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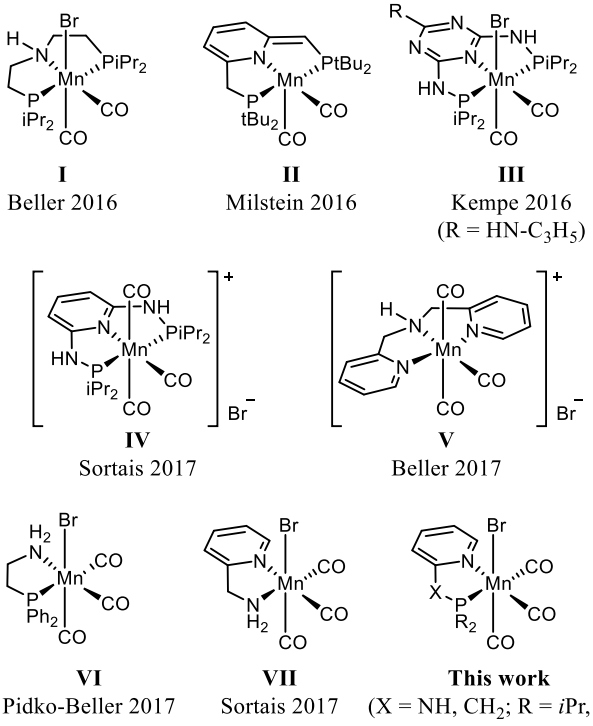
Abstract. Manganese(I) catalysts incorporating readily available bidentate 2-aminopyridinyl-phosphine ligands achieve a high efficiency in the hydrogenation of carbonyl compounds, significantly better than parent ones based on more elaborated and expensive tridentate 2,6-(diaminopyridinyl)-diphosphine ligands. The reaction proceeds with low catalyst loading (0.5 mol%) under mild conditions (50 °C) with yields up to 96%.

Keywords: hydrogenation; manganese; ketones; reduction; P,N-ligands

Hydrogenation with molecular dihydrogen is a clean, atom-economic and efficient reaction that has drawn a huge interest for more than a century from the Nobel Prize of Sabatier in 1912 for heterogeneous hydrogenation to the one of Noyori and Knowles in 2001 for asymmetric hydrogenation.[1] Homogeneous hydrogenation catalysts are usually complexes based on late transition metals including ruthenium, rhodium, iridium, nickel and palladium. In the last decade, iron has emerged as a powerful sustainable alternative candidate in catalysed reduction reactions, as it is the most abundant and inexpensive transition metal.[2] Actually, the level of the activity, and chemo- and enantioselectivity of iron catalytic systems is now comparable to the ones involving noble transition metals.[3] Manganese, being the third most abundant transition metals after iron and titanium, has recently emerged as suitable transition metal for the design of efficient hydrogenation catalysts[4] starting with a seminal contribution of Beller in 2016 using the Mn^{I} complex **I** featuring a tridendate bis(phosphino)amine ligand (Scheme 1).[5]

Soon after, a series of parent Mn^{I} complexes exhibiting a variety of tridendate ligands including nitrogen and phosphorus donor fragments has been successfully applied in hydrogenation[6] and related hydrogen borrowing reactions,[7] selected representative examples being shown in Scheme 1.



Scheme 1. Representative examples of manganese catalysts for redox reactions.

In the course of our investigations directed toward manganese catalysed reduction reactions,[8] we first demonstrated that the PN^3P manganese complex **IV** bearing a 2,6-(diaminopyridinyl)-diphosphine ligand was suitable for the hydrogenation of carbonyl derivatives,[6c] yet with moderate activity compared to PN^5P analogue **III** developed by Kempe[6a] and based on the 2,6-(diaminotriazinyl)-diphosphine ligand. Searching for simpler catalytic system, we found later that the manganese complex **VII** featuring a bidentate picolylamine ligand was significantly more active[6d] than Beller's tridendate dipicolylamine complex **V**[6b] in the case of hydrogen transfer reaction using 2-propanol as the reductant. In the meantime, Pidko and Beller showed that the manganese complex **VI** bearing bidentate phosphinoamine ligand was as active as **I** for the hydrogenation of esters.[5b, 9] In the present contribution, we demonstrate that simple Mn^I complexes bearing readily available phosphino-pyridinyl PN bidentate ligands can achieve a very high efficiency in the hydrogenation of carbonyl compounds.

