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PAPER

Homogeneous catalytic hydrogenation of long-chain esters by an osmium pincer complex and its potential application in the direct conversion of triglycerides into fatty alcohols†

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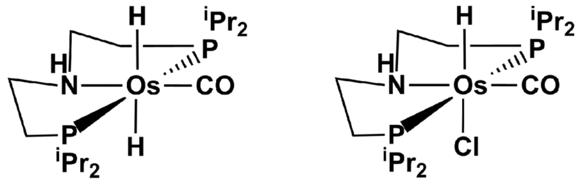
The osmium hydride complexes $OsH_2(CO)[NH(CH_2P^iPr_2)_2]$ (**1**) and $OsHCl(CO)[NH(CH_2P^iPr_2)_2]$ (**2**) were evaluated in the catalytic hydrogenation of hexyl octanoate and *cis*-3-hexenyl hexanoate to alcohols as model substrates for triglycerides. Both complexes achieve full conversion of the saturated ester at 220 °C and 800 psi pressure of hydrogen gas. In the presence of unsaturated substrates, the complexes hydrogenate C═C bonds, but are subsequently ineffective in the reduction of the ester moiety. However complex **1** is capable of hydrogenating fully saturated triglycerides (*i.e.*, hardened fats as obtained by separate initial hydrogenation of seed oils using either **1** or **2** or a standard heterogeneous hydrogenation catalyst) giving cetyl and stearyl alcohols as the main products.

Introduction

Fatty alcohols are important technical products that find extensive application in surfactants.[1] Industrially, they are produced either from fossil petrochemical resources through *Aufbau-Reaktion* and/or *Oxo processes* or by the hydrogenolysis of fatty acid methyl esters (FAME – effectively bio-diesel in turn obtained by methanol transesterification of triglycerides from seed or animal oils/fats) using a copper-chromite based heterogeneous catalyst that operates at high hydrogen pressures (3000–4500 psi ≈ 200–300 atm) and high temperatures (250–300 °C).[2–6] Due to the drastic reaction conditions and high associated costs of this process, substantial effort has been expended to find catalysts that can convert fatty esters to corresponding long-chain alcohols under milder conditions, which would lead to energy savings both in the operation and design-build of plants carrying out this process and therefore be potentially more environmentally friendly. One strategy to achieve this goal is the use of a homogeneous rather than a heterogeneous catalyst system.[7–12] Impressive progress has been made in the homogeneously catalyzed hydrogenation of esters to alcohols using metal–ligand bifunctional ruthenium-based systems that tolerate different functional groups in the substrate and employ mild conditions of hydrogen gas pressure (750 psi ≈ 50 atm) and temperature (25–140 °C).[13–22] Recently, we reported that the osmium complexes **1** and **2** (Chart 1) are versatile and robust dehydrogenation catalysts for primary alcohols to esters showing good air, moisture and thermal stability.[23,24]

Applying the *Principle of Microscopic Reversibility*, we now report the use of these complexes in the hydrogenation of esters and their potential application to the direct conversion of triglyceride seed oils into fatty alcohols, which is made possible through high thermal stability of the osmium *vs.* the previously reported ruthenium-based complexes. To the best of our knowledge, no osmium-based homogeneous catalysts for the hydrogenation of esters have been reported and also to date no homogeneous catalysts have been used for the direct conversion of triglycerides to fatty alcohols. This may be routed in the intrinsic higher temperature stability of osmium *vs.* ruthenium based catalyst systems.

In the context of a desirable greener process for the direct hydrogenolysis of triglycerides to fatty alcohols the use of an osmium-based catalyst deserves comment. The extreme toxicity of osmium in its volatile tetroxide (OsO_4) form, obtained directly from the molten metal and oxygen gas has long been known[25] and the material has even been considered as a chemical weapon by terrorists.[26] This toxicity is however believed to mainly be associated with the powerful oxidizing properties of OsO_4, which is rapidly reduced by tissue and any other biological



1 **2**

Chart 1

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† Electronic supplementary information (ESI) available: Images of 2D NMR spectra of the reaction of complex **1** with *cis*-3-hexenyl hexanoate (3 pages). See DOI: 10.1039/c2gc15960k

environment. Environmental and toxicological data of other more reduced forms of osmium are relatively sparse,[27,28] but both osmium dioxide and osmium metal are considered to be inert.[29] Given that the use of osmium based catalysts proposed here would take place under reducing conditions that cannot generate OsO_4, the use of this metal should therefore not be an issue, but would of course have to be reviewed in a full life-cycle analysis covering all relevant dimensions of an actual process design.

Results and discussion

Hydrogenation of model systems

Hexyl octanoate (HO) was chosen as a GC-analyzable model substrate for the hydrogenation of triglycerides. Reactions were carried out under 800 psi hydrogen pressure (cold at time = 0) at 0.1 mol% catalyst load either in toluene solvent or neat substrate. Table 1 summarizes the results of these reactions as a function of temperature and gives the conversion of the HO substrate and the yields of the expected products 1-hexanol (C6-OH) and 1-octanol (C8-OH) and those of the redistribution and transesterification products hexyl hexanoate (HH) and octyl octanoate (OO). No other products were observed in the GC traces of the reaction mixtures or the gas phase head space of the reactions (by micro-GC) and no precipitates formed in the reaction solutions, *i.e.*, the mass balances of the reactions are complete as stated. At $T >$ 175 °C both complexes are active as catalysts, but the chloro-hydrido complex **2** requires the addition of a base activator (NaO^tBu), generating through loss of HCl the amido complex [Os(H)(CO)(PNP)] **3** *in situ*.[23] Under hydrogen gas, **3** gives rise to the formation of **1**. When used directly **1** is more active than **2**, in particular at lower temperatures. *E.g.*, at 175 °C after 24 h and 800 psi of hydrogen pressure and toluene as a solvent (entry 5, Table 1) 46% conversion was observed when **1** was used as catalyst, while 15% conversion occurred for **2** under the same conditions (entry 7, Table 1). An improvement in the activity was observed when the temperature and/or reaction time was increased. The best conversion was observed when the reactions were performed at 220 °C giving 87% conversion for **1** after 24 h (entry 13, Table 1) and 68% conversion for **2** under the same conditions (entry 15, Table 1). Small amounts of hexyl hexanoate (HH) and octyl octanoate (OO) were detected in the GC traces of reaction mixtures run at 220 °C. The formation of the latter side product is easily understood as a simple transesterification of the 1-octanol reaction product with the starting material, while the formation of HH must be due to the fact that these complexes also catalyze the acceptorless dehydrogenative coupling of alcohols, as reported before.[23] Both complexes show an induction period during the catalytic reactions, as is evident in the hydrogen uptake plots presented in Fig. 1. The reaction is sensitive to the presence of an inert atmosphere. When the reactor was charged under argon atmosphere (glove-box) and then pressurized with hydrogen gas, the activity of complex **2** improves, reaching 82% conversion compared to 67% when the reactor was charged in air (entries 17 and 15, respectively, Table 1). The effect is less pronounced with complex **1**, giving 87% conversion when charged in air *vs.* 93% under argon atmosphere (entries 13 and 16, respectively, Table 1). When neat substrate was used, 57% conversion was observed when **1** was used as catalyst (entry 18, Table 1) and 64% for catalyst **2**. Increasing the hydrogen pressure from 800 to 950 psi at 220 °C did not result in a considerable change in the conversion of the ester to the corresponding alcohols when the reactions were carried out in toluene. However, when neat substrate was used, a 93% conversion was achieved after 24 h when using **1** (with 90%/85% yield of C6-OH/C8-OH and 2% and 3% yield of HH and OO, respectively, entry 20) and 70% conversion when **2** was used (with 61%/45% yield of C6-OH/C8-OH and 2% and 14% yield of HH and OO, respectively, entry 21) as the catalyst.

