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# Manganese-Catalyzed Transfer Hydrogenation of Nitriles with 2-Butanol as the Hydrogen Source

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We report herein the first example of a homogeneous manganese catalyzed transfer hydrogenation of nitriles using 2-BuOH as the hydrogen source. Compound fac-[(CO)$_3$Mn{iPr$_2$P(CH$_2$)$_2$PiPr$_2$}Br] (**Mn-1**, 3 mol%) exhibited catalytic activity in the presence of KO$^t$Bu (10 mol%) for the transfer hydrogenation of benzonitrile to yield a mixture of benzylamine (**BA**) and N-sec-butylidenebenzylamine (**SBA**). Subsequent acidic hydrolysis yielded isolated benzylamine hydrochloride in 96%. The title system featured reversible formation of N-benzylidenebenzylamine (**BBA**) prior to formation of **SBA**. A series of amine hydrochlorides was prepared following this methodology (39–92% isolated yields, 4 examples). Best substrates for this transformation are electron-rich aromatic nitriles, nonetheless electron-deficient aromatic as well as aliphatic nitriles were also hydrogenated. Mechanistic studies suggested coordinatively unsaturated Mn-hydride species performing catalytic turnover.

## 1. Introduction

The catalytic hydrogenation of nitriles is a reaction with high atom economy to synthesize primary amines.[1a–d] Alternative transfer hydrogenation (TH) allows for the use of other hydrogen sources, safer, inexpensive, and if stemming from renewable resources, more environmentally friendly than the use of H$_2$, whose manipulation requires special equipment and whose industrial production from fossil fuels is rather polluting.[2a,b]

Amines are important organic compounds acting as bases and nucleophiles. They are present in biochemical systems and are widely used in industry.[3a] Relevant for this work is the hydrogenation of benzonitrile to benzylamine, used in synthetic textiles, in paints, and as a corrosion inhibitor.[3b]

The hydrogenation of nitriles is challenging in terms of selectivity. Reaction between intermediate primary imines and primary amines leads to formation of secondary imines and ammonia.[1a–d] Thus, secondary imines are a product of partial hydrogenation. Because of their straightforward functionalization, primary amines are the most valued products from nitrile hydrogenation.

Although the TH of nitriles has been known since 1982,[4] reports on this reaction are still scarce. Namely, in heterogeneous catalysis, the synthesis of primary amines has been performed with Raney Ni both in the presence of 2-propanol,[5a] and with the use of formates in ionic liquids.[5b] Formates have also been used as the hydrogen source with catalysts such as Pd/C,[6a] and more recently with Rh composites.[6b] The use of the ammonia-borane adduct in the presence of graphene-supported NiPd nanoparticles allowed for the preparation of primary amines,[7a] and the same hydrogen source was used with Pd-CuFe multimetallic systems able to modulate selectivity toward production of primary or secondary amines.[7b] Additionally, Co-nanoparticles deposited over nitrogen-doped supports catalyzed the synthesis of primary amines and secondary imines with the use of 2-propanol.[8]

In the homogenous arena, the TH of nitriles was reported by the Beller group with the use of [{Ru(p-cymene)Cl$_2$}$_2$] and 1,4-bis(diphenylphosphino)butane as ancillary ligand for the selective preparation of primary amines using 2-butanol as the hydrogen source.[9a] The same group investigated the hydrogenation of nitriles and subsequent N-alkylation with 2-propanol catalyzed by [RuCl$_2$(PPh$_3$)$_3$].[9b] Later on, Liu and coworkers reported the use of Co-PNN pincer complexes along with ammonia-borane as the hydrogen donor to synthesize primary, secondary, and tertiary amines.[10] Simultaneously, the Nikonov group used Ru complexes bearing NHC-ligands for the N-alkenylation of nitriles with 2-propanol,[11a] and recently, the same products were obtained with the use of Ru complexes containing pyrazole ligands.[11b] Also Nikonov and coworkers reported the use of ammonium formate for the preparation of primary amines catalyzed by ruthenium compounds.[11c]

Except for the use of a cobalt pincer complex (vide supra), homogeneous TH of nitriles selective to primary amines has been mainly studied with the use of ruthenium compounds. Hence the extended use of first-row transition metals for this catalytic reaction is still a pending task. In this context, manganese being the third most abundant transition metal in the Earth's crust and a biocompatible element is a very attractive candidate to perform new catalytic protocols, which is a field that continues to grow rapidly.[12]

To the best of our knowledge, there are no examples in the literature on the transfer hydrogenation of nitriles with the use of Mn(I) soluble catalytic precursors.[12d,e,f,h,i] Nonetheless, Mn(I) compounds containing PNP or NNN-pincer ligands have been reported for the TH of alkynes[13] and ketones.[12e,h,14] Additionally, there are examples on the use Mn(I) compounds with

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polydentate ligands,[15a] Shvo-type complexes,[15b] and Mn(I) compounds with N-donor bidentate ligands for the transfer hydrogenation of ketones[16] and aldimines,[17] with 2-propanol as the hydrogen source.

During the course of our investigations on the catalytic hydrogenation of nitriles with the use of Mn(I) compound, fac-[(CO)$_3$Mn{R$_2$P(CH$_2$)$_2$PR$_2$}(OTf)] [R = $^i$Pr (dippe = 1,2-bis(diisopropylphosphino)ethane)], we observed that, when using secondary alcohols as solvents, and in the absence of H$_2$ pressure, benzonitrile was also hydrogenated.[18] Encouraged by this result we decided to investigate independently the TH of nitriles with secondary alcohols as the hydrogen source.

In contrast to our previous report with the use of fac-[(CO)$_3$Mn(dippe)(OTf)] as a catalytic precursor for the hydrogenation of nitriles, in the current work we envisioned compound fac-[(CO)$_3$Mn(dippe)(Br)] (**Mn-1**) as a more practical catalytic precursor since its preparation is straightforward from commercial [MnBr(CO)$_5$], requiring a lesser number of synthetic and purification steps. Also relevant for this work was the use of an analog of **Mn-1**, namely, fac-[(CO)$_3$Mn{$^n$Pr$_2$P(CH$_2$)$_2$P$^n$Pr$_2$}Br], which showed this Br-containing Mn(I)-complex was a suitable catalytic precursor for the hydrogenation of polar bonds,[19] although requiring longer times and higher pressure than with the use of fac-[(CO)$_3$Mn(dippe)(OTf)].[18] Based on this **Mn-1** was chosen as the model catalytic precursor for the TH of benchmark benzonitrile.

## 2. Results and Discussion

Synthesis of **Mn-1** was performed as reported previously;[20] suitable crystals for XRD were obtained from a saturated toluene solution stored at −30 °C for over a week under an argon atmosphere. ORTEP plot for fac-[(CO)$_3$Mn(dippe)Br] (**Mn-1**) is depicted in Figure 1.

