Applied Catalysis A, General 623 (2021) 118280

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Manganese-catalyzed homogeneous hydrogenation of ketones and conjugate reduction of α,β-unsaturated carboxylic acid derivatives: A chemoselective, robust, and phosphine-free in situ-protocol

Thomas Vielhaber, Christoph Topf *

Johannes Kepler University (JKU), Institute of Catalysis (INCA), Linz, 4040, Austria

ARTICLE INFO

Keywords:
Homogeneous hydrogenation
Conjugate reduction
Manganese
Picolylamine
Chelates

ABSTRACT

We communicate a user-friendly and glove-box-free catalytic protocol for the manganese-catalyzed hydrogenation of ketones and conjugated C═C—bonds of esters and nitriles. The respective catalyst is readily assembled in situ from the privileged [$Mn(CO)_5Br$] precursor and cheap 2-picolylamine. The catalytic transformations were performed in the presence of *t*-BuOK whereby the corresponding hydrogenation products were obtained in good to excellent yields. The described system offers a brisk and atom-efficient access to both secondary alcohols and saturated esters avoiding the use of oxygen-sensitive and expensive phosphine-based ligands.

1. Introduction

The first report of a manganese-based pincer complex that effects the homogeneous hydrogenation of carbonyl compounds and nitriles by Beller and coworkers in 2016 [1] has triggered a fast-developing research process in the field of Mn-mediated redox transformations [2–6]. Besides (de)hydrogenation catalysts that incorporate the classic PNP motif in the ligand framework [7–19], active complexes that contain unsymmetrical PNP' [20,21] or (chiral) PNN [22–26] scaffolds, all-nitrogen NNN donor sets [27,28], and mixed donor arrangements such as SNP [29] and CNP [30] are also well known and found widespread applications in a variety organic synthesis protocols.

However, it was soon demonstrated that the redox-activity of manganese catalysts featuring a planar tridentate ligand architecture is faithfully reproduced in their molecularly less complicated PN [31–33], PC [34]-, and PP-ligated [35–38] congeners amongst which the former are readily developed into chiral entities that permit access to the enantioselective synthesis of pertinent secondary alcohols through Mn-catalyzed transfer hydrogenation of ketones [39]. In the same vein, phosphorus-free oxamide ligands have also been demonstrated to enable the syntheses of optically pure alcohols [40]. Rewardingly, the reactivity of these phosphine-based assemblies carries over to manganese coordination compounds that rely on bidentate NN ligands [41–46] which are rather cost-effective and not prone to detrimental oxidation as compared to their PN congeners. These N-ligated manganese species are also amenable to chiral modification(s) thus enabling asymmetric reduction of selected substrates [47].

Strikingly, the popular [$Mn(CO)_5Br$] precursor compound can also function as a decent catalyst in its own right and as such it enables the efficient hydrogenation of quinolines under very mild conditions [48, 49].

Given the vast number of Mn-catalyzed hydrogenation protocols which rely on H_2 gas as the principal reductant [50], it is quite conspicuous that reports on the highly relevant and rewarding conjugate reduction of α,β-unsaturated carbonyl compounds deploying manganese-based catalysts and molecular hydrogen [32] are still scarce in the literature.

Traditionally, the conjugate reduction of α,β-unsaturated esters and related compounds is well centered about the use of copper in combination with phosphine [51] or NHC [52–55] ligands, yet other metals such as titanium have already been found to facilitate the given transformation [56]. In this context, Stryker's classic reagent $[Cu(PPh_3)H]_6$ [57,58] and ligand-modified versions thereof have to be mentioned, too [59,60].

* Corresponding author.
E-mail address: christoph.topf@jku.at (C. Topf).

https://doi.org/10.1016/j.apcata.2021.118280
Received 29 March 2021; Received in revised form 24 June 2021; Accepted 29 June 2021
Available online 2 July 2021

2. Results and discussion

2.1. Catalytic activity of the pre-synthesized manganese(I) complex versus the in situ-system

Based on a recent report by Sortais and co-workers [41] who described the very efficient transfer hydrogenation of various carbonyl compounds with *iso*-propanol enabled by a simple picolylamine-tagged manganese complex [Mn(NN)(CO)$_3$Br], we initially tested the same catalyst in the related and easy-to-envisage reduction of acetophenone using H_2 gas, *t*-BuOK as base additive, and THF as the solvent (Table 1). Although the pre-synthesized catalyst displayed activity in the given hydrogenation process, the overall transformation was sluggish and the desired product, 1-phenylethanol, was obtained in only minute quantities (Table 1, entries 1-2). Notably, the catalyst performance was not significantly increased upon solvent variation and/or changing the nature of the base (Table S1 in the supporting information). The autoclave charging procedure was then performed in the glovebox under an Ar-atmosphere to rule out any possible degradation routes of the single catalytic components due to the exposure to inevitable O_2 and H_2O of an ordinary laboratory atmosphere, but this approach did not improve the catalytic result either (Table 1, entry 3). Notwithstanding these disappointing results, we conducted the same hydrogenation as an in situ-experiment by simply combining the components in the reaction vessel prior to charging the autoclave with the needed H_2 pressure and, to our delight, we observed complete substrate conversion and almost quantitative yield of the secondary alcohol in this case (Table 1, entry 5).

Noteworthy, applying the picolylamine-ligand in an over-stoichiometric amount versus the manganese caused a steep decline of both conversion and yield whereas full collapse of the catalytic performance was observed when the given transformation was carried out without any ligand. Furthermore, it was borne out by experiment that the addition of a base is indispensable for the Mn-complex to develop proper hydrogenation activity (Table 1, entries 6-8).

In order to substantiate the homogeneous nature of the in situ-formed manganese chelate in combination with *t*-BuOK, the reaction was performed in the presence of a few mercury drops [61,62]. Since both substrate-conversion and yield were unaffected by the amalgam-forming agent, we infer that the catalyst acts in a homogeneous manner (Table 1, entry 9).

The yield/time trace recorded for the Mn-catalyzed hydrogenation of acetophenone (Fig. 1) revealed that the active catalyst species is formed after a short induction phase of approximately 30 min. resulting in almost quantitative formation of the desired secondary alcohol. In the case of the pre-synthesized well-defined manganese complex [Mn(NN)(CO)$_3$Br] the catalytic activity developed very slowly and remained poor throughout the given reaction interval.

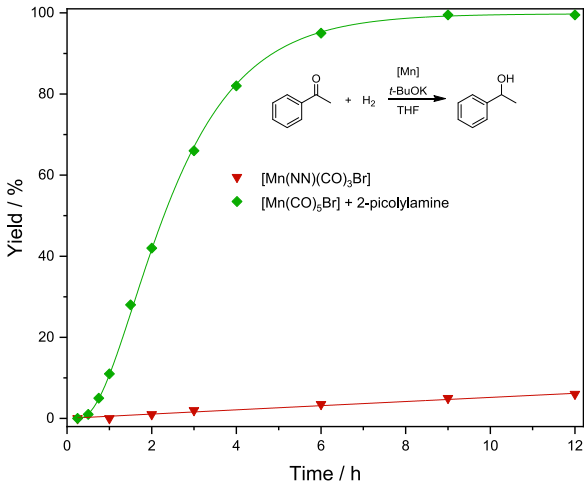
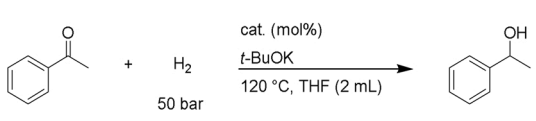
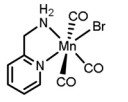


Fig. 1. Catalytic activity of the in situ-system versus the pre-synthesized manganese(I) complex: Yield/time diagram for the hydrogenation of acetophenone to the corresponding alcohol. Reaction conditions: 0.5 mmol acetophenone, 3 mol% [Mn(NN)(CO)$_3$Br] or [Mn(CO)$_5$Br]/2-picolylamine, 3 mol% *t*-BuOK, 2 ml THF, 30 bar H_2, 120 °C, and 12 h. The yields were determined by GC analyses using *n*-dodecane as the internal standard.

