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Hydrogenation of carboxylic esters catalyzed by manganese catalysts supported by bidentate NHC-phosphine ligands

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KEYWORDS. Manganese, hydrogenation, carboxylic esters, N-heterocyclic carbene, phosphine, Earth abundant transition metals

ABSTRACT A series of bidentate manganese complexes with a general structure $[(\kappa^2\text{C},\text{P}-\text{R}_2\text{PCH}_2\text{CH}_2\text{-NHC})\text{Mn}(\text{CO})_3\text{Br}]$ (NHC = N-substituted imidazolylidene) was prepared and fully characterized. These complexes were proven to be efficient catalysts for the hydrogenation of carboxylic ester derivatives with a low catalyst loading (0.5 mol%) in 2-Me-THF at 100 °C in the presence of KHBt_3 . The generality of this hydrogenation was exemplified with more than 25 substrates. Experimental and computational investigations allowed to propose a rational mechanism involving an anionic tricarbonyl manganese hydride complex as the active species.

HIGHLIGHTS

- Hydrogenation of carboxylic esters with manganese catalysts
- Manganese complexes with bidentate P-NHC ligand as efficient catalyst in hydrogenation
- “NH” free manganese catalysts for hydrogenation of carboxylic esters
- Computational investigations suggest an anionic tricarbonyl manganese hydride as the active species

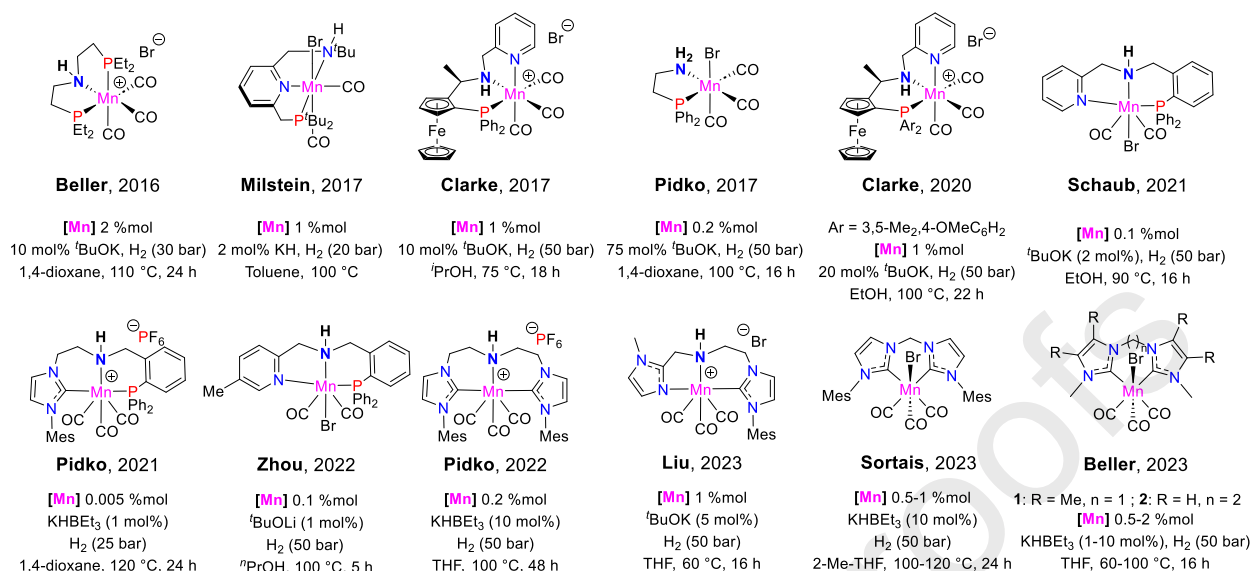
1. Introduction

The reduction of carboxylic esters to alcohols is among the most fundamental reactions in organic chemistry. Among the various reducers that can be used, dihydrogen is undoubtedly the most sustainable reagent compared to metal hydrides, silanes or boranes in terms of atom economy. For this reason, a range of heterogeneous and homogeneous hydrogenation catalysts has been developed for over a century, and the search for more selective and efficient systems under the mildest possible conditions continues to be a major focus.[1]

Within a few years, the application of manganese, an abundant and available 3d transition metal, has gained considerable importance in reduction reactions, mainly due to the stability of the molecular pre-catalysts synthesized.[2-5] Despite this rapid development, in the case of ester hydrogenation, a still limited number of catalytic systems have been described in the literature. In 2016, Beller's group described the first example of hydrogenation of esters to alcohols with a catalyst based on the tridentate PN(H)P MACHO ligand.[6] Later on, Milstein and coll. used a tridentate ligand of the N(H)-Pyridine-P type.[7] The groups of Clarke,[8-11] Schaub[12] and Zhou[13] all showed that ligands based on a Pyridine-N(H)-P architecture were also effective in this transformation. Pidko's group was the first to demonstrate that bidentate amino-phosphine ligands promoted ester reduction, provided that the amount of base used was almost stoichiometric.[14] The same group also evidenced the beneficial effect of an additional N-heterocyclic carbene ligand C_{NHC} -N(H)P ligand on the reduction of formate esters at very low catalytic loadings.[15] The MACHO ligand analog with two carbene donors, $C_{NHC}N(H)C_{NHC}$, also proved an excellent ligand.[16] Finally, Liu's team demonstrated the potential of N-N(H)- C_{NHC} ligands for the hydrogenation of various carboxylic acids, including ester derivatives.[17]

It's important to note that in all these examples, the ligand possesses an NH fragment, paving the way for a bifunctional mechanism. The only catalytic system without an NH fragment is that based on bis-NHC bidentate ligands described recently simultaneously by our group[18] and that of Beller[19]. Very few catalytic systems for hydrogenation with manganese have neither NH fragments nor pyridinyl moieties that can participate in metal-ligand cooperation. Until now, in addition to the bis-NHCs mentioned above, only the diphosphine systems described by Kirchner[20-25] and Garcia[26, 27] and carbene-phosphine systems described by our team[28] have been known in hydrogenation. It is important to note that the catalysts developed by Kirchner have an alkyl ligand on manganese, a crucial feature for the precatalyst activation step without external additives, whereas the phosphine-carbene system carries a bromide ligand and requires an external base to show a catalytic activity. Herein, we show that manganese complexes featuring bidentate NHC-phosphine ligands are excellent catalysts for ester hydrogenation and propose a mechanism highlighting the critical role of the chelating ligand.

Chart 1. Manganese catalysts for hydrogenation of carboxylic esters.