Compound **Mn-1** featured two independent molecules in the asymmetric unit (Figure S9), similar to what was observed for the crystal structures of the Mn(I) complexes, fac-[(CO)$_3$Mn{κ$^2$-P,N-Ph$_2$P(CH$_2$)$_2$NH$_2$}Br],[21] and fac-[(CO)$_3$Mn{$^n$Pr$_2$P(CH$_2$)$_2$P$^n$Pr$_2$}Br].[19] In the solid state, **Mn-1** displayed a manganese atom in a slightly distorted octahedral geometry with two phosphorus and two carbon atoms defining an equatorial plane. A carbonyl and a bromide ligand complete the coordination sphere in axial positions forming an angle of 173.2(2)°. The three carbonyl groups form a facial arrangement, so symmetry for **Mn-1** is C$_s$, consistent with a three-band pattern (2 A′ + A′′) previously observed in the corresponding FTIR (ATR) spectrum and a single signal in $^{31}$P{$^1$H} NMR (Table 1, entry 1). The Mn–P [(2.349(2) and 2.365(2) Å] and Mn–C(CO) [1.844(8) and 1.842(8) Å] lengths in the equatorial plane of **Mn-1** agree with values for the trans P–Mn–CO moieties in fac-[(CO)$_3$Mn{$^n$Pr$_2$P(CH$_2$)$_2$P$^n$Pr$_2$}Br], [2.313(1) and 2.314(1); 1.824(4) and 1.829(4) Å],[19] and in fac-[(CO)$_3$Mn(dippe)(OTf)], [2.350(4) and 2.348(4); 1.840(15) and 1.825(13) Å].[20] The P–Mn-P bite angle of 83.85(7)° in **Mn-1** agrees with the value of 83.07(12)° for fac-[(CO)$_3$Mn(dippe)(OTf)].

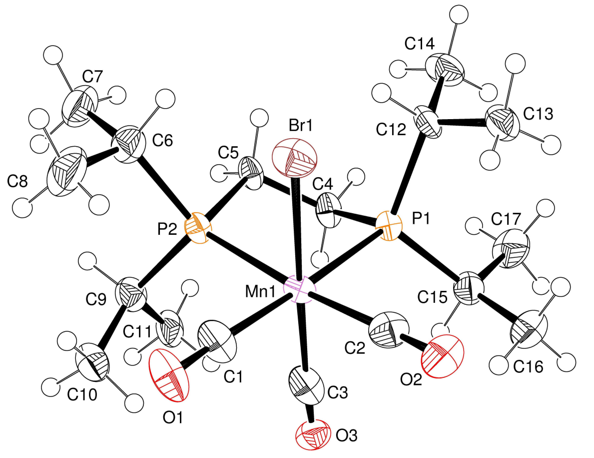


**Figure 1.** ORTEP plot (50 % probability) for **Mn-1**. Selected bond lengths (Å): Mn(1)-P(1) 2.349(2), Mn(1)-P(2) 2.365(2), Mn(1)-C(3) 1.878(10), Mn(1)-C(2) 1.842(8), Mn(1)-C(1) 1.844(8), Mn(1)-Br(1) 2.5378(12), C(1)-O(1) 1.083(9), C(2)-O(2) 1.100(9), C(3)-O(3) 0.972(9). Selected bond angles (deg): P(1)-Mn(1)-P(2) 83.85(7), P(1)-Mn(1)-C(3) 88.9(2), P(1)-Mn(1)-C(2) 94.1(2), P(1)-Mn(1)-C(1) 176.4(2), P(1)-Mn(1)-Br(1) 95.20(6), P(2)-Mn(1)-C(3) 94.8(2), P(2)-Mn(1)-C(2) 174.2(2), P(2)-Mn(1)-C(1) 92.5(2), P(2)-Mn(1)-Br(1) 91.05(6), C(3)-Mn(1)-Br(1) 173.2(2).

**Table 1.** $\nu_{CO}$ and $\delta_P$ Values for fac-[(CO)$_3$Mn{R$_2$P(CH$_2$)$_2$PR$_2$}Br]

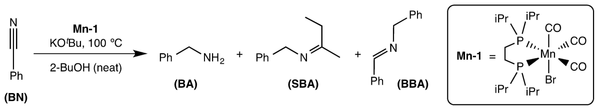
| Entry | Compound | R | [$\nu_{CO}$$^{[a]}$ [cm$^{-1}$]] | | | $\delta_P$$^{[b]}$ [ppm] |
|---|---|---|---|---|---|---|
| | | | A′ | A′′ | A′ | |
| 1 | **Mn-1** | $^i$Pr | 2001[c] | 1922[c] | 1886[c] | 80.5[d] |
| 2 | **Mn-2** | Et | 2001[d] | 1935[d] | 1910[d] | 72.0[d] |
| 3 | **Mn-3** | Cy | 2007[d] | 1941[d] | 1897[d] | 72.5[d] |

[a]For comparison: $\nu_{CO,free}$ = 2155 cm$^{-}$, [b] $^{31}$P{$^1$H} NMR (162 MHz), [c] Data from Ref. [20], [d] Data from this work.

Compound **Mn-1** was assessed as a catalytic precursor for the transfer hydrogenation (TH) of benchmark benzonitrile (**BN**) in the presence of 2-butanol both as the solvent and the hydrogen source. Transfer hydrogenation with 2-propanol was also performed but products from side-reactions such as hydration and aldol condensation were detected by GC-MS (Table S3 and Figures S11 and S12). The use of 2-BuOH thus favored only the formation of products from transfer hydrogenation of **BN**, namely, benzylamine (**BA**), N-sec-butylidenebenzylamine (**SBA**), and N-benzylidenebenzylamine (**BBA**) (Table 2).

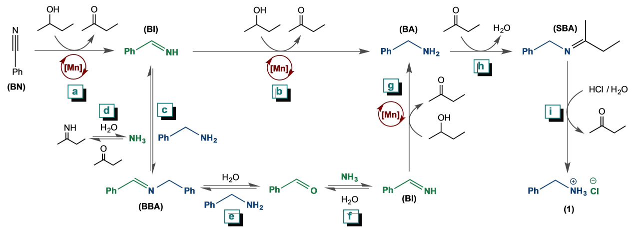
Initial experimental setup comprised the use of 5 mol% **Mn-1**, neat sec-butanol, and sub stoichiometric KO$^t$Bu (10 mol %). **Mn-1** showed moderate performance after 1 h at 100 °C, and complete substrate conversion upon 3 h (Table 2, entries 1 and 2). Selectivity was strongly favored toward the formation of N-sec-butylidenebenzylamine (**SBA**), which is the product of condensation between benzylamine and 2-butanone [Scheme 1, reaction (h)], stemming from dehydrogenation of 2-butanol. 2-butanone was detected in the crude reaction mixture by GC-MS at the end of catalysis. Acidic hydrolysis of the reaction mixture, and thus of **SBA** [Scheme 1, reaction (i)],

**Table 2.** TH of BN with 2-BuOH catalyzed by Mn-1[a]



| Entry | [%] mol Mn-1 | [%] mol KO$^t$Bu | t [h] | Conversion[b] [%] | **BA** [%] | **SBA** [%] | **BBA** [%] |
|---|---|---|---|---|---|---|---|
| 1 | 5 | 10 | 1 | 50 | n.d.[c] | 6 | 44 |
| 2 | 5 | 10 | 3 | > 99 | 30 (95)[d] | 69 | 1 |
| 3 | 5 | 20 | 3 | > 99 | 11 | 83 | 6 |
| 4[e] | 5 | 10 | 3 | > 99 | 60 (92)[d] | 37 | 3 |
| 5 | 4 | 10 | 3 | > 99 | 37 (94)[d] | 58 | 5 |
| 6 | 3 | 10 | 3 | > 99 | 18 (96)[d] | 77 | 4 |
| 7 | 2 | 10 | 3 | 84 | n.d.[c] | 14 | 70 |
| 8[f] | 3 | 10 | 3 | > 99 | 38 (96)[d] | 58 | 4 |
| 9 | 3 | 10 | 1 | 70 | 2 | 3 | 65 |
| 10[g] | 3 | 10 | 3 | 77 | 13 | 12 | 52 |
| 11[g] | 3 | 10 | 6 | 99 | 30 | 56 | 13 |
| 12 | 3 | 5 | 3 | 95 | 42 | 32 | 21 |
| 13 | 3 | 5 | 6 | > 99 | 23 | 70 | 7 |
| 14[h] | 3 | 10 | 3 | n.d.[i] | n.d.[c] | n.d.[c] | n.d.[c] |

