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Hydrogenation of alkenes catalyzed by a non-pincer Mn complex

S. M. Wahidur Rahaman,[†a] Dilip K. Pandey,[†a] Orestes Rivada-Wheelaghan,[a] Abhishek Dubey,[a] Robert R. Fayzullin,[b] and Julia R. Khusnutdinova*[a]

[a] Dr. S. M. W. Rahaman, Dr. Dilip K. Pandey, Dr. O. Rivada-Wheelaghan, Dr. A. Dubey, Prof. J. R. Khusnutdinova
Coordination Chemistry and Catalysis Unit
Okinawa Institute of Science and Technology Graduate University
1919-1 Tancha, Onna, Okinawa, 904-0495, Japan
E-mail: juliak@oist.jp
[b] Dr. R. R. Fayzullin
Arbuzov Institute of Organic and Physical Chemistry
FRC Kazan Scientific Center, Russian Academy of Sciences
8 Arbuzov Street, Kazan, 420088, Russian Federation
† These authors contributed equally.

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Abstract: Hydrogenation of substituted styrenes and unactivated aliphatic alkenes by molecular hydrogen has been achieved using a Mn catalyst with a non-pincer, picolylphosphine ligand. This is the second reported example of alkene hydrogenation catalyzed by a Mn complex. Mechanistic studies showed that a Mn hydride formed by H_2 activation in the presence of a base is the catalytically active species. Based on experimental and DFT studies, H_2 splitting is proposed to occur via a metal-ligand cooperative pathway involving deprotonation of the CH_2 arm of the ligand, leading to pyridine dearomatization.

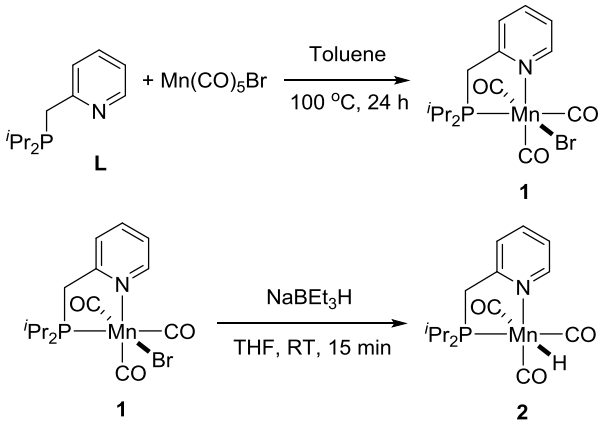
Utilization of earth-abundant metal complexes as a replacement for precious metal catalysts is an important goal in the practical utilization of homogeneously catalyzed processes.[1] Manganese, the third most abundant transition metal in Earth's crust, has started to emerge as a competitive catalyst in hydrogenation[2] and transfer hydrogenation[3] catalysis and shows a wide range of reactivity in the hydrogenation of polar functional groups, including ketones, esters, amides, N-heterocycles, nitriles, carbonates, imides, ureas, and other substrates. Interestingly, many currently reported Mn catalysts tolerated terminal and internal C=C bonds that under the reaction conditions (i.e. typically high H_2 gas pressure).[4] Hydrogenation of nonpolar C=C bond in alkenes is traditionally performed through the use of precious metal catalysts, such as Ir,[5] Rh,[6] Pd[7] and other metals.[8] Recently, a number of studies have been reported on alkene hydrogenation using first-row transition metals: Fe,[9] Co,[10] and Ni complexes.[11] However, currently only one previous example of Mn-catalyzed alkene hydrogenation involving a Mn alkyl complex with a diphosphine ligand was reported by the Kirchner group in 2019.[12] Alkene hydrogenation reactivity still remains an uncommon reactivity mode for Mn homogeneous catalysis.

