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# Hydrogenation of Carbonyl Derivatives Catalysed by Manganese Complexes Bearing Bidentate Pyridinyl-Phosphine Ligands

Duo Wei,<sup>a</sup> Antoine Bruneau-Voisine,<sup>a</sup> Téo Chauvin,<sup>a</sup> Vincent Dorcet,<sup>b</sup> Thierry Roisnel,<sup>b</sup> Dmitry A. Valyaev,<sup>c</sup> Noël Lugan<sup>c</sup> and Jean-Baptiste Sortais<sup>a,c,d,\*</sup>

<sup>a</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Team Organometallics: Materials and Catalysis, 263 av. du Général Leclerc, 35042 Rennes Cedex, France

<sup>b</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Centre de Diffraction X, 263 av. du Général Leclerc, 35042 Rennes Cedex, France

<sup>c</sup> LCC-CNRS, Université de Toulouse, INPT, UPS, 205 route de Narbonne 31077 Toulouse Cedex 4, France. Email : [jean-baptiste.sortais@lcc-toulouse.fr](mailto:jean-baptiste.sortais@lcc-toulouse.fr)

<sup>d</sup> Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05, France.

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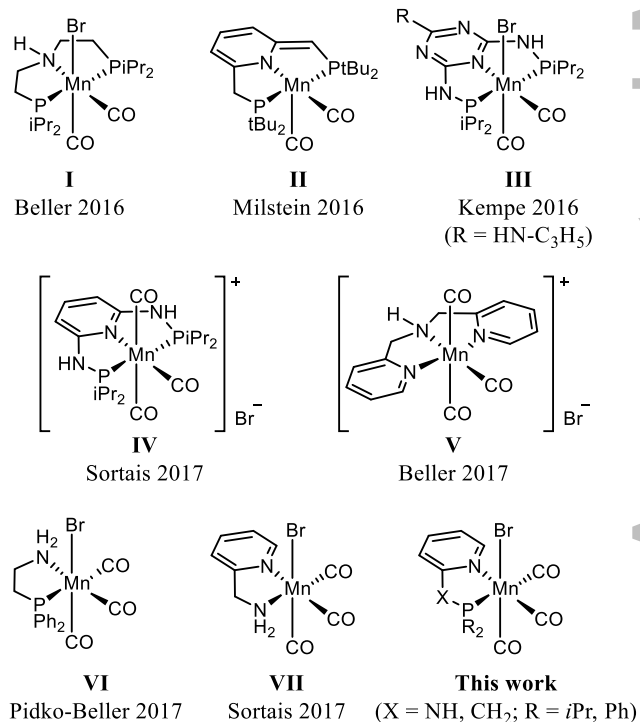
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.201#####>. ((Please delete if not appropriate))

**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.<sup>[1]</sup> 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.<sup>[2]</sup> Actually, the level of the activity, and chemo- and enantioselectivity of iron catalytic systems is now comparable to the ones involving noble transition metals.<sup>[3]</sup> 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<sup>[4]</sup> starting with a seminal contribution of Beller in 2016 using the Mn<sup>I</sup> complex **I** featuring a tridentate bis(phosphino)amine ligand (Scheme 1).<sup>[5]</sup>

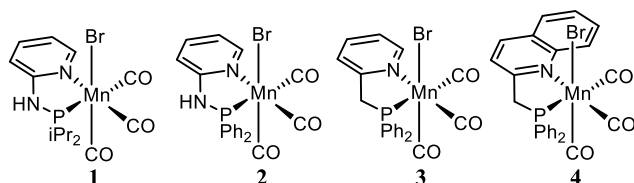
Soon after, a series of parent Mn<sup>I</sup> complexes exhibiting a variety of tridentate ligands including nitrogen and phosphorus donor fragments has been successfully applied in hydrogenation<sup>[6]</sup> and related hydrogen borrowing reactions,<sup>[7]</sup> selected representative examples being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



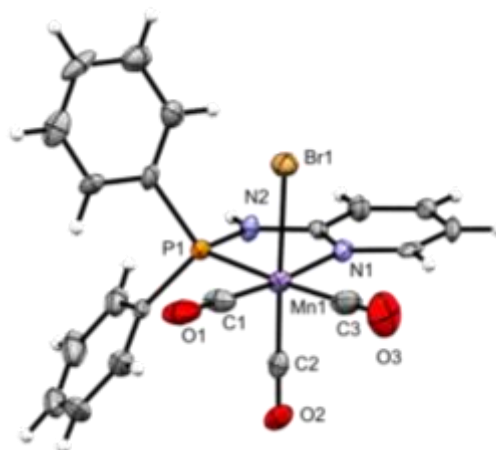
**Scheme 1.** Representative examples of manganese catalysts for redox reactions.

