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Suitable ligands for homogeneous ruthenium-catalyzed hydrogenolysis of esters

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Abstract

Effective hydrogenolysis of dimethyl oxalate to ethylene glycol has been obtained using a catalyst prepared in situ from $Ru(acac)_3$ with the facially coordinating tridentate phosphine ligand $CH_3C(CH_2PPh_2)_3$. This catalyst enabled full and selective conversion in 16 h at [S]/[Ru] = 500 at 80–100 bar hydrogen pressure at 120 °C. This catalyst is far more active than any known homogeneous catalyst able to hydrogenate dimethyl oxalate to ethylene glycol. Several mono-, di- and tridentate P- and N-ligands have been selected and were evaluated, several of which showed (almost) no reactivity. In some cases, for instance when using the meridional coordinating ligand $PhP(C_2H_4PPh_2)_2$, selectivity can be directed toward the semi-hydrogenolysis product methyl glycolate.

Keywords: Hydrogenolysis; Hydrogenation; Esters; Alcohols; Ruthenium; Tripodal phosphine

1. Introduction

In contrast to the hydrogenation of ketones and aldehydes, the hydrogenolysis of esters is troublesome. Esters are a stable class of compounds and, with a few exceptions, are reduced with difficulty and survive most catalytic hydrogenations [1], Scheme 1.

Evaluation of thermodynamic data associated with relevant hydrogenolysis reactions (e.g. the hydrogenolysis of methyl formiate, ethyl acetate), gave an estimation of the cross-over temperature, $\Delta H^\circ/\Delta S^\circ$, at 200–400 K [2] so the equilibrium is favorable at temperatures up to and slightly above ambient temperature. However, the reaction has a high activation barrier and kinetic constraints prevent the reaction from proceeding. At higher temperatures, the entropy change of the reaction becomes more unfavorable, so an optimum temperature should be chosen.

Homogeneous hydrogenolysis of esters, in contrast to its heterogeneous counterpart, is a fairly new development. Ruthenium complexes have been employed in a wide variety of hydrogenation reactions, for instance, ruthenium-catalyzed hydrogenation of alkynes, alkenes, aldehydes and ketones is well established and is extensively documented [3]. However, concerning hydrogenolysis of esters, only a few publications describing successful attempts have appeared

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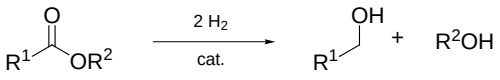


Scheme 1. Hydrogenolysis of esters to alcohols.

on the subject over the years [4,5]. Matteoli et al. have extensively studied the conversion of activated esters, such as dimethyl oxalate using the ruthenium cluster compound $H_4Ru_4(CO)_8(PBu_3)_4$, [6,7] which had proved to be succesful in the hydrogenation of carboxylic acids to the corresponding alcohols [8]. This catalyst showed limited activity for a variety of esters and a lot of different by-products were formed, stemming from esterification, trans-esterification and decarboxylation. Another example of a catalyst applicable for the hydrogenolysis of esters is the complex developed by Grey et al. [9]. The scope of both systems is limited, they are only applicable in the hydrogenolysis of activated esters, such as dimethyl oxalate [10] or fluorinated esters [9].

In view of the general problems with, and the lack of, suitable catalysts for the hydrogenolysis of esters, a search towards more active catalysts was initiated [11]. Interest was directed towards the use of ruthenium complexes having an increased electron density on the ruthenium center, which would enhance the nucleophilicity of the intermediate hydride towards the less polar (as compared to ketones) carbonyl function of the ester.

In this paper we describe the selection of suitable ruthenium complexes and ligands as catalyst precursors for the hydrogenolysis of esters to alcohols. Catalyst precursors were evaluated based on their activity and selectivity in the hydrogenolysis of dimethyl oxalate (**1**), which, due to its structural properties, is activated for hydrogenolysis, and can act as an excellent probe (Scheme 2) [5–10].

