

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201810605 Angew. Chem. 10.1002/ange.201810605

Link to VoR: http://dx.doi.org/10.1002/anie.201810605 http://dx.doi.org/10.1002/ange.201810605

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Base-Free Iron Catalyzed Transfer Hydrogenation of Esters Using EtOH as Hydrogen Source

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Dedication ((optional))

Abstract: Herein, we report on the use of the iron pincer complex Iron-MACHO-BH, in the base-free transfer hydrogenation of esters with EtOH as a hydrogen source. More than 20 substrates including aromatic and aliphatic esters and lactones were reduced affording the desired primary alcohols and diols with moderate to excellent isolated yields. It is also possible to reduce polyesters to the diols with this method, enabling a novel way of plastic recycling. Reduction of the renewable substrate methyl levulinate proceeds to form 1,4-pentanediol directly. The yields are largely governed by the equilibrium between the alcohol and the ethyl ester.

Transfer hydrogenation (TH) processes are an attractive alternative to classical catalytic hydrogenations since the use of expensive high pressure reactors can be avoided.^[1] Most transfer hydrogenations are used to reduce ketones to the corresponding alcohols. Recent work on transfer hydrogenation of more challenging substrates reported the reduction of lactams to tertiary amines via transfer hydrogenation.^[2] Surprisingly only two examples are described in the literature of transfer hydrogenation of esters, which are generally less easily reduced than ketones.^[3] Nikonov established proof of concept for the transfer hydrogenation of ester compounds with isopropanol using the cationic ruthenium complex 1 as catalyst.[3a] Transesterification was a serious problem as the isopropyl esters are reduced much slower. Khaskin screened 9 different ruthenium-based ester hydrogenation catalysts and found that the Ru-NNS pincer catalyst 2 developed by Gusev was the most effective. He also discovered that ethanol is a much more effective reductant than isopropanol. He was able to reduce a wide scope of esters including triglycerides and heterosubstituted esters (Figure 1).^[3b] It is obvious that this is an interesting new methodology which can probably be improved further. Both Nikonov and Khaskin have used KOtBu to activate the catalyst. And indeed in many cases the base accelerates the catalysis beyond this inactivation step.^[4] However, the use of



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such a strong base can be detrimental in the case of basesensitive substrates. Relatively few transfer hydrogenation catalysts are known that function without base.^[5] Another aspect that could be improved is the replacement of the precious metal by a base metal.

Here, we report the use of a non-precious Fe-based catalyst for the transfer hydrogenation of ester compounds in the absence of base. Fe-MACHO-BH (**3**) is an excellent catalyst for the dehydrogenation of alcohols for hydrogen production and for the hydrogenation of a large number of other functionalities.^[6] For that reason, we envisioned the possibility of using this catalyst in the transfer hydrogenation of esters. In a preliminary experiment, methyl benzoate was stirred in the presence of 5 mol% of **3** in a large excess of EtOH at 100 °C. After 24 hours, benzyl alcohol was obtained in 88% GC-yield (Table 1, entry 1). Additionally, 10% of ethyl benzoate was formed due to the transesterification of the substrate with the solvent. Also, ethyl acetate was detected by GC-MS as the by-product resulting

Table 1. Screening of alcohols as the reducing agents for the base-free transfer hydrogenation of esters. $^{\left[a\right] }$

)	4a	Fe cat. 3 ROH 100 °C, 24 h	OH + 4b	4c	R
Entry	Cat.Load. [mol%]	Hydrogen Source	Conv. [%]	Yield of 4b [%]	Yield of 4c [%]
1	5	EtOH	>99	88	10
2 ^[b]	5	MeOH	7	0	0
3	5	iPrOH	95	56	39
4	5	BuOH	>99	40	60
5	3	EtOH/MeOH ^[c]	98	61	35
6	3	EtOH/MeOH ^[d]	41	1	36

[a] Reaction conditions: Substrate (0.5 mmol), alcohol (96 equiv), cat. **3** (5 mol%), 100 °C, 24 hours, conversion and yield determined by GC using dodecane as an internal standard. [b] 25 mol% of 'BuOK was added. [c] 2.5 equiv of MeOH with respect to the substrate. [d] 96 eq of MeOH with respect to the substrate.