Surprised by the marked difference in catalytic activity of the pre-synthesized and the in situ-generated picolylamine-manganese complex, we continued with the investigation of our Mn-based in situ system by standard spectroscopic techniques, viz. NMR and IR spectroscopy. Initially, we aimed to prove the formation of the NN-tagged manganese complex [Mn(NN)(CO)$_3$Br] under hydrogenation conditions upon pairing the manganese precursor [Mn(CO)$_5$Br] with 2-picolylamine inside the autoclave. Indeed, the characteristic signals of the IR and NMR spectra of the thus-obtained organometallic product match those of the pre-synthesized manganese(I) complex and are well in accordance with the literature values (supporting information, Section 8.1) [41]. Secondly, a control experiment was performed to probe the reactivity of the precursor [Mn(CO)$_5$Br] with one equivalent of *t*-BuOK under the authentic reaction conditions. The IR spectrum of the isolated compound was compared to [Mn(CO)$_5$Br] and clearly, a different carbonyl species (Fig. 2, red curve) was formed upon base treatment. Finally, the outcome of the reaction of an equimolar mixture of [Mn(CO)$_5$Br],

Table 1
Comparison of the catalytic hydrogenations of acetophenone to afford 1-phenylethanol facilitated by the pre-synthesized complex [Mn(NN)(CO)$_3$Br] and the same in situ-generated species in the presence of *t*-BuOK[a].





[Mn(NN)(CO)$_3$Br] (cat)

Entry	Catalyst (mol%)	*t*-BuOK (mol%)	t (h)	Conversion (%)	Yield (%)
1	[Mn(NN)(CO)$_3$Br] (3)	6	18	6	6
2	[Mn(NN)(CO)$_3$Br] (3)	3	18	8	8
3[b]	[Mn(NN)(CO)$_3$Br] (3)	3	18	10	9
4	[Mn(CO)$_5$Br] (3) + 2-picolylamine (3)	6	12	98	98
5[c]	[Mn(CO)$_5$Br] (3) + 2-picolylamine (3)	3	12	>99	99
6[c]	[Mn(CO)$_5$Br] (3) + 2-picolylamine (6)	3	12	25	24
7	[Mn(CO)$_5$Br] (3) + 2-picolylamine (3)	0	12	0	0
8	[Mn(CO)$_5$Br] (3)	5	12	0	0
9[c,d]	[Mn(CO)$_5$Br] (3) + 2-picolylamine (3)	3	12	>99	99

[a] 0.5 mmol of acetophenone were used. Conversions and yields were determined by GC analysis using *n*-dodecane as internal standard.
[b] The reaction vial was charged in the glovebox under an Ar-atmosphere.
[c] Applied pressure: 40 bar H_2. [d]Mercury drops were added to the reaction solution.

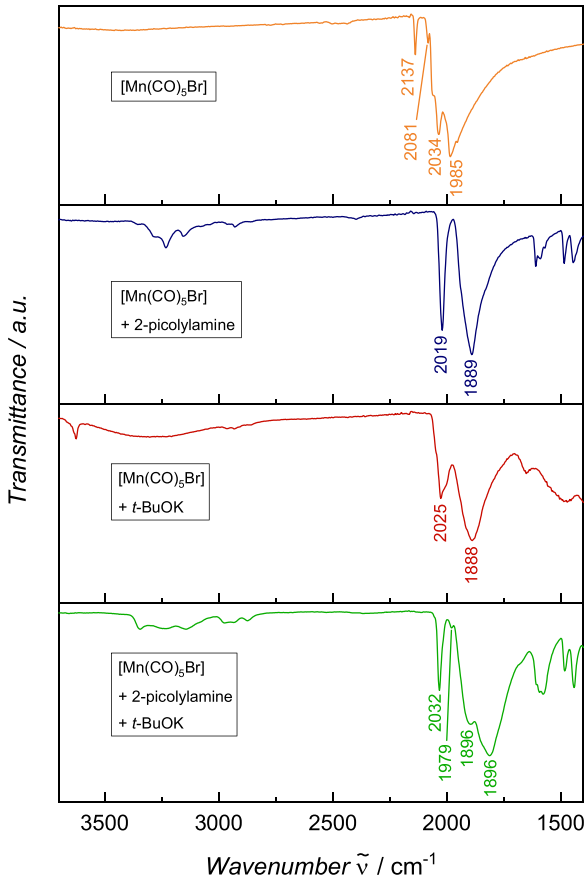


Fig. 2. ATR-IR spectra of $[Mn(CO)_5Br]$ (orange) and isolated products from reactions under hydrogenation conditions (30 bar H_2, 120 °C, 12 h): $[Mn(CO)_5Br]$ + 1 equiv. 2-picolylamine (blue), $[Mn(CO)_5Br]$ + 1 equiv. *t*-BuOK (red); $[Mn(CO)_5Br]$ + 1 equiv. 2-picolylamine + 1 equiv. *t*-BuOK (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

2-picolylamine, and *t*-BuOK in the presence of molecular hydrogen (30 bar H_2, 120 °C, 12 h) was investigated by IR spectroscopy (Fig. 2, green trace). In this case, the formation of another distinct metal carbonyl compound, that turned out to be exceedingly air-sensitive in solution, was observed. The corresponding IR spectra of all relevant Mn species that were obtained in this experiment series are shown in Fig. 2.

To get a glimpse into the understanding of the different catalytic performance of the in situ system and the pre-synthesized catalyst $[Mn(NN)(CO)_3Br]$, NMR experiments were performed under the typical reaction conditions without substrate (0.073 mmol $[Mn(CO)_5Br]$/2-picolylamine or $[Mn(NN)(CO)_3Br]$, 0.073 mmol *t*-BuOK, 0.7 ml THF-d_8, 30 bar H_2, 120 °C, and 12 h). In the case of the Mn in situ system, the ^1H spectrum (Fig. 3, blue spectrum) of the reaction solution showed the presence of several picolylamine species but, unfortunately, it was not possible to detect any hydride species. Notably, a strong spectroscopic feature at 2.60 ppm was observed. The existence of various picolylamine-tagged species was further confirmed by ^{13}C NMR spectroscopy (supporting information, Section 8.3) while also a CO signal was detected at a chemical shift of 239 ppm.

By contrast, NMR studies of the pre-synthesized complex disclosed the presence of one dominant picolylamine species (Fig. 3, red trace) and again, ^{13}C NMR spectroscopy confirmed these findings (supporting information, Section 8.3). Moreover, a CO signal located at identical shift as compared to the in situ system was observed. In addition, the IR spectrum of the isolated product displayed the same absorption pattern in the CO region (see Fig. S29).

Since the well-defined NN-ligated manganese(I) complex $[Mn(NN)(CO)_3Br]$ is known to form a binuclear coordination compound upon reaction with *t*-BuOK [41], we were interested as to whether this dimer is also generated when the given picolylamine-tagged Mn complex is generated in situ. For this purpose, we applied a slightly modified literature procedure using 1,4-dioxane instead of toluene to increase the solubility of *t*-BuOK in that solvent (supporting information, Section 8.8). Analysis of the isolated product by IR spectroscopy and X-ray crystallography confirmed that the dimer *fac*-$[Mn(NN)(CO)_3]_2$ can also be prepared directly from $[Mn(CO)_5Br]$ and 2-picolylamine in the presence of a strong base (Fig. 4).

Curious about the behavior of the synthesized dimer under the given hydrogenation conditions without substrate, the binuclear compound was brought to reaction with H_2 gas (0.016 mmol $[Mn(NN)(CO)_3]_2$, 1.0 ml THF, 30 bar H_2, 120 °C, 12 h) and the isolated compound was then analyzed by IR spectroscopy. Very interestingly, it seems that the isolated species has the same structure as those substances obtained from the reaction of $[Mn(NN)(CO)_3Br]$ with base or from the combination of equimolar amounts of $[Mn(CO)_5Br]$, 2-picolylamine, and base since the recorded IR spectra are almost identical in the CO region (see Fig. S32).