The ligands R_2P–X–Py (**L1**: R = *i*Pr, X = NH; **L2**: R = Ph, X = NH; **L3**: R = Ph, X = CH_2) and Ph_2P–CH_2–Qn (**L4**) were obtained in high yield starting from the appropriate chlorophosphines R_2PCl and 2-aminopyridine (**L1**, **L2**),[10],[11] 2-picoline (**L3**),[12] or 2-methylquinoline (**L4**),[13] respectively, according to literature procedures. The corresponding complexes $Mn(CO)_3Br(\kappa^2P,N$-**L1**-**L4**) (**1**-**4**) (Fig. 1) were readily obtained in excellent yield (87-91%) upon simple heating of an equimolar mixture of $Mn(CO)_5Br$ and the given ligand in toluene at 100 °C overnight. They were fully characterised by IR and NMR spectroscopy, high-resolution mass spectrometry and elemental analysis, and their solid-state structures were determined by single-crystal X-ray diffraction.[14] Perspective views of the complexes are displayed on Figure 2 for complex **2**, and on Figures S15, S17 and S18 for complexes **1**, **3**, and **4**, respectively. All complexes show a typical octahedral environment for the Mn center, the **L1**-**L4** ligands being coordinated in a κ^2P,N mode and the three carbonyl ligands being in facial position.

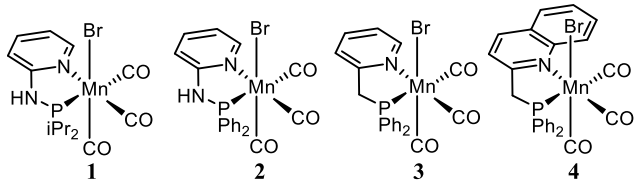


Figure 1. Manganese complexes synthesised for this study.

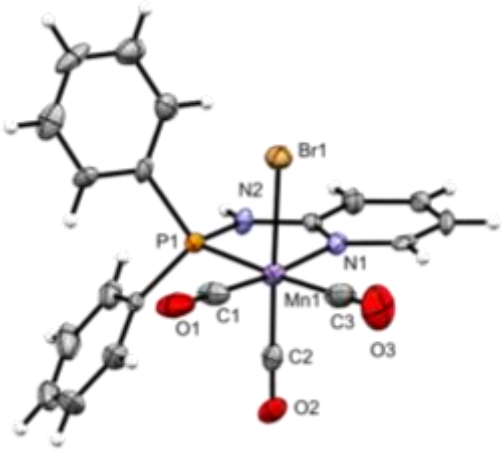
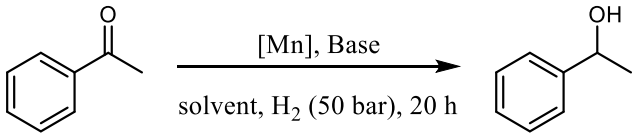


Figure 2. Perspective view of complex **2** with thermal ellipsoids drawn at the 50% probability level.

Table 1. Optimization of the reaction parameters



a1 **b1**

Entry	Catalyst (mol%)	Base (mol%)	Temp. (°C)	Solvent	Yield[b]
1	**1** (5)	*t*BuOK (10)	110	toluene	> 98
2	**1** (1)	*t*BuOK (2)	110	toluene	> 98
3	**1** (1)	*t*BuOK (2)	80	toluene	65
4	**2** (1)	*t*BuOK (2)	80	toluene	90
5	**3** (1)	*t*BuOK (2)	80	toluene	15
6	**4** (1)	*t*BuOK (2)	80	toluene	16
7	**2** (1)	KHMDS (2)	80	toluene	> 98
8	**2** (0.5)	KHMDS (1)	80	toluene	81
9	**2** (0.5)	KHMDS (1)	80	*t*-amyl alcohol	76
10	**2** (0.5)	KHMDS (2)	80	toluene	95
11	**2** (0.1)	KHMDS (1)	80	toluene	43
12	**2** (0.5)	KHMDS (2)	50	toluene	93
13	**2** (0.5)	KHMDS (2)	50	*t*-amyl alcohol	51
14	**2** (0.5)	KHMDS (2)	30	toluene	44
15	-	KHMDS (2)	50	toluene	0
16	**2** (0.5)	-	50	toluene	0
17[c]	**2** (0.5)	KHMDS (2)	80	toluene	93

