399$ nm (1191 L mol^{-1} cm^{-1}); MALDI-TOF mass spectrometry: [(4′-phenyl-2,2′:6′,2″-terpy)$_2$Ru$_2$(μ-OCH$_3$)]$^+$ = $C_{23}H_{33}N_6O_1{}^{102}Ru_2 = 853$, found 855.22; [(4′-phenyl-terpy)Ru(CO)(OTf)]$^+$ = $C_{22}H_{15}F_3N_3O_4{}^{102}Ru_1S_1 = 588$, found 588.05; [(4′-phenyl-terpy)Ru(OTf)]$^+$ = $C_{21}H_{15}F_3N_3O_3{}^{102}Ru_1S_1 = 560$, found 560.06.

Representative procedure for a 1,2-hexanediol deoxygenation experiment: 1,2-Hexanediol stock solution (500 mM 1,2-hexanediol, 100 mM dimethyl sulfone, in sulfolane) was dispensed into a 25.0 mL volumetric flask, HOTf (22 μL, 4 equivalents with respect to catalyst) was added, and the solution mixed well. The catalyst (2.5 mM, 0.5 mol % of substrate concentration) was weighed into a small vial. The stock solution and catalyst were combined in the AE minireactor 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 4.82 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 through 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. At 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. The remainder of the reaction solution was transferred to a large vial for storage. Glycerol deoxygenations were carried out in an analogous manner.

Representative procedure for a glycerol deoxygenation experiment using the 24-well parallel reactor: The catalyst (5 mM, 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 (1000 mM glycerol, 200 mM dimethyl sulfone, in sulfolane) 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 a 10.0 mL volumetric flask and filling to the mark with the catalyst solution. 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 mM, [dimethyl sulfone] = 100 mM, [catalyst] = 2.5 mM, [HOTf] = 10, 20, 30, 40 mM in the sample test tubes. Dimethyl sulfone stock solution (100 mM in sulfolane, 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 aluminum 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.

Acknowledgements

The authors thank Dr. Garry Hanan, Université de Montreal, Montreal, QC for helpful discussions regarding the synthesis of terpy ligands. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), Natural Resources Canada, (NRCAN), the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), the BioCap Canada Foundation and DuPont. Deeb Taher thanks the Deanship of Research, Tafila Technical University for financial assistance for travel to Canada.

---

[1] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem. Int. Ed.* **2007**, *46*, 4434–4440.
[2] C. H. C. Zhou, J. N. Beltramini, Y. X. Fan, G. Q. M. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527–549.
[3] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Chim. Oggi* **2008**, *26*, 32.
[4] Y. Zheng, X. Chen, Y. Shen, *Chem. Rev.* **2008**, *108*, 5253–5277.
[5] R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angew. Chem.* **2006**, *118*, 4086–4089; *Angew. Chem. Int. Ed.* **2006**, *45*, 3982–3985.
[6] D. G. Lahr, B. H. Shanks, *Ind. Eng. Chem. Res.* **2003**, *42*, 5467–5472.
[7] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel, C. Rosier, *Green Chem.* **2004**, *6*, 359–361.
[8] D. G. Lahr, B. H. Shanks, *J. Catal.* **2005**, *232*, 386–394.
[9] A. Perosa, P. Tundo, *Ind. Eng. Chem. Res.* **2005**, *44*, 8535–8537.
[10] M. A. Dasari, P. P. Kiatsimkul, W. R. Sutterlin, G. J. Suppes, *Appl. Catal. A* **2005**, *281*, 225–231.
[11] C. W. Chin, M. A. Dasari, G. J. Suppes, W. R. Sutterlin, *AIChE J.* **2006**, *52*, 3543–3548.

[12] Y. Kusunoki, T. Miyazawa, K. Kunimori, K. Tomishige, *Catal. Commun.* **2005**, *6*, 645–649.

[13] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, *J. Catal.* **2006**, *240*, 213–221.

[14] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, *Appl. Catal. A* **2007**, *329*, 30–35.

[15] T. Miyazawa, S. Koso, K. Kunimori, K. Tomishige, *Appl. Catal. A* **2007**, *318*, 244–251.

[16] J. Feng, H. Fu, J. Wang, R. Li, H. Chen, X. Li, *Catal. Commun.* **2008**, *9*, 1458–1464.

[17] A. Alhanash, E. F. Kozhevnikova, I. V. Kozhevnikov, *Catal. Lett.* **2008**, *120*, 307–311.

[18] M. McCoy, *Chem. Eng. News* **2007**, *85*, 7.

[19] R. R. Dykeman, K. L. Luska, M. E. Thibault, M. D. Jones, M. Schlaf, M. Khanfar, N. J. Taylor, J. F. Britten, L. Harrington, *J. Mol. Catal. A* **2007**, *277*, 233–251.

[20] J. F. Knifton, T. G. James, K. D. Allen, P. R. Weider, J. B. Brown, L. H. Slaugh, US 6.903.044, **2005**.

[21] T. Haas, B. Jaeger, R. Weber, S. F. Mitchell, C. F. King, *Appl. Catal. A* **2005**, *280*, 83–88.

[22] S. Vollenweider, G. Grassi, I. Konig, Z. Puhan, *J. Agric. Food Chem.* **2003**, *51*, 3287–3293.

[23] S. Vollenweider, C. Lacroix, *Appl. Microbiol. Biotechnol.* **2004**, *64*, 16–27, and references therein.

[24] Y. Doleyres, P. Beck, S. Vollenweider, C. Lacroix, *Appl. Microbiol. Biotechnol.* **2005**, *68*, 467–474.