[a] Reactions under an inert atmosphere. Conditions: BN (0.19 mmol), 2-BuOH (3 mL),[b] Determined by GC-MS, [c] Not detected, [d] In parentheses, yield of isolated benzylamine hydrochloride based on initial **BN**, [e] Reaction under an argon stream in an open flask, [f] Hg drop test, [g] T = 90 °C, [h] 3 mol% [Mn(CO)$_5$Br] was used instead of **Mn-1**, [i] Not determined.



**Scheme 1.** Formation and consumption of N-containing species during Mn-catalyzed TH of BN with 2-BuOH

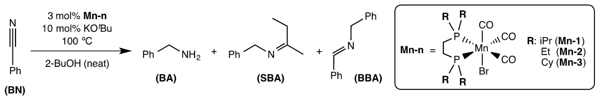
allowed for the isolation of the corresponding benzylamine hydrochloride (**1**) in an excellent yield of 95%, based on initial **BN** (Table 2, entry 2). Purity of 98% for **1** was determined by gas chromatography (Figures S17 and S18). Increasing the amount of base to 20 mol% did not affect **BN** conversion or product selectivity (Table 2, entry 3). The catalytic loading of **Mn-1** was lowered to 3 mol% still observing quantitative substrate conversion after 3 h, and excellent isolated yields (up to 96%) for the corresponding primary amine hydrochlorides (Table 2, entries 5 to 7). Performance of a mercury drop test suggested the catalytic system is homogeneous, as no significant change in conversion, selectivity or yield was observed (Table 2, entry 8). Attempts to lower both the temperature and the amount of base turned out detrimental for performance as longer reaction times (i.e. 6 h) were needed to complete **BN** conversion (Table 2, entries 10–13). Additionally, the need for the ancillary ligand (dippe) was demonstrated as no **BN** conversion was observed with the use of [MnBr(CO)$_5$] as a catalytic precursor (Table 2, entry 14).

With a set of optimal reaction conditions for the use of **Mn-1** as a catalytic precursor (Table 2, entry 6), we also studied the influence of the ancillary ligand in the model reaction. For this purpose, Mn(I) complexes fac-[(CO)$_3$Mn{R$_2$P(CH$_2$)$_2$PR$_2$}Br] [R = Et (depe = 1,2-bis(diethylphosphino)ethane, **Mn-2**); Cy (dcpe = 1,3-bis(dicyclohexylphosphino)ethane, **Mn-3**)] were synthesized from [MnBr(CO)$_5$] and the corresponding commercial diphosphines. FTIR (ATR) spectra for both compounds featured CO bands for a C$_s$ symmetry arrangement, also consistent with singlet signals observed in the corresponding $^{31}$P{$^1$H} NMR traces (Table 1, entries 2 and 3). Assessment of **Mn-2** and **Mn-3** as catalytic precursors is displayed in Table 3.

Compared with the use of dippe with compound **Mn-1** (Table 3, entry 1), reaction became sluggish with depe as ancillary ligand in **Mn-2** (Table 3, entries 2 and 3), whereas with dcpe (**Mn-3**), almost quantitative conversion was reached at the same 3 h, but with a higher amount of **BBA** (Table 3, entry 4). A practically identical product distribution to that for **Mn-1** was achieved with **Mn-3** at a longer reaction time (i.e. 6 h, Table 3, entries 1 and 5).

As displayed in Table 2, for a given catalytic loading of **Mn-1**, formation of the product of partial hydrogenation of benzonitrile (**BBA**), was favored at early stages during heating of the reaction mixture (i.e. 1 h) (Table 2, entries 1, 2, 6, and 9). Since formation of **BBA** is accompanied by production of ammonia, we hypothesized that in an open system, namely, a flask with a condenser under an argon stream, loss of NH$_3$ should direct selectivity toward the formation of **BBA**; however, no significant change neither in conversion nor selectivity was observed (Table 2, entry 4). A more detailed monitoring of the formation and consumption of N-containing species during catalysis was performed using 3 mol% **Mn-1**. Aliquots of a same reaction mixture were analyzed by GC-MS at the time intervals depicted in Figure 2. Accumulation of **BBA** reached its maximum after 1 h and started decreasing simultaneously with the formation of both **BA** and **SBA**, indicating once formed, **BA** condensates immediately with 2-butanone [Scheme 1, reaction

**Table 3.** Influence of the ancillary ligand in the Mn-catalyzed TH of BN with 2-BuOH.[a]



| Entry | R | t [h] | Conversion[b] [%] | **BA** [%] | SBA [%] | **BBA** [%] |
|---|---|---|---|---|---|---|
| 1 | $^i$Pr | 3 | > 99 | 18 | 77 | 4 |
| 2 | Et | 3 | 58 | 19 | 38 | 1 |
| 3 | Et | 6 | 89[c] | n.d.[d] | 85 | n.d.[d] |
| 4 | Cy | 3 | 94 | 31 | 46 | 17 |
| 5 | Cy | 6 | > 99 | 20 | 75 | 5 |

[a] Reactions under an inert atmosphere. Conditions: BN (0.19 mmol), **Mn-n** (5.7 μmol), KO$^t$Bu (0.019 mmol), 2-BuOH (3 mL), [b] Determined by GC-MS, [c] 4% of benzamide was determined, [d] Not detected.

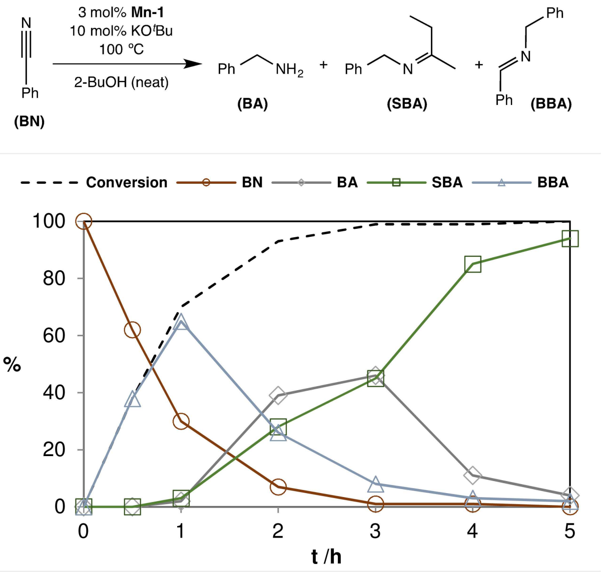


**Figure 2.** Monitoring (GC-MS) of the formation and consumption of N-containing species during the TH of BN with 2-BuOH catalyzed by Mn-1.