In order to more closely mimic the unsaturation found in typical triglyceride oils as obtained from corn, soy, palm, canola, *etc.*, *cis*-3-hexenyl hexanoate was employed as the second model substrate (Scheme 1). Under the same reaction conditions as the optimized reaction using hexyl octanoate as a substrate (800 psi of hydrogen gas, 24 h at 220 °C, reactor charged in air), 100% conversion was observed when **1** was used as the catalyst, however only hexyl hexanoate was obtained as the main product (97%) and only a small trace of 1-hexanol was formed (<3%). An instant color change from colourless to deep brown occurred in the solution when the catalyst was added. The same observation was made when the reactor was charged under inert atmosphere with the reaction giving a marginally improved result (100% conversion, 94% yield of hexyl hexanoate, 2% yield of 1-hexanol and 4% of 1-hexanal). Similarly when **2** was employed as the catalyst a 100% conversion and a quantitative yield of the saturated ester was realized. When the catalytic reactions were analyzed at different times and the hydrogen uptake of these reactions monitored, it was found that the alkene hydrogenation was complete after just 3 h at 220 °C and 800 psi of H_2, but in neither case did further ester hydrogenation to the alcohols take place. However, when after complete hydrogenation of the alkene a second equivalent of either **1** or **2** was added to the reaction mixture and the reactor re-pressurized and re-heated, 67% hexyl hexanoate was converted to 1-hexanol. Also, by visual inspection no further change or deepening of colour was observed in the reaction upon the second catalyst addition.

In order to elucidate the cause of the observed change in colour and apparent reactivity of the osmium complexes upon addition of the unsaturated ester to the catalyst solution a ^1H, ^{13}C and ^{31}P NMR study was carried out. One equivalent of *cis*-3-hexenyl hexanoate was added to a benzene-d_6 solution of **1** and then the reaction was followed by NMR spectroscopy. Under these conditions, the color change in the solution is not as pronounced as when a large excess of unsaturated ester is present as is in the case of the catalytic reaction (substrate : catalyst ratio = 1000 : 1). The comparison of the $^{31}P[^1H]$ NMR spectrum before and after addition of the ester (Fig. 2a *vs.* Fig. 2b) shows the presence of a new species represented by the small new singlet at 57.7 ppm, along with the singlet for the catalyst **1** at δ 64.3 ppm. In the ^1H and $^{13}C[^1H]$ NMR spectra (Fig. 3b and 4b, respectively) initially only the resonances due to the presence of **1** and *cis*-3-hexenyl hexanoate were observed. The NMR tube was then heated to 100 °C (the highest temperature technically available to us in this study) for 4 h during which time the reaction turned yellow. The $^{31}P[^1H]$ NMR spectrum (Fig. 2c) then showed not only the two resonances described above, but also a new singlet at 82.2 ppm assigned to the known yellow-orange amido complex [Os(H)(CO)(PNP)] (**3**) on the basis of our previous studies.[23] The corresponding ^{1}H spectrum shows the presence of two new multiplets at δ 3.15 and 2.81 (Fig. 3c) assignable to the (NCH$_2$) protons in this complex,[31] along with the resonances of both starting materials. After heating to 100 °C for an additional 12 h, the ^{31}P[^{1}H] NMR spectrum (Fig. 2d), showed a relative increase in the amount of the amido complex **3** signal and that of the unknown species at 57.7 ppm at the expense of **1**. In the ^{1}H and ^{13}C[^{1}H] (J-MOD) NMR spectra (Fig. 3d and 4c, respectively) the disappearance of the alkene signals (5.25 and 5.45 ppm) revealed that most of the unsaturated ester had reacted and also a new signal assignable to an aldehyde proton is observed at 9.54 ppm. In the ^{13}C[^{1}H] spectrum (Fig. 4c) several new resonances were observed in the chemical shift region for carbonyls (one at 194 ppm for the CO of **3**) while the peaks for the alkene carbons were no longer observed. The peaks centered at 67.8 and 27.1 ppm represent the osmium amido complex associated CH_2 moieties. This spectroscopic information is consistent with the reaction of the *hydrogen-loaded* catalyst **1** with the unsaturated ester yielding the amido complex **3** and the saturated ester. Under catalytic conditions (*i.e.*, hydrogen atmosphere) **3** can then react with hydrogen gas directly generating **1** and closing the catalytic cycle. Scheme 2 summarizes these reactions. The nature of the species represented by the peak at 57.7 ppm in ^{31}P[^{1}H] NMR however remains unknown, as is its possible role in the deactivation of the catalyst system for ester hydrogenation once exposed to alkene functions. The presence of small amounts of aldehyde suggests that a small amount of ester hydrogenation does in fact take place in a competitive reaction in which the alkene hydrogenation is much faster than that of the ester, *i.e.*, $k_{\text{alkene}} \gg k_{\text{ester}}$. This mirrors the results of the catalytic reaction of the unsaturated ester discussed above in which 2% of 1-hexanol and 4% of 1-hexanal were formed. A deactivation of the catalyst system against esters in the presence of alkenes may be routed in the complete conversion of the catalyst into a presumably inactive species represented by the peak at 57.7 ppm in the ^{31}P[^{1}H] NMR or conceivably a secondary reaction of the amido complex **3** with the alkene function of the unsaturated ester at higher temperatures. *E.g.*, a hydroformylation of the double bond to a branched aldehyde leading to loss of the carbonyl function from the osmium centre could occur, which in turn may render the