[25] K. Y. Wang, M. C. Hawley, S. J. DeAthos, *Ind. Eng. Chem. Res.* **2003**, *42*, 2913–2923.

[26] T. Kurosaka, H. Maruyama, I. Naribayashi, Y. Sasaki, *Catal. Commun.* **2008**, *9*, 1360–1363.

[27] T. Che (Celanese Corporation), US 4.642.394, **1987**.

[28] G. Braca, A. M. R. Galletti, G. Sbrana, *J. Organomet. Chem.* **1991**, *417*, 41–49.

[29] M. Schlaf, *J. Chem. Soc. Dalton Trans.* **2006**, 4645–4653.

[30] D. Pressman, H. J. Lucas, *J. Am. Chem. Soc.* **1942**, *64*, 1953–1957.

[31] Z. Xie, M. Schlaf, *J. Mol. Catal. A* **2005**, *229*, 151–158.

[32] M. Schlaf, P. Gosh, P. J. Fagan, E. Hauptman, R. M. Bullock, *Angew. Chem.* **2001**, *113*, 4005–4008; *Angew. Chem. Int. Ed.* **2001**, *40*, 3887–3890.

[33] C. P. Lau, L. Cheng, *Inorg. Chim. Acta* **1992**, *195*, 133–134.

[34] C.-P. Lau, L. Cheng, *J. Mol. Catal.* **1993**, *84*, 39–50.

[35] R. M. Bullock, *Chem. Eur. J.* **2004**, *10*, 2366–2374.

[36] B. Durham, S. R. Wilson, D. J. Hodgson, T. J. Meyer, *J. Am. Chem. Soc.* **1980**, *102*, 600–607.

[37] P. Bonneson, J. L. Walsh, W. T. Pennington, A. W. Cordes, B. Durham, *Inorg. Chem.* **1983**, *22*, 1761–1765.

[38] D. L. Jameson, L. E. Guise, *Tetrahedron Lett.* **1991**, *32*, 1999–2002.

[39] J. Wang, G. Hanan, *Synlett* **2005**, 1251–1254.

[40] P. A. Lay, A. M. Sargeson, H. Taube, *Inorg. Synth.* **1986**, *24*, 291–299.

[41] T. Togano, N. Nagao, M. Tsuchida, H. Kumakura, K. Hisamatsu, F. S. Howell, M. Mukaida, *Inorg. Chim. Acta* **1992**, *195*, 221–225.

[42] B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 1404–1407.

[43] S. A. Adeyemi, A. Dovletoglou, A. R. Guadalupe, T. J. Meyer, *Inorg. Chem.* **1992**, *31*, 1375–1383.

[44] B. Cornils, W. A. Herrmann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**, pp. 87–88.

[45] Detailed results of this screen are given in the Supporting Information.

[46] H. Brunner in *Homogeneous Hydrogenation, Vol. 1* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**, pp. 195–212.

[47] See the Supporting Information for images of the NMR spectra of all complexes described.

[48] CCDC 733652 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[49] G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas, A. H. White, *Aust. J. Chem.* **1984**, *37*, 929–945.

[50] In our hands attempts to synthesize and isolate these hydride complexes were unsuccessful.

[51] R. H. Prince, K. A. Raspin, *J. Chem. Soc. A* **1969**, 612–618.

[52] G. Domazetis, B. Tarpey, D. Dolphin, B. R. James, *Chem. Commun.* **1980**, 939–940.

[53] Y.-Z. Chen, W. C. Chan, C. P. Lau, H. S. Chu, H. L. Lee, G. Jia, *Organometallics* **1997**, *16*, 1241–1246.

[54] J. N. Coalter, J. C. Huffman, K. G. Caulton, *Organometallics* **2000**, *19*, 3569–3578.

[55] See the Supporting Information for an image of the GC-MS trace and spectrum obtained.

[56] The p*K*a of protonated NMP (aqueous scale) is approximately −0.5, that is, substantially higher than that of H_3O^+ (−1.74), which due to solvent leveling is the strongest acid present in the sulfolane/water mixtures. p*K*a values from J. March, *Advanced Organic Chemistry*, 6th ed., Wiley-Interscience, New York, **2006**.

[57] 3500 mmol L^{-1}glycerol, 0.35 mol% catalyst, 5 equiv of H_2WO_4 in 25 mL NMP and 80 mmol L^{-1} DMS as an ISTD.

[58] 500 mmol L^{-1} of glycerol, 100 mmol L^{-1} DMS, 0.5 mol% ruthenium catalysts and 8 equivalents of H_2WO_4 (with respect to ruthenium).

[59] R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504–7507; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363.

[60] M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman, R. M. Bullock, *Adv. Synth. Catal.* **2009**, *351*, 789–800.

[61] H. Konno, A. Kobayashi, K. Sakamoto, F. Fagalde, N. E. Katz, H. Saitoh, O. Ishitani, *Inorg. Chim. Acta* **2000**, *299*, 155–163.

[62] C. Creutz, M. H. Chou, *J. Am. Chem. Soc.* **2007**, *129*, 10108–10109.

[63] L. E. Manzer, US 6.593.481 B1, **2003**.

[64] L. E. Manzer, US 7.019.155, **2006**.

[65] E. C. Constable, A. M. W. C. Thomson, *New J. Chem.* **1992**, *16*, 855–867.

[66] E. C. Johnson, B. P. Sullivan, D. J. Salmon, S. A. Adeyemi, T. J. Meyer, *Inorg. Chem.* **1978**, *17*, 2211–2215.

Received: May 27, 2009