(h)]. At 3 h, **BA** reached its highest concentration and continued to condensate with ketone forming **SBA**. At longer reaction times (i.e. 3 to 5 h) condensation became predominant yielding a mixture containing 94% **SBA** after 5 h. Reversibility between the formation of **BBA** and **BA** is proposed to happen as depicted in Scheme 1.

Among the ways to control selectivity toward the formation of **BA** over **BBA**, is the use of ammonia or metal hydroxides.[22] In this case both alternatives are plausible, namely, since in situ produced $NH_3$ remains in solution, even in an open system (vide supra), it can perform aminolysis of **BBA** [Scheme 1, back reaction (c)] to yield **BA** back and intermediate benzylideneamine (**BI**). Additionally, ammonia might react reversibly with 2-butanone to yield 2-butanimine [Scheme 1, reaction (d)], but the latter was not detected during monitoring by CG-MS. On the other hand, water produced by condensation between **BA** and 2-butanone [Scheme 1, reaction (h)] can perform hydrolysis of **BBA** under basic conditions, meaning it is held by hydroxide species, to yield benzaldehyde [Scheme 1, forward reaction (e)], which regenerates intermediate **BI** upon reaction with ammonia [Scheme 1, forward reaction (f)]. Hydrolysis pathway is more likely to enhance **BBA** consumption since its concentration stops increasing only after water starts to form (Figure 2, t > 1 h).

The title transfer hydrogenation was investigated with other nitriles (Figure 3). Optimized reaction conditions for **BN** were successfully extended to aromatic nitriles bearing electron-releasing substituents. Therefore, p-methoxy (**2**) and p-methyl (**3**) benzylamine hydrochlorides were obtained in 89 and 92% yield, respectively. 4-ethynylbenzonitrile was assessed under hydrogenation conditions but the nitrile moiety was not converted neither to imine nor amine functionality. Instead, C–C triple bond was hydrogenated unselectively to the corresponding vinyl (6%) and ethyl (7%) groups with low conversion (13%) of the substrate as determined by CG-MS. For aromatic nitriles bearing electron-withdrawing substituents, transfer hydrogenation did not perform well under the same reaction conditions used for electron-rich aromatic substrates. For instance, model p-trifluoromethyl benzonitrile was converted to the corresponding amine hydrochloride **5** in 39% isolated yield, under more forcing conditions (i.e. 5 mol% **Mn-1**, 22 h). Despite this fair isolated yield, no reactions leading us to suspect about low tolerance to $CF_3$ group were observed, as

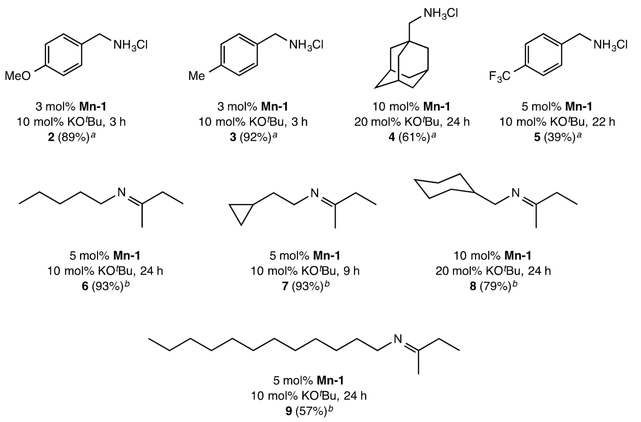


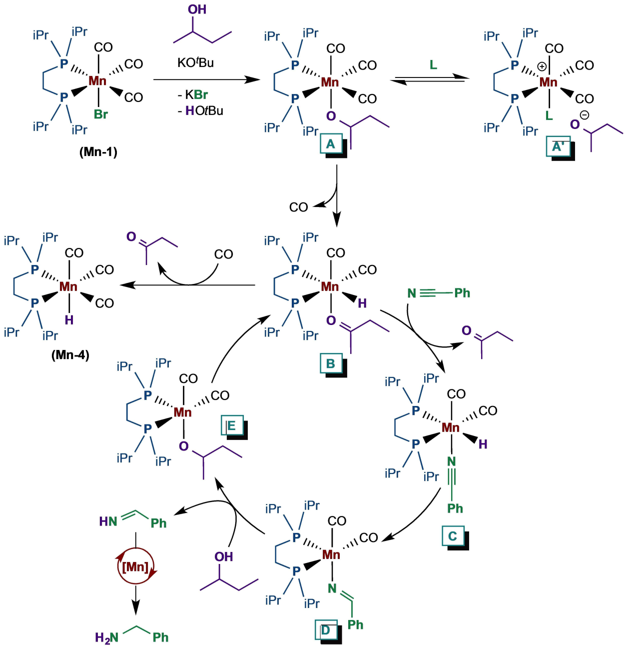
**Figure 3.** Substrate scope for the TH of nitriles with 2-BuOH catalyzed by Mn-1. Reactions under an inert atmosphere. Conditions: Nitrile (0.19 mmol), 2-BuOH (3 mL), 100 °C. (a) Yields are for isolated amine hydrochlorides. (b) Yields determined by area normalization in GC-MS.

displayed in Table S5. Changes in reactivity toward TH between electron-rich and electron-deficient aromatic nitriles might rather be a direct consequence of the differences in the coordinating character of the substrates as explained later in the text.

On the other hand, aliphatic nitriles were also challenging to reduce, probably due to increased steric hindrance if compared with para-substituted electron-rich aromatic nitriles. In the case of relevant adiponitrile, which was successfully hydrogenated in our previous report,[18] a slow and unselective reaction was observed under the transfer hydrogenation conditions used in this work (i.e. 3 mol% **Mn-1**, 10 mol% KO$^t$Bu, 3 h, 100 °C, 3 mL 2-BuOH). In this case, 27% conversion was observed with selectivity of 48, 19, and 33% toward hemi reduction, cyclization, and condensation products (See Figures S38-S41 for details). When the reaction time was increased to 28 h, several unidentified products were detected by GC-MS; to note, no hexanediamine could be detected. Regarding aliphatic mono nitriles, catalytic loadings of 5 to 10 mol% **Mn-1** were necessary to observe good to excellent yields for compounds **6** to **8** (79–93%). In the case of lauronitrile, which was hydrogenated to N-sec-butylidene-n-dodecyl amine (**9**), a maximum yield of 57% was observed regardless of the catalytic loading used (either 5 or 10 mol% **Mn-1**). Finally for 1-adamantanecarbonitrile, yet also forcing conditions were needed for TH, we were able to isolate the corresponding amine hydrochloride (**4**) in 61% yield, since it was the only product derived from TH of aliphatic nitriles for which acidic hydrolysis at room temperature performed well. For the rest of the nitriles, only yields based on area normalization by GC-MS could be determined, as depicted in Figure 3.

Considering a mechanistic proposal for the title TH reaction, we hypothesized the use of KO$^t$Bu would allow for the creation of a vacant site at the Mn-coordination sphere in the 18e complex, fac-[(CO)$_3$Mn(dippe)Br] (**Mn-1**), upon metathesis to yield KBr precipitating out of the reaction mixture (Scheme 2, from **Mn-1** to **A**).