Aiming to obtain reactivity in the hydrogenation of alkenes, we decided to focus on Mn complexes with P,N-donor ligands. Among Mn hydrogenation catalysts, the use of aliphatic or pyridine-based pincer PNP and PNN ligands remains predominant up to date.[13] In the case of pyridine-based PNP and PNN pincer ligands, mechanistic studies suggest that the reactivity of these complexes involves CH_2-arm deprotonation in the presence of a strong base, leading to pyridine ring dearomatization, with the ligand further participating in H_2 splitting.[14] Considering the simplicity of a bidentante diphosphine ligand used by Kirchner *et al.* in the hydrogenation of alkenes and a few other recent examples of phosphine-based bidentate ligands used in Mn-catalyzed hydrogenation or hydrogen borrowing reactions of polar substrates,[15] we have chosen a non-pincer, bidentate picolylphosphine ligand for initial studies. We found that Mn complexes supported by this non-pincer ligand show catalytic activity in alkene hydrogenation. The mechanistic studies reported in this work elucidate the role of the ligand that enables this reactivity.

The ligand **L** can be easily prepared according to the literature procedure.[16] The neutral manganese(I) bromo complex can be prepared through the reaction of $Mn(CO)_5Br$ with the ligand **L** in a toluene solution under reflux to give complex **1** in 88% yield (Scheme 1). This complex was isolated and characterized by NMR, IR, UV-vis spectroscopies, X-ray diffraction (XRD), elemental analysis, and electrospray ionization mass spectrometry (ESI-MS). The $^{31}P\{^1H\}$ NMR spectrum shows a single phosphorus peak at 78.8 ppm, and $^{13}C\{^1H\}$ NMR spectrum shows three peaks of the carbonyl groups at 225.3, 224.8, and 216.9 ppm. The FT-IR spectrum shows carbonyl stretching peaks at 2009, 1900, and a shoulder at 1887 cm^{-1}. ESI-MS analysis detected the presence of a cationic $[M\text{-}Br]^+$ fragment at m/z 348.0553 resulting from the loss of a bromide ligand. The solid-state structure was established by XRD and is shown in Figure 1, a. Complex **1** features a distorted octahedral Mn center with *fac*-tricarbonyl orientation and Mn1–C1, Mn1–C2 and Mn1–C3 distances of 1.8016(13), 1.8433(14), and 1.7904(14) Å, respectively.[17]

Considering that Mn hydrides are likely to be active catalysts in hydrogenation reactions, we then synthesized a hydride complex **2** by treatment of **1** with $NaBHEt_3$ solution in THF at room temperature (RT) (Scheme 1). Complex **2** was isolated in 64% yield and characterized by XRD (Figure 1, b), NMR, IR, UV-vis spectroscopies, and elemental analysis. Complex **2** features a similar *fac*-arrangement of three carbonyls, with a significantly longer Mn1–C3 distance of 1.8182(16) Å compared to complex **1** (1.7904(14) Å) due to the stronger *trans*-influence of the hydride ligand. Hydrogen atom H1 at the Mn-center,

present in the *cis*-position relative to phosphine, was found from Fourier difference maps and Mn1–H1 interatomic distance is equal to 1.50(2) Å. The ^{1}H NMR spectrum shows a characteristic peak of a Mn–H at –4.46 ppm as a doublet split by the phosphorus atom ($^{2}J_{HP}$ = 56.7 Hz), and the phosphorus peak appears at 104.02 ppm in the ^{31}P{^{1}H} spectrum. Three carbonyl peaks are also observed in the ^{13}C NMR spectrum at 227.4, 225.2, and 222.8 ppm. The IR stretching peaks of carbonyls appear at lower frequencies compared to complex **1**, 1970, 1857, 1835 cm^{-1}, reflecting stronger π-backdonation from the more electron rich Mn center in a hydride complex.



Scheme 1. Synthesis of Mn complexes with picolylphosphine ligand.