2. Results and discussion

2.1. Synthesis of the ligands and complexes

In line with our work on the hydrogenation of carbonyl derivatives by manganese complexes,[28-31], we explored the reduction of esters, which represents a greater challenge due to the low electrophilicity of the C=O bond, with NHC-phosphine manganese complexes. We first evaluated complex **1**, possessing a carbene-phosphine ligand with a methylene bridge, which was found to be an excellent catalyst for the hydrogenation of ketones.[28] Under the operating conditions determined for ketones (complex **1** (1 mol%), 20% ^tBuOK, THF, 100 °C, 20 h, 50 bar, Table 1, entry 1), the hydrogenation of methyl benzoate as a model substrate led to the formation of benzyl alcohol in a moderate but promising yield (37%, 77% conversion).

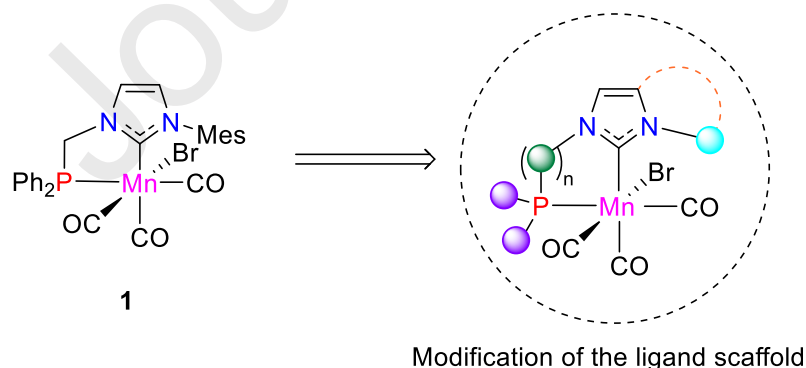
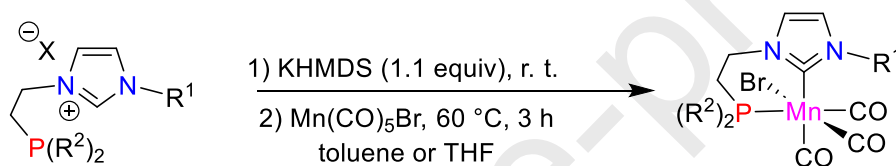


Figure 1: Strategy followed to develop new Mn(I) catalysts based on NHC-phosphine ligands.

In order to improve the performance of the system, we first extended the family of catalysts by modifying the key structural elements of the ligand (Figure 1). First, the length of the spacer between the phosphine moiety and the N-heterocycle was extended from methylene (complex **1**) to ethylene (complexes **2-6**) in order to see the impact on the activation of H₂. The steric hindrance and the electronic properties of the substituents on the nitrogen of the NHC ring were modulated (from mesityl (**2**), to methyl (**3**) and isopropyl (**4**)), as well as the nature of the N-heterocycle itself (imidazole (**2-5**) and imidazo[1,5-a]pyridine (**6**)).[32-34] Finally, the nature of the substituents on the phosphorus atom was changed from aryl to alkyl groups (phenyl (**2-4, 6**) and cyclohexyl (**5**)).

All the ligands were prepared according to a two-step procedure following protocols from the literature.[35-39] Starting from the corresponding N-substituted-imidazoles, quaternization with 1,2-dichloroethane afforded the desired chloro(β -chloroethyl)imidazolium salts, which were then converted to the desired preligands by nucleophilic substitution with KPPH₂. In order to prevent bromide/chloride exchange during the complexation onto Mn(CO)₅Br, imidazolium salts with non-coordinating anions such as tosylate or hexafluorophosphate were selected.



L2.HOTs - R₁ = Mes, R₂ = PPh₂, X = OTs

L3.HPF₆ - R₁ = Me, R₂ = PPh₂, X = PF₆

L4.HPF₆ - R₁ = iPr, R₂ = PPh₂, X = PF₆

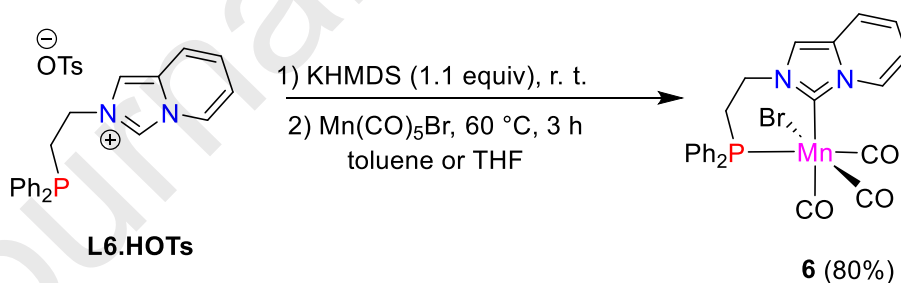
L5.HOTs - R₁ = Mes, R₂ = PCy₂, X = OTs

2 - R₁ = Mes, R₂ = PPh₂ (90%)

3 - R₁ = Me, R₂ = PPh₂ (85%)

4 - R₁ = iPr, R₂ = PPh₂ (98%)

5 - R₁ = Mes, R₂ = PCy₂ (88%)



Scheme 1: Synthesis of NHC-phosphine complexes **2-6** from the corresponding imidazolium salt precursors.

The coordination to Mn(CO)₅Br took place at 60 °C in THF or toluene after *in situ* deprotonation of the imidazolium salts with KHMDS (Scheme 1). Complexes **2-6** were obtained as yellow powders in excellent yields (80-98%). In the solid state, compounds **2-6** were fairly stable in air and moderately sensitive to light, as they can be weighted under air and stored for several months safe from light. All the complexes were fully characterized by classical spectroscopic techniques.

IR spectra in solution displayed a classical pattern for a facial arrangement of tricarbonyl complexes. The molecular structures were all ascertained by X ray diffraction analysis (Figure 2).