$^1$H NMR analysis of a mixture containing **Mn-1** and KO$^t$Bu in a molar ratio 3:10, in neat 2-BuOH heated at 100 °C during 1 h, featured formation of fac-[(CO)$_3$Mn(dippe)H] (**Mn-4**) (signature signal at $\delta_H$ −9.24, t, $^2J_{HP}$ = 48 Hz),23 and at least one additional hydride-species (Figure S59). The corresponding $^{31}$P{$^1$H} NMR spectrum displayed signature signals for **Mn-4** ($\delta_P$ 115.9),[23] free dippe ($\delta_P$ 9.2), and no signal for **Mn-1**, indicating this is consumed in the presence of KO$^t$Bu (Figure S60). Detection of hydride species in this mixture also indicates after creation of a vacant site, β-hydride elimination takes place, likely as depicted in Scheme 2 (from **A** to **B**). As depicted in Scheme 2, participation of **Mn-4** is not considered during catalytic turnover since previously, such compound proved to be inert in this type of reactions.[18]



**Scheme 2.** Mechanistic proposal for the TH of BN with 2-BuOH catalyzed by Mn-1.

On the other hand, $^1$H NMR analysis of a mixture containing **Mn-1**, KO$^t$Bu, 2-BuOH, and PhCN in a molar ratio 1:1:1:3 in THF-d$_8$, after heating at 100 °C for 1 h (Figure S64), featured signals for **Mn-4**, and an additional hydride whose chemical shift and multiplicity matched the one observed during our previous investigations.[18] Based both on the $^2J_{HP}$ values (103 Hz, 51 Hz) and the intensity of the peaks observed in Figure S64 (For analysis of multiplets see Figure S65 and Table S6, entry 3), signal at $\delta_H$ −8.7 is likely a double of doublets (dd), consistent with structures of the type **B** or **C** in Scheme 2. To note is the fact that in structures like **B** or **C**, any other neutral ligand (L), such as ammonia, THF-d$_8$, benzylamine, **BBA**, or **SBA**, might coordinate to the Mn-core competing for the vacant site. Equatorial arrangement in these complexes would feature J values such as $^2J_{HP,cis} \neq {}^2J_{HP,trans}$, matching the data obtained from the corresponding $^1$H NMR spectrum.

$^{31}$P{$^1$H} NMR trace for the same mixture displayed signature signals for unreacted **Mn-1** at $\delta_P$ 80.5 (Table 1, entry 1), free dippe ($\delta_P$ 9.2), and **Mn-4** ($\delta_P$ 115.9) (Figure S67). Also a broad signal was observed centered at $\delta_P$ 88.6, that is typically a $\delta_P$ value around which signals for species containing the "fac-[(CO)$_3$Mn(dippe)(L)]$^+$" cation are observed in THF-d$_8$ (L = neutral ligand; e.g. PhCN $\delta_P$ 87, $H_2O$ $\delta_P$ 86.8, PhC(O)NH$_2$ $\delta_P$ 87.8, 2-BuOH $\delta_P$ 86).[18,20] In this case, alkoxides might account as counter ions for stabilizing fac-[(CO)$_3$Mn(dippe)(L)]$^+$ (L = PhCN or 2-BuOH) (Scheme 2, **A′**). Signals around $\delta_H$ 8.6 in $^1$H NMR (Figure S63) support this proposal since they can be assigned to coordinated PhCN.[20] This observation is consistent with formation of a vacant site due to reaction between **Mn-1** and KO$^t$Bu in the presence of neutral ligands. GC-MS analysis of this reaction mixture revealed the presence of PhCN and HO$^t$Bu, confirming deprotonation of 2-BuOH by KO$^t$Bu, and suggesting fac-[(CO)$_3$Mn(dippe)(PhCN)](2-butoxide) (Scheme 2, **A′**) might be present in solution. Detection of **BBA** and 2-butanone also by GC-MS confirmed the transfer hydrogenation activity of the model reaction (Figures S73–S75).

Further NMR monitoring of the same reaction mixture was performed upon heating at 100 °C for additional 2 h. Recorded $^{1}H$ NMR spectrum featured signals for **Mn-4** and the doublet of doublets aforementioned (Figure S69). Since once formed, **Mn-4** remains unaltered in solution,[18] intensity for its corresponding triplet was compared with the intensity of the doublet of doublets, likely stemming from a structure like **B** or **C** (Scheme 2), After heating for 1 and 3 h (Figure S71 and Table S6), the concentration of the latter hydride decreased. The corresponding $^{31}P\{^{1}H\}$ NMR spectra displayed at least two couples of multiplets that might account for species of the type **B** or **C**, such as $\delta_{\text{P,cis to H}} \neq \delta_{\text{P,trans to H}}$ (Figures S67 and S70). When compared with the intensity of the signature signal for inert **Mn-4**, the aforementioned signals exhibited the same behavior observed for their presumed counterpart in the corresponding $^{1}H$ NMR spectra (i.e. intensity of the presumed signals for active hydrides decreased, see also Figure S72), so supporting the proposal of species of the type **B** or **C** participating during catalytic turnover, as depicted in Scheme 2.

Formation of **C** triggers the actual hydrogenation process by a sequence of nitrile insertion into an Mn-hydride bond (Scheme 2, from **C** to **D**), followed by electrophilic abstraction to yield benzylideneamine and **E**, which after β-hydride elimination, regenerates the proposed catalytically active species **B**.

Based on NMR experiments (Figures S67 and S70), although ancillary phosphine (dippe) is lost during catalytic turnover, leading to an amount of catalyst decomposition, its participation cannot be ruled out based on control experiment displayed in Table 2 (entry 14). Moreover, this helps explaining why a relatively high catalytic loading is necessary to observe good performance for the TH reaction (compare entries 6 and 7 in Table 2), especially when using nitriles that, based on their steric or electronic features, are less prone to coordinate to the manganese-core (Figure 3).

Finally, regarding the ancillary ligand performance, since dippe, depe, and dcpe exhibited no significant differences in their electronic behavior in the corresponding **Mn-n** compounds ($\nu_{CO}$ values in Table 1, entries 1 to 3), the less steric hindrance inherent to Et substituents in **Mn-2** compared to $^{i}Pr$ in **Mn-1** or Cy in **Mn-3**, seems to play a role in deactivation, probably favoring ligand dissociation, leading to partial loss of catalytic performance with the use of **Mn-2** as a catalytic precursor (Table 3, entries 1 to 5).

## 3. Conclusions

We performed the transfer hydrogenation (TH) of benzonitrile with 2-butanol both as the hydrogen source and the solvent, using fac-[(CO)$_3$Mn(dippe)Br] (**Mn-1**) as a catalytic precursor (3 mol%) to favor the formation of N-sec-butylidenebenzylamine, which after acidic hydrolysis allowed for the isolation of benzylamine hydrochloride in excellent yield (96%).

This system featured reversible formation of the partial hydrogenation product **BBA** likely due to hydrolysis under basic conditions followed by aldehyde amination. Substoichiometric base (10 mol% KO$^{t}$Bu) proved to participate in the creation of a vacant site in 18e complex **Mn-1**, and in deprotonation of the alcohol, needed to start the actual TH process.

Besides inert compound fac-[(CO)$_3$Mn(dippe)H] (**Mn-4**), detection of other Mn-hydrides led us to propose in situ formation of coordinatively unsaturated Mn-hydride compounds by β-elimination, performing catalytic turnover. Catalyst deactivation was proposed to depend on ancillary ligand dissociation, based on the performance of catalytic precursors fac-[(CO)$_3$Mn{R$_2$P(CH$_2$)$_2$PR$_2$}Br] [R = Et (**Mn-2**), Cy (**Mn-3**)].

