

Manganese-catalyzed transfer hydrogenation of aldimines

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Abstract: The reduction of imines to amines via transfer hydrogenation was achieved promoted by phosphine-free manganese(I) catalyst. Using isopropanol as reductant, in the presence of *t*BuOK (4 mol%) and manganese complex [Mn(CO)₅Br(κ²-N,N-PyCH₂NH₂)] (2 mol%), a large variety of aldimines (30 examples) were typically reduced in 3 hours at 80 °C with good to excellent yield.

The development of catalysts based on earth abundant 3d transition metals, as sustainable and economical alternative to precious transition metals, is one of the current challenge in the field of homogeneous catalysis.^[1] In the case of reduction reactions,^[2] despite its natural abundance, the potential of manganese^[3] was disregarded until recently compared to iron,^[4] cobalt,^[5] and nickel.^[6]

Indeed, the first efficient manganese based catalyst for hydrogenation of polar bonds was reported latterly, in 2016, by the group of Beller.^[7] Since then, hydrogenation catalysts were developed for the reduction of carbonyl derivatives,^[8] nitriles,^[9] esters,^[10] amides,^[11] carbonates,^[12] and CO₂.^[13] To our knowledge, only two examples of hydrogenation of imines are reported, one with a manganese nano-sheet^[14] and one with an aminophosphinepyridine manganese catalyst developed by our group.^[15] As an alternative to molecular dihydrogen (or hydrosilanes^[16]) as reductants, secondary alcohols, typically isopropanol, are convenient source of hydrogen.^[17] Advantages of transfer hydrogenation over hydrogenation are that reduction reactions can be performed in conventional equipments, *i.e.* without requiring the use of high-pressure autoclaves, and that alcohols are usually benign chemicals, safer to handle than dihydrogen.

Compared to hydrogenation, only a few catalytic systems based on manganese were developed for transfer hydrogenation reactions, including the asymmetric version (Scheme 1).^[8f, 18] The first system was developed by the group of Beller, with a

tridentate ligand, namely dipicolamine, for the reduction of ketones.^[18a] Zirakzadeh and Kirchner reported the application of a chiral catalyst supported by a tridentate PNP ligand bearing a ferrocenyl moiety for the enantioselective production of alcohols.^[18b] Similar catalytic system, developed by Clarke, performed the reduction of ketones in the presence of alcohols, but required hydrogen pressure to exhibit enantioselectivity.^[8f] More recently, the groups of Leitner^[18c] and Morris,^[18d] reported respectively an aminotriazole and a chiral tridentate manganese catalyst efficient in transfer hydrogenation reactions. Our group demonstrated that simple manganese complex based on a bidentate aminomethylpyridine ligand could perform with high efficiency the reduction of ketones and aldehydes, even at room temperature.^[18e] We also showed that the combination of [Mn(CO)₅Br], as commercial manganese precursor, and a diamine ligand, for example ethylenediamine or a chiral diamine, namely (1*R*,2*R*)-*N,N*-dimethyl-1,2-diphenylethane-1,2-diamine, could promote the (asymmetric-) transfer hydrogen of carbonyl compound.^[18f]

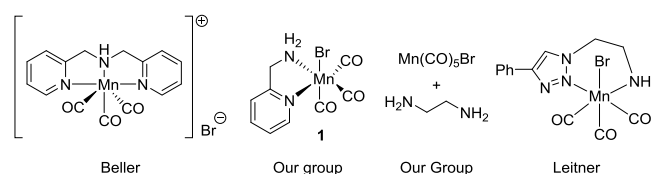
So, to date, manganese-catalyzed transfer hydrogenation reactions were limited to the reduction of ketones and aldehydes. Furthermore, examples of reduction of imines via this methodology involving non-noble metals such as iron,^[19] nickel,^[20] and cobalt^[21], are quite scarce. Starting from this statement, and taking into account the importance of amines in organic synthesis,^[22] we found relevant to explore the manganese-catalyzed reduction of imines by hydrogen transfer^[23] as a complementary method in the chemist tool box to hydrogenation,^[24] hydrosilylation^[25] or hydrogen borrowing,^[2b] for example.

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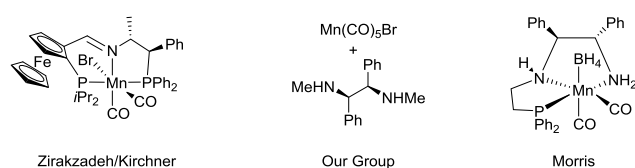
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Transfer hydrogenation



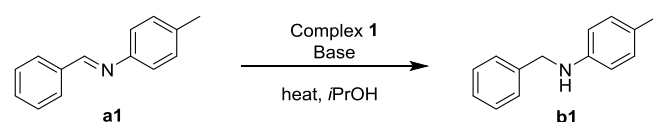
Asymmetric transfer hydrogenation



Scheme 1. Manganese catalysts used in transfer hydrogenation.