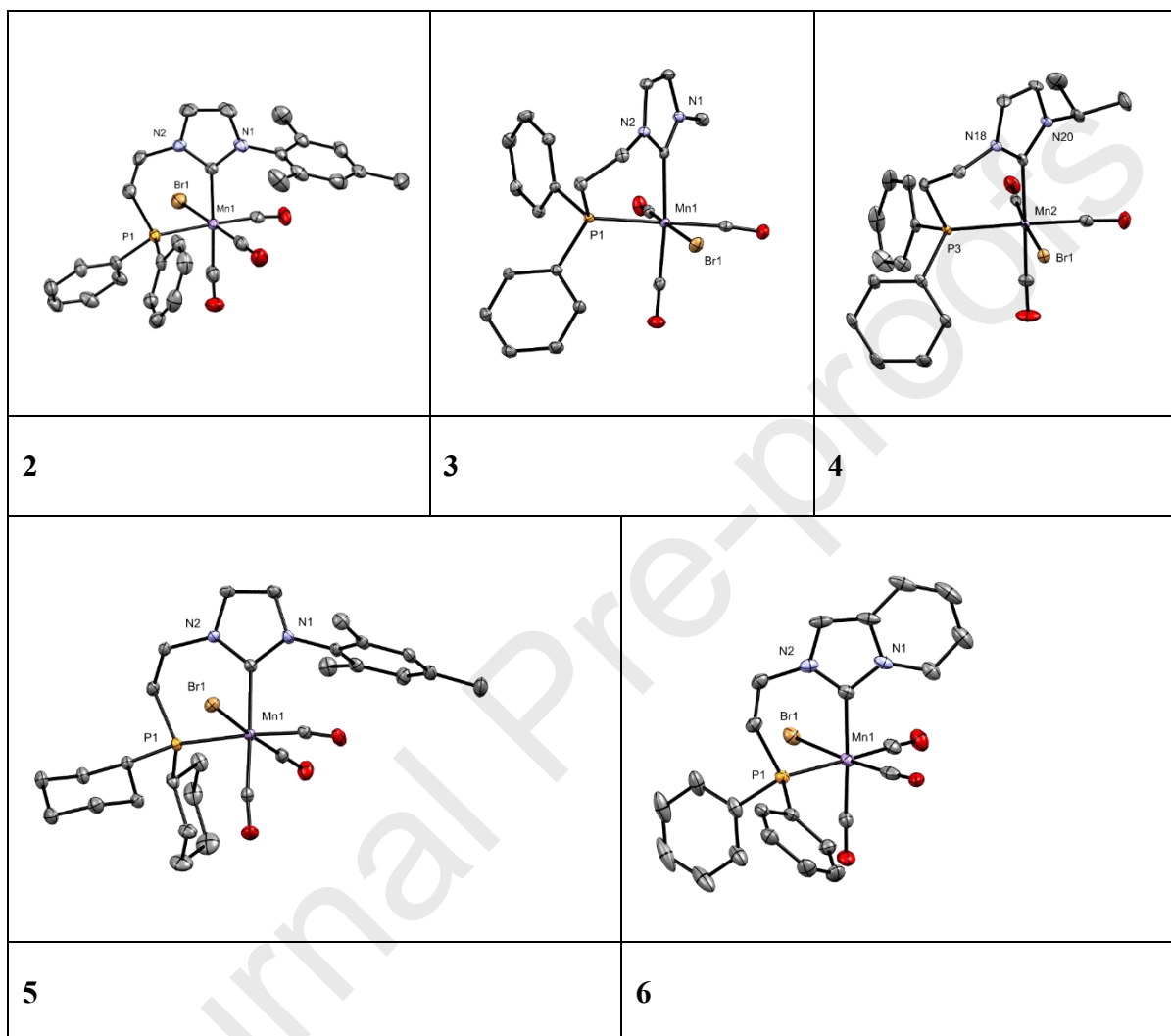


Figure 2: Perspective views of complexes 2-6 with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms were omitted for clarity.

In order to evaluate the importance of the structure of the ligand on the catalytic activity, i.e. the key structural parameter of the bidentate phosphino-carbene ligand, a series of complexes with a closely related structure was prepared. In particular, we have selected two ligands in which the phosphine moiety was substituted by a tertiary amine[40] in complex 7 and a pyridine[41] in complex 8. In order to evaluate the importance of the carbene fragment, two complexes bearing diphosphine ligands, namely bis-diphenylphosphinoethane (dppe)[42] and bis-dimethylphosphinoethane (dmpe)[43] (complexes 9 and 10, Chart 2) have been included in the library of benchmark catalysts. Finally, complex 11 having two monodentate ligands, a phosphine and an NHC, was prepared for comparison's sake with the bidentate analogues.

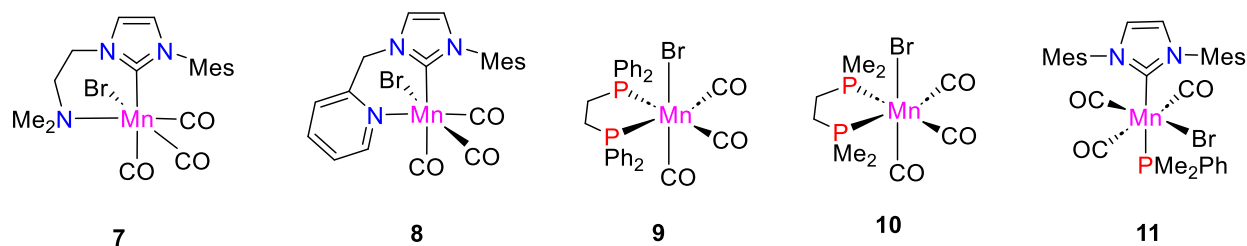


Chart 2: Manganese catalysts **7-11** selected as benchmark catalysts.

2.2. Optimization of the hydrogenation reaction

With these complexes in hand, the reduction of methylbenzoate **a1** as model substrate with dihydrogen was optimized (Tables 1, 2, S1, S2, and S3). First, complexes **1** and **2** were compared. Using complex **2**, displaying an ethylene bridge between the phosphine and the N-heterocycle moieties, instead of a methylene bridge present in complex **1**, methyl benzoate **a1** was completely reduced to the benzylalcohol **b1** with a total selectivity (entries 1-2). Indeed, benzyl benzoate **a2** resulting from the transesterification of the starting ester **a1** with the formed alcohol **b1** was not detected. Complex **2** was therefore selected for further optimization. With ^tBuOK as the additive, a decrease in temperature to 80 °C (entry 3) or in catalyst loading to 0.5 mol% (entry 4), or in hydrogen pressure to 30 bar (entry 5) leads to a decrease in conversion. The effect of the cation of the base was also investigated (Table S1, entries 9, 11 and 12), showing a favorable effect of potassium ion over lithium and sodium. Several solvents were then evaluated (Table S2). In tert-amyl alcohol, only the tert-amyl benzoate ester was formed (100%) resulting from the transesterification of ester **a1**. Among THF, toluene, dioxane, cyclopentylmethyl ether and 2-Me-THF, the latter, recognized as a green solvent able to stabilize organometallic reagents,[44, 45] significantly improved the activity of the catalytic system compared to THF (Table S2 and Table 1, entry 6), allowing to reach nearly full conversion at a pressure of 30 bar of H₂. In order to activate bromo-manganese complexes, triethylborohydride salts were also tested as an alternative to classical alcoholic bases (Table S3), that have been used previously with iron[46], cobalt[47, 48] or even manganese[15] in hydrogenation reactions. To our delight, with KHBET₃, the catalyst loading could be lowered to 0.5 mol% without any loss of activity (Table 1, entry 7) and even to 0.2 mol% (91% yield, entry 8). Lowering the quantity of KHBET₃ from 10 to 2.5 mol% induced a slight decrease in both conversion and selectivity (entry 9). Finally, blank reactions in the absence of additive or catalyst (Table 1, entries 10-11), demonstrated the importance of each component of the catalytic mixture.