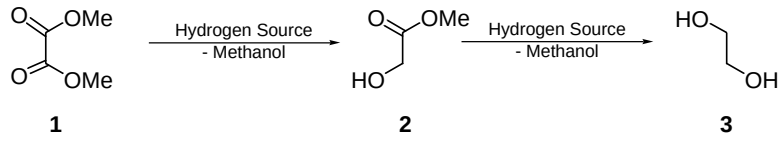
2. Results and discussion

2.1. Selection of ruthenium precursor

A number of initial experiments were performed to find a suitable ruthenium catalyst precursor for the hydrogenolysis of dimethyl oxalate (**1**) to the corresponding diol, ethylene glycol (**3**). It is known that the conversion of the ester proceeds in two steps. In the first step, dimethyl oxalate is converted to methyl glycolate (**2**), which is subsequently converted to ethylene glycol (**3**, Scheme 2) [9].

The first experiments were conducted using readily available and stable ruthenium starting materials such as $RuCl_2(PPh_3)_4$, which is known to be an excellent catalyst precursor for the transfer hydrogenation of ketones and aldehydes [12]. When $RuCl_2(PPh_3)_4$ was applied as catalyst precursor for the hydrogenolysis of dimethyl oxalate, 37% conversion of ester **1** was observed using THF [10]. The catalyst precursor, however, showed poor selectivity and only a 12% yield of **2** was isolated after 16 h. No formation of **3** was observed; the remainders are unidentified side-products. Methyl glycolate is less susceptible to undergo hydrogenolysis compared to dimethyl oxalate, because the ester function of the former is no longer activated by the presence of an electron withdrawing group. It is known that for further hydrogenolysis of the α-hydroxy ester to the diol, increased reaction temperatures (180 °C instead of 120 °C) and reaction times are required [8].

For this active catalyst, reaction conditions were varied. First, the focus was at the solvent for the reaction. An interesting solvent to perform the conversion of dimethyl oxalate to ethylene glycol and methanol would be methanol itself. Matteoli et al. found for their catalyst that alcoholic solvents increased selectivity for ethylene glycol (**3**) [5,7]. When methanol was used, 51% of the starting ester was converted to



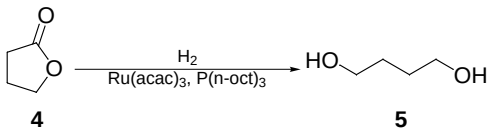
Scheme 2. Hydrogenolysis of dimethyl oxalate (**1**) via methyl glycolate (**2**) to ethylene glycol (**3**).

2. Apparently, hydrogenolysis is halted at the stage of the intermediate product **2** and further hydrogenolysis to **3** was not observed under the standard conditions using $RuCl_2(PPh_3)_4$.

Our experiments revealed that conversion of the substrate is influenced by the presence of water in the reaction medium: when commercial methanol was used in the catalytic reaction, conversions and yields are lower compared to use of dry methanol. The presence of water may lead to hydrolysis of the ester resulting in the formation of the corresponding acids that in turn can lead to inactive carbonyl species formed by decarbonylation of the acid in the presence of ruthenium.

All reactions conducted thus far were performed using a well-defined ruthenium^{II} precursor. Although conversion of the substrate is observed, catalyst activity is low and only partial hydrogenolysis to **2** is observed and other (undefined) side-products are formed. In order to increase the conversion of the substrate and to facilitate the formation of ethylene glycol (**3**), several readily available ruthenium starting materials that can act as a pre-catalyst were screened. An appealing route towards an active catalyst is the formation of the catalyst in situ by reduction of a Ru^{III} starting material in the presence of a suitable ligand under catalytic conditions, thus forming an active system. It was previously reported by Hara et al. that an in situ prepared catalyst derived from $Ru(acac)_3$ and phosphine type ligands was suitable in the hydrogenation of γ-lactones (**4**) to α,ω-diols (**5**, Scheme 3) [13].