In line with our research program to develop manganese complexes for reduction reactions,^[8d, 26] we have selected the well-defined Mn(I) complex **1** (Scheme 1) featuring an 2-(aminomethyl)-pyridine ligand for this study as it was the most efficient catalyst for the reduction of carbonyl derivatives.^[18e] Besides, the synthesis of this complex is very straightforward, as **1** can be obtained in high yield in only one step from commercially available reactants.^[18e]

Table 1. Optimization of the parameters of the reduction of imine with catalyst **1**.^[a]



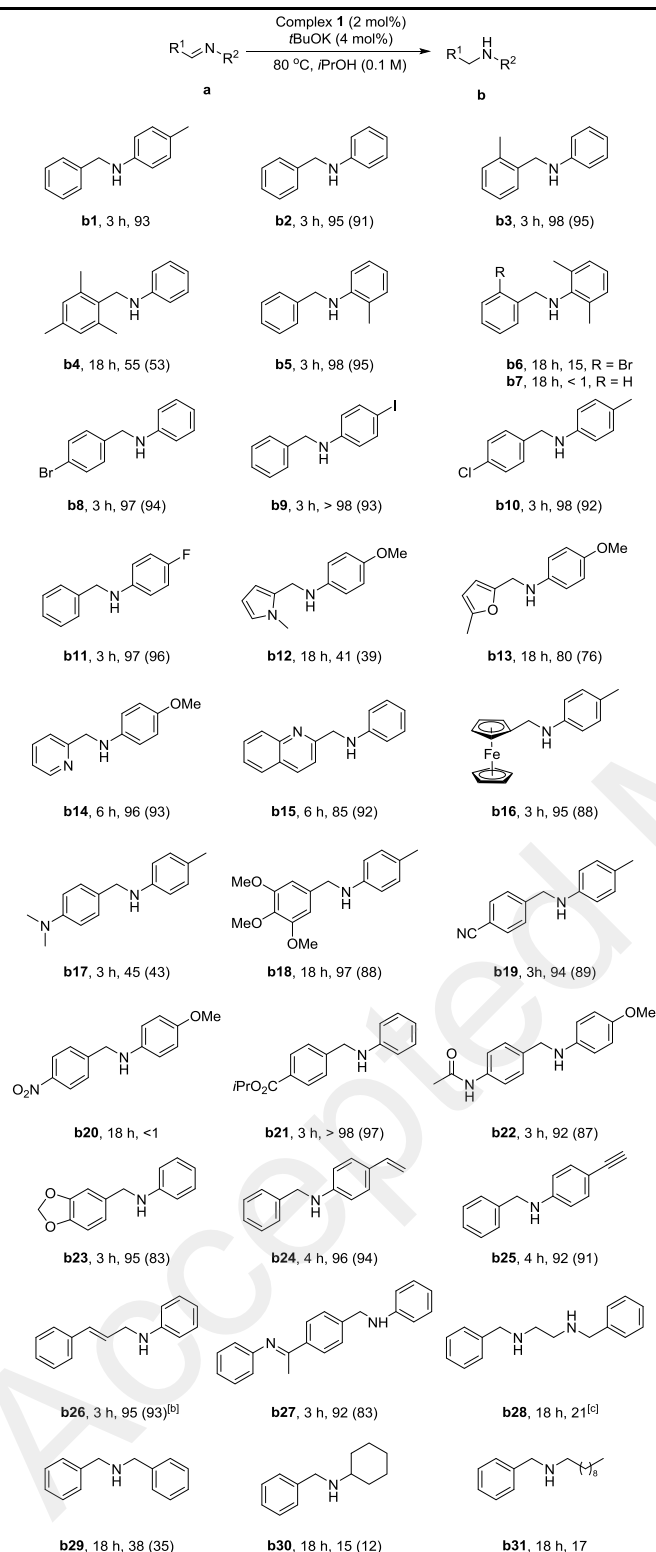
Entry	Loading (mol%)	Base (mol%)	Conc. (mol.L ⁻¹)	Temp. (°C)	Time (h)	Conv. (%)
1	1	<i>t</i> BuOK (2)	0.16	80	1.5	77
2	1	<i>t</i> BuONa (2)	0.16	80	1.5	63
3	1	KHMDS (2)	0.16	80	1.5	77
4	1	KOH (2)	0.16	80	1.5	65
5	1	Na ₂ CO ₃ (2)	0.16	80	1.5	15
6	1	K ₃ PO ₄ (2)	0.16	80	1.5	12
7	1	<i>t</i> BuOK (2)	0.5	80	1.5	58
8	1	<i>t</i> BuOK (2)	0.1	80	1.5	82
9	1	<i>t</i> BuOK (2)	0.05	80	1.5	83
10	1	<i>t</i> BuOK (2)	0.1	80	3	88
11	1	<i>t</i> BuOK (2)	0.1	50	3	29
12	1	<i>t</i> BuOK (2)	0.1	30	3	7
13	2	<i>t</i> BuOK (4)	0.1	80	3	93
14	0.5	<i>t</i> BuOK (2)	0.1	80	3	60
15	0	<i>t</i> BuOK (4)	0.1	80	3	<1
16 ^[b]	2	<i>t</i> BuOK (4)	0.1	80	3	94

