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## Manganese – new prominent actor in transfer hydrogenation catalysis

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**Abstract:** Transfer hydrogenation processes catalyzed by manganese organometallic complexes are comprehensively reviewed. The reaction scope includes the reduction of aldehydes, ketones, imines, polyaromatic nitrogen heterocycles, esters, nitriles and semi-hydrogenation of internal alkynes. Special attention is devoted to ligand design for Mn-catalyzed asymmetric transfer hydrogenation of prochiral ketones leading to enantiomerically-enriched alcohols.

**Keywords:** Transfer hydrogenation, Manganese, Bidentate ligands, Pincer ligands, Asymmetric catalysis

### 1. Introduction.

Transfer hydrogenation (TH) is a reduction process that involves hydrogen donors (H<sub>2</sub>-donor) such as primary and secondary alcohols (typically isopropanol), diols (such as ethyleneglycol), formic acid, and aminoboranes to cite a few, instead of molecular H<sub>2</sub>. For this reason, TH is considered as a safer alternative to direct hydrogenation but also easier to operate since it does not require any use of high-pressure equipment such as autoclaves or Fischer porter vessels.

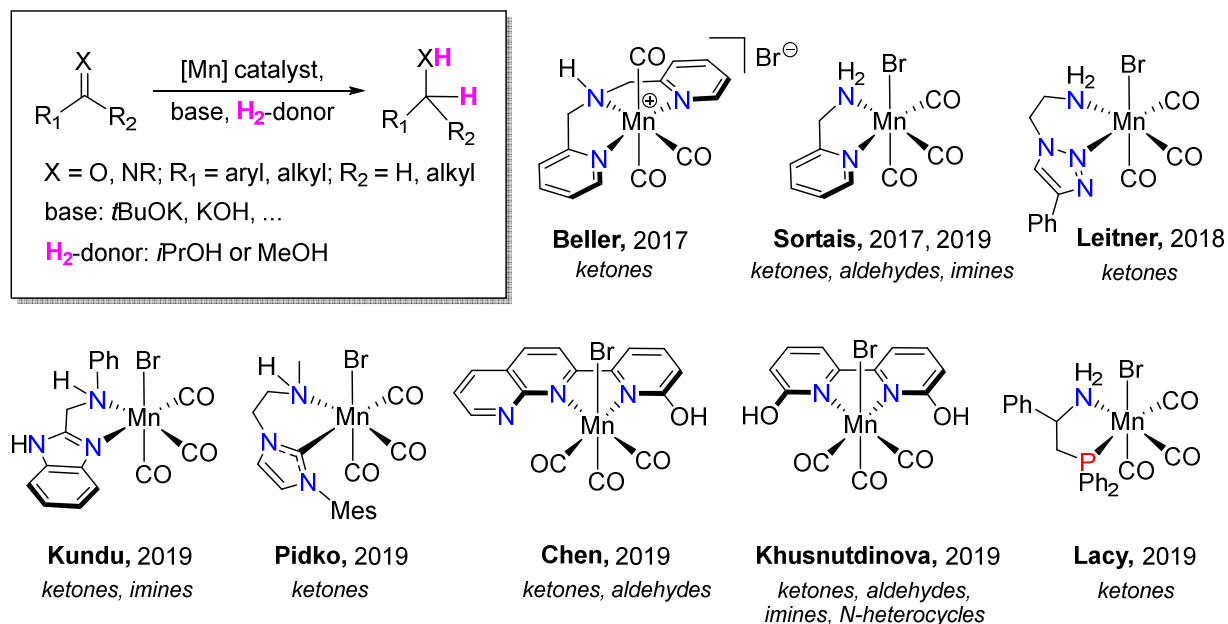
The first example of late-transition metal-catalyzed TH reaction was reported in 1964 by Henbest and Mitchell with an iridium complex in the presence of isopropanol as the hydrogen donor for the reduction of cyclohexanone in cyclohexanol [1,2]. Later on, in 1973, Blum and Sasson reported the TH of diones with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> [3,4]. Since then, many examples have flourished in literature with noble metals [5-7].

If noble metals arguably proved to be very efficient and selective, they are nevertheless quite toxic and very expensive due to their rarity and limited availability. Therefore, interest in non-noble metals has been revived, and several catalytic systems based on late first row transition metals such as iron [8,9] or cobalt [9], have emerged as powerful TH promoters. Contrary to the former 3d transition metals, manganese was disregarded at first, most certainly, because it has long been considered as a metal promoting mainly oxidation reactions. It was not until 2017 and seminal Beller's work that the first catalysts for the TH of ketones to alcohols appeared in literature [10].