We started from $RuCl_3$ and PPh_3 and added activated zinc to facilitate the reduction of Ru^{III} to Ru^{II}. The initial attempt proved to be successful and indeed an active catalyst was formed, however, the activity of this catalyst system was lower than when starting from $RuCl_2(PPh_3)_4$. Presumably, the formation of the catalyst is not optimum under these conditions (15% yield with a turnover frequency of only 0.2/h) and the chlorides introduced with $RuCl_2(PPh_3)_4$ and $RuCl_3$ may be hampering the reaction. In order to prevent the presence of chlorides in the reaction mixture, the Ru^{III} complex $Ru(acac)_3$, a succesfull catalyst precursor for the hydrogenation of cyclic esters (Scheme 3) [14], was used as the starting material. Indeed with this catalyst precursor, with activated zinc as the reducing agent, a large increase in activity was observed (Table 1, entry 4), showing that the formation of the catalyst in situ from $Ru(acac)_3$ provides an easier and more efficient route towards the active species that is involved in catalysis. Using $Ru(acac)_3$ and PPh_3, already 73% of the starting material **1** was converted to methyl glycolate **2**; hydrogenolysis of this α-hydroxy ester to the diol **3** was, again, not observed. The amount of ligand added does not influence the rate of the reaction significantly (turnover frequency (TOF) 1.1/h for ligand/Ru = 12 compared to 0.9 for ligand/Ru = 5.88). The role of the zinc additive can be ascribed to two influences. Metallic zinc acts as a reducing agent in the conversion of the Ru^{III} starting



Scheme 3. The hydrogenation of γ-butyrolactone (**4**) to 1,4-butanediol (**5**).

Table 1
Selected ruthenium precursors for the hydrogenolysis of dimethyl oxalate (**1**)[a]

Catalyst	Solvent	Ru (μmol)	Ligand/Ru	DMO (mmol)	Conversion (%)	Yield (%)		TOF (mol mol^{-1} h^{-1})
						2	**3**	
$RuCl_2(PPh_3)_4$	THF	25.5		1.28	37	12	0	0.4
$RuCl_2(PPh_3)_4$	MeOH	22.4		1.37	51	20	0	0.8
$RuCl_3 + PPh_3$	MeOH	37.9	3.62	0.87	44	15	0	0.2
$Ru(acac)_3 + PPh_3$	MeOH	19.6	5.88	0.99	73	36	0	0.9
$Ru(CO)_2(OAc)_2(PBu_3)_2$[b]	MeOH				100	18	82	0.9

[a] General conditions: $pH_2 = 80$ bar, $T = 120\,^{\circ}C$; TOF: turnover frequency = amount of alcohol formed (mmol)/h/amount of catalyst (μmol). TOF is determined as an average value after 17 h.

[b] $T = 180\,^{\circ}C$, $pH_2 = 200$ bar; $t = 144$ h, [5].

material to Ru^{II}, furthermore, the formed Zn^{II} acts as a Lewis acid and can activate the ester carbonyl function by coordinating to it, hence rendering it more prone to attack by the ruthenium catalyst [9].

At this point it was assumed that the formation of the actual catalyst is initiated by the hydrogenation of the acetyl acetonate ligands on the ruthenium center to 2,4-pentanediol. Indeed, amounts of 2,4-pentanediol were recovered in a separate experiment, confirming the hydrogenation of the acetyl acetonate ligands.

2.2. Ligand selection

Common ligands, such as mono-, di- and tridentate ligands based on N- and P- donor systems, as displayed in Fig. 1, were selected and evaluated in the ruthenium-catalyzed hydrogenolysis of dimethyl oxalate. The chemistry of ruthenium complexes containing these types of ligands is generally well documented and a wide range of catalyst precursors is available. Some examples are the hydrogenation of olefins (using 1,10-phenanthroline (**9**) or trispyrazolylborate (**12**)) [14,15] and the transfer hydrogenation of ketones and aldehydes (using 1,10-phenanthroline (**9**) [16], bis(diphenylphosphine)ethane (**11**) [16] or 2,2′,6′,2″-terpyridine (**13**) [17]). Other examples include triphenylarsine (**7**), $PhP(CH_2CH_2PPh_2)_2$ (**14**), $CH_3C(CH_2PPh_2)_3$ (**15**), [18] and $(PPh_2C_2H_4PPhCH_2)_2$ (**16**) [19].