In the course of our investigations directed toward manganese catalysed reduction reactions,<sup>[8]</sup> we first demonstrated that the PN<sup>3</sup>P manganese complex **IV** bearing a 2,6-(diaminopyridinyl)-diphosphine ligand was suitable for the hydrogenation of carbonyl derivatives,<sup>[6c]</sup> yet with moderate activity compared to PN<sup>5</sup>P analogue **III** developed by Kempe<sup>[6a]</sup> 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<sup>[6d]</sup> than Beller's tridentate dipicolylamine complex **V**<sup>[6b]</sup> 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.<sup>[5b, 9]</sup> In the present contribution, we demonstrate that simple Mn<sup>I</sup> complexes bearing readily available phosphino-pyridinyl PN bidentate ligands can achieve a very high efficiency in the hydrogenation of carbonyl compounds.

The ligands R<sub>2</sub>P–X–Py (**L1**: R = *i*Pr, X = NH; **L2**: R = Ph, X = NH; **L3**: R = Ph, X = CH<sub>2</sub>) and Ph<sub>2</sub>P–CH<sub>2</sub>–Qn (**L4**) were obtained in high yield starting from the appropriate chlorophosphines R<sub>2</sub>PCl and 2-aminopyridine (**L1**, **L2**),<sup>[10],[11]</sup> 2-picoline (**L3**),<sup>[12]</sup> or 2-methylquinoline (**L4**),<sup>[13]</sup> respectively, according to literature procedures. The corresponding complexes Mn(CO)<sub>3</sub>Br(κ<sup>2</sup>P,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)<sub>5</sub>Br 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.<sup>[14]</sup> 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<sup>2</sup>P,N mode and the three carbonyl ligands being in facial position.

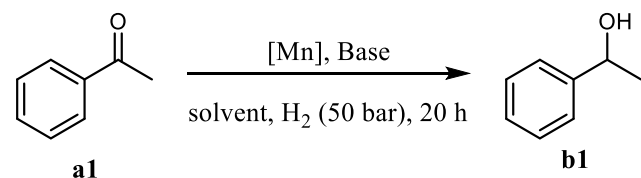


**Figure 1.** Manganese complexes synthesised for this study.



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

**Table 1.** Optimization of the reaction parameters



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

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

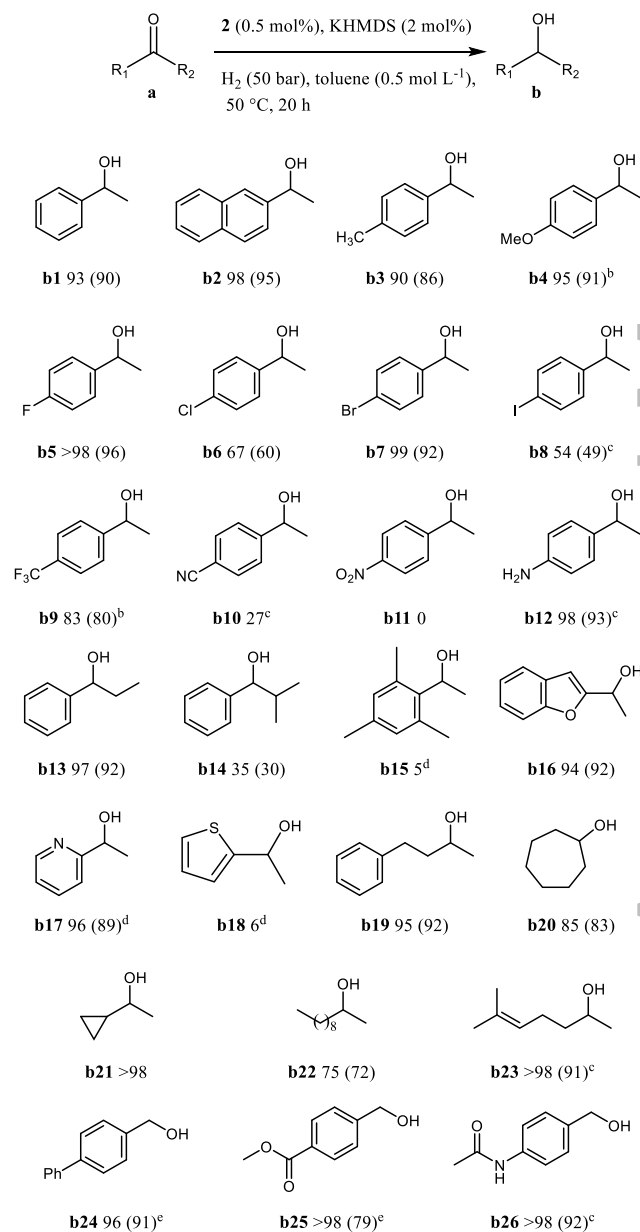
NMR. <sup>c</sup> 300 equiv. of Hg (vs **2**) were added before H<sub>2</sub> in the reaction mixture.