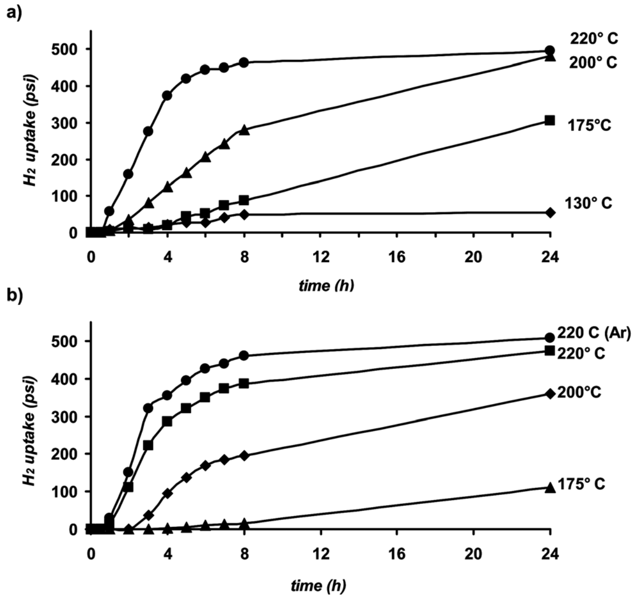
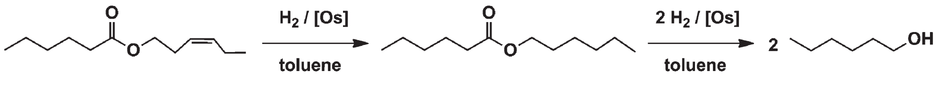


Fig. 1 Hydrogen uptake for the catalytic hydrogenation of hexyl octanoate in toluene at different temperatures using (a) **1** and (b) **2** as catalyst (presented as the pressure drop in the reactor at temperature).[30]

Table 1 Hydrogenation of hexyl octanoate to 1-hexanol and 1-octanol using osmium complexes **1** and **2**[a]

Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Conversion (%)	C6-OH/C8-OH (%)	HH[d]/OO[e] (%)
1	1	Toluene	130	8	0	—	—
2	1	Toluene	130	24	9	9/10	—
3	2	Toluene	130	24	0	—	—
4	1	Toluene	175	8	4	4/4	—
5	1	Toluene	175	24	46	45/47	—
6	2[b]	Toluene	175	8	0	—	—
7	2[b]	Toluene	175	24	15	15/16	—
8	1	Toluene	200	8	44	44/43	—
9	1	Toluene	200	24	69	62/72	—
10	2[b]	Toluene	200	8	16	16/17	—
11	2[b]	Toluene	200	24	46	45/47	—
12	1	Toluene	220	8	63	63/62	—
13	1	Toluene	220	24	87	77/82	3/4
14	2[b]	Toluene	220	8	49	48/50	—
15	2[b]	Toluene	220	24	68	62/62	1/4
16	1[c]	Toluene	220	24	88	70/82	3/4
17	2[b,c]	Toluene	220	24	82	72/77	2/5
18	1	Neat	220	24	57	54/46	0/6
19	2[b]	Neat	220	24	64	55/31	2/17
20	1[f]	Neat	220	24	93	90/85	2/3
21	2[b,f]	Neat	220	24	70	61/45	2/14

[a] Reaction conditions: 0.1 mol% of osmium catalyst in 25 mL total volume. Total amount of substrate in the reactions in toluene solvent was 37 mmol. P_{H_2} = 800 psi. Conversion and yield were determined by quantitative GC against authentic samples. Cyclohexane was used as internal standard. [b] NaO^{t}Bu was used as the co-catalyst. [c] The reactor was charged under argon atmosphere. [d] Hexyl hexanoate. [e] Octyl octanoate. [f] P_{H_2} = 950 psi.



Scheme 1

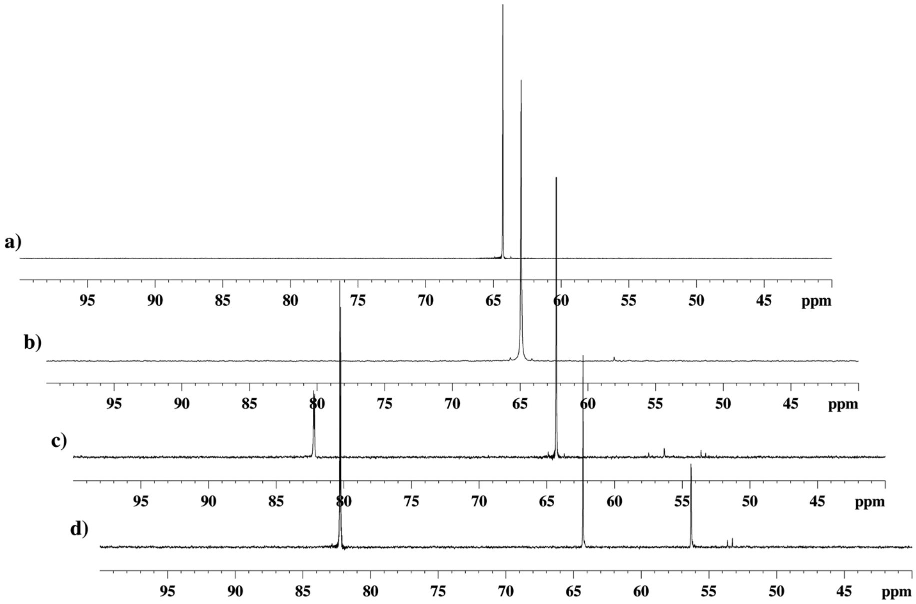


Fig. 2 ^{31}P[^{1}H] NMR spectra in benzene-d$_6$ of: (a) complex **1**. (b) Reaction of **1** and *cis*-3-hexenyl hexanoate at room temperature. (c) Same reaction after 4 h at 100 °C. (d) Same reaction after another 12 h at 100 °C.