from the dehydrogenation of the hemiacetal obtained from the formed acetaldehyde and another molecule of ethanol. Examples where EtOH is used as the hydrogen source are rare in the literature.^[3b, 7] This could be due to its known ability to poison catalysts via decarbonylation of the acetaldehyde, forming less reactive carbonyl complexes. In addition, acetaldehyde can undergo condensation reactions with the starting materials or products before it is scavenged as ethyl acetate. Furthermore, its dehydrogenation is both kinetically and

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thermodynamically less favored than that of secondary alcohols like iPrOH.^[7a, 7f] Thus, other sources of hydrogen were also tried. In line with the findings of Nikonov, use of iPrOH resulted in only 56% of the desired product (Table 1, entry 3). Use of n-Butanol also led to a slower reaction and poorer selectivity to benzyl alcohol. The use of MeOH led to very low conversions even when a base was added. (Table 1, entry 2) Similar results were obtained with an equimolar mixture of MeOH and EtOH (Table 1, entry 5). When the amount of MeOH in the mixture was reduced to 2.5 equiv, the benzylic alcohol yield increased to 61% yield (Table 1, entries 4). This result clearly suggests catalyst poisoning by MeOH. Next, the reaction conditions were optimized and the results are summarized in Table 2.

Table 2. Optimization of the reaction conditions.[a]



[a] Reaction conditions: substrate (0.5 mmol), cat. 3, 100 $^{\circ}\text{C}$, 24 hours, conversion and yield determined by GC using dodecane as an internal standard.

Reducing the catalyst loading to 4 mol%, a lower yield of the desired product was obtained (Table 2, entry 2). Similarly, increasing or reducing the number of equivalents of EtOH (compared to optimal 96 equiv) causes a decrease of conversion towards benzyl alcohol (Table 2, entries 3-4). The effect of temperature was also tested. At 80 °C a similar result was obtained (Table 2, entry 5). Running the reaction at 60 °C resulted in a significant drop of the yield (Table 2, entry 7).

Intrigued by the inability to achieve full conversions, a kinetic profile of the reaction was performed using 3 at three different concentrations as well as the analogous Ru-MACHO-BH (3b)[8] and Mn-MACHO-BH (3c)^[9] catalysts. (ESI, S3, Figure1 and 2). As expected, with 3 transesterification of the starting material to compound 4c was the fastest reaction. Then, the desired alcohol 4b was obtained via the reduction of both esters. Interestingly, the reaction reaches the maximum yield after only 7 hours. This suggests that an equilbrium has been reached. It seems that under the reaction conditions the dehydrogenation of the benzyl alcohol to the aldehyde and its further reaction with ethanol followed by a second dehydrogenation gives the ethyl benzoate. To check the feasibility of the reverse reaction, benzyl alcohol (4b) was submitted to a reaction with ethyl acetate in ethanol. In this experiment, 5% of ethyl benzoate and 3% of benzyl acetate were the only observed products (ESI, S4). The other monitorings were then performed with the Ru and Mn analogues of the Fe complex **3** (ESI, S3). Monitoring the Ru-catalyzed reaction with the defined protocol, very similar results were obtained (ESI3, Figure 2). Interestingly, the final ratio between benzyl alcohol (**4b**) and ethyl benzoate (**4c**) was 3:1 in both cases (ESI, S3, Figure1). These results confirm that the transfer hydrogenation process is governed by the equilibrium between EtOH, benzyl alcohol (**4b**) and ethyl benzoate (**4c**). On the other hand, with the Mn-PNP-BH complex **3c** only ethyl benzoate (**4c**) was obtained. (ESI, S3, Figure2).

Next, the scope and limitations of the transfer hydrogenation with Fe-MACHO-BH were explored using 5 mol% of catalyst at 100 °C. Under these conditions a wide variety of aromatic esters were reduced. Results are summarized in Scheme 1. Nonsubstituted aromatic esters were smoothly reduced to the desired alcohols with isolated yields up to 86 % (Scheme 1, 4-6). Ester 7a, which also contains a ketone group, was completely reduced to the corresponding diol with 80% isolated yield (Scheme 1, 7b). High vields were obtained when p-fluoro (8a) and p-chloro (9a) substituted benzoic acid methyl esters were used as the substrates. However, the transfer hydrogenation of methyl p-bromobenzoate(10a) resulted in only 14% yield of the alcohol. Likewise, p-nitrobenzoate 11a only afforded the desired product in 5% yield (Scheme 1, 11a). A possible explanation for this behaviour is that the alcohol formed is too acidic, and therefore binds to the metal thus deactivating the catalyst. pamine-substituted methyl esters 12a and 13a were completely