The binuclear manganese complex was then tested for its ability to catalyze the reduction of acetophenone without the addition of external base under standard hydrogenation conditions (3 mol% $[Mn(NN)(CO)_3]_2$, 0.5 mmol acetophenone, 2 ml THF, 30 bar H_2, 120 °C, 12 h). In this case, 1-phenylethanol was obtained in a rather modest yield of only 55 %.

To conclude, IR study on the reaction products under hydrogenation conditions indicated that the same carbonyl species were formed regardless of whether the dimer $[Mn(NN)(CO)_3]_2$ or the combinations $[Mn(NN)(CO)_3Br]$/*t*-BuOK and $[Mn(CO)_5Br]$/2-picolylamine/*t*-BuOK, respectively, were used as the hydrogenation reaction setup. However, the ^1H NMR spectrum of the reaction solution pertinent to the in situ system turned out to be rather complicated on comparison with the spectrum obtained from the reaction mixture that corresponds to the application of the well-defined Mn-complex. Notably, this intricate pattern is due to the presence of several picolylamine-based species.

2.2. Optimization of the reaction conditions

To improve upon the results obtained in THF, we first embarked on a solvent variation study to find proper alternatives with respect to the reaction medium. Indeed, when the title transformation was conducted in 1,4-dioxane we obtained results which are similar to those observed in THF (see Table S5 in the supporting information for details). However, as the dioxane did not significantly outperform its smaller ring congener, we adhered to the use of THF owing to its lower price and advantageous boiling point that allows for convenient removal from the reaction mixture.

We then substituted the *t*-BuOK additive by other strong bases, viz. MeONa, *t*-BuONa, and Cs_2CO_3, but since this approach resulted in a steep decline of the catalyst activity (Table S4 in the supporting information), we decided to use the potassium alcoholate throughout. Noteworthy, the in situ-system tolerates a slight excess of *t*-BuOK without loss of activity but upon adding more than two equivalents versus the Mn-catalyst a pronounced decrease of the catalytic performance was observed (Table 2, entries 1-2). In fact, this is a rather unusual behavior considering that related catalytically active metal centers held by deprotonable NH motifs perform significantly better on increasing the base-loading [31,63]. On the other hand, applying less than one equivalent of *t*-BuOK resulted in a decrease of the both substrate-conversion and yield (Table 2, entry 3). Consequently, the activity of the $[Mn(CO)_5Br]$-picolylamine assembly depends on a delicate balance of base, metal, and the ligand.

Having optimized the metal-to-base-ratio as well as the physical parameters, viz. temperature and H_2-pressure (Table 2, entries 4-7), we finally sought to reduce the catalyst amount. Regrettably, a prompt and

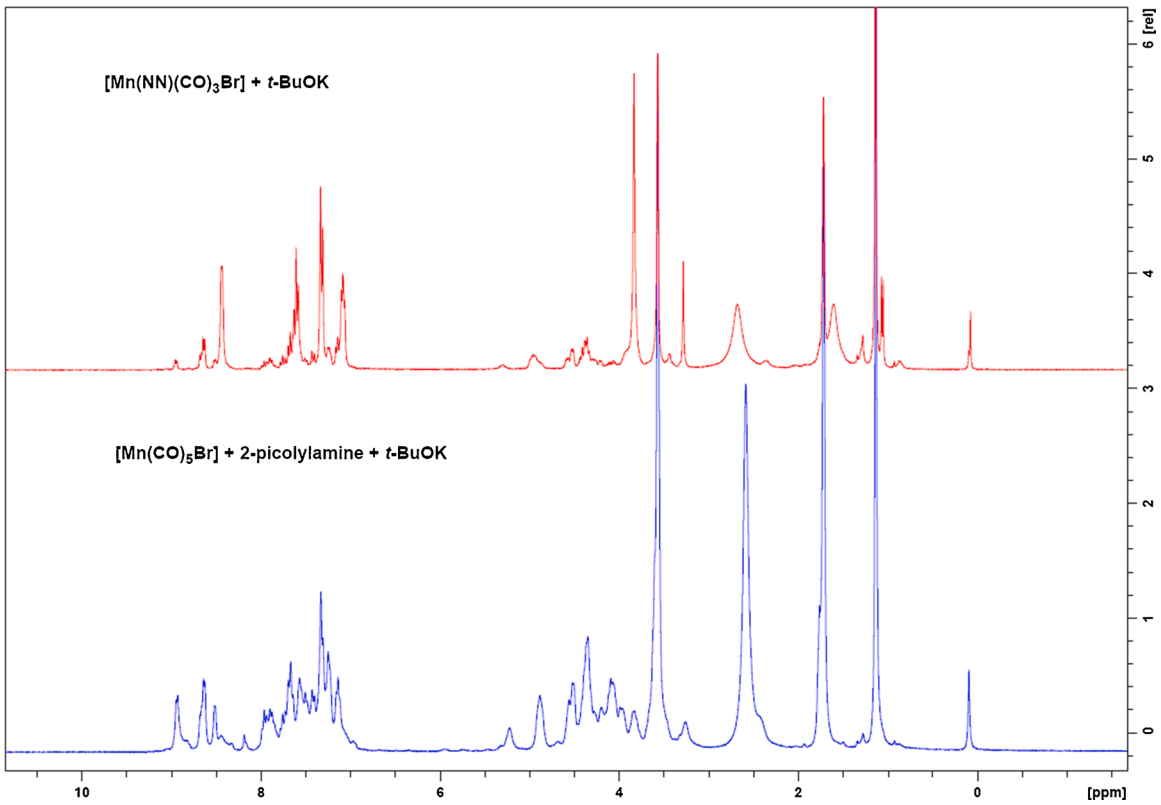


Fig. 3. ^{1}H NMR spectra of the reaction mixtures in the presence of H_2 (30 bar, 12 h, 120 °C) in THF-d_8: [$Mn(CO)_5Br$] + 2-picolylamine + t-BuOK (blue); [$Mn(NN)(CO)_3Br$] + t-BuOK (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

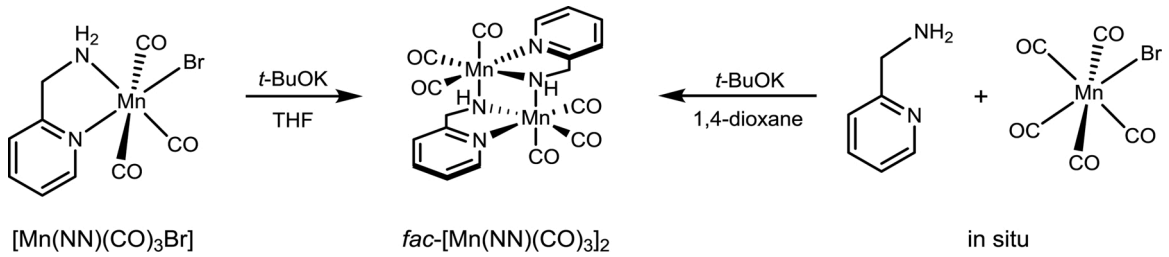


Fig. 4. Formation of the binuclear Mn-carbonyl compound from the pre-synthesized [$Mn(NN)(CO)_3Br$] upon reaction with *t*-BuOK in THF [41]. The reaction also occurs when the respective NN-ligated manganese(I) complex is prepared in situ.

marked decrease of the catalytic performance resulted if the [$Mn(CO)_5Br$] precursor was used in quantities less than 3 mol% (entries 8-11).