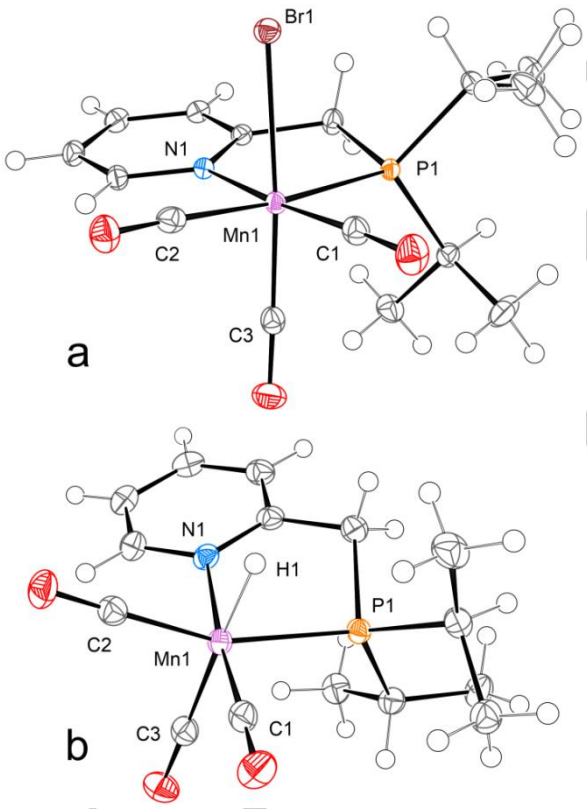


Figure 1. ORTEP of **1** (a) and **2** (b) at 50 % probability level according to SC XRD data. Selected interatomic distances [Å]: Br1–Mn1 2.5341(2), Mn1–P1 2.3159(3), Mn1–N1 2.1082(11), Mn1–C1 1.8016(13), Mn1–C2 1.8433(14), Mn1–C3 1.7904(14) for **1**; Mn1–P1 2.2615(4), Mn1–N1 2.1003(12), Mn1–C1 1.7826(16), Mn1–C2 1.8068(15), Mn1–C3 1.8182(16), Mn1–H1 1.50(2) for **2**.[17]

We then tested the catalytic activity of complex **1** in the presence of KO^{t}Bu in hydrogenation of alkenes. Initial optimization using styrene as a standard showed that the reaction proceeds selectively in the presence of 4 mol% of **1** and 10 mol% of KO^{t}Bu at 100 °C and 30 bar H_2 to give ethylbenzene as the only product in 86% yield after 24 h (Table 1, entry 1), while lowering temperature to 26 °C (entry 2) or H_2 pressure to 10 bar (entry 3) led to diminished yields of 31% and 8.5%, respectively. Reaction in benzene as a solvent also gave nearly quantitative conversion to ethylbenzene under standard conditions (entry 4).

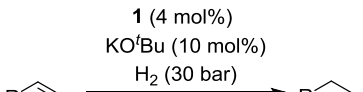
High yields were obtained in hydrogenation of electron-rich alkenes under analogous conditions as well as for *para*-trifluoromethyl-substituted styrene (entries 5-7). Styrenes containing electron-withdrawing substituents were generally less reactive, however, good yields were obtained for *para*- and *meta*-fluorostyrene, and *para*-chlorostyrene after prolonged reaction time, 48 h (entries 8-10). *meta*-Bromo substituted styrene gave only moderate yield even after prolonged reaction time. This could be due to partial hydrodebromination that could deactivate the catalyst: a trace amount (<3%) of ethylbenzene was also detected among the reaction products by GC-MS. An ester-functionalyzed styrene showed poor yield, which could be due to side reactions involving the ester functionality.