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<sup>3</sup>P catalyst **IV**,<sup>[6c]</sup> *i.e.* complex **1** (5 mol%), *t*BuOK (10 mol%) as the base, toluene, 110 °C, H<sub>2</sub> (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).<sup>[15]</sup> 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.<sup>[16]</sup> 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.

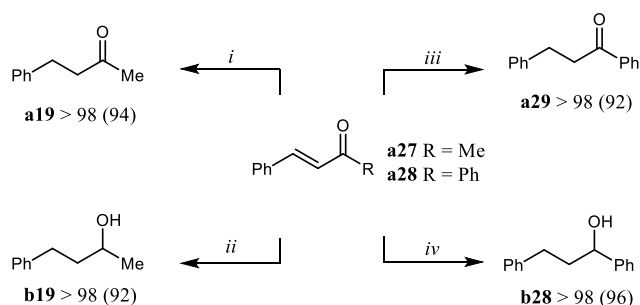
**Table 2.** Scope of the hydrogenation of carbonyl derivatives under the catalysis of **2**.<sup>a</sup>



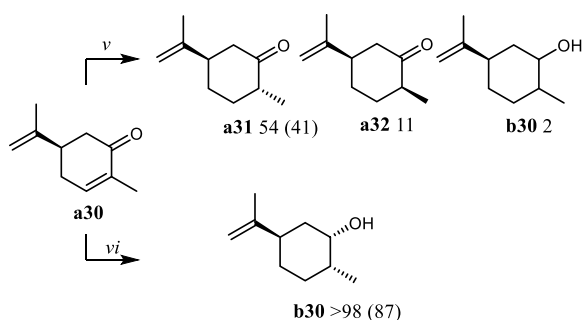
<sup>a</sup> General conditions: ketone (2 mmol), H<sub>2</sub> (50 bar), **2** (0.5 mol%), KHMDS (2 mol%), toluene (4 mL, 0.5 mol.L<sup>-1</sup>),

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

In the case of  $\alpha,\beta$ -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 harsher 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<sup>[17]</sup> **a31** and **a32**. Under harsher conditions, dihydrocarveol<sup>[18]</sup> **b30** was obtained in high yield (87%). In both cases, the non-conjugated C=C bond remained intact. Compared to the reduction of  $\alpha,\beta$ -unsaturated aldehydes by aliphatic PNP manganese catalysts **I**,<sup>[5a]</sup> where the unsaturated alcohols were produced selectively, and to the reduction of  $\alpha,\beta$ -unsaturated esters,<sup>[5b]</sup> 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,  $\text{H}_2$  (50 bar), toluene, 18 h  
 ii) **2** (5 mol%), *t*BuOK (10 mol%), 80 °C,  $\text{H}_2$  (50 bar), toluene, 18 h  
 iii) **2** (2 mol%), *t*BuOK (5 mol%), 80 °C,  $\text{H}_2$  (50 bar), toluene, 18 h  
 iv) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C,  $\text{H}_2$  (50 bar), toluene, 22 h



- v) **2** (1 mol%), *t*BuOK (2 mol%), 80 °C,  $\text{H}_2$  (50 bar), toluene, 18 h  
 vi) **2** (5 mol%), *t*BuOK (10 mol%), 100 °C,  $\text{H}_2$  (50 bar), toluene, 18 h

## Scheme 2. Selective reduction of conjugated enones.

In conclusion, a series four  $\text{Mn}^{\text{I}}$  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  $\text{Mn}(\text{CO})_3\text{Br}(\kappa^2\text{-P,N-Ph}_2\text{PN(H)Py})$  (**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.<sup>[6a, 6e]</sup> In terms of catalyst design and taking the  $\text{PN}^3\text{P}$   $\text{Mn}^{\text{I}}$  complex **IV** as reference,<sup>[6c]</sup> 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.<sup>[19]</sup> Indeed, the use of the PN  $\text{Mn}^{\text{I}}$  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.<sup>[6c]</sup>

## 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  $\text{H}_2$  (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  $\text{Mn}^{\text{I}}$  complexes and for catalytic products, see the Supporting Information.

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## COMMUNICATION

## Hydrogenation of Carbonyl Derivatives Catalysed by Manganese Complexes Bearing Bidentate Pyridinyl-Phosphine Ligands

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Duo Wei, Antoine Bruneau-Voisine, Téo Chauvin, Vincent Dorcet, Thierry Roisnel, Dmitry A. Valyaev, Noël Lugan and Jean-Baptiste Sortais\*