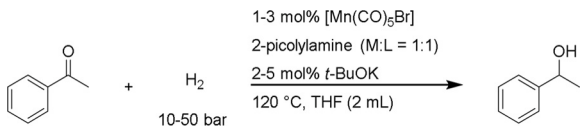
2.3. Catalytic hydrogenation of ketones

After the systematic variation of the reaction conditions, we went straight ahead to elaborate the scope and limitations of the given Mn-based hydrogenation protocol (Table 3). First, we probed the aptitude of the given catalytic system to cope with steric hindrance imposed by the substrate substitution pattern and for that purpose we introduced α-branching at the CH_3-group of the parent acetophenone **a1**; in a related experiment the pertinent methyl group was substituted for the phenyl motif. To our delight, substrates **a2-a5** were fully converted into their corresponding alcohols, indicating that the presence of additional or longer alkyl chains as well as arene moieties do not hamper the catalyst.

The bulky kindred naphthalene derivatives **a6** and **a7** as well as the methyl acetophenones **a8-a10** were also neatly transformed into the desired secondary alcohols giving rise to excellent yields in each case. Noteworthy, the position of the appendant CH_3-group did not have a measurable impact on the catalyst performance.

With respect to the halide-functionalized ketones **a11-a21** the catalytic system sharply discriminates between two sets. The hydrogenation of the fluoro- and chloro-substituted acetophenones **a11-a17** as well as the disubstituted substrate **a14** featuring both an electron-withdrawing- and electron-donating group produced the desired tagged alcohols in quantitative yield, albeit with a slight modification of the standard reduction protocol for *ortho*-chloroacetophenone **a15**. On the other hand, all tested brominated acetophenone derivatives **a18-a20** were not amenable to reduction under the optimized reaction conditions. Consequently, both H_2-pressure and temperature were increased (50 bar, 120 °C) whereby prolonging the reaction time (20 h) but the conversion still remained inferior, especially for the *ortho*- and *meta*-substituted bromoacetophenones **b18** and **b19**. The same negative result was obtained for the related iodo-compound **a21** which proved to be almost unreactive in the given hydrogenation process. The reactivity of halo-acetophenones thus seems to be strongly dominated by the

Table 2
Optimization of the reaction conditions for the reduction of acetophenone catalyzed by the in situ formed manganese catalyst[a].



Entry	[Mn(CO)$_5$Br] (mol%)	*t*-BuOK (mol%)	*t* (h)	*p* (bar)	Conversion (%)	Yield (%)
1	3	9	12	50	67	67
2	3	4	12	50	>99	99
3	3	2	12	40	89	89
4[b]	3	3	12	40	98	97
5	3	3	12	30	>99	99
6	3	3	5	20	42	42
7	3	3	16	10	26	25
8	2.5	5	12	40	18	17
9	2.5	2.5	12	40	79	79
10	2	2	18	50	27	27
11	1	2	18	50	4	4

[a] 0.5 mmol of acetophenone were used. Conversions and yields were determined by GC analysis using *n*-dodecane as internal standard.
[b] The reaction temperature was 100 °C. M:L denotes the molar ratio of the manganese versus the picolylamine-ligand.

electronegativity of the attached halide species which is, however, intrinsically related to the size of the respective atom.

Our Mn-based catalytic system also mediated the reduction of pharmaceutically relevant CF_3-tagged acetophenones, viz. **a22** and its disubstituted congener **a24**, to generate the corresponding trifluoromethyl-alcohols in excellent yields. Interestingly, we observed a subtle but decisive effect of the alkyl chain length that is in direct proximity of the ketone group. If we subjected the immediate homologous propiophenones **a23** and **a25** to the same hydrogenation process, the catalytic transformation was sluggish and the alcohols **b23** and **b25** were produced in very low yields (17 % and 23 %, respectively).

Along with aromatic ketones, (benzannulated) cyclic substrates that incorporate the carbonyl group directly in the ring (**b26**-**b30**) were also completely converted to afford the corresponding secondary alcohol in very good yields. Notably, the ring size affected the catalyst activity in that six-membered rings required higher H_2 pressure and prolonged reaction time (**b26** and **b27** versus **b28**).

To our regret, methyl ketones with an attached pyridine core were either not at all (**a31**) or poorly (**a32**, **a33**) converted into the desired products **b31**-**b33** presumably due to inhibition of the active Mn-center through the strongly ligating sp^2 nitrogen atom of the pertinent heterocycle.

Finally, the chemoselectivity of the manganese in situ-system was examined by testing substrates that incorporate one additional reducible motif, viz. CN-functionalized acetophenone **a34**, isophorone **a35**, and the aldehyde-tagged ketone derivative **a37** (see Section 4 in the supporting information). With the exception of the latter, the ketone group was selectively reduced to produce the target alcohols **b34** and **b35** in very good yields. On the contrary, the aldehyde-bearing acetophenone **a37** was exhaustively hydrogenated to the bis-alcohol **b37**. Quite remarkably, on applying benzaldehyde derivatives devoid of an acetyl group on the arene moiety as substrates, we observed either only traces of the respective primary alcohol or no product at all.

In stark contrast to the selectivity observed in the case of the reduction of isophorone **34a**, the hydrogenation of *trans*-chalcone **a36** produced a mixture of saturated alcohol **b36** and ketone **c36** (Fig. 5). Since no evidence for the formation of allyl alcohol **d36** was found, it is tempting to assume that the given Mn-catalyzed transformation is considerably biased towards the reduction of the C = C-bond. However, the intermediate formation of **d36** through hydrogenation of the ketone group in enone **a36** and its direct isomerization to the ketone **c36** via a combined Mn-mediated dehydrogenation-hydrogenation sequence is also conceivable [64]. Indeed, when a pristine portion of commercial **d36** was subjected to the reaction conditions from Fig. 5, but in the absence of H_2 gas, the given allyl alcohol was completely converted to the ketone **c36** [65]Fig. 5.

2.4. Hydrogenation of cinnamic acid ester derivatives

The pleasing results obtained in the hydrogenation of *trans*-chalcone **a36** encouraged us to test the in situ-generated [Mn(NN)(CO)$_3$Br] for its ability to selectively reduce cinnamate derivatives (Table 4). Applying the optimized reaction conditions established for the acetophenone hydrogenation resulted in virtually full conversion of the methyl cinnamate **c1** (95 %, Table S6 in the supporting information). On exchanging THF for 1,4-dioxane as solvent we actually achieved complete substrate conversion while the corresponding saturated ester product was isolated in very good yield (86 %). The alkyl cinnamates **c2**-**c4** gave rise to the same excellent yields, in fact irrespective of the degree of branching in the esterifying alcohol. Rather bulky substrates such as **c5** and **c6** did not hamper the course of the catalytic transformation either, allowing the synthesis of **d5** and **d6** in almost quantitative yields without debenzylation taking place in the ester part. Quite remarkably, the in situ-prepared Mn-catalyst smoothly converted allyl cinnamate **c7** into the targeted hydrogenation product without compromising the C═C—bond of the allyl motif. However, a higher catalyst loading (5 mol% versus 3 mol%) and slightly reinforced reaction conditions had to be applied in order to achieve this important result (50 bar H_2 and 20 h reaction time versus the standard values of 30 bar H_2 and 12 h).

Placing electron-releasing groups on the phenyl ring of the cinnamic acid ester did not markedly affect the catalyst performance. Yet, in case of the methyl cinnamates **c8** and **c9** the conditions had to be modified (50 bar H_2, 100 °C and 20 h) so as to maintain full substrate conversion and decent yield.

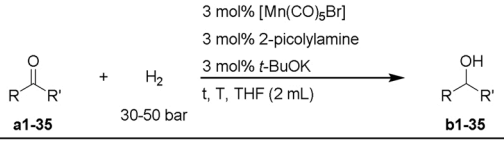
Regarding the halide-functionalized esters **c11**-**c14** we did not observe any unwanted hydro-dehalogenation processes for the fluoro- and chloro-compounds whereby the corresponding products were isolated in good yields ranging from 80 % to 89 %. Most notably, the respective bromo-derivatives were also amenable to the given hydrogenation which is in stark contrast to the results obtained for the brominated acetophenones **a18**-**a20** (vide supra). However, the reaction conditions had to be adjusted (6 mol% catalyst loading, 50 bar, 24 h, 100 °C) which again demonstrated a somewhat detrimental decreased-electronegativity-effect of the appendant bromide substituent. With respect to **d13** and **d14** we detected 3-phenyl methyl cinnamate in the GC–MS spectra which is indicative of concomitant hydro-debromination that occurred during the course of the Mn-catalyzed hydrogenation.