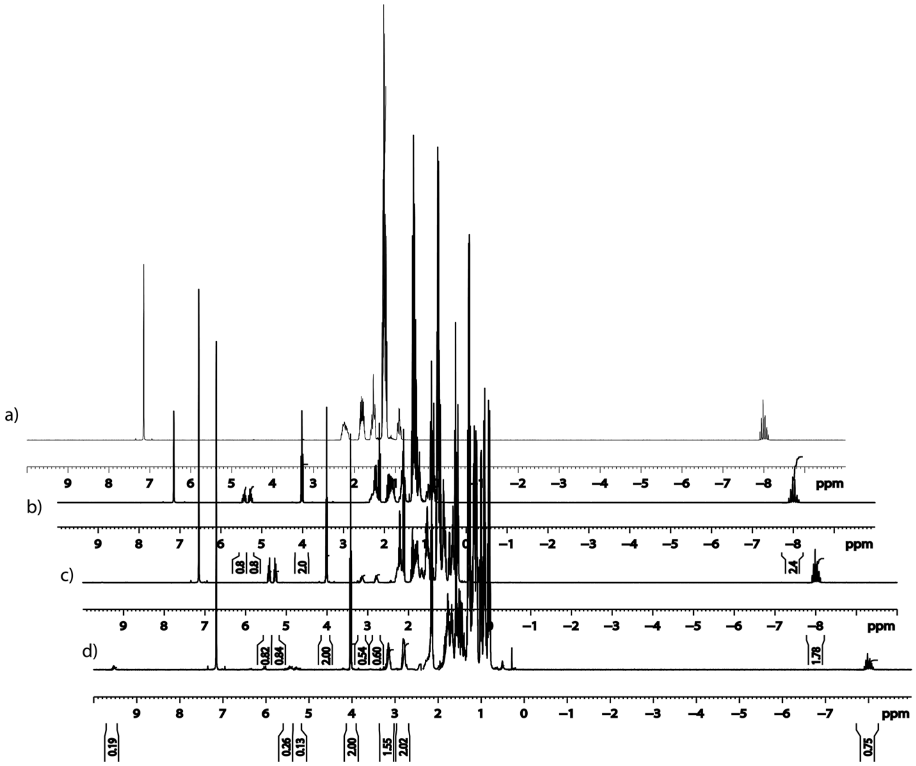


Fig. 3 ^{1}H NMR spectra in benzene-d$_6$ of: (a) complex **1**. (b) Reaction of **1** and *cis*-3-hexenyl hexanoate at room temperature. (c) Same reaction after 4 h at 100 °C. (d) Same reaction after 16 h at 100 °C.

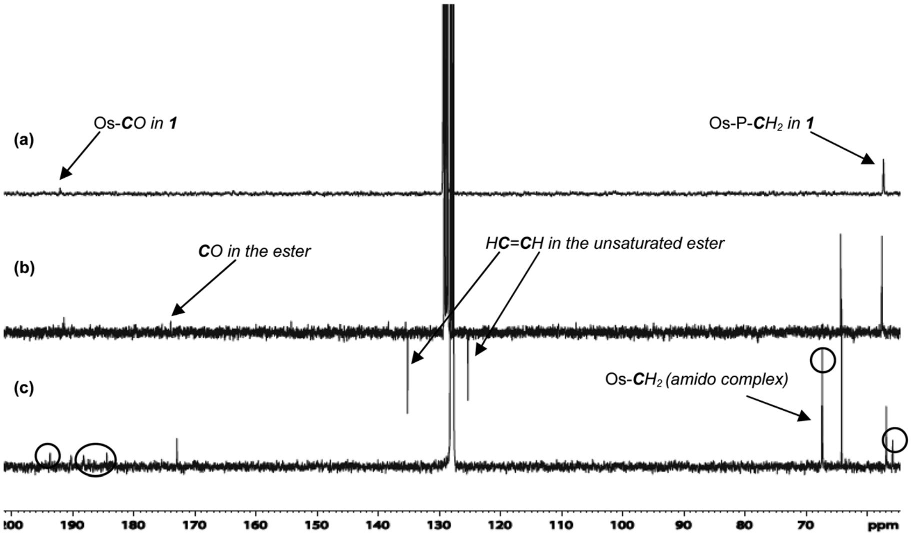
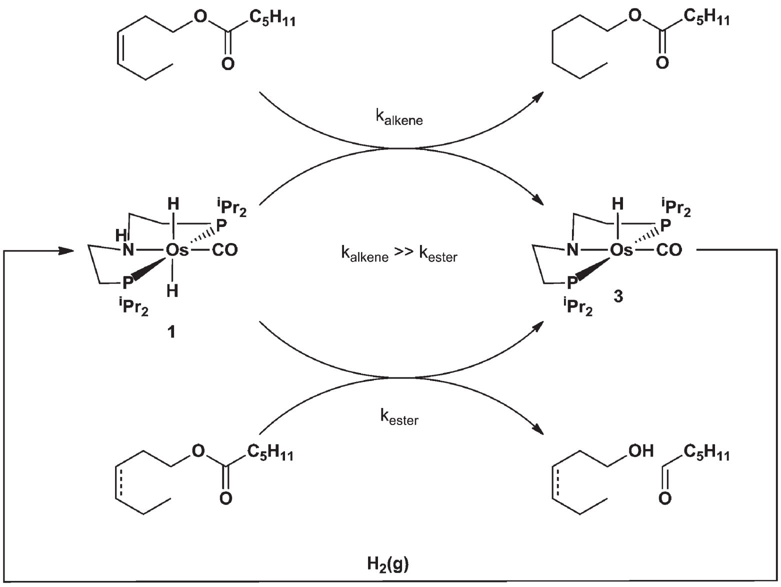


Fig. 4 $^{13}C[^1H]$ NMR spectra in benzene-d_6 of: (a) complex **1**. (b) Reaction of **1** and *cis*-3-hexenyl hexanoate at room temperature. (c) Same reaction after 12 h at 100 °C.



Scheme 2

resulting species inactive for ester hydrogenations. As the study of the system in solution at temperatures relevant to the catalytic ester hydrogenation ($T \geq 175$ °C – *cf.* Fig. 1 and Table 1) is at present beyond our technical capabilities, we are however not able to provide experimental evidence for this hypothesis.