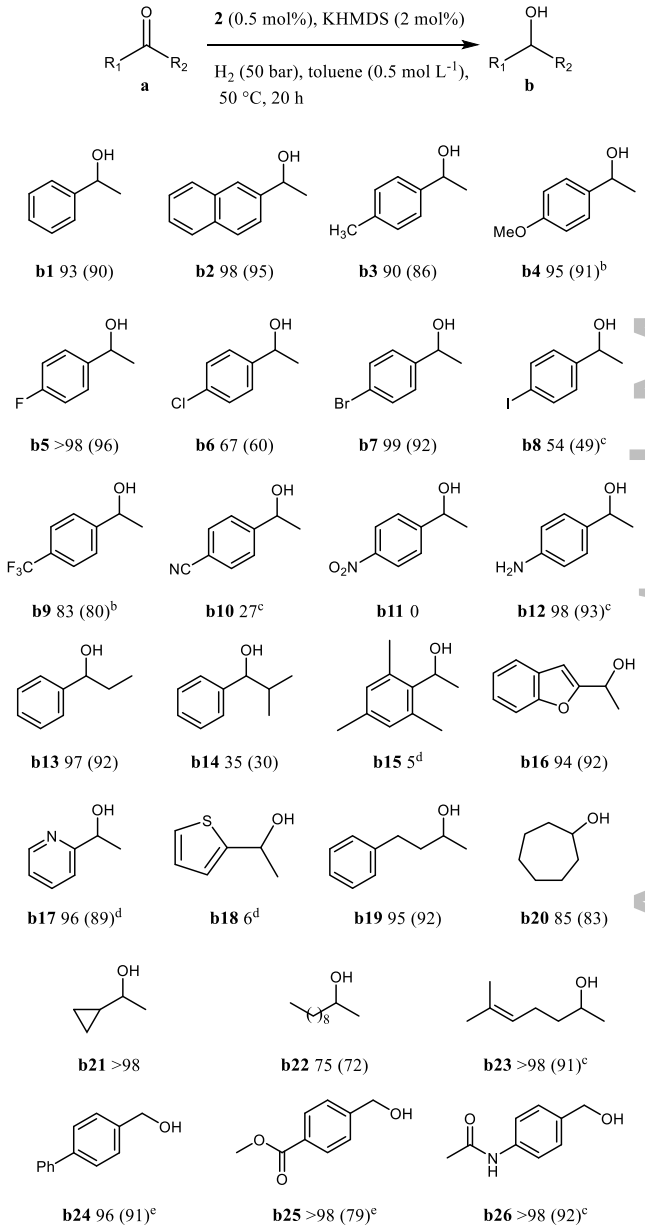
[a] Typical conditions: in an autoclave, **2** (0.5 mol%), toluene (4 mL), ketone (2 mmol), KHMDS (2 mol%), H_2 (50 bar) were added in this order. [b] Yield determined by GC and ^1H

NMR. [c] 300 equiv. of Hg (vs **2**) were added before H2 in the reaction mixture.

The catalytic activity of the new complexes **1-4** was then evaluated for the reduction of ketones under hydrogenation conditions (Table 1). Under the previously optimized reaction conditions determined for the PN^3P catalyst **IV**,[6c] *i.e.* complex **1** (5 mol%), *t*BuOK (10 mol%) as the base, toluene, 110°C, H_2 (50 bar), 22 h, a full conversion of acetophenone **a1** to the corresponding alcohol **b1** was obtained (entry 1). The catalyst loading could be reduced to 1 mol% without any degradation of the activity (Table 1, entry 2). The performance of the four complexes was then compared at 80 °C (entries 3-6): complex **1** exhibiting the amino-bridged diisopropylphosphino-pyridinyl bidentate ligand **L1** gave a moderate conversion (65%), whereas the diphenylphosphino derivative **2** gave the alcohol in 90% yield. Disappointingly, complexes **3** and **4** featuring the methylene–bridged PN bidentate ligands **L3** and **L4** led to low conversion (15 and 16% respectively, entries 5 and 6). The nature of the base was optimized using **2** as pre-catalyst. KHMDS (potassium bis(trimethylsilyl)amide) appeared to be the best one leading to a full conversion with 1 mol% of complex and 2 mol% of base at 80 °C in toluene (entry 7). With this base, the catalyst loading could be even decreased to 0.5 mol% (entries 8-10). With 0.1 mol% of catalyst a TON of 430 was achieved (entry 11). The temperature could also be lowered to 50 °C without significant loss of efficiency (entries 12-13). At 30 °C, however, the conversion dropped to 44% (entry 14). The influence of the solvent and of the pressure was also evaluated (see ESI, Tables S1 and S2). Notably, *tert*-amyl alcohol was found to be suitable for this reaction at 80 °C, as an alternative greener solvent (entries 9 and 13).[15] Control experiment showed that the presence of Hg has no influence on the reaction (entry 17 vs entry 10). Eventually, the optimal condition selected were catalyst **2** (0.5 mol%), KHMDS (2 mol%), toluene, 50 bar of hydrogen, 20 h (entry 10).