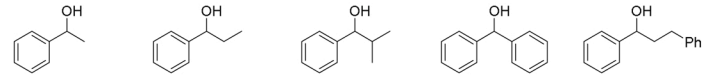
The introduction of a cyano group on the arene ring was not as well accommodated as was the case with the related CN-labelled acetophenone **a33** (vide infra) and hence cinnamate **d15** was only isolated in a mediocre yield of 75 %. Diesters **c16** and **c17** displayed considerable reactivity towards the conjugate hydrogenation of their C = C-bonds though the yield of the former was surprisingly low considering its rather simple molecular architecture.

The most surprising feature of the in situ-prepared [Mn(NN)(CO)$_3$Br] complex is its ability to even reduce tetra-substituted C = C-bonds at 100 °C in crowded esters such as **c18** and **c19**. Upon applying a H_2-pressure of 50 bar and a reaction time of 20 h the isolated yields of both desired products were well above 70 %. Accordingly, the conjugated C = C-bond of the less sterically congested α-phenyl cinnamyl nitrile **c20** was fully hydrogenated upon applying lower H_2-pressure (30 bar) and a shorter reaction time (12 h).

To further explore the limitations of the Mn-based in situ-system presented herein, we expanded the substrate panoply by ethyl-*β*-methyl cinnamate **c21** (Table 5). Regrettably, we soon realized that this compound cannot compete with those listed in Table 4 with respect

Table 3
Scope and limitation of the ketone-hydrogenation catalyzed by in situ-prepared $[Mn(NN)(CO)_3Br]$[a].





b1
>99% **A**
99% (88%)

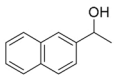
b2
>99% **A**
99% (94%)

b3
>99% **A**
99% (95%)

b4
>99% **A**
99% (99%)

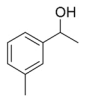
b5
>99% **A**
99%

b6
>99% **A**
99% (99%)



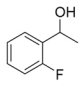
b7
>99% **A**
99% (98%)

b8
>99% **A**
99% (92%)

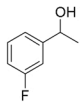


b9
>99% **A**
99% (88%)

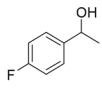
b10
>99% **A**
99% (94%)



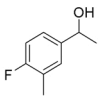
b11
>99% **A**
99% (85%)



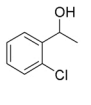
b12
>99% **A**
99%



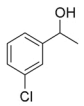
b13
>99% **A**
99% (89%)



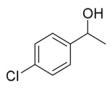
b14
>99% **A**
99% (94%)



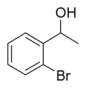
b15
>99% **B**
99%



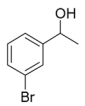
b16
>99% **A**
99% (96%)



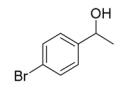
b17
>99% **A**
99% (97%)



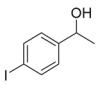
b18
8% **C**
7%



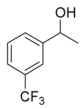
b19
7% **C**
6%



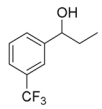
b20
35% **C**
32%



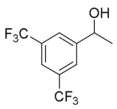
b21
5% **C**
4%



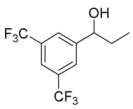
b22
>99% **C**
99%



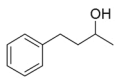
b23
18% **C**
17%



b24
>99% **A**
99% (72%)



b25
25% **A**
23%



b25
>99% **A**
98%

b26
>99% **C**
99%

b27
>99% **C**
99%

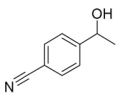
b28
>99% **A**
99%

b30
>99% **C**
99% (98%)

b31
0% **A**

b32
35% **A**
35 %

b33
21% **A**
19%



b34
92% **C**
91%

b35
>99% **D**
86%[b]

[a] A 0.5 mmol amount of the ketone was used. Reaction conditions: **A**: 30 bar H_2, 120 °C, 12 h; **B**: 50 bar H_2, 100 °C, 12 h; **C**: 50 bar H_2, 120 °C, 20 h; **D**: 50 bar H_2, 120 °C, 24 h. Conversions (upper value) and yields (lower value) were determined by GC analysis using *n*-dodecane as internal standard. In case of **b8-b10** *n*-hexadecane was used as the standard. Isolated yields are given in parentheses. [b]Isolated yield.

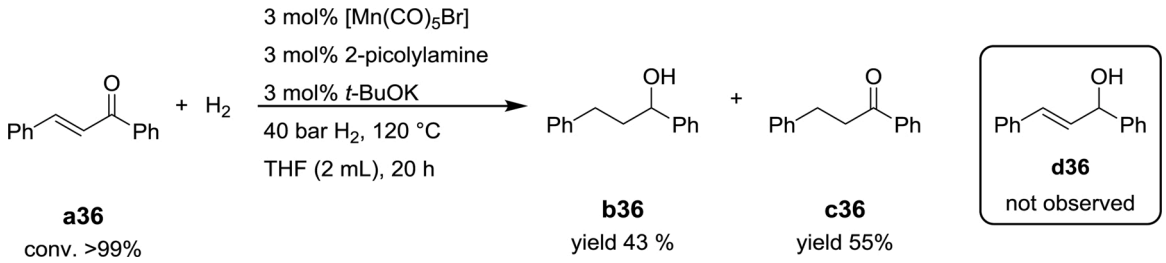


Fig. 5. Hydrogenation of *trans*-chalcone (0.5 mmol) using H_2 gas effected by the in situ-formed manganese catalyst. A mixture that was solely composed of saturated alcohol **b36** and ketone **c36** was obtained. The substituted allyl alcohol **d36** was not detected, presumably due to its quantitative Mn-catalyzed isomerization to yield ketone **c36** [65]. Conversion and yields were determined by GC analysis using *n*-dodecane as internal standard.

to catalytic activity. On applying the optimized reaction conditions found for the methyl cinnamate reduction (vide supra), the substrate-conversion was as low as 34 %. Even on doubling the H_2-pressure and using significantly higher catalyst loadings we only achieved 87 % conversion after a reaction time of 48 h. Thus, we did not pursue the reduction of ethyl-β-methyl cinnamate any further in this work. The fact that the congested olefins **c18** and **c19** do exhibit considerable activity is explained by the presents of the appendant CN-groups that exert a strong electron-withdrawing effect that eventually activates the C = C-motif towards nucleophilic attack of a hydride.

In order to verify whether the method reported herein is applicable to synthesize larger quantities of hydrogenation products a scale-up experiment (5 mmol) was performed using methyl cinnamate as substrate. Indeed, the respective ester product was obtained in good yield (79 %) and was easily separated from the reaction mixture by vacuum distillation (see Section 5 in the supporting information). Hence, the given catalytic protocol allows a scale-up by at least a factor of ten, thus rendering this operationally simple system a sound method for the synthesis of various saturated esters.

3. Conclusion

We presented a convenient, robust, and phosphine-free Mn-based in situ-protocol for the chemoselective hydrogenation of selected ketones and cinnamate derivatives using molecular H_2. The key constituents, viz. the organometallic Mn-precursor and the picolylamine ligand, are readily available through commercial channels whereby the catalytic assembly is readily prepared on simply combining the components in the reaction vessel under an ordinary laboratory atmosphere. Notably, the in situ-system heavily outperforms the analogous method which relies on the pertinent pre-synthesized Mn-catalyst.

The catalytic hydrogenation of ketones was well-compatible with the presence of phenyl F- and Cl-substituents in that detrimental hydrodehalogenation was not observed in both cases. However, the reduction of the carbonyl group failed to occur in related compounds containing Br- and I-motifs while potentially reducible CN-groups are also tolerated by the given system.