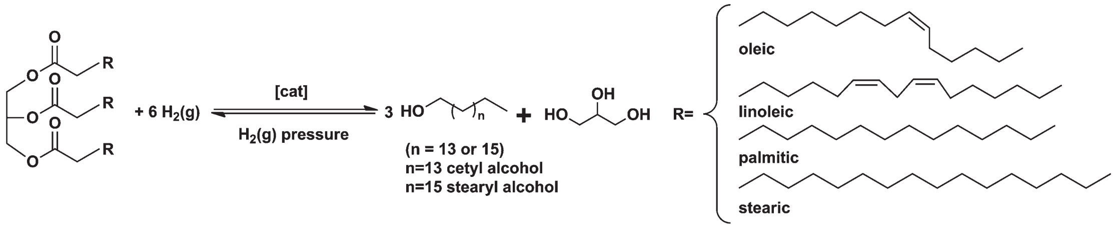
In order to overcome the incompatibility of the osmium catalysts **1** and **2** with alkenes, the conversion of unsaturated esters to saturated alcohols was subsequently carried out in two separate steps. First the hydrogenation of the C═C bond in the 3-hexenyl hexanoate model substrate was carried out using Pd–C as catalyst and only the subsequent reduction of the resulting saturated hexyl hexanoate using **1** as a catalyst. As anticipated the hydrogenation of the alkene with Pd–C proceeds at much milder conditions. After 60 min at 70 °C and 600 psi pressure of H_2 total conversion of the unsaturated substrate to hexyl hexanoate is achieved. After the removal of the heterogeneous catalyst by filtration, catalyst **1** was added and the second hydrogenation was performed at the previously established reaction conditions (220 °C for 24 h and 800 psi of H_2) resulting in 67% conversion with a 64% yield of 1-hexanol and 3% yield of n-hexane.[32] When the Pd catalyst was not removed from the reaction mixture, the only product observed was n-hexane with full conversion of the substrate.

Direct hydrogenation of triglycerides

The encouraging results described above, prompted us to carry out a preliminary study using the same methodology in a direct conversion of triglycerides (*i.e.*, canola, soybean, corn or palm oil) to the corresponding fatty alcohols and glycerol (Scheme 3).

The oils consist of ~80–90% unsaturated (mainly oleic and linoleic acids) and 10–20% saturated (mainly palmitic and stearic acids) acid glycerol esters.[33] The experiments were carried out analogous to the reactions performed with the *cis*-3-hexenyl hexanoate model substrate. Solutions of 10 mL seed oil (a mixture of canola/soybean oil, commercial brand, $\rho \approx 0.92$ g mL^{-1}) in 15 mL of toluene were used to perform the experiments. The alkene functionalities in the seed oil were hydrogenated at 800 psi of H_2 for 4.5 h at 100 °C, using Pd–C as the catalyst. Complete conversion to the saturated form of the oil was confirmed by ^{1}H and ^{13}C[^{1}H] NMR spectroscopy (Fig. 5 and 6a, respectively), in which the alkene proton peaks at 5.9 ppm are no longer present after the hydrogenation and the shifting of the characteristic glycerol backbone proton signals (6.8–4.4 ppm) to higher fields. The saturation of the oil was also evident from the margarine-like physical appearance of the reaction mixture upon cooling to ambient temperature after the first hydrogenation.

The heterogeneous catalyst was then removed by hot filtration of the melted reaction mixture. The second hydrogenation was carried out using complex **1** as the catalyst. In order to estimate the amount of catalyst needed, it was assumed that the triglyceride was composed of pure stearic acid ester (MW = 956 g mol^{-1}), *i.e.*, the reaction was assumed to contain ~9.5 mmol of triglyceride. Using the solid residue containing the saturated triglyceride and toluene the hydrogenation reaction was performed using 0.1 mol% or 0.3 mol% of **1**, 950 psi of H_2 and 220 °C for 24 h consuming ~200 or ~300 psi of hydrogen gas, respectively. Applying the virial theorem for a non-ideal behaviour of hydrogen gas, neglecting the vapour pressures of the solvent, substrate and products and scaling to the 6 mol equivalents of hydrogen required for a full conversion of the substrate to the



Scheme 3

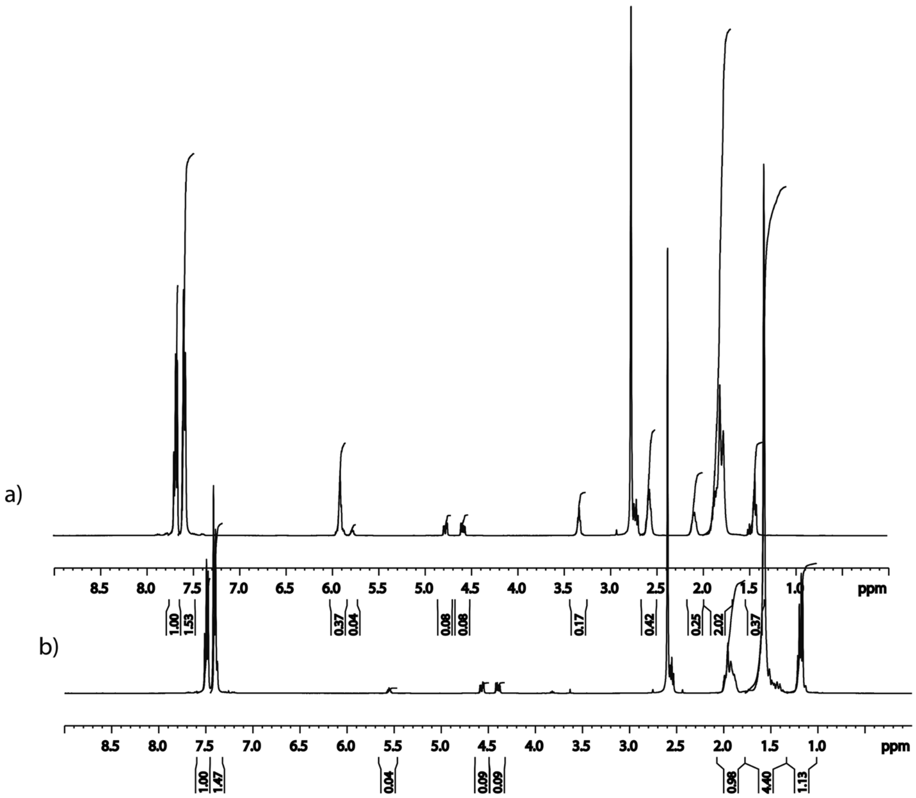


Fig. 5 ^{1}H NMR ($CDCl_3$) spectra of (a) a toluene solution of unsaturated seed oil and (b) a toluene solution of seed oil after the hydrogenation of the alkenes.