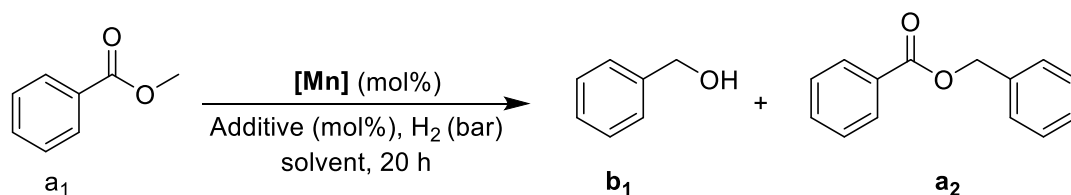


Table 1: Optimization of the parameters for the hydrogenation of methyl benzoate **a1** catalyzed by complex **2**.

Entry	[Mn] (mol%)	Solvent	Additive (mol%)	H ₂ (bar)	Temp (°C)	Conversion ^[b] (%)	NMR yield ^[b]	
							b ₁	a ₂
1	1 (1)	THF	^t BuOK (20)	50	100	77	37	40
2	2 (1)	THF	^t BuOK (20)	50	100	>98	>98	-
3	2 (1)	THF	^t BuOK (20)	50	80	70	55	15
4	2 (0.5)	THF	^t BuOK (20)	50	100	94	92	2
5	2 (1)	THF	^t BuOK (20)	30	100	89	83	6
6	2 (1)	2-Me- THF	^t BuOK (20)	30	100	>98	92	8
7	2 (0.5)	2-Me- THF	KHBEt ₃ (10)	50	100	98	98 (96)	-
8	2 (0.2)	2-Me- THF	KHBEt ₃ (10)	50	100	97	91	6
9	2 (0.5)	2-Me- THF	KHBEt ₃ (2.5)	50	100	93	81	11
10	2 (1)	THF	-	50	100	0	0	-
11	-	2-Me- THF	KHBEt ₃ (10)	50	100	10	<2	9

[a] Experimental procedure: catalyst, solvent (1.5 mL), ester (1 mmol) and additive were introduced under inert atmosphere in this order into an autoclave, the latter was then rapidly pressurized with H₂ to the required pressure and heated in an oil bath under stirring for 20 h at the indicated temperature.

[b] Conversions and yields were determined by ¹H NMR. Isolated yield in parenthesis.

Table 2: Screening of manganese catalysts **1-11** for the hydrogenation of methylbenzoate **a1**.

Entry	[Mn] (mol%)	Conversion ^[b] (%)	NMR yield	
			b ₁	a ₂
1	1 (0.5)	90	31	59
2	2 (0.5)	98	98 (96)	-
3	2 (0.1)	90	67	23
4	3 (0.5)	58	25	33
5	4 (0.5)	>98	>98	-
6	4 (0.1)	65	11	54
7	5 (0.5)	90	87	3
8	6 (0.5)	25	2	23
9	7 (0.5)	10	0	10

10	8 (0.5)	32	14	18
11	9 (0.5)	6	1	5
12	10 (0.5)	35	1	34
13	11 (1)	8	1	7

[a] Experimental procedure: an autoclave was loaded with an ester solution (1 mmol) in 2-Me-THF (1 mL) and a solution of complex which was prepared in 0.5 mL of 2-Me-THF and activated with a solution of KHBET_3 (10 mol%; 1M in THF) for 30 min in that order, then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring for 24 h at 100 °C.

[b] Conversions determined by ^1H NMR spectroscopy. Isolated yield in parentheses.

Complexes **1-11** were tested under optimized conditions (Table 1, entry 7). Complexes **1-5**, bearing bidentate NHC-phosphine ligand, displayed all moderate to good activity for the reduction of methylbenzoate, complex **2** being the most efficient one (Table 2, entries 1-7). In order to discriminate complexes **2** and **4**, the catalytic charge was lowered to 0.1 mol% (entries 3 and 6), affording a TON of 670 for complex **2**. Complex **7** with a chelating tertiary amine was totally inactive. Complex **8**, with a pyridinyl fragment, displayed some activity even if the loading of catalyst used in this comparative study is very low (entry 10). For complexes **9** and **10** (entries 11 and 12), featuring diphosphinoethane ligands, only **10** with alkyl substituents on the phosphorus atom exhibited a moderate activity. Those results are in line with the results of Kirchner[20-24] and Garcia,[26, 27, 49] who have shown that bis-dialkylphosphinoethane manganese complexes were active in various hydrogenation and transfer hydrogenation reactions, while bis-diarylphosphino-complexes were inactive. Finally, the importance of the bidentate nature of the ligand was highlighted by the absence of conversion obtained with the complex **11** bearing monodentate ligands, namely IMes and PMe_2Ph .

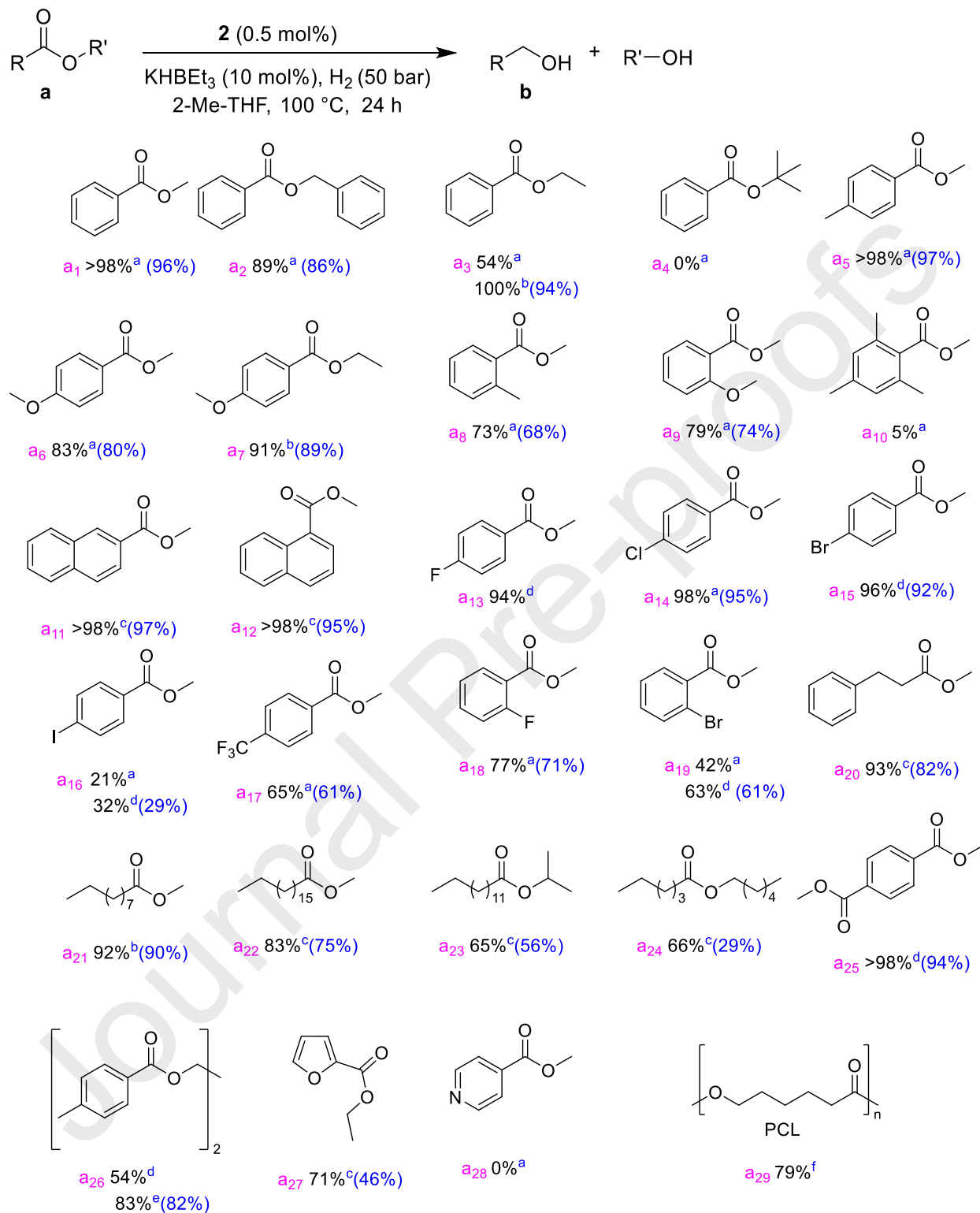
2.3. Scope of the hydrogenation reaction