The activity of the catalytic system with these ligands in the in situ hydrogenolysis of dimethyl oxalate to ethylene glycol with $Ru(acac)_3$ as the ruthenium source has been summarized in Table 2. A first screening of ligands revealed that best results were obtained for phosphine type ligands. Although ligands containing nitrogen donor atoms such as 1,10-phenanthroline (**9**) or 2,2′,6′,2″-terpyridine (**13**) have proven to be active in the hydrogenation of ketones, they show no activity in the hydrogenolysis of dimethyl oxalate, even at higher temperatures and pressures no conversion was observed.

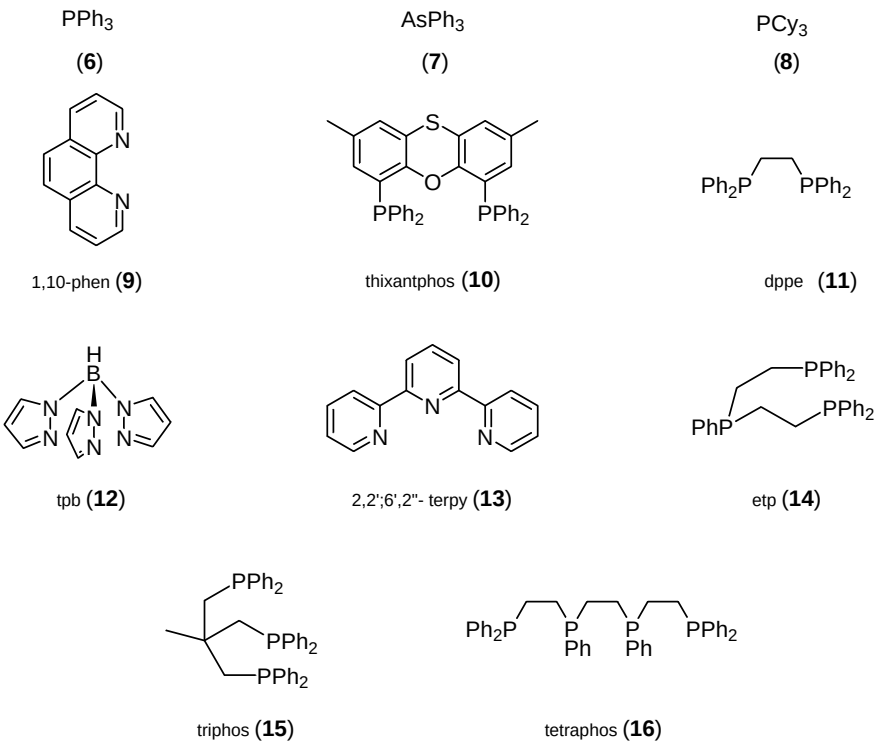


Fig. 1. Ligands used in hydrogenolysis of dimethyl oxalate to ethylene glycol.