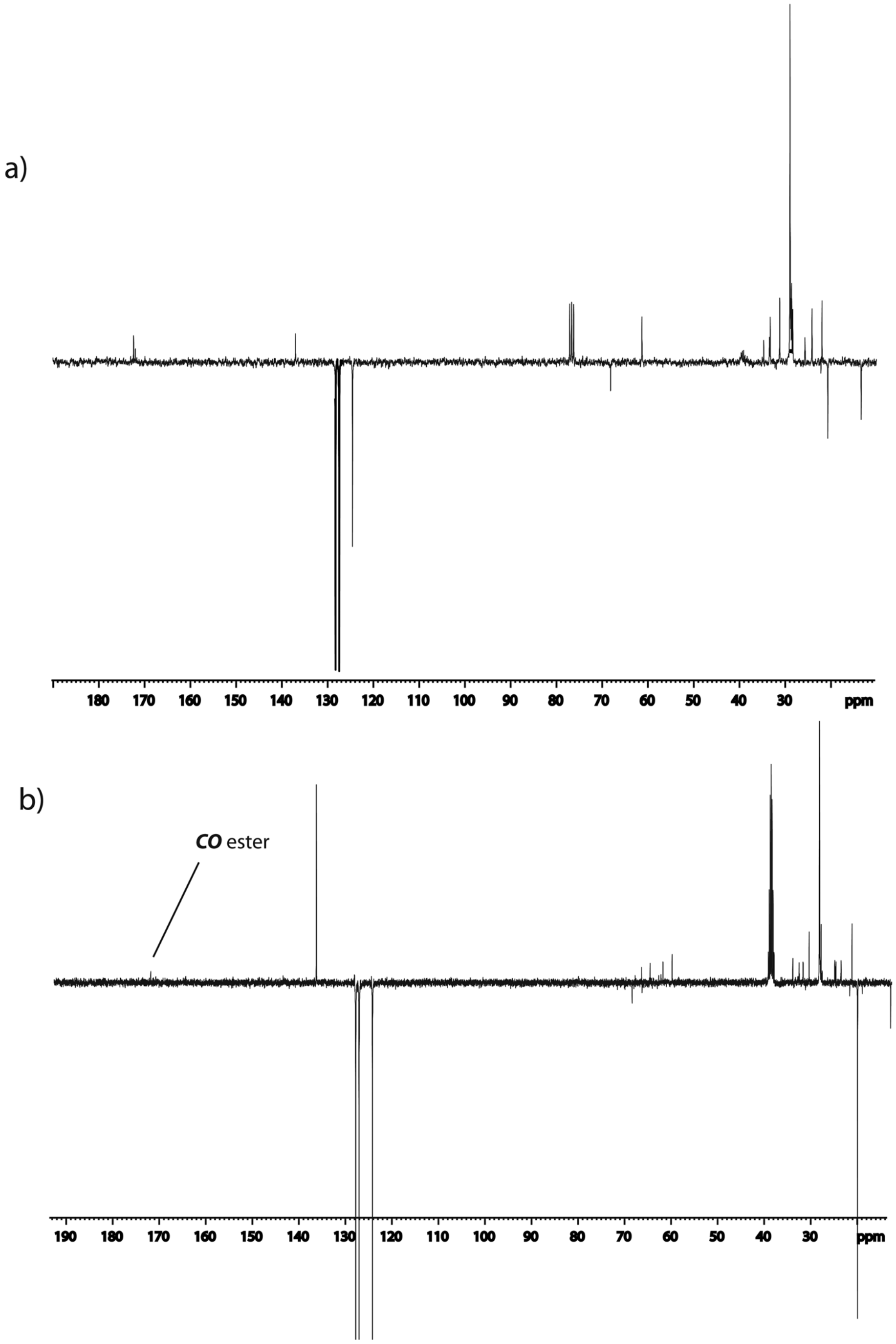


Fig. 6 $^{13}C[^1H]$ NMR spectra of toluene solutions of (a) the fully saturated seed oil ($CDCl_3$) and (b) the final product of the ester hydrogenation reaction catalyzed by **1** (DMSO-d_6).

corresponding fatty alcohols the observed pressure drops reflect conversions of ~60% for the 200 psi pressure drop and ~90% for the 300 psi pressure drop.[34] The ^1H NMR spectrum (recorded in DMSO-d_6 at 70 °C) of the mixture after the hydrogenation reaction (Fig. 7a) no longer showed the well defined signals for the glycerol protons of the saturated triglyceride at 4.4, 4.6 (CH_2–O) and 5.6 (*CH–O*) ppm (Fig. 5b), but instead a group of new signals between 3 and 4.3 ppm interpreted as originating from a complex blend of mono- and diglycerides, with the larger broad multiplet centered at ~3.45 ppm assigned to the presence of CH_2–O moieties of the fatty alcohols formed. They correspond to a group of new peaks between 63 and 73 ppm also assigned to the fatty alcohols in the $^{13}C[^1H]$ NMR spectrum (J-MOD) of the reaction mixture (Fig. 6b),[35] which also shows small amounts of remaining ester carbonyl groups due to the presence of the mono- and diglycerides. The GC-MS traces of a toluene extract of the reaction mixture showed cetyl and stearyl alcohols as the main volatile products verified against the traces and fragmentation patterns of authentic samples (Fig. 8).