Scheme 1. Transfer hydrogenation of aromatic esters. [a] Reaction conditions: substrate (0.5 mmol), 96 equiv of EtOH (2800 μ L), Fe cat. 3 (5 mol%, 9,7 mg), 100 °C, 24 hours reaction time in a pressure tube covered from light. All yields are isolated unless mentioned otherwise. [b] Yield corresponds to saturated alcohol. [c] Mn cat. 3c (5 mol%) was used. The product is ethyl 3-(p-methoxyphenyl)propanoate. [d] Yield is calculated by dividing the amount of benzyl alcohol by 2 [e] Substrate (0.21 mmol), 120 equiv of EtOH (2100 μ L). 7.5 mol% of Fe cat. 3 (5 mol%, 97.5 mg). [g] Yield determined by GC.

inactive. This can possibly be explained by the high affinity of amines for the metal center, which leads to deactivation of the

catalyst. α,β -Unsaturated esters **14a** and **15a** were also reduced to the corresponding saturated alcohols with high isolated yields. Unfortunately, it is not possible to keep the conjugated double bond intact as the saturated alcohols were obtained as the products.

On the other hand, Mn-PNP-BH **3c** was able to reduce only the C=C double bond in compound 15a. Homogeneous base metal-catalyzed reductions of alkenes and alkynes have been reported before with iron-,^[10] cobalt-,^[11] and nickel-based^[12] catalysts and most of them use hydrogen sources other than EtOH. This is the first example of the use of a manganesebased pincer-catalyst for the TH of a C=C bond using EtOH as hydrogen donor. The heteroaromatic ester **16a** could be reduced quantitatively.

To test the robustness of the system, the reaction with 9a was scaled up 10 times resulting in a 95% isolated yield of the desired alcohol.



17a R = $(CH_2)_4CH_3$ (77%) **18a** R = $(CH_2)_2C(O)CH_3$ (97%)^[b] **19a** R = $(CH_2)_7CH=CH(CH_2)_7CH_3$ (92%)^[c]

20a R = $(CH_2)_3CH=CH_2 (53\%)^{[C]}$ **21a** R = $(CH_2)_3CH=CH_2 (63\%)^{[C]}$



Scheme 2. Transfer hydrogenation of aliphatic esters [a] Reaction conditions: substrate (0.5 mmol), 96 equiv of EtOH (2800 μ L), Fe cat. 3 (5 mol%, 9.7 mg), 100 °C, 24 hours reaction time in a pressure tube covered from light. All yields are isolated unless mentioned otherwise. [b] 7.5 mol% of cat. 3. [c] Yield corresponds to unsaturated alcohol. [d] 5 mol% of cat. 3 per equiv of ester moiety and 123 equiv of EtOH (3600 μ L) were used. [e] Substrate (0.25 mmol of basic unit of the polymer), 5 mol% of cat. 3 per equiv of ester moiety is used.

Gratifyingly, aliphatic esters could be reduced in good yields in the same fashion (Scheme 2). For instance, methyl hexanoate (17a) was reduced to 1-hexanol with an isolated yield of 77%. The potential and relevance of adipic acid dimethyl ester (22a), methyl levulinate (18a) and methyl oleate (19a) for renewable chemistry is very well known.^[13] For this reason, their applications have been studied by many groups in both academia and industry in the last decades. Few catalytic systems in the literature are reported to reduce methyl levulinate (18a) to 1,4 pentandiol.^[14] We were glad to see how methyl levulinate was reduced to the corresponding diol in almost quantitative yield (Scheme 2, 18a). Adipic acid dimethyl ester (22a) was converted to the diol in 99% yield. Methyl oleate (19a) was converted to the unsaturated alcohol in 92% yield. Isolated double bonds in the substrates remained untouched.