Table 2
Ligand variations in the homogeneous hydrogenolysis of dimethyl oxalate[a]

Ligand	Ru (μmol)	Ligand/Ru	DMO (mmol)	Conversion (%)	Yield (%)		TON	[TOF][b] (h^{-1})
					2	**3**		
None	15.8	0.0	0.96	18	2	0	1	[0.0]
Monodentate phosphines								
PPh_3 (**6**)	19.6	5.9	0.99	73	36	0	18	[0.9]
PCy_3 (**8**)	19.3	4.6	0.89	7	1	0	0	[0.0]
Didentate phosphines								
Thixantphos (**10**)[c]	20.0	0.0[c]	1.24	0	0	0	0	[0.0]
$Ph_2PC_2H_4PPh_2$ (**11**)	16.1	3.0	0.88	18	11	0	6	[0.4]
Tridentate phosphines								
$PhP(C_2H_4PPh_2)_2$ (**14**)	20.1	1.7	1.14	76	67	0	38	[2.5]
$CH_3C(CH_2PPh_2)_3$ (**15**)	21.1	1.4	1.77	100	1	95	160	[10.0]
Tetradentate phosphines								
$(CH_2PPhC_2H_4PPh_2)_2$ (**16**)	22.8	1.0	0.96	91	85	0	36	[2.2]
Other ligands/catalysts								
$AsPh_3$ (**7**)	16.8	8.9	1.41	1	0	0	0	[0.0]
1,10-Phenanthroline (**9**)	20.3	6.4	1.04	20	0	0	0	[0.0]
Trispyrazolylborate (**12**)	19.1	2.3	9.25	14	1	0	3	[0.2]
2,2′:6′2″-Terpyridine (**13**)	15.6	1.8	0.89	11	0	0	0	[0.0]

[a] General conditions: 12 ml methanol, $pH_2 = 80$ bar, $T = 120\,^{\circ}C$, 0.3 mol% Zn.
[b] TON: turnover number = amount of alcohol formed (mmol)/amount of catalyst (mmol); TOF: turnover frequency = amount of alcohol formed (mmol) per h/amount of catalyst (μmol). TON and TOF were determined as an average after the standard reaction time of 16 h.
[c] Was applied as the complex $H_2Ru(thixantphos)_2$.

2.3. Monodentate ligands

Using simple monodentate coordinating phosphine ligands gave rise to the formation of only the mono-hydrogenated methyl glycolate (**2**). For example, in the case of PPh_3 (**6**), 73% of the starting material is converted with a selectivity of 50% for methyl glycolate (other products are unidentified). As mentioned, it was assumed that an increased electron density on the ruthenium catalyst would enhance the attack of the catalyst on the electrophilic carbonyl carbon atom of the ester, thus increasing the rate of conversion to the alcohol. For this reason, the more basic PCy_3 (**8**) was employed. However, catalyst activity was found to decrease when using this ligand, presumably as a result of its stronger donor properties and steric bulk, which tend to stabilize and screen the ruthenium complex too much. In the ruthenium-catalyzed hydrogenation of aldehydes, it has been suggested that the initial step is the reversible dissociation of a phosphine ligand *trans* to a hydride [20]. Contrary to expectation, despite favorable dissociation of the ligand, catalyst activity is reduced to zero using $AsPh_3$ (**7**).

2.4. Didentate ligands

Polyphosphines are often favored over monodentate phosphines and generally exhibit excellent bonding towards transition metals, leading to an increased basicity or nucleophilicity at the metal [19]. Didentate phosphine ligands of the type $R_2PCH_2CH_2PR_2$ (R: alkyl and aryl), have proven to be a useful class of supporting ligands in organometallic complexes and catalysis and significant research efforts have been devoted to the investigation of ruthenium hydrides bearing didentate phosphines [21].

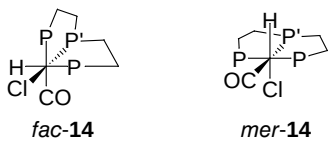
Several didentate ligands were applied in the hydrogenolysis of dimethyl oxalate (**1**). The application of the ligand dppe (**11**, R: $-C_6H_5$) proved successful, and 18% of the ester was converted with the formation of only a small amount of undefined side-products.

The phosphine ligand thixantphos (**10**) [22] was available as its ruthenium hydride complex $H_2Ru(thixantphos)_2$ and was used as such. This complex showed no activity.