TH reported herein is sensitive to coordinating properties of the substrates. The most challenging nitriles exhibited electronic or steric features hindering coordination so that they compete with catalyst deactivation. For these substrates, more forcing conditions (i.e. higher base or catalytic loading) are needed to observe very good to moderate yields.

Current work in our group is underway on the use of these Mn compounds in hydrogenation of other relevant substrates, and on a more detailed mechanistic understanding of the reactions presented herein.

## Experimental Section

### General Considerations

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques in an inert-gas/vacuum double manifold or under an argon atmosphere (Praxair 99.998) in an MBraun Unilab Pro SP glovebox (&λτ“;1 ppm $H_2O$ and $O_2$). All liquid reagents were purchased as reagent grade and degassed before use. Anhydrous benzonitrile and the rest of the nitriles were purchased from Aldrich and stored in the glovebox before use. Regular toluene (J. T. Baker, reagent grade) was dried and distilled from sodium/benzophenone. Regular isopropanol (J. T. Baker, reagent grade) was dried and distilled from manganese/iodine. Regular THF and hexanes (J. T. Baker) were dried and degassed in an MB-SPS-800. Solvents were stored in the glovebox before use. Anhydrous sec-butanol (Aldrich, 99.5%) was stored in the glovebox as received. Deuterated solvents (THF-d$_8$, DMSO-d$_6$, $CDCl_3$, $D_2O$) were purchased from Cambridge Isotope Laboratories. THF-d$_8$ and DMSO-d$_6$ were stored over 3 Å molecular sieves inside the glovebox before use. NMR spectra were recorded at room temperature on the following spectrometers: Bruker Avance 300 MHz and Bruker Avance III 400 MHz. Wilmad (0.38 mm) NMR tubes equipped with a J. Young valve were used for analyzing the samples. NMR signals were processed using the Mnova software (MestreLab Research). $^{1}H$ chemical shifts ($\delta_H$) are reported in ppm and relative to the residual proton resonance of the solvent: THF-d$_8$ 3.58 (1), 1.72 (1); $CDCl_3$ 7.26 (1). $^{31}P\{^{1}H\}$ NMR chemical shifts ($\delta_P$) are reported in ppm and relative to external 85% $H_3PO_4$. Coupling constants (J values) are given in Hz. The following abbreviations are used for the NMR data: s = singlet; d = doublet; t = triplet, m = multiplet; and br = broad. Elemental analysis experiments were performed on a Perkin Elmer 2400. FTIR (ATR) analyses were performed on a Perkin-Elmer Spectrum 400 (4000–400 cm$^{-1}$). GC-MS determinations were performed using an Agilent Technologies G3171A equipped with the following column: 5% phenylmethylsilicone, 30 m × 0.25 mm × 0.25 μm. The $^{i}Pr_2P(CH_2)_2P^{i}Pr_2$ (dippe) ligand was synthesized from $Cl_2P(CH_2)_2PCl_2$ (Aldrich) and a 2.0 M THF solution of $^{i}PrMgCl$ (Aldrich).[24] The ligands $Cy_2P(CH_2)_2PCy_2$ (dcpe) and $Et_2P(CH_2)_2PEt_2$ (depe) were purchased from Aldrich and Strem Chemicals, respectively, and stored in the glovebox as received. [MnBr$(CO)_5$] (Strem Chemicals) was purified by sublimation at 70 °C under reduced pressure (0.005 mmHg) and stored in the glovebox before use. Complex **Mn-1** was synthesized from [MnBr$(CO)_5$] and dippe as reported previously.[20]

Synthesis and characterization of fac-[$(CO)_3$Mn{$R_2P(CH_2)_2PR_2$}(Br)] [R = Et (depe, **Mn-2**), Cy (dcpe, **Mn-3**)].

In a Schlenk flask, 0.18 mmol (50 mg) of freshly sublimed [MnBr$(CO)_5$] for **Mn-2** or 0.38 mmol (100 mg) for **Mn-3** were suspended in toluene (3 mL). To this mixture, a solution of depe (41.3 mg, 0.20 mmol) or dcpe (169.0 mg, 0.40 mmol) in toluene (5 mL) was added dropwise via syringe, allowing the evolved CO to vent to the inert gas/ vacuum double manifold. A condenser was adapted to the Schlenk flask and the reaction mixture was refluxed for 60 minutes. After that, the yellow solution was evaporated under reduced pressure. The solid residue was washed with hexanes (3 × 2/3 mL) at room temperature and dried under vacuum for 1 h. Toluene was added to form a saturated solution that was stored at −30 °C for 48 h. Crystals of **Mn-2** were triturated and washed with hexane (3 × 2/3 mL) and dried under vacuum for 6 h. In the case of crystals of **Mn-3**, last step was repeated 3 times. **Mn-2** and **Mn-3** were obtained as yellow powders. **Mn-2** (59 mg, 76 %). $^1$H (400 MHz, $CDCl_3$) 2.30–2.13 (m, 1H, $CH_2$), 2.06–1.71 (m, 2H, 2$CH_2$), 1.21 (sept, J = 7.6 Hz, 3H, 2$CH_3$). $^{31}$P{$^1$H} (162 MHz) 72.0 (s). FTIR (ATR) $\nu_{C\text{-}H}$ (cm$^{-1}$) 2967.79 m, 2936.86 m, 2910.82 w, 2879.75 w; $\nu_{C\text{-}O}$ (cm$^{-1}$) 2001.20 s, 1934.51 s, 1910.28 s. Anal. Calcd for **Mn-2**, $C_{13}H_{24}BrMnO_3P_2$: C, 36.73; H, 5.69. Found: C, 36.91; H, 5.76. **Mn-3** (89 mg, 69 %). $^1$H (400 MHz, $CDCl_3$) 2.55–2.45 (m, 1H, CH), 2.18 (d, J = 11.6 Hz, 1H, CH), 2.02–1.70 (m, 12H, 6$CH_2$), 1.63–1.40 (m, 3H, $CH_2$, CH), 1.34–1.26 (m, 6H, 3$CH_2$), 0.89-0.86 (m, 1H, CH). $^{31}$P{$^1$H} (162 MHz) 72.5 (s). FTIR (ATR) $\nu_{C\text{-}H}$ (cm$^{-1}$) 2920.71 s, 2850.90 s; $\nu_{C\text{-}O}$ (cm$^{-1}$) 2007.38 s, 1941.44 s, 1897.46 s.

Synthesis of benzylamine hydrochloride (**1**) via transfer hydrogenation of benzonitrile with 2-butanol catalyzed by **Mn-1** and subsequent acidic hydrolysis with HCl.

In the glovebox, a 2-BuOH solution of benzonitrile (20 mg, 0.19 mmol) was added to a 2-BuOH suspension of **Mn-1** (2.8 mg, 5.7 μmol). This mixture was added to a 2-BuOH solution of KO$^t$Bu (2.2 mg, 0.019 mmol) and stirred manually. The yellow solution was transferred to a 25 mL Schlenk tube (Synthware Glass) (3 mL 2-BuOH total volume). The reaction mixture was stirred into an oil bath at 100 °C during 3 h. Then, the content of the flask was exposed to air and filtered through Celite® 545 (Merck) to remove a white precipitate. To the filtrate were added 0.4 mL of an aqueous HCl (1 M) solution and stirred for 2 h at room temperature. Solvent and volatiles were removed by heating and the white residue was washed with fresh hexanes (3 × 1 mL) and ethyl acetate (3 × 1 mL). **1** was obtained as a white crystalline powder (26.8 mg, 96 %). MS (EI): m/z 106 [M−1 (100)], 107 [M$^+$ (56)], 108 [M + 1 (4)].