This breakthrough was the starting point for enormous progress in this field in parallel with the extensive development of Mn-catalyzed hydrogenation processes,[11-15] whether through the design of new efficient ligands and their combination with different hydrogen donors, the development of a chiral version of this reaction (abbreviated ATH for asymmetric transfer hydrogenation), or the broadening of the application scope to a wider range of substrates. All these aspects will be highlighted in this review.

### 2.1. Reduction of ketones, aldehydes, imines, nitroarenes and N-heterocycles

In 2017, Beller reported the first example of Mn-based pre-catalyst for TH supported by a tridentate NNN ligand, namely dipicolylamine (Figure 1) [10]. This catalytic system was highly efficient for the reduction of (hetero)aryl and alkyl ketones affording the corresponding alcohols in excellent yields (up to 99%), under mild conditions (70 °C, 2 mol% of base) using 1 mol% catalyst loading. This Mn-based catalytic system showed an excellent chemoselectivity towards ketones over other reducible functions (esters, nitriles) and no deactivation for the substrates containing potentially coordinating O-, S- and N-groups. The same year, our group demonstrated that tridentate ligands were not mandatory to stabilize the catalyst [16]. High TON up to 2000 and TOF up to 3600 h<sup>-1</sup> were recorded at 80 °C in the presence of 0.5 mol% of Mn-based catalyst supported by very simple and inexpensive bidentate 2-(aminomethyl)pyridine ligand and the reaction can proceed even at 30 °C albeit more slowly. It should be noted that this Mn-NN catalyst allowed reduction of aldehydes unlike Beller's system with negligible amounts of aldol-type condensation products and preserved conjugated C=C bonds. The ligand's system was even simplified further as catalyst generated *in situ* from Mn(CO)<sub>5</sub>Br and ethylenediamine proved to efficiently promote TH of ketones with the same catalyst charge [17].



**Figure 1.** Mn-based catalytic systems for transfer hydrogenation of carbonylated substrates.

These promising results paved the way to further investigations performed by the groups of Leitner,[18] Kundu,[19] Khusnutdinova,[20] Pidko [21] and Chen [22]. They contributed to the field by expanding the library of catalytic systems for the reduction of ketones and aldehydes. Most of these systems relies on bidentate tricarbonyl Mn-NN complexes and are selective for C=O bond reduction. However, TH of chalcones catalyzed by PN complex developed by Lacy [23] proceeds selectively at the conjugated C=C bond, being consistent with the results of hydrogenation of these substrates using related Mn-PN complex [24]. Although demonstrating reasonable activities, there was still a gap to be bridged to approach the activity recorded with catalytic systems involving noble metals. Pidko and coll.[21] demonstrated that the replacement of one N-donor moiety in NN ligand by a N-heterocyclic carbene (NHC) resulted in a significant improvement in Mn-catalyzed TH of ketones. Indeed, such a Mn-NC system could operate at 75 ppm of catalyst loading at 60 °C with TON up to *ca.* 17000.

A further step has been taken in the field when the groups of Kundu,[19] Khusnutdinova [20] and Sortais [25] demonstrated that their catalytic systems were also able to reduce imines,

which are more reluctant substrates towards TH. The catalyst developed by Khusnutdinova was particularly active for the reduction of aldimines, the corresponding amines were produced in good to excellent yields up to 96% in the presence of 0.5 mol% of catalyst at 80 °C. Its applicability could be extended to the TH of polyaromatic nitrogen heterocycles. Although the scope remains rather limited (4 examples, yields up to 94%), this protocol represents the first example in the field. Finally, selective TH of 2-nitropyridine to form the corresponding amine was recently reported by Morrill using 5 mol% of  $[(iPr_2PNHPyNHPiPr_2)Mn(CO)_3]Br$  in MeOH at 110-130 °C [26]. Nitro compounds  $ArNO_2$  with more electron-donating aryl groups under these conditions afforded the corresponding  $ArNHMe$  products probably as a sequence of TH and aniline alkylation with methanol [27].