[a] Reaction conditions: Under inert atmosphere, a 20 mL Schlenk tube was filled sequentially with the imine **a1** (0.5 mmol), anhydrous 2-propanol, complex **1**, and the base. The reaction was heated in an oil bath. Conversion was determined by ¹H NMR spectroscopy [b] In the presence of Hg (300 equiv.).

The conditions of the reaction were optimized for the reduction of *N*-benzylidene-4-methylaniline **a1** in 2-propanol as solvent (Table 1). At 80 °C, in the presence of *t*BuOK (2 mol%) and manganese complex **1** (1 mol%), the corresponding amine **b1**, namely *N*-benzyl-4-methylaniline, was formed in 77% yield. Various bases were first screened (entries 1-6), showing that *t*BuOK and KHMDS gave the best results (77%, entries 1 and 3). Interestingly, common base KOH could also be used, albeit affording a slightly

lower conversion than the former bases (65%, entry 4) The concentration of the reaction mixture is often crucial for the reduction of carbonyl derivatives, as transfer hydrogenation is a reversible reaction.^[27] Therefore, the influence of the concentration of **a1** was examined ranging from 0.5 to 0.05 mol.L⁻¹. An optimal concentration of 0.1 mol.L⁻¹ (entries 1, 7-9) was identified. With 1 mol% catalyst, lengthen the reaction time (3 h) allowed to improve the conversion to 88% (entry 10). However, lowering the temperature had a detrimental effect on the -activity as the conversion dropped to 39% at 50 °C and to 7% at 30 °C (entries 11 and 12). A satisfying yield (93%) was obtained using 2 mol% of catalyst and 4 mol% of *t*BuOK at 80 °C after 3 h (entry 13). Finally, lowering the catalyst loading to 0.5 mol% resulted in a moderate TON of 120 (**1**, 3 h, 60% conversion, entry 14). It is worth noting that under the optimized conditions, but in the absence of manganese complex **1**, no reaction occurred (entry 15, Table S2), demonstrating a metal-catalyzed reduction.^[28] Additionally, the reaction proceeded in the presence of Hg (300 equiv.) without observing any significant changes in reactivity (Table 1, entry 16), suggesting a homogeneous catalytic system. Given the promising activity of catalyst **1** for the reduction of aldimine **a1**, we then investigated its potential for the more challenging reduction of ketimines, with *N*-[1-phenylethylidene]-aniline as a model substrate (See Table S1). Even under harsh conditions (**1** (5 mol%), *t*BuOK (10 mol%), 130 °C, 18 h), the corresponding amine was obtained in low yield (20%), demonstrating that this catalytic system is not suitable for the reduction of ketimines.

Having optimized the conditions for the reduction of aldimines (complex **1** (2 mol%), *t*BuOK (4 mol%), *i*PrOH (C = 0.1 mol.L⁻¹), 80 °C, 3 h), we then explored the scope of this transformation (Table 2). In general, a large variety of aldimines, prepared by the condensation of benzaldehyde with aniline derivatives, was reduced in high yield. Steric hindrance has an influence as increasing the number of *ortho* substituents on both the benzaldehyde (**a3**, **a4**) or the aniline (**a5**, **a6**) moieties, from one to two, led to the sterically hindered amines **b4** and **b6** in lower yield than **b3** and **b5**. The steric hindrance on the aniline moieties has a more drastic influence than on the benzaldehyde part (**b4** vs **b7**). Halogen substituents (F, Cl, Br, I) were well tolerated (**b8**-**b11**, isolated yield > 90%), and no product resulting from dehalogenation was detected. Interestingly, heteroaromatic imines (**a12**-**a15**) affording *N*-substituted-aminomethylheterocycles (**b12**-**b15**) were also surprisingly reduced without significant loss of activity. It should be noticed that the structure of the reaction products are very similar to the one of the ligand used to support the manganese center, namely 2-(aminomethyl)-pyridine. Under the conditions of the catalysis, a dynamic exchange of ligands can not be ruled out. Since diverse diamines proved to be active ligands in transfer hydrogenation of ketones, such an exchange may not alter the reduction.^[18f] Likewise, organometallic 4-methyl-*N*-(ferrocenylmethylidene)-aniline **a16** was totally reduced and led to the corresponding amine **b16** in excellent isolated yield (88%). The tolerance toward various functional groups such as amino (**a17**), methoxy (**a18**), cyano (**a19**), nitro (**a20**), ester (**a21**), amido (**a22**), acetal (**a23**), vinyl (**a24**) and alkynyl (**a25**) groups was tested.