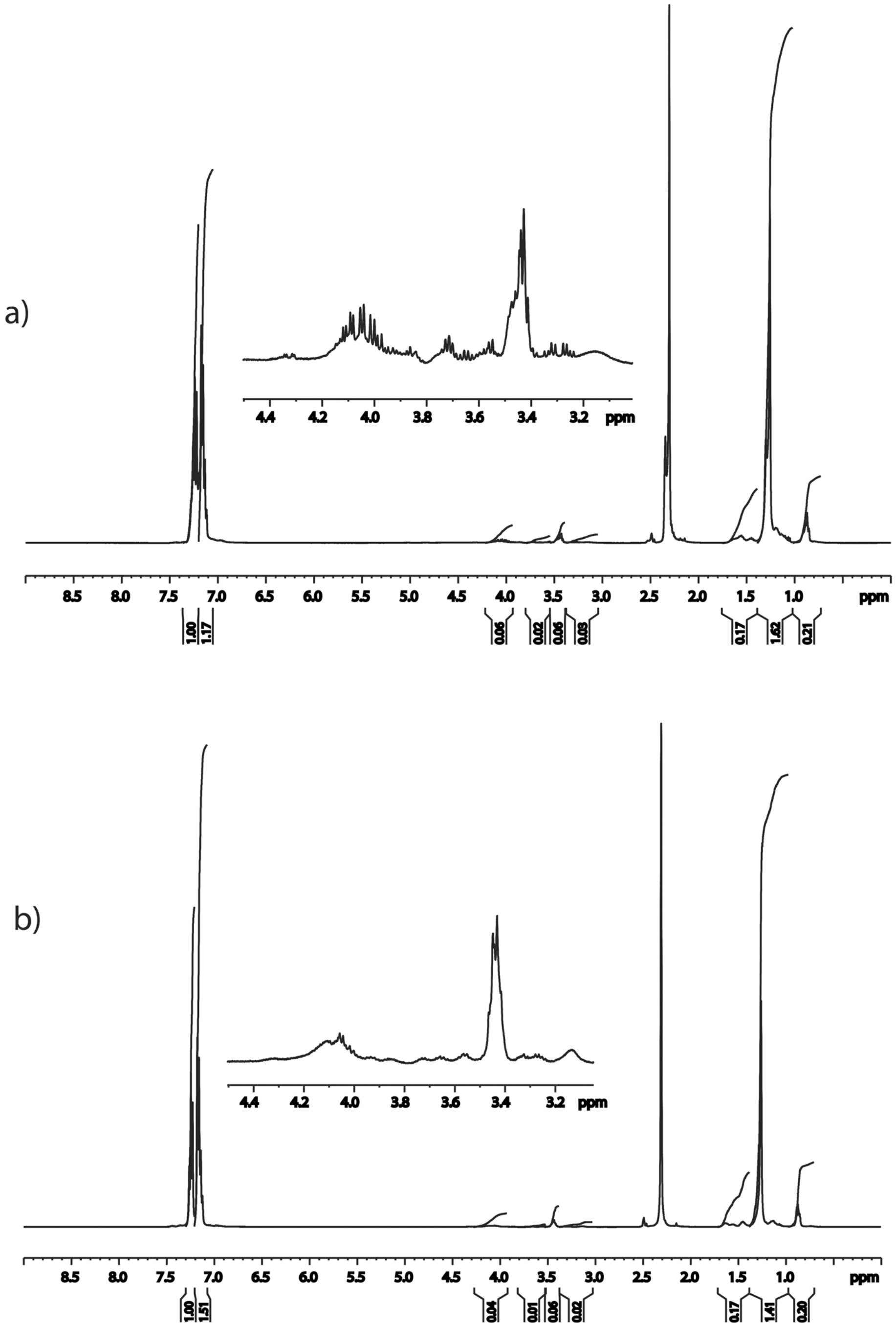


Fig. 7 ^{1}H NMR spectra (70° C, DMSO-d$_6$) of toluene solution reaction mixtures of the ester hydrogenations using (a) 0.1 mol% of **1** catalytic hydrogenation reaction and (b) 0.3 mol% of **1**.

Conclusion

The osmium complexes OsH$_2$(CO)[NH(CH$_2$P^{i}Pr$_2$)$_2$] (**1**) and OsHCl(CO)[NH(CH$_2$P^{i}Pr$_2$)$_2$] (**2**) are active catalysts in the hydrogenation of esters with the latter requiring the addition of base as an activator. Both complexes are also active in the hydrogenation of alkenes, although, when they are used as catalyst in the reduction of unsaturated esters once the alkene has been hydrogenated, no subsequent reduction of the carbonyl moiety was observed. With a separate initial saturation of any carbon–carbon double bonds present in the triglyceride using a standard alkene hydrogenation catalyst, complex **1** is capable of directly converting seed oils (canola/soybean) into fatty alcohols at temperatures and pressures significantly lower than those required for the heterogeneous catalysts typically employed, but at higher temperature than those tolerated by the previously described ruthenium-based homogeneous ester hydrogenation catalysts, for which however no triglyceride hydrogenation/hydrogenolysis has been demonstrated to date.[13,14] Whether or not the osmium-based systems will be viable for an actual technical application

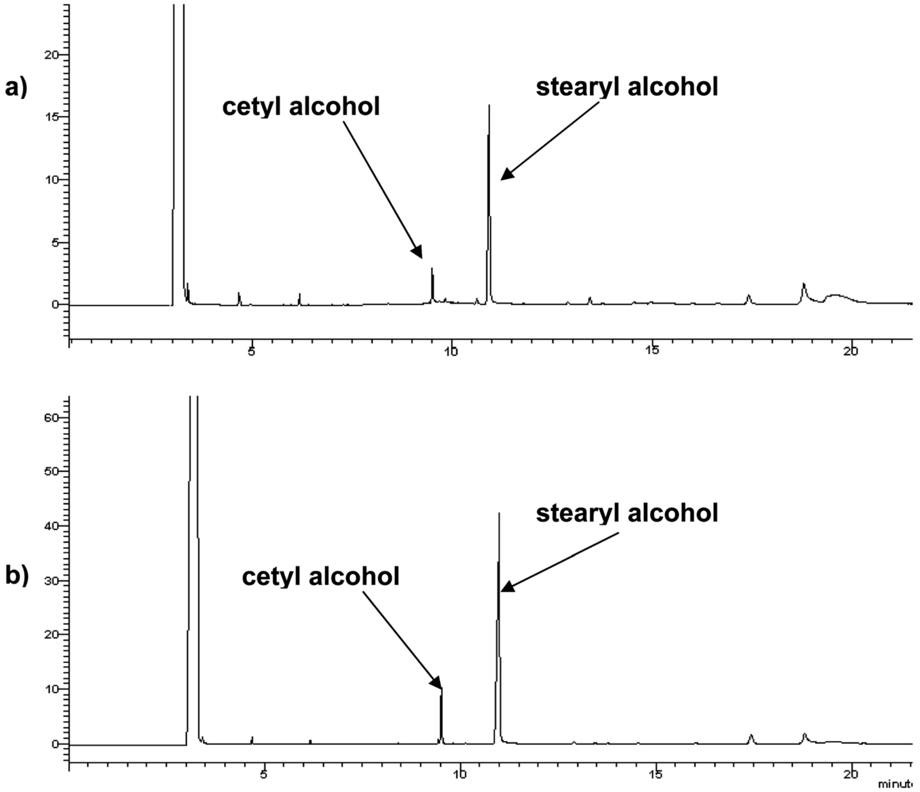


Fig. 8 GC-MS traces of the reaction mixture of ester hydrogenation reaction using (a) 0.1 mol% of **1** and (b) 0.3 mol% of **1** as the catalyst.

will in large part depend on their recyclability, which was not investigated in this first study. The high temperature stability of the catalysts suggests that this may possibly be achieved by removal of the products through vacuum distillation.