Having identified the best manganese complex and the optimum conditions for the reduction of methylbenzoate **a1** (complex **2** (0.5 mol%), KHBET_3 (10 mol%), H_2 (50 bar) in 2-Me-THF for 24 h at 100 °C), the limits of this catalytic system were assessed. Firstly, variation of the alkyl moiety of the alkylbenzoates (**a1-a4**) evidenced that steric hindrance had a strong influence on catalytic activity, as tert-butylbenzoate **a4** was not converted to alcohols at all. With ethylbenzoate **a3**, conversion was 90% after 24 h, but the NMR yield in benzyl alcohol was only 54%, with 36%

benzylbenzoate as by-product. Extending the reaction time to 48 h led to a quantitative NMR yield in benzylalcohol. Electron-donating groups on the aromatic ring, such as methyl and methoxy, in the para and ortho positions are well tolerated (**a5-a10**). For methyl naphthoate esters (**a11** and **a12**), the formation of hindered naphthyl naphthoate explained the harsher conditions (1 mol%, 48 h) required to obtain high yields. Halogenated methyl benzoates (**a13-a19**) substituted in the para or ortho positions by fluoro, chloro, bromo, iodo to a lesser extent and trifluoromethyl moieties, are reduced without noticeable deactivation of the catalyst. Next a series of aliphatic esters **a20-24**, usually more difficult to reduce than aromatic ones, were converted to alcohols in good yield in the presence of 0.5 or 1 mol% catalyst for 48 h. Diester such as dimethylterephthalate **a25** was reduced to 1,4-dimethanol benzene in high yield. In contrast, diester **a26**, affording ethylene glycol as co-product, was more difficult to reduce. The deleterious effect of ethylene glycol on the catalyst was verified by performing the reduction of methylbenzoate **a1** in the presence of this diol (0.5 equiv, conditions a) affording only 62% of benzyl alcohol. A similar effect has been reported by Clarke with ruthenium based catalysts.[50]

Finally, heteroaromatics such as 2-ethylfuroate **a27** were reduced, albeit, methyl isonicotinate **a28** was not. In order to confirm the compatibility of this system with heterocycles, competitive experiments, i.e. the hydrogenation of methyl benzoate **a1** in the presence of heterocycles has been performed (conditions [a] of scheme 2, See SI, Table S4): in the presence of pyridine and thiophene, the hydrogenation proceeds and the benzyl alcohol was formed (52 and 57% yield respectively), while in the presence of pyrrole, no conversion was obtained. Some substrates were not reduced such as methyl p-hydroxybenzoate and methyl p-aminobenzoate, probably due to the acidic character of the hydroxyl or amino moiety, as well as methyl p-cyano and p-nitrobenzoate (See SI, Table S5). Gratifyingly, the scope could also be extended to polyesters such as polycaprolactone **a29** (Aldrich, Mw = 14 000), as 1,6-hexanediol was obtained in good yield (79%).

Scheme 2: Scope of the hydrogenation of carboxylic esters catalyzed by manganese complex **2**.



[^a] Experimental procedure: an autoclave was loaded with a solution of ester (1 mmol) in 2-Me-THF (1 mL) and a solution of **2** (0.5 mol%) in 2-Me-THF, which was first preactivated with KHBEt₃ (10 mol%, 1M in

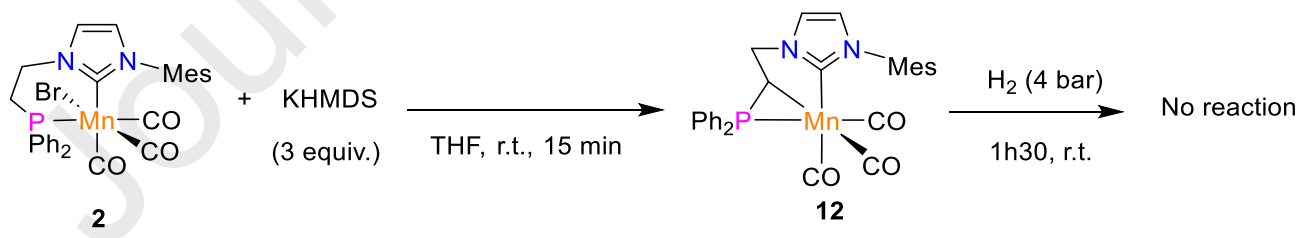
THF) for 30 min, in this order. Then the autoclave was immediately pressurized with hydrogen (50 bar) and kept under stirring in an oil bath for 24 h at 100 °C. Yields were determined by ^1H NMR, with isolated yields being given in parentheses. [b] **2** (0.5 mol%), 100 °C, 48 h. [c] **2** (1 mol%), 100 °C, 48 h. [d] **2** (1 mol%), 100 °C, 24 h. [e] **2** (5 mol%), 120 °C, 48 h. [f] **2** (5 mol%), 100 °C, 24 h, 2-Me-THF (1 mL) and anisole (1 mL) as solvent.

2.4. Mechanism of the hydrogenation reaction

We then investigated the mechanism of this hydrogenation from an experimental and computational point of view. DFT studies were carried out with a dispersion corrected hybrid functional and an implicit model for the solvent (THF). Natural bond orbital (NBO) analyses of the stationary points of the potential energy surface have been carried out. Full computational details are given in the SI.

