Recent Advances in Manganese(I)-Based Catalysts for Hydrogenations of Aldehydes, Ketones, and Esters

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Abstract: Sustainable chemistry that uses accessible, benign, and inexpensive materials has always been a major goal for industry. As catalytic reactions play an important role in different chemical industries, it is necessary to enhance the activity of the catalysts and to substitute precious metal catalysts by more abundant metal catalysts. In this context, using Mn for hydrogenations of C=O bonds is a potential replacement of precious metal in catalysis. Mn^{I} complexes, with their commercial availability, have been widely used to react with many ligand systems to produce catalysts that are active toward hydrogenations of aldehydes, ketones, and esters. The dominating ligand type in this area is pincer type, which shows stability and tuning ability advantages. Mn^{I} pincer catalysts, inspired by metal-ligand cooperativity mechanism, show great activity in a wide range of hydrogenation substrates. Unlike pincer Mn^{I} catalysts, non-pincer Mn^{I} catalysts usually exhibit unconventional mechanisms and alternative ligand systems but still retain high catalytic activity toward specific substrates. Explorations of new catalytically promoting ligands for Mn complexes are expected to be seen in the near future.

I. Introduction

Hydrogenations are among the most important chemical transformations in academic research and industries of perfumes,[1] detergents,[2] and pharmaceuticals.[3,4] In terms of green chemistry, hydrogenation is a sustainable process because one of the main reactants is hydrogen gas that can be obtained from clean, abundant, and low-cost resources. Moreover, when the demands of renewable sources of energy are in high consideration, hydrogenation reactions play a promising role due to their ability to produce alternative fuels such as alcohols and biofuels.[5] In particular, the reductions of CO_2 and carbonyl compounds to useful alcohols through hydrogenations have been advanced; however, these reactions have a high activation energy and, therefore, require the presence of a catalyst.

The first, well-established, and most active hydrogenation catalysts are made of precious metals (ruthenium, rhodium, iridium, platinum, osmium, and palladium).[3,6-9] In 2001, Noyori and coworkers presented a breakthrough in this area by introducing the bifunctional metal–ligand catalysis for the hydrogenation of carbonyl compounds.[6] With precious-metal

catalysts, carbonyl compounds can be hydrogenated under mild conditions (1-7 atm and < 100 ^{o}C).[3,6,7] In the last decade, inexpensive transition metals such as Fe, Co, Ni, Mn, and Cu are preferred for higher environmental and economical sustainability. For C=O bond hydrogenations, the use of Fe was first discovered by Milstein and coworkers in their report on the first Fe-based catalyst for hydrogenation of esters.[10] Following this seminal work, many Fe and Co compounds featuring mono- and multi-dentate ligands have been successfully utilized for the catalysis of carbonyl hydrogenations; however, most of such Fe- and Co-catalysts up to date have a significantly lower catalytic performance (i.e. high catalyst loading and low conversion percentage) than the Ru-based complexes and require expensive and toxic oxide bases as activators.[6,9-13] The ultimate goal for modern hydrogenation catalyst design is to make catalysts that (1) require simple preparations, (2) use low-cost and environmentally benign reactants, solvents, and additives, and (3) exhibit high catalytic performance under mild conditions.

Recently, manganese(I) complexes have become of increasing interest because manganese is inexpensive, highly abundant, and biocompatible. Although Mn compounds have been known for their applications in oxidation and coupling reactions due to the high redox potential and the coordination state of the metal center, catalytic application of Mn complexes for hydrogenations are still limited compared to Fe, Co, and Ni. In 2016, the first examples of Mn-catalysts for hydrogenations of carbonyl compounds were introduced independently by the Beller group[14] and the Kempe group.[15] The trend of catalyst design has also shifted from using Fe and Co to Mn in the past 5 years (**Figure 1**); however, the efficiency and practicality of these Mn compounds are still far from satisfactory. The future of this young area relies on the art of ligand design. Ligands used for these manganese complexes are mainly pincer-type ligands. Attempts to apply non-pincer-type ligands to Mn^{I}-based coordination complexes have introduced a variety of multidentate ligands with N- and/or P-donor fragments that led to enhancements in catalytic performance and better understanding about the mechanism of the catalytic hydrogenations of carbonyl compounds.