Synthesis of amine hydrochlorides **2–5** via transfer hydrogenation of nitriles with 2-butanol catalyzed by **Mn-1** and subsequent acidic hydrolysis with HCl.

In the glovebox, 2-BuOH solutions of p-methoxybenzonitrile (p-MeOBN, 25.3 mg, 0.19 mmol), p-tolunitrile (p-MeBN) (22.3 mg, 0.19 mmol), 1-adamantanecarbonitrile (1-AdCN, 31.3 mg, 0.19 mmol), or p-trifluoromethylbenzonitrile (p-$CF_3$BN, 32.5 mg, 0.19 mmol) were added to 2-BuOH suspensions of **Mn-1** (2.8 mg, 5.7 μmol for p-MeOBN and p-MeBN; 9.3 mg, 0.019 mmol for 1-AdCN; and 4.7 mg, 9.5 μmol for p-$CF_3$BN). The mixtures were added to 2-BuOH solutions of KO$^t$Bu (2.2 mg, 0.019 mmol for aromatic nitriles and 4.4 mg, 0.038 mmol for 1-AdCN) and stirred manually. The yellow solutions were transferred to 25 mL Schlenk tubes (Synthware Glass) (3 mL 2-BuOH total volume each). The reaction mixtures were stirred into an oil bath at 100 °C during 3, 22, or 24 h. The content of each flask was exposed to air and filtered through Celite® 545 (Merck) to remove white precipitates. To each filtrate were added 0.4 mL of an aqueous HCl (1 M) solution and stirred for 2 h in the case of aromatic nitriles, and overnight for the aliphatic one, at room temperature. Solvent and volatiles were removed by heating and the white residues were washed with fresh hexanes (3 × 1 mL) and ethyl acetate (3 × 1 mL). Amine hydrochlorides were obtained as white crystalline powders. **2** (29.8, 89 %). MS (EI): m/z 136 [M−1 (100)], 137 [M$^+$ (49)], 138 [M + 1 (4)]. **3** (22.3, 92 %). MS (EI): m/z 120 [M−1 (100)], 121 [M$^+$ (42)], 122 [M + 1 (4)]. **4** (23.9, 61 %). MS (EI): m/z 164 [M−1 (11)], 165 [M$^+$ (100)], 166 [M + 1 (12)]. **5** (15.7 mg, 39 %). MS (EI): m/z 174 [M−1 (100)], 175 [M$^+$ (53)], 176 [M + 1 (4)].

Transfer hydrogenation of valeronitrile, cyclopropylacetonitrile, cyclohexanecarbonitrile, and lauronitrile with 2-butanol catalyzed by **Mn-1**.

In the glovebox, 2-BuOH solutions of valeronitrile (ValCN, 16.1 mg, 0.19 mmol), cyclopropylacetonitrile (cPrMeCN, 15.4 mg, 0.19 mmol), cyclohexanecarbonitrile (CyCN, 20.7 mg, 0.19 mmol), or lauronitrile (LauCN, 34.5 mg, 0.19 mmol) were added to 2-BuOH suspensions of **Mn-1** (4.7 mg, 9.5 μmol; and 9.3 mg, 0.019 mmol for CyCN). The mixtures were added to 2-BuOH solutions of KO$^t$Bu (2.2 mg, 0.019 mmol; and 4.4 mg, 0.038 mmol for CyCN) and stirred manually. The yellow solutions were transferred to 25 mL Schlenk tubes (Synthware Glass) (3 mL 2-BuOH total volume each). The reaction mixtures were stirred into an oil bath at 100 °C during 9 or 24 h. The content of each flask was exposed to air and filtered through Celite® 545 (Merck) to remove white precipitates. 1 μL of aliquot of each reaction crude was analyzed by GC-MS to determine the conversion of nitrile and the yield of each TH product by area normalization. Attempts to isolate the corresponding amine hydrochlorides at room temperature were unsuccessful for these substrates. **6** (93 %) MS (EI): m/z 140 [M−1 (100)], 141 [M$^+$ (62)]. **7** (93 %) MS (EI): m/z 138 [M−1 (100)], 139 [M$^+$ (84)]. **8** (79 %) MS (EI): m/z 166 [M−1 (100)], 167 [M$^+$ (94)], 168 [M + 1 (12)]. **9** (57 %) MS (EI): m/z 238 [M−1 (100)], 239 [M$^+$ (78)], 240 [M + 1 (17)].

## X-Ray Structure Determination

Suitable single crystal of **Mn-1** mounted on a glass fiber were studied with Oxford Diffraction Gemini "A" diffractometer with a CCD area detector ($\lambda_{MoK\alpha}$ = 0.71073 Å, monochromator: graphite) source equipped with a sealed tube X-ray source at 130 K. Unit cell constants were determined with a set of 15/3 narrow frame/runs with1° in ω scans. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans[25a] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by a global refinement of 5016 reflections with 3.759 < θ < 26.190°. Collected data were corrected for absorbance by using analytical numeric absorption correction.[25b] Structure solution and refinement were carried out with the SHELXS-2014[25c] and SHELXL-2014;[25d] Wingx v2014.1[25e] software was used to prepare material for publication. Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 – F_c^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C–H = 0.98–1.0 Å and with -Uiso(H) = 1.2Ueq(C) for methine and methylene groups and Uiso(H) = 1.5Ueq(C) for methyl groups. C23, C24, C25 and C23B, C24B, C25B are disordered over two sites with occupancies 0.77:0.23, on the other hand C26, C27 C28 and C26B, C27B, C28B are disordered over two sites with occupancies

0.72:0.28. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary material number CCDC 1937366. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail:deposit@ccdc.cam.ac.uk.

## Supporting Information

Featuring crystallographic data for complex **Mn-1** and detailed multinuclear NMR spectra for the synthesized compounds and for the monitoring of reactions described in the main text. Also includes GC traces for catalytic reactions, and mass spectra for imines detected in the crudes of reaction, and for isolated amine hydrochlorides.

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## *Conflict of Interest*

The authors declare no conflict of interest.

**Keywords:** Amines · catalysis · manganese · nitriles · transfer hydrogenation

[1] a) S. Gomez, J. A. Peters, T. Maschmeyer, *Adv. Synth. Catal.* **2002**, *344*, 1037–1057; b) H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, *Adv. Synth. Catal.* **2003**, *345*, 103–151; c) S. Werkmeister, K. Junge, M. Beller, *Org. Process Res. Dev.* **2014**, *18*, 289–302; d) D. B. Bagal, B. M. Bhanage, *Adv. Synth. Catal.* **2015**, *357*, 883–900.

[2] a) D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621–6686; b) P. Häussinger, R. Lohmüller, A. M. Watson, Hydrogen 2. Production. Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany., 2011; DOI: 10.1002/14356007.o13_o03

[3] a) P. Roose, K. Eller, E. Henkes, R. Rossbacher, H. Höke. Amines, Aliphatic. Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2015; DOI: 10.1002/14356007.a02_001.pub2; b) L. Heuer. Benzylamine. Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2006; DOI: 10.1002/14356007.a04_009.pub2.