## 2.2. Reduction of carboxylic acid derivatives

Unlike carbonyl derivatives, carboxylic acid derivatives are more difficult to hydrogenate. In this respect, the results reported by Garcia's group in transfer hydrogenation of nitriles to amines constitute an important breakthrough in the field (Figure 2) [28]. Though TH of benzonitrile with 2-butanol catalyzed with Mn-diphosphine complex **Mn1** initially leads to a mixture of target  $BnNH_2$  and its condensation products with 2-butanone  $BnN=C(Me)Et$  and benzaldehyde  $BnN=C(H)Ph$ , they could all be converted to the corresponding ammonium salt upon acidic treatment. The choice of the  $H_2$ -donor appeared to be crucial for the selectivity of this transformation, since the use of more classical isopropanol led to undesired hydration and aldol condensation processes. Under optimized conditions, excellent selectivity was reached at 3 mol% of catalyst loading at 100°C for 3h in the presence of 10 mol% of *t*BuOK affording  $[BnNH_3]Cl$  in 96% isolated yield. While the presence of electron-donating groups such as *p*-Me and *p*-OMe was well tolerated, *p*- $CF_3C_6H_4CN$  bearing electron-withdrawing group was more reluctant to reduction and only 39% product yield was obtained despite an increase in of the catalytic charge to 5 mol%. Aliphatic nitriles can also undergo TH using this system, but higher catalyst loading (5 to 10 mol%) was required to achieve good conversions.

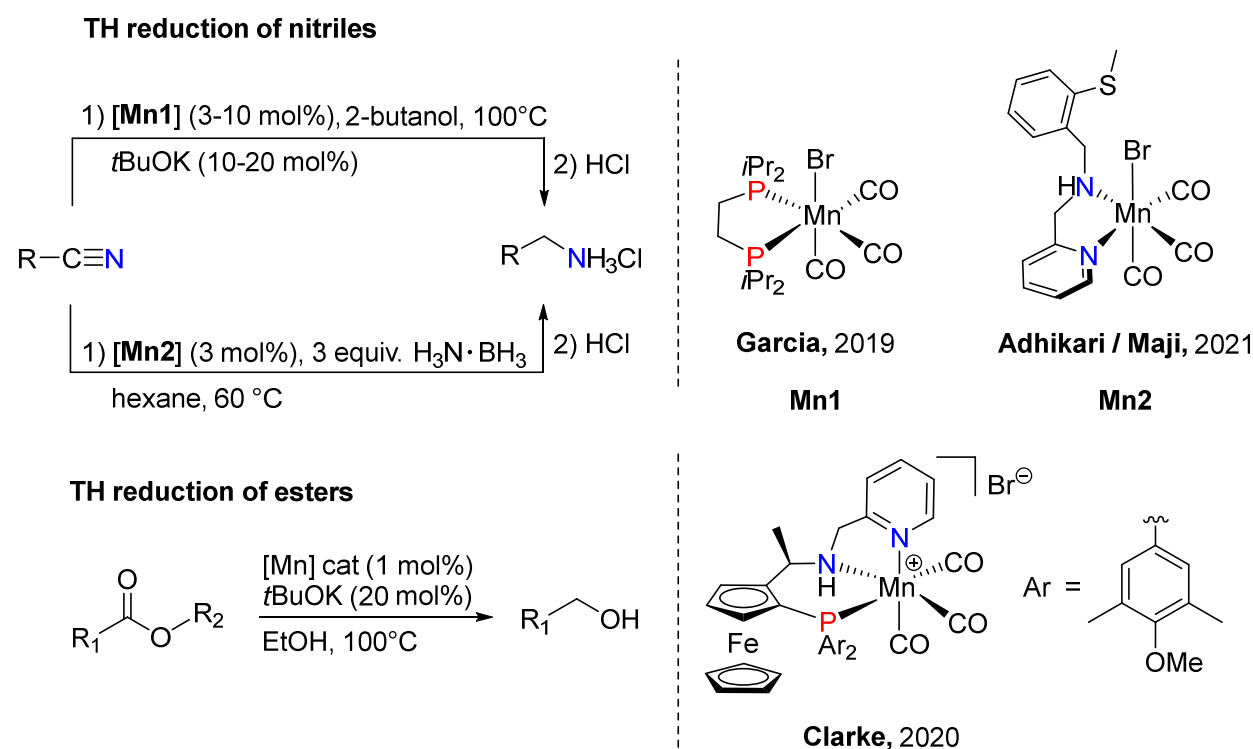


Figure 2. Mn-based catalytic systems for TH of carboxylic acid derivatives.