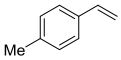
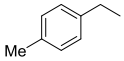
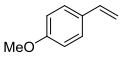
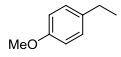
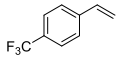
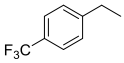
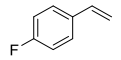
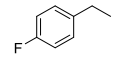
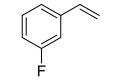
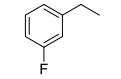
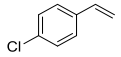
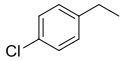
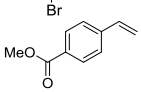
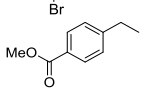
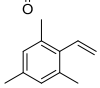
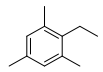
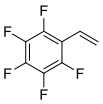
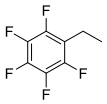
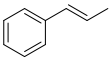
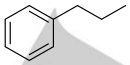
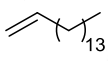
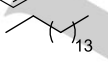
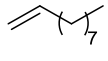
Steric hindrance significantly diminished the catalytic activity and poor yields were obtained for *ortho*-substituted substrates such as both electron-poor 2-chlorostyrene (entry 11) and electron-rich 2,4,6-trimethylstyrene (entry 14), as well as 2,3,4,5,6-pentafluorostyrene (entry 15), the yields in the latter case were likely lower due to a combination of both steric and electronic factors.

1,2-Disubstituted alkenes were generally less reactive with a steric factor playing an important role: only α-methylstyrene gave the product in good yield after 48 h (entry 16), while the more sterically hindered 1,1-diphenylstyrene gave poor yield (entry 17). Low reactivity was also observed for an internal alkene, trans-β-methylstyrene (entry 18). Unactivated aliphatic terminal alkenes gave moderate to good yields after 48 h (entries 19-22). No migration of the double bond to give internal alkenes was observed under these reaction conditions according to GC-MS and NMR analyses. Unactivated acyclic internal alkenes, *trans*-4-octene and *cis*-4-octene, remained mostly unreacted (ca. 20% conversion after 48 h under standard conditions). In the case of *cis*-4-octene, partial isomerization to *trans*-4-octene and only a small amount of *n*-octane was detected.

Interestingly, hydrogenation of 1,5-cyclooctadiene selectively produced *cis*-cyclooctene as a major product in high yield, without detectable amounts of cyclooctane or isomerized cyclooctadienes. Accordingly, attempted hydrogenation of *cis*-cyclooctene under the same conditions left most of the starting material unreacted. Similar selective hydrogenation of only one double bond in cyclic dienes was reported for some other homogeneous, precious metal-catalyzed reactions.[18] In contrast, full hydrogenation of both double bonds in 1,5-cyclooctadiene catalyzed by a Mn diphosphine complex was reported by Kirchner *et al*.[12]

Table 1. Hydrogenation of alkenes catalysed by **1**. [a]



Entry	Substrate	Product	Time [h]	NMR yield [%][b]
1			24	86
2[c]			24	31
3[d]			24	8.5
4[e]			24	97
5			24	97
6			24	76
7			24	76
8			48	95
9			48	86
10			48	84
11			48	45
12			48	56
13			48	34
14			48	28
15			48	23
16			48	74
17			48	25
18[f]			48	12
19			48	83
20			48	63
21			48	82
22			48	70
23			48	92[g]
24		n.d. [h]	48	n.d. [h]

[a] Solution containing 0.5 mmol of alkene, 4 mol% of **1**, 10 mol% of KO^{t}Bu in 5 mL of 1,4-dioxane was heated at 100 °C under 30 bar H_2. [b] Yield of alkene determined by NMR by integration vs. internal standard mesitylene. All reactions were repeated at least 2 times. [c] At room temperature. [d] Under 10 bar of H_2. [e] In benzene-d_6 as a solvent. [f] 1% admixture of *cis*-isomer was present. [g] Cyclooctane or isomeric cyclooctadienes were not detected by NMR and GC-MS; conversion of 1,5-cyclooctadiene 99%. [h] No product detected; >97% of starting material was found unreacted.