Next, we explored the substrates scope amenable for the PN manganese precatalyst **2** in hydrogenation (Table 2). In general, arylketones bearing both electron withdrawing and electron donating substituents were reduced in very good yields. In the case of halogenated ketones, fluoro- and bromo-derivatives (**a5**, **a7**) were well tolerated with low catalyst loading, whereas chloro- and iodo-substituted ketones (**a6**, **a8**) were not fully reduced, even under slightly forcing conditions. Steric hindrance had a noticeable influence as increasing the length and the branching of the alkyl chains from methyl (**a1**), ethyl (**a13**) to isopropyl (**a14**) induced a significant drop in the conversion (93% for **b1**, 97% for **b13** to 35% for **b14**). In line with these observations 2',4',6'-trimethylacetophenone **a15** was not reduced with this system. Among the various coordinating functional groups, primary amines **a12**, benzofurane **a16**, and pyridine **a17** were tolerated, but required a higher catalyst loading. Conversely, cyano-derivatives **a10** was reduced in very low yield, and nitro **b11** and thiophene **b18** moieties completely inhibited the reaction.[16] A series of aliphatic and cyclic ketones was reduced smoothly (**b19**-**b23**). Isolated tri-substituted C=C double bond in **a23** remained completely intact during the hydrogenation process. In order to confirm this selectivity, a series of competitive reduction of acetophenone, in the presence of 1-decene, 5-decene and 5-decyne, respectively, were conducted. In all the cases, the reduction of the ketone proceeds without the reduction of the insaturated C-C bond (See Table S3). Finally, *para*-substituted benzaldehydes (**a24**-**a26**) were also reduced to the corresponding benzylic alcohols in high yields showing the tolerance toward ester (**b25**) and amide (**b26**) groups.

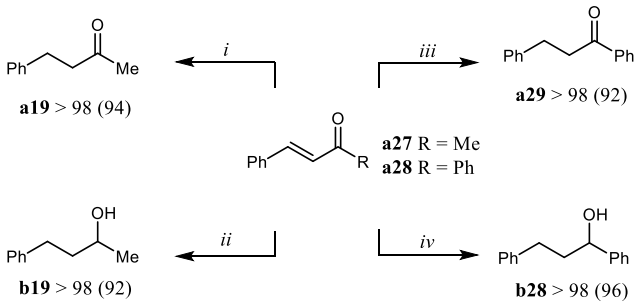
Table 2. Scope of the hydrogenation of carbonyl derivatives under the catalysis of **2**.[a]



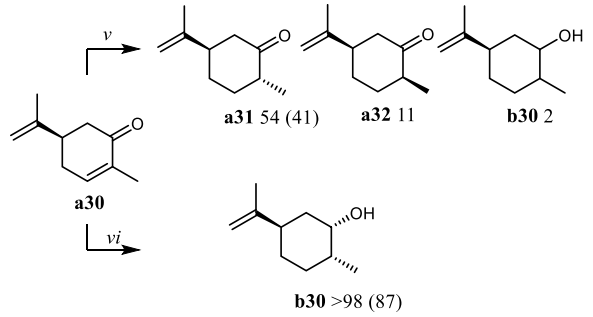
[a] General conditions: ketone (2 mmol), H_2 (50 bar), **2** (0.5 mol%), KHMDS (2 mol%), toluene (4 mL, 0.5 mol.L^{-1}),

50 °C, 20 h. Conversion determined by ^{1}H NMR, isolated yield in parentheses. [b] **2** (0.5 mol%), KHMDS (2 mol%), 80 °C. [c] **2** (1 mol%), *t*BuOK (2 mol%), 80 °C. [d] **2** (5 mol%), *t*BuOK (10 mol%), 80 °C. [e] **2** (1 mol%), *t*BuOK (2 mol%), 50 °C.