Using ammonia-borane as H<sub>2</sub>-donor, Adhikari and Maji developed very recently a chemo-divergent reduction of nitriles to primary amines or secondary amines by using n-hexane or isopropanol as solvent, respectively, using 3 mol% of complex **Mn2** supported by hemilabile tridentate SNN ligands (Figure 2) [29]. Unsymmetrical products ArCH<sub>2</sub>NHR were even readily obtained by reduction of nitriles ArCN in the presence of external primary amines RNH<sub>2</sub>.

In 2020, Clarke and co-workers reported the first example of TH of ester catalyzed by a ferrocene-based Mn(I) complex using ethanol as the H<sub>2</sub>-donor (Figure 2).[30] The catalytic system displayed high activity and the catalyst loading could be reduced to 1 mol% at 100 °C in the presence of *t*BuOK (20 mol%). Good tolerance to halogen and heterocycles was observed, whereas the presence of cyano or amino group was detrimental to the activity. The scope of the reaction was successfully extended to aliphatic esters as well as to esters derived from ethanol, methanol and isopropanol. It is worth noting that (*S*)-Naproxen was successfully reduced using this protocol in 82% yield, however with the chiral center epimerization.

### 2.3. Stereoselective reduction of alkynes to alkenes via TH

Another milestone in the field was reached thanks to the discovery of Mn-based stereoselective transfer semi-hydrogenation of alkynes into alkenes. In 2018, two catalytic systems were reported both involving the use of ammonia borane as H<sub>2</sub>-donor and Mn(II) pre-catalysts, but leading to complementary stereoselectivity (Figure 3). [31,32] The groups of El-Sepelgy and Azofra performed the stereoselective transfer semi-hydrogenation of aromatic and aliphatic alkynes to (*Z*)-alkenes using Mn(II) pre-catalyst (1 mol%) supported by tridentate PNP ligands in the presence of 1 equiv. of H-donor in methanol at 60°C. [31] High yields (up to 98%) and stereoselectivities (up to >99:1 *Z/E* ratio) were obtained on a broad scope of internal alkynes. On the other side, Driess and coll. succeeded to reverse the stereoselectivity of the reaction by using N-heterocyclic silylene Mn(II) pre-catalysts (1 mol%) and (*E*)-alkenes were produced in high conversions and stereoselectivities at 55°C.[32] Although the latter catalytic system tolerates the presence of sensitive functional groups, limitations appeared regarding the reduction of dialkyl substrates. Indeed, 6-dodecyne was reduced with lower conversion (67%) and without any stereoselectivity and no reduction was observed with disilylated alkyne derivatives.

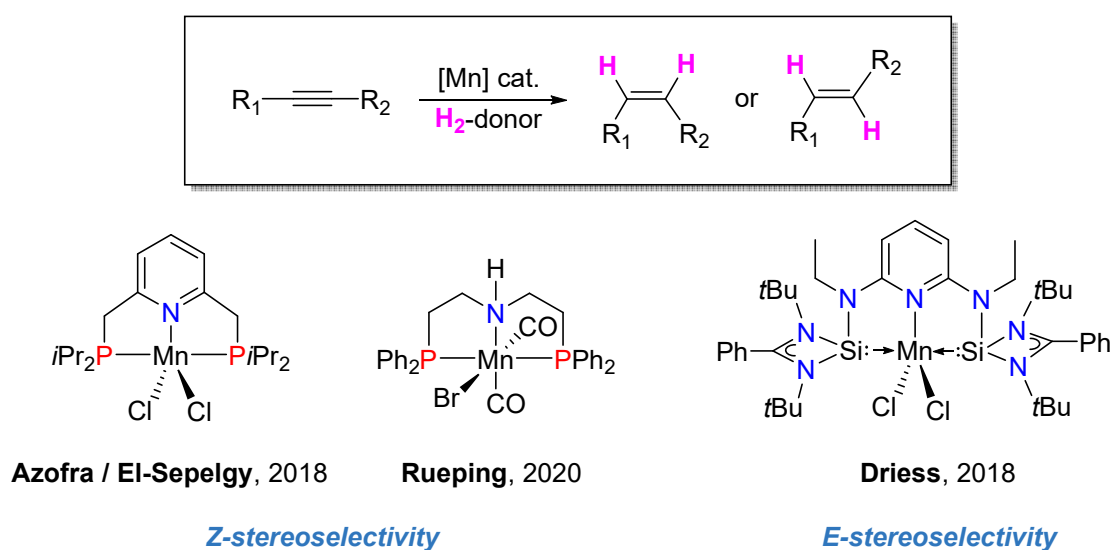


Figure 3. Mn-based catalytic systems for transfer semi-hydrogenation of alkynes.