As to the cinnamate hydrogenation, a vast array of saturated esters was accessible including those which are derived from challenging tetra-substituted starting materials containing a CN-group in the α-position. Given the initial results on the reduction of ethyl-β-methyl cinnamate, the introduced Mn-in situ-system is likely to be developed into a more active (chiral) version that enables effective (enantioselective) syntheses of branched saturated esters.

4. Experimental section

4.1. General information

All chemicals were purchased from Acros Organics, Alfa Aesar, Merck (including Sigma Aldrich), Roth, TCI, VWR, or Fluorochem, and were used as received without further purification. For the addition of 2-picolylamine, a 10 µl Hamilton Gastight® syringe (Model 1701 RN) was used. Hydrogenation reactions were performed in a 300 ml autoclave from Parr Instruments GmbH and the employed hydrogen was purchased from Linde Gas GmbH (5.0 purity). Dry solvents were either purchased from Acros Organics or drawn off from a MB-SPS-7 solvent system (M. Braun GmbH). GC–MS analyses were carried out on a Shimadzu GC–MS QP-2020 with helium carrier gas from Linde Gas GmbH (5.0 purity). Infrared spectroscopy was performed in the solid state on a Bruker Alpha II and high-resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL. NMR measurements were carried out on a Bruker Avance 300 MHz and 500 MHz spectrometer. Spectra for different cores were recorded as follows: 300 MHz for ^{1}H NMR, 75.5 MHz for ^{13}C NMR, and 470.5 MHz for ^{19}F NMR. Chemical shifts are listed in parts per million (ppm) on the delta scale (δ). Axis calibration of the ^{1}H and ^{13}C NMR spectra is based on the non-deuterated solvent as reference [66]. The active $[Mn(NN)(CO)_3Br]$ complex and the manganese dimer $[Mn(NN)(CO)_3]_2$ were prepared in accordance with the literature procedure [41]. Vacuum distillation for product isolation in the scale-up experiment was performed with the Glass-Oven B-585 from Büchi.

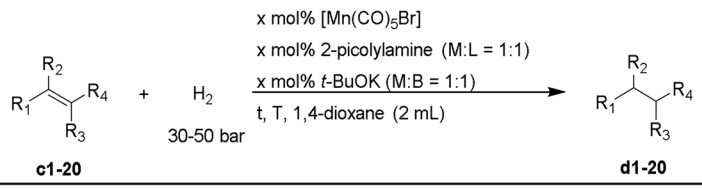
4.2. Safety statement concerning high-pressure hydrogenation

The H_2 pressure tank (200 bar, 50 l) was placed in a safety storage cabinet with an installed tapping unit whereby the gas container was connected to a control panel that allowed for fine adjustment of the H_2 pressure used for the hydrogenation reactions. The autoclave charging procedure was performed in a fume hood that was equipped with a sensor which was wired to a magnetic valve. The latter instantaneously stops the gas supply in case of any H_2 leakage that might occur during the filling procedure. Furthermore, both optical and acoustic alarm signals are triggered whenever free flammable gas is detected inside the hood.

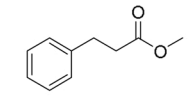
4.3. Representative procedure for the catalytic hydrogenation reactions

A 4 ml glass vial was sequentially charged with solid $[Mn(CO)_5Br]$ (0.015−0.030 mmol), the substrate (0.5 mmol), 2-picolylamine (0.015−0.030 mmol), and a magnetic stirring bar. The reaction components were then dissolved in THF (2 ml) or 1,4-dioxane (2 ml) whereupon the resulting yellow solution was then gently stirred (200 rpm) for a period of 5 min. Whilst stirring, the glass vial was sealed with the septum cap. Hereafter, solid *t*-BuOK (0.015−0.030 mmol) was added to the reaction mixture upon which the reaction vessel was again sealed with a septum cap which was then penetrated with a needle. Notably, the base addition was carried out without stirring. After that, the glass vial was placed in a drilled aluminum liner which was promptly transferred into the 300 ml autoclave. Once tightly sealed, the latter was purged five times with H_2 (20 bar per cycle) before being pressurized to the desired value. The autoclave was then placed on a pre-heated stirring plate and heated up to the required reaction temperature. On completion of the hydrogenation reaction, the autoclave was allowed to

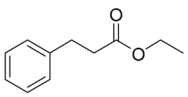
Table 4
Scope and limitation of the cinnamate hydrogenation mediated by the in situ-formed [Mn(NN)(CO_3)Br][a].



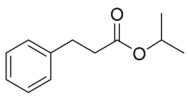
c1-20 **d1-20**



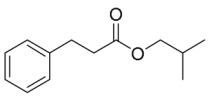
d1
3 mol%
>99% (86%) **A**



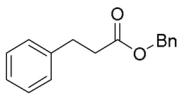
d2
3 mol%
>99% (90%) **A**



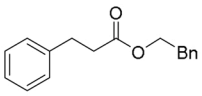
d3
3 mol%
>99% (90%) **A**



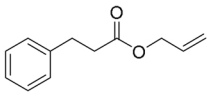
d4
3 mol%
>99% (92%) **A**



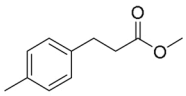
d5
3 mol%
>99% (92%) **A**



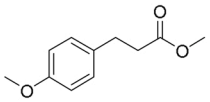
d6
3 mol%
>99% (91%) **A**



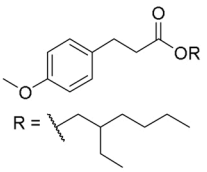
d7
5 mol%
>99% (87%) **B**



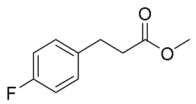
d8
3 mol%
>99% (90%) **B**



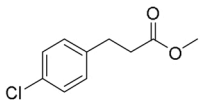
d9
3 mol%
>99% (84%) **B**



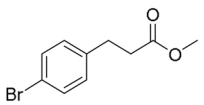
d10
3 mol%
>99% (94%) **A**



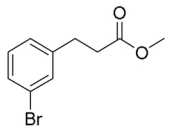
d11
3 mol%
>99% (82) **A**



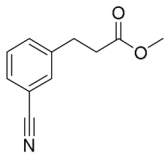
d12
3 mol%
>99% (89%) **B**



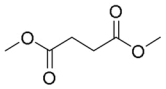
d13
6 mol%
>99% (85%) **C**



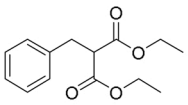
d14
6 mol%
>99% (80%) **C**



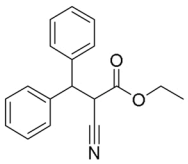
d15
5 mol%
>99% (75%) **D**



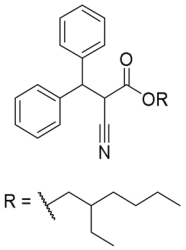
d16
5 mol%
>99% (64%) **B**



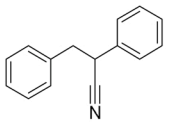
d17
3 mol%
>99% (83%) **A**



d18
5 mol%
>99% (75%) **B**



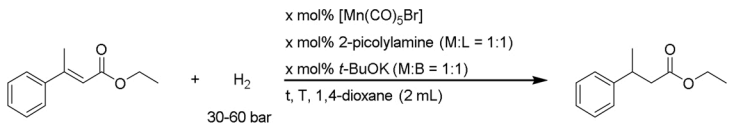
d19
5 mol%
>99% (73%) **B**



d20
3 mol%
>99% (78%) **A**

[a] 0.5 mmol of the substrate were used. Reaction conditions: **A**: 30 bar H_2, 12 h, 120 °C; **B**: 50 bar H_2, 20 h, 100 °C; **C**: 50 bar H_2, 24 h, 100 °C; **D**: 50 bar H_2, 24 h, 120 °C. Conversions were determined by GC analysis using *n*-hexadecane as internal standard. Isolated yields are given in parentheses. The amount x of [Mn(CO)$_5$Br], 2-picolylamine, and *t*-BuOK is given in mol% directly under the short description of the corresponding product.