2.5. Tri- and tetradentate ligands

Tridentate ligands for catalysis are well documented and have been used in a variety of catalytic experiments (such as hydrogenation of aldehydes and ketones) using different ruthenium complexes [19,23]. Suarez and Fontal [19], Sung and co-workers [24] showed that ruthenium^{II} complexes containing diphosphines that form larger chelate ring sizes exhibit higher catalytic activity in the hydrogenation of aldehydes. Chelate ring opening was regarded as the rate determining step in similar catalytic processes. In complexes containing larger chelate rings, this process should be faster, and enhance activity. Moreover, since poly-phosphine complexes usually have two or more chelate rings, the chelate effect is augmented and the number of undesired isomers, which often appear in octahedral complexes with monodentate or didentate ligands, is diminished. Continuing along these lines, we first attempted the use of $PhP(CH_2CH_2PPh_2)_2$ (**14**), which has the capability to coordinate in a facial as well as in a meridional fashion to transition metals, such as ruthenium. This ligand has previously been investigated in the complex $RuHCl(CO)(PhP(CH_2CH_2PPh_2)_2)$ (Fig. 2), which was used as as a catalyst for the hydrogenation of alkenes (e.g. cyclohexene) and ketones (e.g. cyclohexanone and propanal) [18].

Employing **14**, catalyst activity increased appreciably although the ester was converted solely into the α-hydroxy ester **2**. The coordination mode of **14** in the hydrogenolysis of **1** has not been determined and different isomers can co-exist, nevertheless, this experiment showed that a tridentate ligand is preferred over equivalent amounts of didentate or monodentate ligands.



fac-**14** *mer*-**14**

Fig. 2. Coordination modes for the ligand etp in $RuHCl(CO)(PPh(CH_2CH_2PPh_2)_2)$ [18].

Forcing a tridentate ligand into a facially coordinating fashion, as for example with the tripodal ligand triphos (**15**), the catalyst displays very high activity and selectivity in the hydrogenolysis of **1** and almost complete conversion towards **3** is observed. Decreasing the Ru/substrate ratio further increased the turnover number (TON) to 860 (TOF 54). The high activity in this case is explained by the forcing conformation of the ligand compared to the other ligands, including **14**. For the other ligands, formation of several coordination isomers can be envisaged, that apparently are inactive. Application of tetradentate ligands as in **16** was not successful, selectivity to the semi-hydrogenated product **2** was observed again.

3. Conclusion

A valuable and easily available catalyst precursor for the hydrogenolysis of dimethyl oxalate to ethylene glycol has been obtained. The catalytic system appeared to be most efficient when $Ru(acac)_3$ was used in combination with the facially coordinating tripod ligand $CH_3C(CH_2PPh_2)_3$. This catalyst enabled the full conversion of the diester into the corresponding diol in high yields and selectivity under relatively mild conditions. Compared to the known catalysts [4,12] reported by Matteoli and co-workers [8] and Grey et al. [4,9] (the only previously reported homogeneous catalyst able to hydrogenate dimethyl oxalate to ethylene glycol), this catalyst is far more active. By selecting different ligands, the product of the reaction can be chosen. For example, when using the meridional coordinating ligand $PhP(C_2H_4PPh_2)_2$, dimethyl oxalate is almost exclusively converted into methyl glycolate whereas the use of $MeC(CH_2PPh_2)_3$ leads to the exclusive formation of ethylene glycol.

4. Experimental section

4.1. General

All manipulations, except hydrogenolysis experiments (see later), were carried out using standard Schlenk techniques in a dried nitrogen atmosphere.

Solvents (obtained from Acros Organics) were dried according to standard procedures [25], distilled prior to use and stored in a dried nitrogen atmosphere. Hydrogen gas (purity 5.0, 99.999%) was obtained in 10 m^3 cylinders from Hoek Loos B.V., Holland, and used without additional purification or drying.