Later Rueping and coll. reported that methanol could also act as an hydrogen donor for *Z*-selective transfer semi-hydrogenation of alkynes using 2 mol% of Mn(I) pre-catalyst bearing PNP ligand.[33] In this case, the addition of 2 equivalents of weak base Cs<sub>2</sub>CO<sub>3</sub> was required and the reaction proceeds under rather harsh conditions at 130-150 °C. However, a variety of aromatic and aliphatic (*Z*)-alkenes was obtained by this procedure including substrates containing various nitrogen and sulfur heterocycles. Deuterium labelling experiments performed in the presence of CD<sub>3</sub>OD evidenced the *cis*-selective hydrogen incorporation onto the alkyne giving important information regarding a plausible catalytic cycle.

## 2.4. Asymmetric transfer hydrogenation of ketones

Due to the importance of chiral alcohols in industry, and the low price and toxicity of manganese, it became evident to investigate the development of chiral catalysts for asymmetric hydrogenation of ketones. The first report was made by Zirakzadeh and Kirchner in 2017, who investigated the implementation of a Mn(I) catalyst supported by a tridentate PNP ferrocenyl-based chiral ligand. [34] The catalytic system displayed high activity and selectivity, acetophenone was reduced in 95% conversion in 85% *ee* (room temperature, 1 mol% catalyst loading, 4 mol% of *t*BuOK). While *para*-substitution of the phenyl group of aryl ketones did not affect the enantioselectivity to great extent, stereoselectivity dropped to 20 and 46% with acetyl ferrocene and tetralone, respectively. <sup>1</sup>H NMR spectroscopy experiments and theoretical calculations demonstrated that the catalytic cycle involves the formation of a monohydride dicarbonyl Mn(I) catalytic intermediate and suggest that an outer sphere transfer of hydrogen occurs without direct ligand participation. In the same vein, Clarke and coll.[35] investigated the implementation of a Mn(I) catalyst derived from a closely related ferrocenyl tridentate PNN ligand in ATH of ketones. The enantiomeric induction recorded was modest under ATH conditions, whereas hydrogen pressure profoundly improved the catalysts efficiency.