Experimental

General

NMR spectra were recorded on a 400 MHz instrument. ^{1}H NMR chemical shifts are reported in ppm *versus* residual protons in deuterated solvents as follows: 7.27 ppm $CDCl_3$, 7.16 ppm C_6D_6, 2.49 ppm DMSO-d_6. ^{13}C[^{1}H] NMR chemical shifts are reported in ppm *versus* residual ^{13}C in the solvent: 77.0 ppm $CDCl_3$, 128.4 ppm C_6D_6, 39.5 ppm DMSO-d_6. ^{31}P NMR shift are reported *versus* 85% H_3PO_4 as an external standard. Industrial grade hydrogen gas was used for all hydrogenation experiments. An Autoclave Engineers (AE) Minireactor with a 50 mL stainless steel (316SS) reactor vessel was employed for the all hydrogenation reactions. Where indicated the reactor body was charged inside an inert-gas dry-box (Argon) and sealed before exposure to the atmosphere. GC analyses were performed on a Varian 3800 using a 30 m/0.25 mm/0.025 mm medium polarity DB-1701 column. Quantitative analysis of the 1-hexanol, 1-octanol, hexyl octanoate and *cis*-3-hexenyl hexanoate experiments was performed through a three-level calibration against authentic samples using cyclohexane as the internal standard (100 mmol L^{-1}). Quantification for all other substrates was approximated using the GC-FID response factor for 1-hexanol or 1-octanol, respectively, corrected for the effective carbon number.[36] GC-MS analyses of the reaction solutions were conducted using a Varian 3800 GC/Saturn 2000 MS using column and GC methods as for the GC analyses. Control reactions carried out in toluene solutions in the absence of catalysts **1** and **2** gave no hydrogenated products.

Materials

Toluene and cyclohexane (dry solvent, Fisherbrand) was degassed and dried using 3 Å molecular sieves in an LC Technology Solutions Solvent Purification System. $CDCl_3$, C_6D_6, and DMSO-d_6 were purchased from Cambridge Isotope Labs. Hexyl hexanoate was purchased from SAFC Supply Solutions and *cis*-3-hexenyl hexanoate was purchased from TCI America. Both esters were passed through a neutral alumina column and degassed through a series of freeze–pump–thaw cycles. Seed oil (a mixture of canola/soybean oil according to the label of a commercial brand obtained from a local supermarket) was used as received. $OsH_2(CO)[NH(CH_2P^iPr_2)_2]$ (**1**) and $OsHCl(CO)[NH(CH_2P^iPr_2)_2]$ (**2**) were synthesized according to the literature.[23,24] Pd–C (5% Pd) was purchased from Aldrich.

Representative procedure for the hydrogenation of esters

In the glove box a 25.0 mL volumetric flask was charged with hexyl octanoate (8.6 g, 37 mmol), cyclohexane (210 mg, 2.5 mmol), and the catalyst (0.037 mmol), using toluene as a solvent. When **2** was used as the catalyst NaO^tBu (9 mg, 0.09 mmol) was also added. Then, the solution was transferred to a vial, sealed and removed from the glove box. The reactor vessel was charged with this toluene solution. The reactor was then flushed out 3 times with H_2 gas (approx. 600 psi) and then pressurized to the working pressure with H_2 gas, and allowed to equilibrate for 2 min. Stirring was set at about 200 rpm and the reactor was heated to the reaction temperature. Samples were taken at 1, 2, 4, and 8 h from reaching the set operating temperature *via* the sample tube, which was first flushed with 0.5 mL of the reaction mixture to ensure cross-contamination from an earlier sample did not occur. After 24 h the reactor heating was turned off and the reactor placed in an ice bath for 30 min to condense any volatile products. The reactor was vented, opened, and a final sample taken for GC analysis.

Representative procedure for hydrogenation of seed oil (canola/soybean oil mixture)

In the glove box a 25.0 mL volumetric flask was charged with 10 mL of seed oil, using toluene as a solvent. Then, the solution was transferred to a vial, sealed and removed from the glove box. The mini-reactor vessel was charged with this toluene solution and 200 mg of Pd–C. was added. The reactor was then pressurized to 800 psi with H_2 gas, and allowed to equilibrate for 2 min. Stirring was set at about 200 rpm and the reactor was heated to 100 °C for 4 h. After 24 h the reactor heating was turned off and the reactor placed in an ice bath for 30 min. The reactor was then vented, opened, and a sample of the waxy solid was taken for NMR analysis. The Pd heterogeneous catalyst was removed by hot filtration using celite and then the osmium catalyst **1** (6 or 18 mg = 0.1 or 0.3 mol%), using toluene as a solvent (10 mL) was added to the white solid mixture reaction. The reactor was then flushed out 3 times with H_2 gas (approx. 600 psi) and then pressurized to 950 psi with H_2 gas, and allowed to equilibrate for 2 min. Stirring was set at about 200 rpm and the reactor was heated at 220 °C. After 24 h the reactor heating was turned off and the reactor placed in an ice bath for 30 min. The reactor was vented, opened, and a final sample taken for GC and NMR analysis. The presence of fatty alcohols was confirmed by comparison with retention time and mass spectrum of authentic samples.

Reactivity of 1 with *cis*-3-hexenyl hexanoate

In the glove box 25 mg of **1** (0.047 mmol) were dissolved in C_6D_6 in a Teflon sealed NMR tube. Then, *cis*-3-hexenyl hexanoate was added (9 mg, 0.047 mmol). The solution turns slightly brown and NMR spectra were recorded. Then, the reaction was heated to 100 °C using an oil bath. The reaction was monitored after 4 and 16 h of heating by NMR.

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30 The fact that the hydrogen uptake data presented here do not directly correspond to the stoichiometries of the quantitative yields as determined by GC (see Table 1) reflects the strongly non-linear response of the non-ideal hydrogen/toluene gas phase composition in the reactor headspace as a function of total pressure at the reaction temperature, which lies above the boiling point of toluene. *E.g.*, a 6-fold increase in conversion as a function of time (entries 4 and 5, Table 1) does not translate to the same amount of pressure drop in the reactor, which shows an only 3-fold increase in apparent uptake. This is because the mole fraction of hydrogen in the gas phase decreases exponentially with decreasing pressure. For a quantitative treatment of this phenomenon see J. J. Simmick, H. M. Sebastian, H.-M. Lin and K.-C. Chao, *J. Chem. Eng. Data*, 1978, **4**, 339–340.

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