Complexes **1** and **2** are structurally very similar, differing only in the length of the alkyl bridge linking the phosphine and the NHC moieties, methylene and ethylene-type respectively. We showed, previously, that the stoichiometric activation of H_2 with complex **1** in the presence of base involved the formation of a metallacyclic complex, characterized spectroscopically, resulting from the deprotonation of the C-H carbon atom in alpha position to the phosphorus atom.[28] This intermediate was particularly unstable, with half-live time of around 30 min at r.t.. Nevertheless, when the addition of KHMDS to a solution of **1** was performed under an atmosphere of H_2 , the quantitative formation of the corresponding manganese hydride complex was observed at r.t. within a few minutes, showing its high reactivity towards H_2 .

When complex **2** was treated with KHMDS in THF at r.t. under an argon atmosphere within 15 min, a new Mn complex **12**, characterized by a chemical shift at δ_{P} -12.7 ppm in ^{31}P NMR, was formed quantitatively (Scheme 3 and S1-2 and S8). The molecular structure obtained by X-ray diffraction provided clear evidence of the formation of a three-membered metallacycle resulting from deprotonation of the CH_2 group in alpha position to phosphorus (Figure 3, left).[51, 52]



Scheme 3: Synthesis and reactivity of cyclometalated complex **12** from NHC-phosphine complex **2**.

This complex **12** is stable at r.t. under an inert atmosphere. However, when **12** was exposed to H_2 (4 bars, r.t., 1h30 to 72 h and then 80 °C for 1 h), the formation of the corresponding hydride

complex was not detected, only partial degradation was observed over elongated period of time (See SI, Figures S8-12). Therefore **12** does not activate H_2 , and thus does not seem to be an active species in the catalytic cycle. From a computational perspective, a consistent observation emerges that direct activation of H_2 from **12** demands an excessively high activation energy ($38.46 \text{ kcal.mol}^{-1}$), rendering it inaccessible. Furthermore, when **12** was employed as a catalyst without any other additive for the reduction of methyl benzoate under the optimized conditions (0.5 mol%, 50 bar, 100°C , 24 h) no conversion was detected after the reaction (See SI).

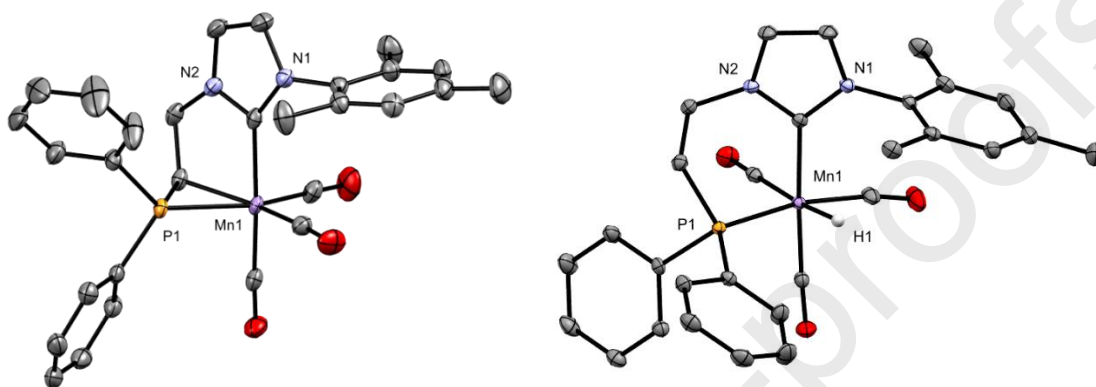
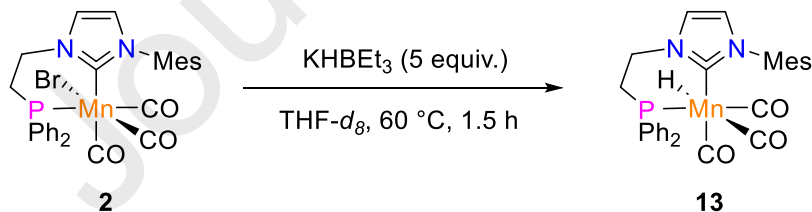


Figure 3: Perspective views of complexes **12** and **13** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms were omitted for clarity.

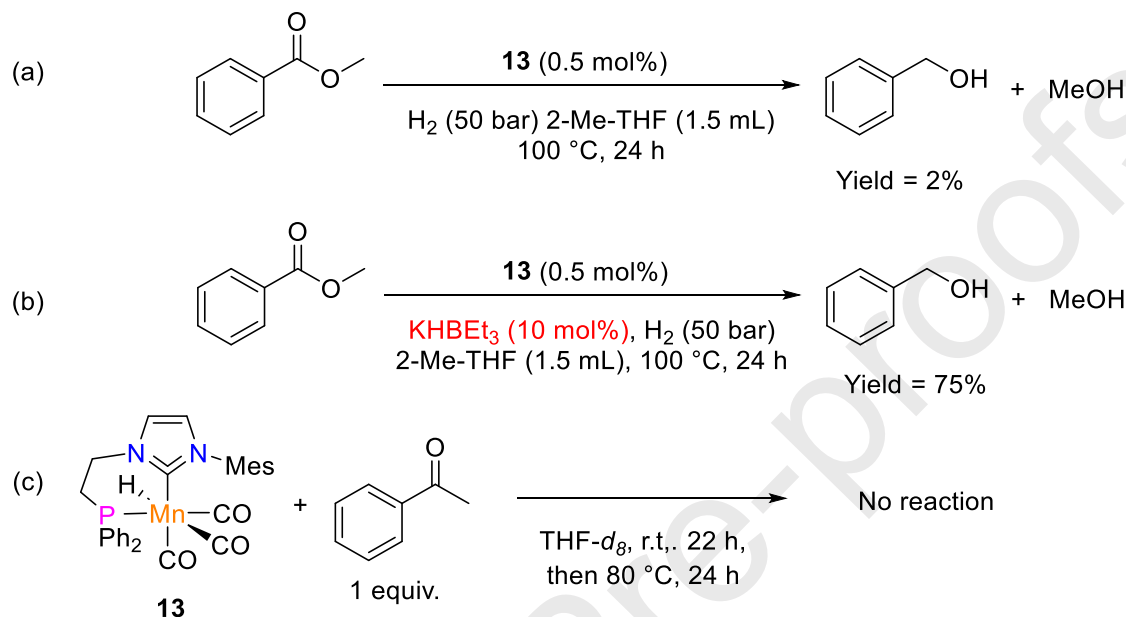
As KHBET_3 was found to be a better activator than $t\text{BuOK}$ (Table 1), complex **2** was reacted stoichiometrically with KHBET_3 (5 equiv.) in $\text{THF-}d_8$. After 30 min at rt, no change was detected by multi-nuclear NMR spectroscopy. Increasing the reaction temperature to 60°C , led to the full conversion of the brominated complex **2** into a new hydride complex **13** after 1.5 h, characterized by a single signal at δ_{P} 65.0 ppm in ^{31}P NMR and a doublet at δ_{H} -7.0 ppm ($^2J_{\text{HP}} = 49.3 \text{ Hz}$) in ^1H NMR (Scheme 4, Figures S13-16). Complex **13** was also synthesized by reaction of **2** with NaBH_4 in ethanol in 80% yield and fully characterized, including by X-ray diffraction analysis (Figure 3, right).