Table 5
Catalytic performance of the Mn-based in situ-system for ethyl-β-methyl cinnamate[a].



c21 d21

Entry	$[Mn(CO)_5Br]$ (mol%)	T / °C	p (bar)	t (h)	Conversion (%)
1	3	120	30	12	34
2	5	100	50	20	41
3	5	120	40	48	71
4	7	120	60	48	87

[a] 0.5 mmol of the ester were used. Conversions were determined by GC analysis using *n*-hexadecane as internal standard. The hydrogenation product was verified by GC analysis. M:L and M:B denotes the molar ratio of the manganese versus the picolylamine-ligand and *t*-BuOK, respectively.

reach room temperature. Afterwards, the remaining gas was slowly released upon which the reaction mixture was degassed through briefly stirring on air. Finally, *n*-dodecane (12 mg) or *n*-hexadecane (20 mg) were added and an aliquot of 30 µl was taken from the solution, mixed with acetone (1 ml) whereupon the resulting solution was analyzed by GC.

4.4. General procedure for the isolation of the alcohol products

The solvent was removed at the pump upon which the obtained residue was mixed with a 2:1-by-volume-mixture of DCM/*n*-pentane (2 ml). The suspension was filtered through a pad of silica (3 cm height in a Pasteur pipette) and the solid phase was then washed with diethyl ether (3 ml). Finally, the filtrate was evaporated to dryness, leaving behind the product alcohol.

4.5. General procedure for the isolation of the α,β-hydrogenated esters

The solvent was removed *in vacuo* and the residue was taken up in a 2:1-by-volume-mixture of DCM/*n*-pentane (2 ml). The thus-obtained suspension was filtered over a pad of silica (3 cm height in a Pasteur pipette) whereupon the solid phase was washed with the same DCM/*n*-pentane mixture (6 ml). Eventually, the filtrate was evaporated to dryness so as to afford the hydrogenated product. Column chromatography over silica using a mixture of *n*-heptane/ethyl acetate as eluent was performed in order to remove persistent impurities.

CRediT authorship contribution statement

Thomas Vielhaber: Methodology, Validation, Investigation, Visualization, Writing - original draft. **Christoph Topf:** Funding acquisition, Project administration, Supervision, Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was funded by the Linz Institute of Technology (Project LIT-2019-8-SEE-113, Manganese Catalysts for (Enantioselective) Redox Transformations and we gratefully thank Univ.-Prof. Dr. Marko Hapke from the INCA for fruitful discussions and the generous support. Moreover, we are much obliged to DI Thomas Bögl from the department of Analytical Chemistry at JKU for performing the HR-MS measurements of the various hydrogenation products.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118280.

References

[1] S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, J. Am. Chem. Soc. 138 (2016) 8809–8814, https://doi.org/10.1021/jacs.6b03709.
[2] M. Garbe, K. Junge, M. Beller, Eur. J. Org. Chem. (2017) 4344–4362, https://doi.org/10.1002/ejoc.201700376, 2017.
[3] F. Kallmeier, R. Kempe, Angew. Chem. Int. Ed. 57 (2017) 46–60, https://doi.org/10.1002/anie.201709010.
[4] A. Mukherjee, D. Milstein, ACS Catal. 8 (2018) 11435–11469, https://doi.org/10.1021/acscatal.8b02869.
[5] T. Zell, R. Langer, ChemCatChem 10 (2018) 1930–1940, https://doi.org/10.1002/cctc.201701722.
[6] N. Gorgas, K. Kirchner, Acc. Chem. Res. 51 (2018) 1558–1569, https://doi.org/10.1021/acs.accounts.8b00149.
[7] S. Elangovan, M. Garbe, H. Jiao, A. Spannenberg, K. Junge, M. Beller, Angew. Chem. Int. Ed. 55 (2016) 15364–15368, https://doi.org/10.1002/anie.201607233.
[8] M. Andérez-Fernández, L.K. Vogt, S. Fischer, W. Zhou, H. Jiao, M. Garbe, S. Elangovan, K. Junge, H. Junge, R. Ludwig, M. Beller, Angew. Chem. Int. Ed. 56 (2016) 559–562, https://doi.org/10.1002/anie.201610182.
[9] F. Kallmeier, T. Irrgang, T. Dietel, R. Kempe, Angew. Chem. Int. Ed. 55 (2016) 11806–11809, https://doi.org/10.1002/anie.201606218.
[10] M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier, K. Kirchner, J. Am. Chem. Soc. 138 (2016) 15543–15546, https://doi.org/10.1021/jacs.6b10433.
[11] S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel, M. Beller, Nat. Commun. 7 (2016), https://doi.org/10.1038/ncomms12641.
[12] A. Bruneau-Voisine, D. Wang, T. Roisnel, C. Darcel, J.-B. Sortais, Catal. Commun. 92 (2017) 1–4, https://doi.org/10.1016/j.catcom.2016.12.017.
[13] A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, J. Catal. 347 (2017) 57–62, https://doi.org/10.1016/j.jcat.2017.01.004.
[14] Y. Wang, Z. Shao, K. Zhang, Q. Liu, Angew. Chem. Int. Ed. 57 (2018) 15143–15147, https://doi.org/10.1002/anie.201809333.
[15] H. Li, D. Wei, A. Bruneau-Voisine, M. Ducamp, M. Henrion, T. Roisnel, V. Dorcet, C. Darcel, J.-F. Carpentier, J.-F. Soulé, J.-B. Sortais, Organometallics 37 (2018) 1271–1279, https://doi.org/10.1021/acs.organomet.8b00020.
[16] M. Glatz, B. Stöger, D. Himmelbauer, L.F. Veiros, K. Kirchner, ACS Catal. 8 (2018) 4009–4016, https://doi.org/10.1021/acscatal.8b00153.
[17] P. Ryabchuk, K. Stier, K. Junge, M.P. Checinski, M. Beller, J. Am. Chem. Soc. 141 (2019) 16923–16929, https://doi.org/10.1021/jacs.9b08990.
[18] S.C. Mandal, K.S. Rawat, S. Nandi, B. Pathak, Catal. Sci. Technol. 9 (2019) 1867–1878, https://doi.org/10.1039/c9cy00114j.
[19] A. Bruneau-Voisine, L. Pallova, S. Bastin, V. César, J.-B. Sortais, Chem. Commun. 55 (2019) 314–317, https://doi.org/10.1039/c8cc08064j.
[20] A. Zirakzadeh, S.R.M.M. de Aguiar, B. Stöger, M. Widhalm, K. Kirchner, ChemCatChem 9 (2017) 1744–1748, https://doi.org/10.1002/cctc.201700042.
[21] Z. Tan, B. Xiong, J. Yang, C. Ci, H. Jiang, M. Zhang, J. Catal. 392 (2020) 135–140, https://doi.org/10.1016/j.jcat.2020.09.036.
[22] V. Papa, J.R. Cabrero-Antonino, E. Alberico, A. Spanneberg, K. Junge, H. Junge, M. Beller, Chem. Sci. 8 (2017) 3576–3585, https://doi.org/10.1039/c7sc00138j.
[23] M.B. Widegren, G.J. Harkness, A.M.Z. Slawin, D.B. Cordes, M.L. Clarke, Angew. Chem. Int. Ed. 56 (2017) 5825–5828, https://doi.org/10.1002/anie.201702406.
[24] M.B. Widegren, M.L. Clarke, Org. Lett. 20 (2018) 2654–2658, https://doi.org/10.1021/acs.orglett.8b00864.
[25] A. Kumar, T. Janes, N.A. Espinosa-Jalapa, D. Milstein, Angew. Chem. Int. Ed. 57 (2018) 12076–12080, https://doi.org/10.1002/anie.201806289.
[26] J.C. Borghs, M.A. Tran, J. Sklyaruk, M. Rueping, O. El-Sepelgy, J. Org. Chem. 84 (2019) 7927–7935, https://doi.org/10.1021/acs.joc.9b00792.