In the case of α,β-unsaturated 4-phenylbut-3-en-2-one **a27**, under the standard conditions, a 13:87 mixture of fully reduced product **b19** and ketone **a19** was obtained. Interestingly, under milder conditions, at 30 °C, the saturated ketone **a29** was obtained selectively, while under hasher ones, at 80 °C, the saturated alcohol **b19** was obtained quantitatively (Scheme 2, i and ii). Similarly, chalcone **a28** could be reduced selectively to 1,3-diphenylpropan-1-one **a29** or to 1,3(diphenylpropan-1-ol **b28** (Scheme 2, iii and iv). The reduction of (*R*)-carvone **a30**, bearing both a conjugated and a non-conjugated C=C bond, under mild conditions, led to the formation of a mixture of isomer of dihydrocarvone[17] **a31** and **a32**. Under harsher conditions, dihydrocarveol[18] **b30** was obtained in high yield (87%). In both cases, the non-conjugated C=C bond remained intact. Compared to the reduction of α,β-unsaturated aldehydes by aliphatic PNP manganese catalysts **I**,[5a] where the unsaturated alcohols were produced selectively, and to the reduction of α,β-unsaturated esters,[5b] where solely saturated alcohols were obtained, the present catalytic system allows to reduce exclusively the conjugated C=C double bond, supplementing the previously described ones.



i) **2** (0.5 mol%), KHMDS (2 mol%), 30 °C, H_2 (50 bar), toluene, 18 h
ii) **2** (5 mol%), *t*BuOK (10 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
iii) **2** (2 mol%), *t*BuOK (5 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
iv) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C, H_2 (50 bar), toluene, 22 h



v) **2** (1 mol%), *t*BuOK (2 mol%), 80 °C, H_2 (50 bar), toluene, 18 h
vi) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C, H_2 (50 bar), toluene, 18 h

Scheme 2. Selective reduction of conjugated enones.

In conclusion, a series four Mn^I complexes bearing readily available phosphino-pyridinyl PN bidentate ligands have been prepared, fully characterized, and their catalytic activity was evaluated in the hydrogenation of aldehydes and ketones. The complex $Mn(CO)_3Br(\kappa^2P,N\text{-}Ph_2PN(H)Py)$ (**2**) showed good performances for the hydrogenation of carbonyl derivatives under mild conditions with low catalyst loading and satisfying functional group tolerance, compared to the most active catalytic systems.[6a, 6e] In terms of catalyst design and taking the PN^3P Mn^I complex **IV** as reference,[6c] it appears that simplifying the ancillary tridentate ligand to a bidentate ligand by removing one of its wingtip led to a dramatic increase of the activity of resulting catalytic system.[19] Indeed, the use of the PN Mn^I complex **2** allowed reducing the catalyst loading by a factor of ten, and lowering the temperature from 130 °C to 50 °C, still keeping the same level of activity and chemoselectivity.[6c]

Experimental Section

General procedure for hydrogenation reactions: in an argon filled glove box, an autoclave was charged with complex **2** (5.0 mg, 0.5 mol%) and anhydrous toluene (4.0 mL), followed by ketone (2.0 mmol) and potassium bis(trimethylsilyl)amide (KHMDS, 8.0 mg, 2 mol%), in this order. The autoclave is then charged H_2 (50 bar). The mixture was stirred for 20 hours at 50 °C in an oil bath. The crude residue was purified by column chromatography.

For full experimental details for the synthesis of Mn^I complexes and for catalytic products, see the Supporting Information.

Acknowledgements

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[16] In a competitive experiment, we found that the reduction of acetophenone in the presence of 4-nitrotoluene, was completely inhibited (see Supporting Information Table S3).

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[18] X. Chen, X. Gao, Q. Wu, D. Zhu, *Tetrahedron: Asymmetry* **2012**, *23*, 734-738.

[19] Mechanistic studies to rationalize the enhancement of activity are under investigations.

COMMUNICATION

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