Scheme 4: Synthesis of NHC-phosphine Mn hydride complex **13**.

The hydride complex **13** was used as a precatalyst for the hydrogenation of methylbenzoate in the absence of KHBET_3 in an autoclave (**13** (0.5 mol%), methylbenzoate, 1 mmol, 2-Me-THF, H_2 , 50

bar, 100 °C, 24 h) but no conversion was detected (Scheme 5 and Figure S17). This absence of catalytic activity is in agreement with the absence of reaction between **13** and acetophenone (or methylbenzoate) observed when both compounds were mixed and heated at 80 °C for 24 h (See Scheme 5 and Figures S18-19). Interestingly, the catalytic activity of **13** was restored if a catalytic amount of KHBEt_3 was added to the reaction mixture (See Scheme 5 and Figure S20).[53]



Scheme 5: Catalytic and stoichiometric reactions with Mn hydride complex **13**.

It therefore appears that the 18-electron saturated complex **13** with three carbonyl ligands and a hydride is not an active species involved in the catalytic cycle. This hypothesis was also supported by the calculations, as no transition state could be found approaching the neutral hydride **13** and a ketone.[54-57]

Alternatively, 16-electron manganese hydride dicarbonyl complex was proposed by Kirchner as the active species, in the case of bidentate diphosphine ligand and by Beller in the case of bis-NHC ligand. To evaluate this hypothesis, first, Me_3NO (10 mol%) was added to a catalytic reaction as additive, instead of KHBEt_3 , in the presence of **13** (0.5 mol%) as precatalyst; but no conversion was detected after 24 h at 100 °C for the hydrogenation of methylbenzoate (50 bar of H_2 , Figure S21).

Another classical way to promote the decarbonylation of one CO ligand is irradiation with UV light. First, hydride complex **13** was irradiated at 365 nm, at r.t. in $\text{THF-}d_8$, but mainly decomposition was observed (Figure S22-23). However, when the irradiation of **13** was carried out in the presence of an excess of acetophenone (5 equiv.), two new complexes with very closed ^{31}P NMR chemical shifts ($\delta_{\text{P}} 33.9 \text{ ppm}$ and $\delta_{\text{P}} 33.4 \text{ ppm}$) were formed quantitatively. The presence of characteristic ^1H NMR signals from the 1-phenylethanol moiety (Figures S24-27) suggests the formation of alkoxy complexes as two diastereoisomers resulting from the insertion of the ketone into the Mn-H bond. The transfer of the metal-bonded hydride to the ketone was confirmed by

repeating the experiment using the deuterated hydride manganese complex, and the transfer of the deuterium atom to the carbonyl moiety was clearly observed. (Figure S28-29).

When the same reaction was carried out in the presence of H₂ (4 bar H₂, 5 equiv. acetophenone), the same complexes were obtained, without the reduction of the excess of ketone to 1-phenylethanol (Figure S30). However, if the same reaction mixture was then heated at 80 °C for 24 h, the ketone was converted to alcohol (83% conversion, Figure S31). At the end of the reaction, the only detectable complex was the hydride complex **13** (Figure S32). This seems to indicate that the tricarbonyl hydride is a dormant form of the active species and confirms the absence of decarbonylation during the catalytic reaction. Calculations also indicate that the decarbonylation of **13** is energetically particularly unfavorable (35.04 kcal/mol compared to the complex **13**) and thus unlikely to occur.

Given that the alpha position to phosphorus is deprotonatable, as evidenced by the formation of the cyclometalated complex **12**, and building on the work of the Kempe,[58] Liu[59] and Mösh Zanetti[60] groups involving anionic hydrides as the active species in hydrogenation with manganese complexes, we considered an anionic hydride resulting from the deprotonation of hydride **13** as the active species.[61] Experimentally, we could not gather unambiguous evidence of the presence of such species, we therefore investigated computationally this pathway. Acetophenone was regarded as a model substrate for this hydrogenation reaction. For the calculated structure of the anionic complex **I**, the Mn-H and Mn-P distances are slightly longer, 1.582 Å and 2.329 Å, respectively, vs. 1.570 Å and 2.248 Å, respectively, for **13**. Additionally, the P-C(H) bond is significantly shorter ie 1.748 Å, vs. 1.846 Å for **13**.

The overall reaction is found to be exergonic ($\Delta_rG^\circ = -6.93$ kcal/mol) and requires a Gibbs activation energy of 27.66 kcal·mol⁻¹ relative to that of the separate reagents (Figure 4). The reaction sequence begins with the weak interaction of the substrate with the hydride complex **I**, leading to adduct **II** (4.97 kcal·mol⁻¹ less stable than the separated species). The next elementary step, which serves as the rate determining step (27.66 kcal·mol⁻¹ compared to the separated reactants), involves the hydride transfer while the substrate remains in the second sphere.[62] Notably, this transfer is facilitated by electrophilic assistance from a CO ligand. The transition state structure **TS II-III** reveals that the oxygen atom of the substrate is significantly close to the carbon atom of a CO ligand (2.247 Å). The resulting intermediate **III** (14.79 kcal·mol⁻¹) corresponds to an alcoholate with the transferred hydrogen pointing toward the metal center (Mn···H: 2.025 Å) while the oxygen remains in interaction with a carbonyl ligand, the Mn-C-O angle, 148°, is significantly bent. This electrophilic assistance from a CO ligand is partially retained throughout the subsequent steps of the mechanism. The next step, through the transition state **TS III-IV** (23.21 kcal·mol⁻¹), corresponds to an isomerization process: the formed intermediate **IV** (16.06 kcal·mol⁻¹) shows the alcoholate interacting with both the metal center and a CO ligand. The coordination (for which no transition state could be determined) of molecular hydrogen then occurs, leading to intermediate **V**, with an energy of 16.36 kcal·mol⁻¹ compared to the separated reactants. The structure of this intermediate **V** reveals a slightly elongated H-H bond: 0.817 Å. The subsequent step involves the heterolytic cleavage of H₂ (**TS V-VI** with a free energy of 26.62 kcal·mol⁻¹ and a H···H bond length of 0.835 Å), leading to the hydrogenation product and the regeneration of the catalytic species (**VI**, -3.58 kcal·mol⁻¹), which forms an adduct with

the alcohol. The release of the formed alcohol is then energetically favorable ($\Delta rG^\circ = -6.93$ kcal·mol⁻¹).