[4] G. R. Brown, A. J. Foubister, *Synthesis* **1982**, *12*, 1036–1037.

[5] a) R. C. Mebane, D. R. Jensen, K. R. Rickerd, B. H. Gross, *Synth. Commun.* **2003**, *33*, 3373–3379; b) X. Chen, S. Zhou, C. Qian, *Arkivoc* **2012**, 128–136.

[6] a) M. Vilches-Herrera, S. Werkmeister, K. Junge, A. Börner, M. Beller, *Catal. Sci. Technol.* **2014**, *4*, 629–632; b) L. Liu, J. Li, Y. Ai, Y. Liu, J. Xiong, H. Wang, Y. Qiao, W. Liu, S. Tan, S. Feng, K. Wang, H. Sun, Q. Liang, *Green Chem.* **2019**, *21*, 1390–1395.

[7] a) H. Göksu, S. F. Ho, Ö. Metin, K. Korkmaz, A. Mendoza-García, M. S. Gültekin, S. Sun, *ACS Catal.* **2014**, *4*, 1777–1782; b) L. Liu, Y. Liu, Y. Ai, J. Li, J. Zhou, Z. Fan, H. Bao, R. Jiang, Z. Hu, J. Wang, K. Jing, Y. Wang, Q. Liang, H. Sun, *iScience* **2018**, *8*, 61–73.

[8] J. Long, K. Shen, *ACS Catal.* **2017**, *7*, 275–284.

[9] a) S. Werkmeister, C. Bornschein, K. Junge, M. Beller, *Chem. Eur. J.* **2013**, *19*, 4437–4440; b) S. Werkmeister, C. Bornschein, K. Junge, M. Beller, *Eur. J. Org. Chem.* **2013**, 3671–3674.

[10] Z. Shao, S. Fu, M. Wei, Z. Zhou, Q. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 14653–14657; *Angew. Chem.* **2016**, *128*, 14873–14877.

[11] a) V. H. Mai, G. I. Nikonov, *Organometallics* **2016**, *35*, 943–949; b) I. D. Alshakova, B. Gabidullin, G. I. Nikonov, *ChemCatChem.* **2018**, *10*, 4860–4869; c) V. H. Mai, S. H. Lee, G. I. Nikonov, *ChemistrySelect* **2017**, *2*, 7751–7757.

[12] a) D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* **2016**, *308*, 191–235; b) J. R. Carney, B. R. Dillon, S. P. Thomas, *Eur. J. Org. Chem.* **2016**, 3912–3929; c) W. Liu, L. Ackermann, *ACS Catal.* **2016**, *6*, 3743–3752; d) B. Maji, M. K. Barman, *Synthesis* **2017**,*49*, 3377–3393; e) M. Garbe, K. Junge, M. Beller, *Eur. J. Org. Chem.* **2017**, 4344–4362; f) F. Kallmeier, R. Kempe, *Angew. Chem. Int. Ed.* **2018**, *57*, 46–60; *Angew. Chem.* **2018**, *130*, 48–63; g) N. Gorgas, K. Kirchner, *Acc. Chem. Res.* **2018**, *51*, 1558–1569; h) A. Mukherjee, D. Milstein, *ACS Catal.* **2018**, *8*, 11435–11469; i) G. A. Filonenko, R. van Putten, E. J. Hensen, E. A. Pidko, *Chem. Soc. Rev.* **2018**, *47*, 1459–1483; j) Y. Hu, B. Zhou, C. Wang, *Acc. Chem. Res.* **2018**, *51*, 816–827; k) S. Waiba, M. K. Barman, B. Maji, *Synlett* **2019**, *30*, 12–20.

[13] A. Brzozowska, L. M. Azofra, V. Zubar, I. Atodiresei, L. Cavallo, M. Rueping, O. El-Sepelgy, *ACS Catal.* **2018**, *8*, 4103–4109.

[14] K. Z. Demmans, M. E. Olson, R. H. Morris, *Organometallics* **2018**, *37*, 4608–4618.

[15] a) J. Schneekönig, K. Junge, M. Beller, *Synlett* **2019**, *30*, 503–507; b) N. V. Shvydkiy, O. Vyhivskyi, Y. V. Nelyubina, D. S. Perekalin, *ChemCatChem* **2019**, *11*, 1602–1605.

[16] a) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J.-B. Sortais, *Org. Lett.* **2017**, *19*, 3656–3659; b) O. Ferraté-Martínez, C. Werlé, G. Franciò, W. Leitner, *ChemCatChem* **2018**, *10*, 4514–4518; c) K. Ganguli, S. Shee, D. Panja, S. Kundu, Dalton. Trans. DOI 10.1039/c8dt05001e; d) A. Dubey, S. M. W. Rahaman, R. R. Fayzullin, J. R. Khusnutdinova, *ChemCatChem* DOI 10.1002/cctc.201900358.

[17] D. Wei, A. Bruneau-Voisine, M. Dubois, S. Bastin, J.-B. Sortais, *ChemCatChem* DOI 10.1002/cctc.201900314.

[18] J. A. Garduño, J. J. García, *ACS Catal.* **2019**, *9*, 392–401.

[19] S. Weber, B. Stöger, K. Kirchner, *Org. Lett.* **2018**, *20*, 7212–7215.

[20] J. A. Garduño, A. Arévalo, M. Flores-Alamo, J. J. García, *Catal. Sci. Technol.* **2018**, *8*, 2606–2616.

[21] 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.* **2017**, *56*, 7531–7534; *Angew. Chem.* **2017**, *129*, 7639–7642.

[22] S. Gomez, J. A. Peters, T. Maschmeyer, *Adv. Synth. Catal.* **2002**, *344*, 1037–1057.

[23] Compare data with Ref. 18.

[24] F. G. N. Cloke, V. C. Gibson, M. L. H. Green, V. S. B. Mtetwa, K. Prout, *J. Chem. Soc. Dalton Trans.* **1988**, 2227–2229.

[25] a) Agilent CrysAlis PRO and CrysAlis RED. Agilent Technologies, Yarnton, England, **2013**; b) R. C. Clark, J. S. Reid, *Acta Crystallogr.* **1995**, *A51*, 887–897; c) G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3–8; d) G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8; e) L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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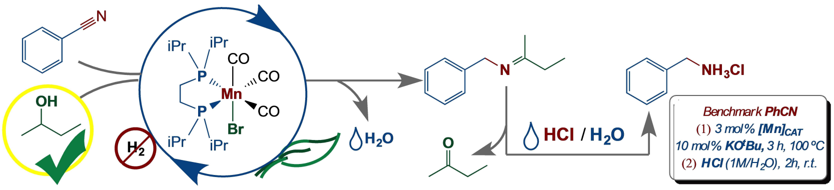

**Mn does the trick**: The first manganese-catalyzed homogeneous transfer hydrogenation of nitriles is reported herein. Benzonitrile was converted to benzylamine and N-sec-butylidenebenzylamine using 3 mol% of a Mn(I) precatalyst, 10 mol% of base, and neat 2-butanol as the hydrogen source. After acidic hydrolysis benzylamine hydrochloride was isolated in 96% yield. Substrate scope includes preparation of 4 amine hydrochlorides, and 5 alkylidene aliphatic amines. Mechanistic studies featured Mn-hydride species performing the elementary steps.

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**Manganese-Catalyzed Transfer Hydrogenation of Nitriles with 2-Butanol as the Hydrogen Source**