We also tested the reactivity of catalyst **1** in combination with KO^{t}Bu in catalytic hydrogenation of terminal alkynes, 1-pentadecyne and phenylacetylene. 1-Pentadecyne was hydrogenated completely with *n*-pentadecane in high yield, with only a trace amount of pentadecene detected. However, phenylacetylene gave low conversion (ca. 30%) and poor yields of ethylbenzene (12%) and styrene (6%), suggesting that activated terminal alkynes might negatively affect the catalyst's activity due to either steric factors or unfavorable side-reactions deactivating the catalyst.

Scheme 2. Hydrogenation of terminal alkynes catalyzed by **1**/KO^{t}Bu.

Base was required to activate complex **1** for catalysis, with the control reaction showing no reactivity in its absence (Table 2, entry 1). However, efficient hydrogenation of styrene could still be observed with the amount of base lowered to 5 mol% (Table 2, entry 2). Although some hydrogenated product was also obtained in the presence of precursor $Mn(CO)_5Br$ as a catalyst and 10 mol% KO^{t}Bu, the yield was significantly lower, showing that the picolylphosphine ligand is required for the observed high catalytic activity. Finally, no reaction was observed in the absence of a Mn catalyst. No inhibition was observed in the presence of a drop of mercury or substoichiometric amounts of PPh_3, while a large excess of PPh_3 was required to observed inhibition (Table S2), consistent with a homogeneously-catalyzed reaction.[19]

Considering that Mn hydrides are commonly proposed as reactive intermediates in hydrogenation, we also tested the catalytic activity of isolated complex **2** in the base-free hydrogenation of styrene. Under standard conditions, ethylbenzene was obtained in 67% yield (Table 2, entry 5). Addition of the base led to an increased yield of 92% under analogous conditions (Table 2, entry 6).

Table 2. Effect of base and Mn catalyst on styrene hydrogenation.

Entry	Catalyst [mol%]	KO^{t}Bu [mol%]	Time [h]	NMR yield [%]
1	**1** (4 mol%)	none	24	n.d. [a]
2	**1** (4 mol%)	5 mol%	24	86
3	none	10 mol%	24	n.d. [a]

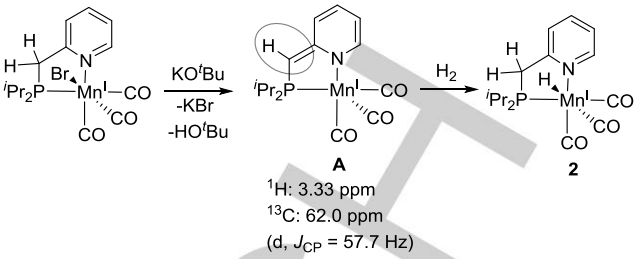
4	$MnBr(CO)_5$ (4 mol%)	10 mol%	24	20
5	**2** (4 mol%)	none	24	67
6	**2** (4 mol%)	10 mol%	24	92

[a] n.d. – not detected.

Based on these results, we proposed that Mn hydride **2** is a viable intermediate in alkene hydrogenation (Scheme 3). To confirm this idea, we reacted isolated complex **2** with *ca.* 1 equiv. of styrene at 80 °C in the absence of H_2 gas in C_6D_6 solution. Under these conditions, gradual conversion of styrene into ethylbenzene was observed accompanied by the disappearance of the Mn–H signal (Figure S14). After prolonged heating (65 h) in the absence of H_2 or excess substrate, partial degradation is observed, likely leading to free ligand release. However, after the standard reaction time, the ^{31}P peak of the hydride **2** remains predominant (≥90%) after heating for 27 h, and the characteristic phosphorus-split doublet at -4.46 ppm corresponding to a Mn-H peak of complex **2** is clearly observed after heating for 27-65 h (Figures S14-S15). These experiments show that the picolylphosphine-containing hydride **2** is a viable intermediate under catalytic conditions. Similar results were obtained when the reaction was performed in dioxane at 100 °C, showing formation of ethylbenzene by reacting styrene with complex **2** (Figures S16-S17).