Another important topic for green chemistry is the recycling of polymers via conversion to the monomers.^[15] Interest on this will keep growing in the following years because of accumulation of waste from polymers has become a significant issue in the last decades. Despite recent advances in polymer recycling ^[16] many challenges are still unsolved in this field. One of these is the design of catalysts capable challenges of depolymerisation with sufficient rate and turnover number.[17] Only three Ru based homogeneous catalytic systems have been reported to be capable of polyester deconstruction under mild conditions.^[18] To the best of our knowledge, no examples exist in the literature on the depolymerization of polyesters via transferhydrogenation. Dynacol 7360 (23a) is made from adipic acid and 1,6-hexandiol. When this substance was submitted to our protocol, 1,6-hexanediol was obtained in 87% isolated yield. This result opens the possibility to recycle polyesters by deconstructing them to their monomers using a complete new,



Scheme 3. Transfer hydrogenation of lactones [a] Reaction conditions: substrate (0.5 mmol), 96 equiv of EtOH (2800 μ L), Fe cat. 3 (5 mol%, 9.7 mg), 100 °C, 24 hours reaction time in a pressure tube covered from light. All yields are isolated unless mentioned otherwise. [b] Product is γ -Valero lactone (GVL). Yield is based on the single peaks observed by GC and products were characterized by GC-MS. [c] 25 mol% of EtONa was used.

It is also possible to reduce lactones using this method. When 6- and 7-membered lactones were tested under our base free protocol, the corresponding diols were obtained with very high yields (Scheme 3, 24a, 25a). α-Angelica lactone (26a), a 5membered unsaturated lactone that can be derived from sugars, underwent reduction of only the double bond whereas the ester function remained intact (ESI, S6). However, it was possible to obtain the corresponding diols from the 5 membered ring lactones when 25 mol% of EtONa was added to the reaction mixture. As representative examples, α -Angelica lactone (26a) and Whiskey lactone (27a) afforded the desired diols in >99% and 70% isolated yields respectively (Scheme, entries 4-5). We assume that the function of the base is to enable the ring opening of the lactone to the hydroxy-ester, which is the entity that is reduced to the diol. Another possible explanation for the role of the base is that hydrogenation of the ester enolate takes place as was recently proposed by Milstein and co-workers in the cobalt-pincer catalysed hydrogenation of esters.^[19]

In conclusion, we have developed the very first Fe-catalyzed base-free transfer hydrogenation of esters. The protocol uses environmentally friendly and renewable EtOH as hydrogen donor and mild conditions. The scope includes aromatic esters, aliphatic esters and lactones. Important substrates stemming from renewable resources like methyl oleate and α -Angelica

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lactone were also reduced to the corresponding alcohols. Furthermore, methyl levulinate was successfully reduced to 1,4-pentanediol in a one pot reaction. Importantly, we were able to depolymerize a polyester to the diol using a transfer hydrogenation protocol for the first time. Thus, this reaction may have a future in the recycling of plastic waste. We assume a mechanism, similar to the one reported before by $us^{[7e]}$ and Beller and co-workers (S9, p27).^[6b,c]

Experimental Section

General procedure for transfer hydrogenations

In an overnight dried 5 mL glass pressure tube equipped with a stirring bar, the ester (0.5 mmol) was dissolved in EtOH (2800 µL, 96 equiv) under argon atmosphere. Dodecane as internal standard was added (60 µL) followed by Fe catalyst 3 (9,8 mg, 5mol%). The tube was sealed and covered from light. The reaction was stirred vigorously for 24 hours at 100 °C. After this time, the pressure tube was cooled to room temperature, the reaction mixture was filtered over a pad of silica and solvents were removed under reduced pressure. The resulting product was purified by а flash column chromatography (SiO₂: cyclohexane:AcOEt, ratio depending on the substrate). For monitoring, a stainless steel autoclave equipped with an auto sampler was used and the reaction was scaled up 3 times. The rest of the procedure is identical.

Acknowledgements

We thank the State of Mecklenburg-Vorpommern for funding.

Conflict of Interest

The authors declare no conflict of interest

Keywords: base-free • transfer hydrogenation • Iron • ester compounds • ethanol

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Even plastic can be reduced!

Transfer hydrogenation of esters and lactones with EtOH can be effected using 5 mol% of Fe-MACHO-BH as catalyst. This catalyst does not need any base activation, thus resulting in very high selectivities.



R.A. Farrar-Tobar, B. Wozniak, Dr. A. Savini, Dr. S. Hinze, Dr. S. Tin, Prof. Dr. J.G. de Vries*



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