$Ru(acac)_3$ was purchased from Acros Organics and $RuCl_3{\cdot}xH_2O$ was obtained from Johnson and Matthey, both were used as received. $RuCl_2(PPh_3)_4$ was prepared according to a literature procedure [26]. Ligands and substrates were obtained commercially from Acros Organics. All solid ligands were purified by recrystallization from a boiling hexanes solution. Liquid compounds were distilled under reduced pressures prior to use.

4.2. Autoclave setup

All experiments were conducted in a homebuilt stainless steel batch reactor (autoclave) designed for reactions under pressures up to 130 bar. The autoclave consisted of a thick-walled (thickness = 1.5 cm) beaker of approximately 200 ml. A wider ring was welled around the top side of the beaker for closing purposes. In this outer ring a deeper lying opening allowed for the placement of a Viton® *o*-ring to ensure an air-tight seal with the lid of the autoclave. The lid was attached to outer ring around the beaker by tightening six bolts in a crosswise manner. Three Swagelok™ connections on the lid of the autoclave allowed for the placement of a manometer combined with the gas inlet, a connector for a thermocouple (PT-100) and a sample valve allowing the introduction of the sample. The entire autoclave setup was protected against overpressure by the variable relief valve set at 105 bar. To heat the contents of the autoclave, the autoclave was placed in an electrically heated oven that was regulated by a Jumo dTRON-16 controller with feedback from the PT-100 thermocouple. Mixing of the contents of the autoclave was achieved by placing the entire setup (autoclave and oven) onto a normal magnetic stirrer plate.

4.3. Hydrogenolysis experiments

All hydrogenolysis experiments were standardized with respect to temperature, pressure and reaction time. Solid materials were weighed in air and transferred to a Schlenk vessel that was subsequently closed by a rubber septum. The Schlenk vessel was subsequently flushed with nitrogen to remove traces of oxygen. A syringe was used to introduce solvents, liquid substrates and additives under exclusion of air. The catalyst mixture consisted of a 15 ml solution of the catalyst precursor and the appropriate ligand (for exact amounts, see Tables 1 and 2). In some cases, additional heating was required to dissolve all the starting materials and to obtain a homogeneous solution. If the solution was heated, it was allowed to cool to room temperature prior to the addition of the substrate. Addition of the substrate was achieved by a syringe.

Before introducing the solution into the autoclave, the autoclave was evacuated and carefully flushed three times with dry nitrogen. The mixture of substrate and catalyst, prepared as earlier, was then introduced in the autoclave by connecting a canula to one of the available Swagelok™ connectors. By reducing the pressure inside the autoclave, the solution, was introduced into the reaction vessel. While stirring, the autoclave was flushed three times with 25 bar of dihydrogen gas before applying the final pressure of 80 bar. The autoclave was slowly heated to 120 °C to prevent a possible overshoot in temperature and left stirring over a period of 16 h. After the reaction, the autoclave was allowed to reach room temperature and the pressure was slowly released to 1 bar. The contents in the autoclave were transferred to a 100 ml one-necked round-bottomed flask, and the solvent was removed in vacuo using a rotary evaporator. A sample from the reaction mixture was taken for NMR and GC analysis.

Catalytic conversions were verified using gas chromatography and ^{1}H NMR spectroscopy. Gas chromatographic analysis was carried out using a Varian 3300 gas chromatograph equipped with a DB-5 capillary column (length = 30 m, internal diameter ∅ = 0.32 mm, film thickness = 1 μm) and a FID detector. Injection and detection temperatures were set at 250 °C. After (splitless) injection, the temperature of the GC was kept at 70 °C for a period of 2 min, after which the GC was heated at 20 °C/min to the final temperature of 230 °C, at which it remained for 5 min before cooling down to 70 °C.

^{1}H NMR spectra were recorded on a Varian Mercury 300 or a Bruker AMX 300 spectrometer and

were referenced to tetramethylsilane (TMS). All samples were measured at 20 °C in deutero-chloroform (99.8 at.% D, Cambridge Isotope Laboratories, Inc.) as the solvent.

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