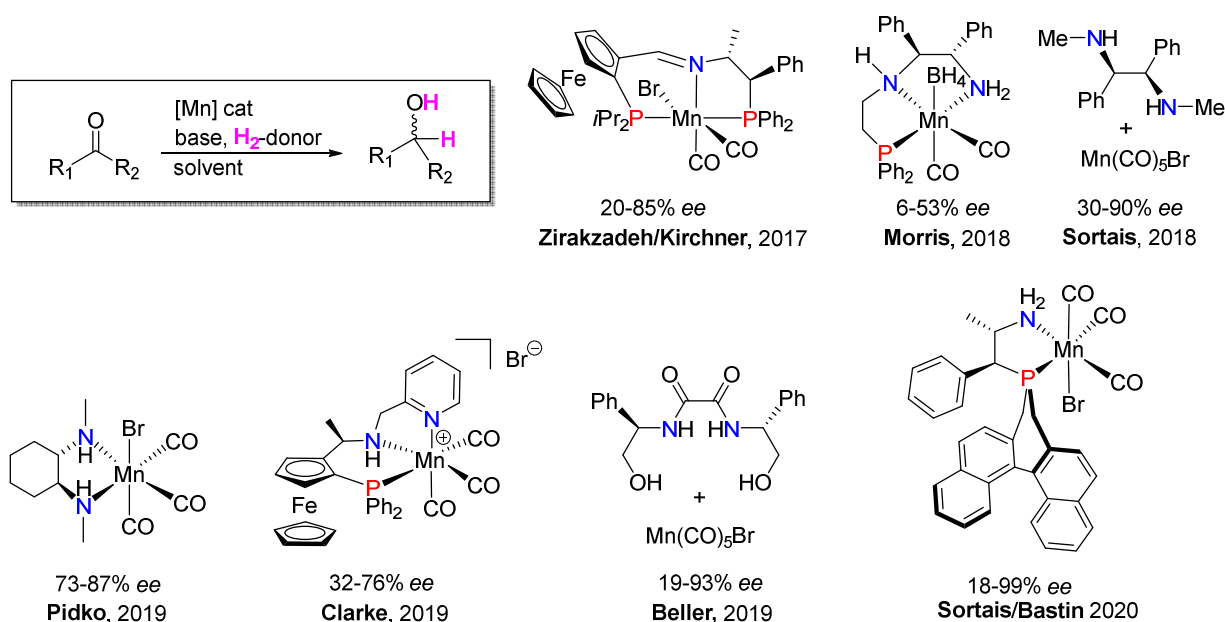


Figure 4. Mn-catalyzed ATH of prochiral ketones

When developing a catalytic system, different aspects have to be considered before envisaging any industrial application. First, the number of additives should be limited. Large-amount of base is often used to activate the pre-catalyst, but reduces functional group tolerance. It is in this context that the catalytic system developed by Morris reveals all its importance since it constitutes the first example of a catalytic system operating in the absence of base.[36] During the course of a study aiming at evaluating the catalytic efficiency of manganese complexes

supported by chiral tri- and tetradentate ligands in ATH, they have isolated a borohydride complex capable of reducing ketones under base-free conditions for the first time. Another point to take into account is the total cost of catalysts. If the replacement of noble metals by base metals lower the price of hydrogenation catalysts, it should be noted that the price of the chiral ligand is non-negligible. With this in mind, the Beller's group has focused its research on the application of inexpensive commercial ligands in ATH. They have tested C<sub>2</sub>-symmetric potentially tetradentate ligands derived from cheap chiral aminoalcohols.[37] While catalyst systems based on these ligands in combination with Mn(CO)<sub>5</sub>Br have led to poor enantiomeric excesses (36% *ee* for the best) in the hydrogenation of aromatic ketones, these systems have proven to be particularly effective in the TH of dialkyl ketones. The reduction of the cyclohexyl methyl ketone led to the corresponding alcohol with 88% *ee*. While catalytic system generated *in situ* from Mn(CO)<sub>5</sub>Br and ONNO-ligand was efficient for the reduction of different (hetero)cyclic alkyl ketones with *ee* up to 93%, the replacement of manganese with iron and ruthenium did not reach the same efficiency. Indeed, iron salts associated with chiral oxamide ligands were unable to reduce cyclohexyl methyl ketone and use of ruthenium precursors did not allow to surpass the enantioselectivity obtained with Mn-based system. Though the catalytic systems described above rely on the use on tri- and tetradentate chiral ligands, our group showed that the combination of simpler bidentate diamine ligands with Mn(CO)<sub>5</sub>Br can also conduct to efficient catalytic systems with *ee* values up to 90% obtained using commercially available (1*R*,2*R*)-*N,N'*-dimethyl-1,2-diphenylethane-1,2-diamine.[17] This work was complemented by Pidko and coll. in 2019, who performed a detailed experimental and theoretical mechanistic study with well-defined Mn catalysts based on (1*R*,2*R*)-*N,N'*-dimethyl-1,2-diaminocyclohexane scaffold.[38] As part of our research on bidentate ligands in reduction, we have investigated the implementation of chiral aminophosphines in ATH.[39] It emerges from our study that a bulky binepine moiety on the phosphorus atom is necessary to get excellent enantioselectivities (up to 99%) for hindered carbonyl derivatives.

## Conclusion and perspectives

Since the discovery of the efficiency of Mn-based catalysts in transfer hydrogenation reactions in 2017, the field has been in constant evolution. A large number of catalytic systems has been developed by playing on the ligand design, the choice of the hydrogen donors and the optimization of the reaction conditions, which resulted in significant progress in terms of catalytic activity, (enantio)selectivity and application scope. These promising results shows a great potential for future development of Mn-catalyzed TH processes and open the way for industrial applications. The biocompatibility of manganese, its low cost and its abundance in the Earth's crust compared to noble metals are all elements in favor of the future application of Mn-based catalytic systems in flavor and fragrance industries as well as for the synthesis of pharmaceutical and agrochemical products.

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### Highlights:

Mn complexes can catalyze transfer hydrogenation of C=O, C=N, C=C, C≡N and C≡C bonds

Mn-catalyzed transfer hydrogenations often display high chemo- and stereoselectivity

Chiral Mn complexes have good potential for enantioselective reduction processes

### TOC graphic