To probe the formation of Mn–H from pre-catalyst **1** and H_2, we first reacted **1** with H_2 (1 atm) in the presence of KO^{t}Bu (2.5 equiv.) in C_6D_6. After 6 h at RT, the signal corresponding to Mn–H was observed at –4.46 ppm, and a new phosphorus signal appeared at 104.6 ppm, indicative the formation of a Mn hydride **2** from pre-catalyst **1** and H_2 in the presence of a base (Figures S18-S19). Similarly, formation of **2** was observed by ^{31}P NMR in dioxane at RT upon reacting **1** with KO^{t}Bu and H_2 at RT, however, limited stability was observed upon heating at 100 °C for several hours (Figure S20).

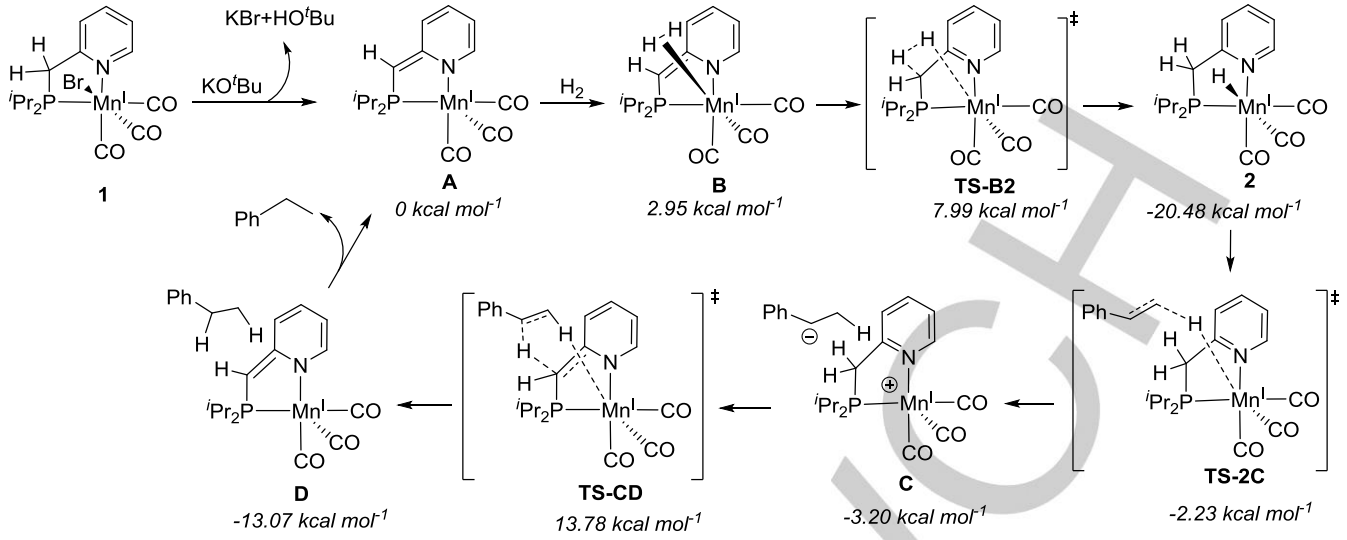
Considering that picolylphosphine ligand **L** in **1** contains an acidic CH_2, we hypothesized that deprotonation of the methylene arm could occur prior to hydrogen activation. When complex **1** was reacted with KO^{t}Bu in the absence of H_2, the formation of a new complex **A** was observed, although the reaction was not selective and several other species were present, presumably due to low stability of the deprotonated species in the absence of substrate. Species **A** was characterized by the presence of a singlet at 3.33 ppm in ^1H NMR spectrum, which was assigned to a deprotonated methylene CHP arm (Figures S21-S25). This signal correlates with the signal of the carbon at 62.0 ppm as shown by HMQC experiment, which appears as a P-coupled doublet (J_{CP} = 57.7 Hz) and it was identified as a CH group based on a ^{13}C DEPT experiment. These values are similar to methyne CHP group chemical shifts reported for deprotonated (^{tBu}PNP*)Mn(CO)$_2$ and (^{tBu}PNP*)Mn(CO)$_3$ complexes by the Milstein group (proton signal at 3.82 and 3.78 ppm, respectively, and carbon signal at 71.4 or 67.5 ppm respectively, split by P-atoms) and analogous complexes.[14a, 20]



Scheme 3. Proposed formation of complex **A** and its reactivity with H_2.