Remarkably, unlike the hydrogenation mechanisms proposed for other Mn(I)-based catalysts, this out-of-sphere mechanism does not require prior dissociation of a strong ligand. It is worth emphasizing that a transition state similar to **TS I-II** could not be determined from a neutral complex. The NBO analysis of both species, **13** and **I**, indicates that deprotonation of the precursor enhances hydricity, with the natural charge of the hydride being -0.08e for **13** and -0.61e for **I**, respectively. It is also noteworthy that this mechanism involves the electrophilic assistance of a CO ligand. Numerous attempts to find transition states involving different conformations where this donor-acceptor interaction would be impossible have been unsuccessful.

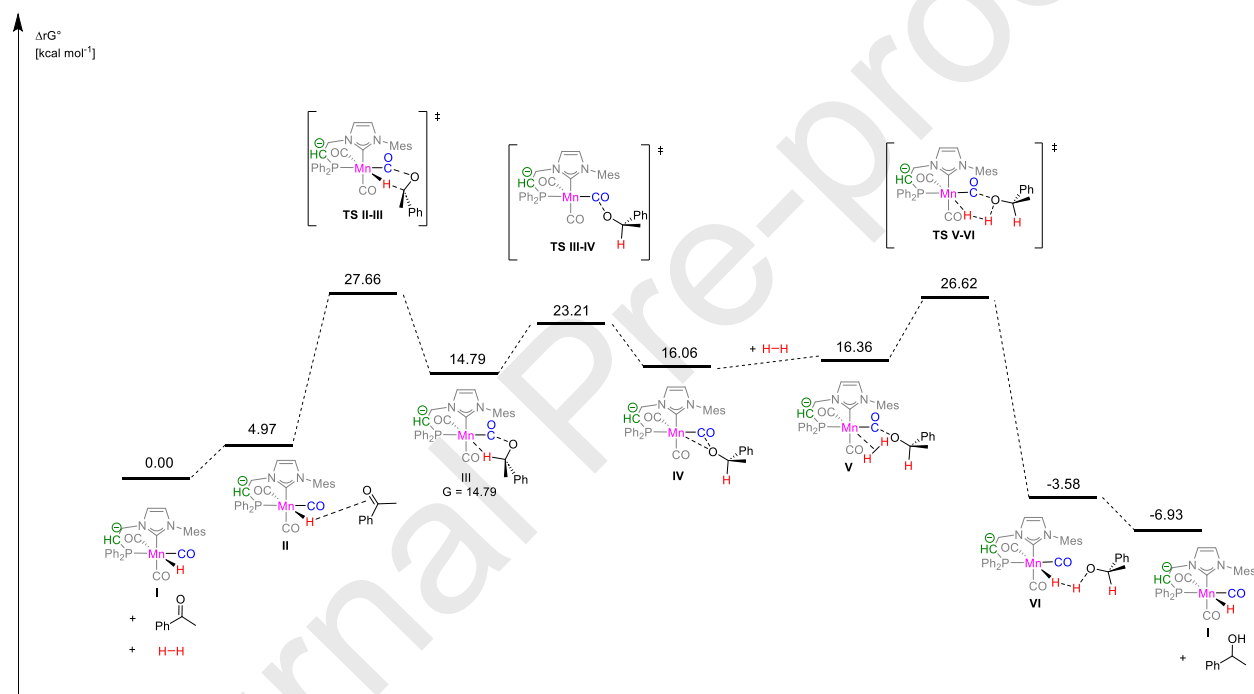


Figure 4: Energy profile of the proposed mechanism for the hydrogenation of acetophenone.

3. Conclusion

In summary, we have developed a family of manganese(I) complexes featuring bidentate NHC-phosphine ligands able to promote the reduction of esters with molecular hydrogen at low catalyst loading (0.5 mol%) in the presence of KHBET₃ as activator. The structural variations on the ligands highlighted that both the NHC and the phosphine moieties are crucial to reach high activities in catalysis, notably with an ethylene bridge between the two donor fragments. In addition, theoretical study revealed that the active species is an anionic manganese hydride complex,

resulting from the deprotonation of the CH₂ moiety in alpha position to the phosphorus atom. This mechanism is original as: i) the acidity of the ligand is involved to generate the active species but does not participate in the activation of H₂ via a cooperative mechanism, ii) the decoordination of a strongly binding carbonyl ligand is not necessary to liberate a vacant site and the electrophilic assistance of a CO ligand facilitates the hydride transfer onto the substrate via an outer sphere mechanism. This finding allows to envision more simple, non-cooperative bidentate ligands in manganese catalysis.

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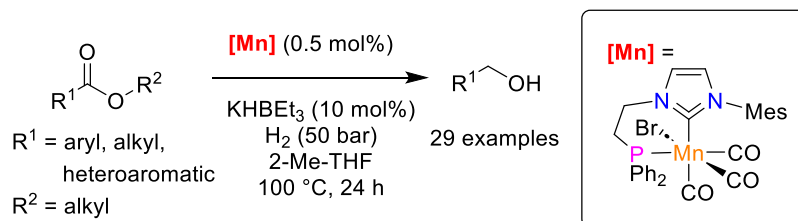
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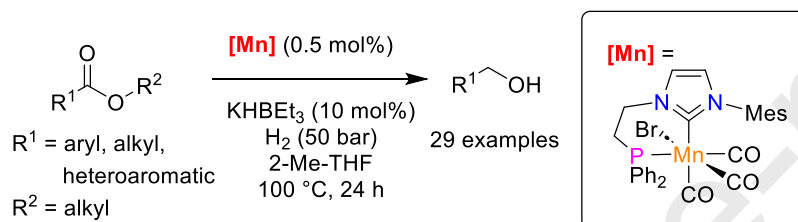
[61] In the catalytic conditions, we assume that the excess of KHBET_3 reduces the ester affording $\text{K[ROBEt}_3]$ which is in equilibrium with KOR and BEt_3 in 2-Me-THF.

[62] The first step, which corresponds to the rate determining one, has also been studied with an ester (methyl benzoate) as a model substrate. The calculated activation barrier was found to be $0.73 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta rG^\ddagger = 28.39 \text{ kcal}\cdot\text{mol}^{-1}$) greater than that associated with the benzophenone substrate, much below the accuracy of such DFT calculations. It therefore seems reasonable to assume that the mechanism found for the acetophenone substrate is representative.

GRAPHICAL ABSTRACT



GRAPHICAL ABSTRACT



HIGHLIGHTS

- Hydrogenation of carboxylic esters with manganese catalysts
- Manganese complexes with bidentate P-NHC ligand as efficient catalyst in hydrogenation
- “NH” free manganese catalysts for hydrogenation of carboxylic esters
- Computational investigations suggest an anionic tricarbonyl manganese hydride as the active species

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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