[27] M. Perez, S. Elangovan, A. Spannenberg, K. Junge, M. Beller, ChemSusChem 10 (2016) 83–86, https://doi.org/10.1002/cssc.201601057.
[28] S. Budweg, K. Junge, M. Beller, Chem. Commun. 55 (2019) 14143–14146, https://doi.org/10.1039/c9cc07337j.
[29] V. Zubar, J. Sklyaruk, A. Brzozowska, M. Rueping, Org. Lett. 22 (2020) 5423–5428, https://doi.org/10.1021/acs.orglett.0c01783.
[30] W. Yang, I.Y. Chernyshov, R.K.A. van Schendel, M. Weber, C. Müller, G. A. Filonenko, E.A. Pidko, Nat. Commun. 12 (2021), https://doi.org/10.1038/s41467-020-20168-2.
[31] R. van Putten, E.A. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E.J.M. Hensen, M. Beller, L. Lefort, E.A. Pidko, Angew. Chem. Int. Ed. 56 (2017) 7531–7534, https://doi.org/10.1002/ange.201701365.
[32] D. Wei, A. Bruneau-Voisine, T. Chauvin, V. Dorcet, T. Roisnel, D.A. Valyaev, N. Lugan, J.-B. Sortais, Adv. Synth. Catal. 360 (2017) 676–681, https://doi.org/10.1002/adsc.201701115.
[33] D. Wei, A. Bruneau-Voisine, D.A. Valyaev, N. Lugan, J.-B. Sortais, Chem. Commun. 54 (2018) 4302–4305, https://doi.org/10.1039/c8cc01787e.
[34] R. Buhaibeh, O.A. Filippov, A. Bruneau-Voisine, J. Willot, C. Duhayon, D. A. Valyaev, N. Lugan, Y. Canac, J. Sortais, Angew. Chem. Int. Ed. 58 (2019) 6727–6731, https://doi.org/10.1002/anie.201901169.
[35] S. Weber, B. Stöger, K. Kirchner, Org. Lett. 20 (2018) 7212–7215, https://doi.org/10.1021/acs.orglett.8b03132.
[36] S. Weber, B. Stöger, L.F. Veiros, K. Kirchner, ACS Catal. 9 (2019) 9715–9720, https://doi.org/10.1021/acscatal.9b03963.
[37] J.A. Garduño, M. Flores-Alamo, J.J. García, ChemCatChem 11 (2019) 5330–5338, https://doi.org/10.1002/cctc.201901154.
[38] S. Weber, L.F. Veiros, K. Kirchner, Adv. Synth. Catal. 361 (2019) 5412–5420, https://doi.org/10.1002/adsc.201901040.
[39] K. Azouzi, A. Bruneau-Voisine, L. Vendier, J.-B. Sortais, S. Bastin, Catal. Commun. 142 (2020) 106040, https://doi.org/10.1016/j.catcom.2020.106040.
[40] J. Schneekönig, K. Junge, M. Beller, Synlett 30 (2019) 503–507, https://doi.org/10.1055/s-0037-1611669.
[41] A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, Org. Lett. 19 (2017) 3656–3659, https://doi.org/10.1021/acs.orglett.7b01657.
[42] A. Dubey, L. Nencini, R.R. Fayzullin, C. Nervi, J.R. Khusnutdinova, ACS Catal. 7 (2017) 3864–3868, https://doi.org/10.1021/acscatal.7b00943.
[43] D. Wei, A. Bruneau-Voisine, M. Dubois, S. Bastin, J. Sortais, ChemCatChem 11 (2019) 5256–5259, https://doi.org/10.1002/cctc.201900314.
[44] S. Waiba, S.K. Jana, A. Jati, A. Jana, B. Maji, Chem. Commun. 56 (2020) 8376–8379, https://doi.org/10.1039/d0cc01460e.
[45] L. Zhou, D. Liu, H. Lan, X. Wang, C. Zhao, Z. Ke, C. Hou, Catal. Sci. Technol. 10 (2020) 169–179, https://doi.org/10.1039/c9cy02112d.
[46] I. Fokin, I. Siewert, Chem. Eur. J. 26 (2020) 14137–14143, https://doi.org/10.1002/chem.202002075.
[47] D. Wang, A. Bruneau-Voisine, J.-B. Sortais, Catal. Commun. 105 (2018) 31–36, https://doi.org/10.1016/j.catcom.2017.10.028.
[48] V. Papa, Y. Cao, A. Spannenberg, K. Junge, M. Beller, Nat. Catal. 3 (2020) 135–142, https://doi.org/10.1038/s41929-019-0404-6.
[49] Z. Wang, L. Chen, G. Mao, C. Wang, Chin. Chem. Lett. 31 (2020) 1890–1894, https://doi.org/10.1016/j.cclet.2020.02.025.
[50] Y. Wang, L. Zhu, Z. Shao, G. Li, Y. Lan, Q. Liu, J. Am. Chem. Soc. 141 (2019), https://doi.org/10.1021/jacs.9b09038, 177337–17349.
[51] H. Shimizu, T. Oshima, K. Mashima, T. Nagano, N. Sayo, T. Saito, Synlett (2009) 3143–3146, https://doi.org/10.1055/s-0029-1218347.
[52] B.M. Zimmermann, S.C.K. Kobosil, J.F. Teichert, Chem. Commun. 55 (2019) 2293–2296, https://doi.org/10.1039/C8CC09853K.
[53] F. Lazreg, F. Nahra, C.S.J. Cazin, Coord. Chem. Rev. 293–294 (2015) 48–79, https://doi.org/10.1016/j.ccr.2014.12.019.
[54] J.D. Egbert, C.S.J. Cazin, S.P. Nolan, Catal. Sci. Technol. 3 (2013) 912–926, https://doi.org/10.1039/C2CY20816D.
[55] V. Jurkauskas, J.P. Sadighi, S.L. Buchwald, Org. Lett. 5 (2003) 2417–2420, https://doi.org/10.1021/ol034560p.
[56] A.D. Kosal, B.L. Ashfeld, Org. Lett. 12 (2010) 44–47, https://doi.org/10.1021/ol9024315.
[57] W.S. Mahoney, D.M. Brestensky, J.M. Stryker, J. Am. Chem. Soc. 110 (1988) 291–293, https://doi.org/10.1021/ja00209a048.
[58] W.S. Mahoney, J. Stryker, J. Am. Chem. Soc. 111 (1989) 8818–8823, https://doi.org/10.1021/ja00206a008.
[59] B.A. Baker, Ž.V. Bošković, B.H. Lipshutz, Org. Lett. 10 (2008) 289–292, https://doi.org/10.1021/ol702689v.
[60] A. Pelšs, E.T.T. Kumpulainen, A.M.P. Koskinen, J. Org. Chem. 74 (2009) 7598–7601, https://doi.org/10.1021/jo9017588.
[61] J.A. Widegren, R.G. Finke, J. Mol. Catal. A Chem. 198 (2003) 317–341, https://doi.org/10.1016/S1381-1169(02)00728-8.
[62] R.H. Crabtree, Chem. Rev. 112 (2012) 1536–1554, https://doi.org/10.1021/cr2002905.
[63] P.A. Dub, J.C. Gordon, Nat. Rev. Chem. 2 (2018) 396–408, https://doi.org/10.1038/s41570-018-0049-z.
[64] T. Xia, B. Spiegelberg, Z. Wei, H. Jiao, S. Tin, S. Hinze, J.G. de Vries, Catal. Sci. Technol. 9 (2019) 6327–6334, https://doi.org/10.1039/C9CY01502G.
[65] The authors gratefully thank a reviewer for drawing their attention to this Mn-mediated isomerization process that provides an alternative rationale for the fact that the respective allyl alcohol was not detected in the reaction mixture.
[66] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, Organometallics 29 (2010) 2176–2179, https://doi.org/10.1021/om100106e.