Based on the above experiments, we propose the mechanism in Scheme 4, which was studied by DFT using M06L functional and SDD(Ru)/6-311++G(d,p)(C,H,N,P,O) basis sets, with the Gibbs energies solvent-corrected using the CPCM model.[21] In this mechanism, deprotonation of the methylene arm and removal of bromide from **1** in the presence of KO^{t}Bu leads to the formation of **A**, with the dearomatized pyridine ring coordinating to a square-pyramidal Mn center. H_2 coordination gives rise to the hydrogen complex **B**. Further H_2 heterolytic splitting via a metal-ligand cooperative pathway leads to the formation of a Mn hydride and re-protonation of the methylene arm. This is followed by a hydride and a proton transfer to the β- and α-carbons of styrene (Figure S71), respectively, similar to the mechanism proposed by Jones *et al.* for alkene hydrogenation catalyzed by Fe PNP pincer complexes.[9a] The proposed mechanism is consistent with observation of hydride **2** formed upon the reaction of **1** with a base, which further reacts with styrene upon heating. However, without a more detailed computational study, we cannot completely exclude possible competing reaction pathways that involve H_2 activation with an assistance of an external base or other alternative pathways.

In conclusion, we report a rare example of Mn-catalyzed hydrogenation of aromatic and aliphatic alkenes using a ~~simple,~~ non-pincer Mn complex. A range of non-sterically hindered, electron-rich and some electron-poor, fluoro- or chloro-substituted styrenes could be hydrogenated in good yields under a hydrogen pressure of 30 bar. Unactivated aliphatic terminal alkenes also afforded alkanes in moderate to good yields after sufficient reaction time. Steric hindrance reduces the catalytic activity leading to poor yields in case of ortho-substituted styrene and acyclic internal alkenes, while selective hydrogenation of only one double bond was observed in 1,5-cyclooctadiene to give *cis*-cyclooctene in good yield. Experimental mechanistic studies showed that a Mn-hydride formed by H_2 activation by **1** in the presence of a strong base is likely the catalytically active species. Deprotonation of the methylene arm was shown to occur prior to H_2 activation, which occurs via a cooperative process between the ligand and metal.



Scheme 4. Proposed mechanism for Mn-catalyzed alkene hydrogenation. The relative solvent-corrected Gibbs energies are shown in italics (kcal mol^{-1}).

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Keywords: manganese • alkene hydrogenation • metal-ligand cooperation • hydride complexes • P,N-donor ligand

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[21] See the Supporting Information for details.

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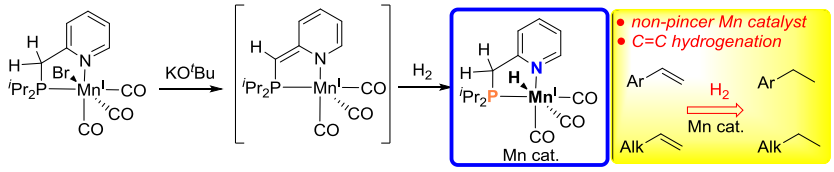

Simple non-pincer, P,N-donor Mn complex catalyzes hydrogenation of styrene and non-activated alkenes. Experimental and DFT studies highlight the role of the ligand deprotonation in enabling H_2 activation by a Mn-H intermediate via a metal-ligand cooperative pathway.

Institute and/or researcher Twitter usernames: @KhusnutdinovaU