Table 1. Generality of the reduction of aldimines catalyzed by complex 1.^[a]

[a] Reaction conditions: Under inert atmosphere, a 20 mL Schlenk tube was filled sequentially with the imine (0.5 mmol), anhydrous 2-propanol (5 mL), complex 1 (3.3 mg, 2 mol%), and *t*BuOK (2.2 mg, 4 mol%). The reaction was heated in an oil bath at 80 °C for 3 h. Conversion was determined by ¹H NMR spectroscopy. Isolated yield in parenthesis. [b] Isolated as mixture containing 20% of saturated amine. [c] complex 1 (6.6 mg, 4 mol%), *t*BuOK (4.4 mg, 8 mol%)

Except for the nitro-substituted imine (**a20**),^[29] all the functional groups did not affect the catalytic system and remained intact after the reduction. In the case of the conjugated imine (**a26**), the unsaturated amine **b26** was obtained as major product (80%) along with 20% of the corresponding saturated amine.

The inability of our catalytic system to reduce ketimines allowed the selective reduction of substrates displaying both ketimine and aldimine moieties. Gratifyingly, for the diimine **a27** derived from 4-formylacetophenone, only the aldimine moiety was reduced affording the corresponding amino-ketimine **b27**. Finally, imines bearing aliphatic substituents were difficult to convert to the desired amines (**b28-b31**, yield 17%-38%).

In conclusion, we reported the first application of Mn-based catalyst in transfer hydrogenation of imines. We have shown that manganese (I) pre-catalyst bearing a 2-aminomethylpyridine ligand catalyzes efficiently the transfer hydrogenation of aldimines in the presence of *i*PrOH as reductant under mild conditions (2 mol% catalyst, 4 mol% base, 80 °C, 3 to 18 h). The catalytic process displayed a high tolerance towards a large variety of functional groups. This protocol enlarges the scope of reactions catalyzed by manganese, highlighting the rising potential of this transition metal in homogeneous catalysis.

Experimental Section

Typical catalytic reduction. A 20 mL Schlenk tube was charged with imine (0.5 mmol), anhydrous isopropanol (5.0 mL), manganese complex 1 (3.3 mg, 2 mol%), and *t*BuOK (2.2 mg, 4 mol%) under argon, in that order. Then the mixture was stirred at 80 °C in an oil bath for 3 h. After cooling to room temperature, the solution was diluted with ethyl acetate (2.0 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with ethyl acetate (2x2.0 mL). The filtrate was evaporated and the crude residue was purified by column chromatography (SiO₂, mixture of petroleum ether/ethyl acetate as eluent) to afford the desired product.

Acknowledgements

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Keywords: manganese • imines • reduction • transfer hydrogenation • amines

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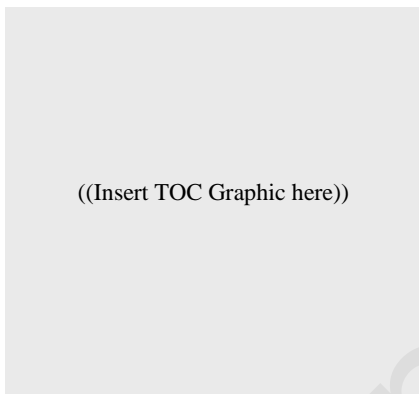
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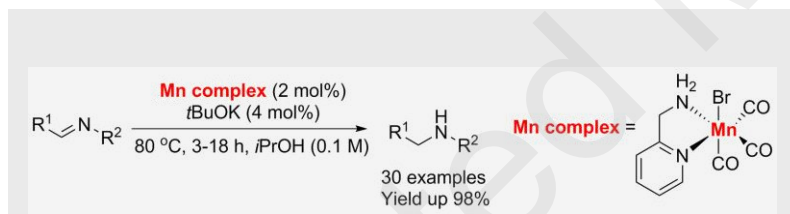
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Using isopropanol as reductant, in the presence of *t*BuOK and manganese complex $[\text{Mn}(\text{CO})_3\text{Br}(\kappa^2\text{N,N-PyCH}_2\text{NH}_2)]$, a large variety of aldimines (30 examples) were reduced to the corresponding amines with good to excellent yield.

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Jean-Baptiste Sortais*

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**Manganese-catalyzed transfer
hydrogenation of aldimines**