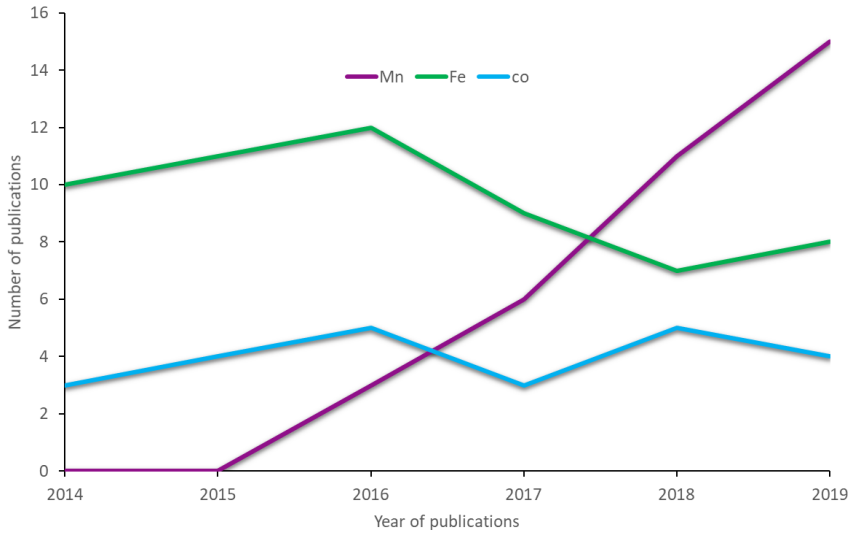


Figure 1. Recent publication trends in studies on Fe-, Co-, and Mn-catalysts for hydrogenation of carbonyl compounds*

In this review, recent advances in catalytic hydrogenations of carbonyl compounds with Mn^{I}-based catalysts are presented. The focus of this review is centered around the ligand design and ligand effect on the catalytic efficiency. In particular, several recent types of ligands that have been used for hydrogenation catalysts will be introduced. For each type of ligand, the preparation and performance of catalysts will be shown, followed by discussion about the proposed mechanisms that will lead to the current challenges and prospects in this field.

II. Manganese Catalysts with Pincer Ligands

II. A. Overview and Mechanism

The advantages of using pincer-type ligands are the well-understood and simple preparation for metal complexes, the tunable electronic and steric properties, and the well-define and stable structure.[16] Because each part of the ligand structure is responsible for different properties of the complex, adjusting these parts gives rise to a variety of pincer compounds with desired properties. The steric hindrance, bite angle, and electron density of

*Data retrieved from Clarivate.webofknowledge.com (Accessed January 30th, 2020). Number of publications is the number of times key terms appear in title or abstract. Key terms include but are not limited to "hydrogenation catalyst", "metal-catalyzed hydrogenation", and "metal catalyst for hydrogenation", where metal can be Fe, Co, or Mn.

pincer complexes are impacted by the L group, linker arms Y, and the nature of the electron withdrawing or donating group R (**Figure 2**). Chirality for these compounds can also be achieved by adjusting the L group, while the electronic properties can also be tuned by using different central donor X (N or C).[7,17] Moreover, the tridentate mode nature results in the high stability of pincer complexes. For example, the first Mn(I) hydrogen catalysts reported by the Beller group show outstanding stability with no evidence of decomposition after 25 days stored in air.[14] Due to these features and the versatile synthetic access, pincer complexes have been extensively studied and used industrially as catalysts.[18]

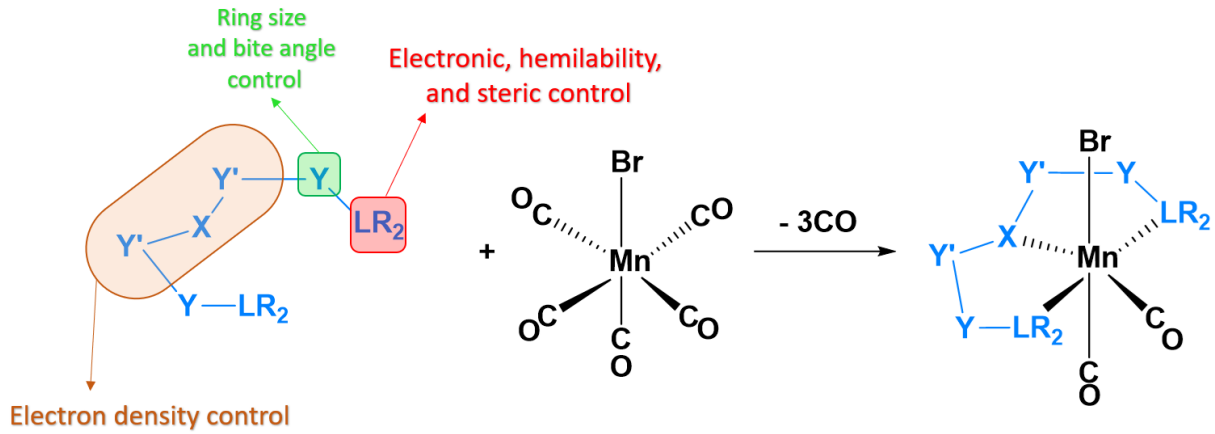


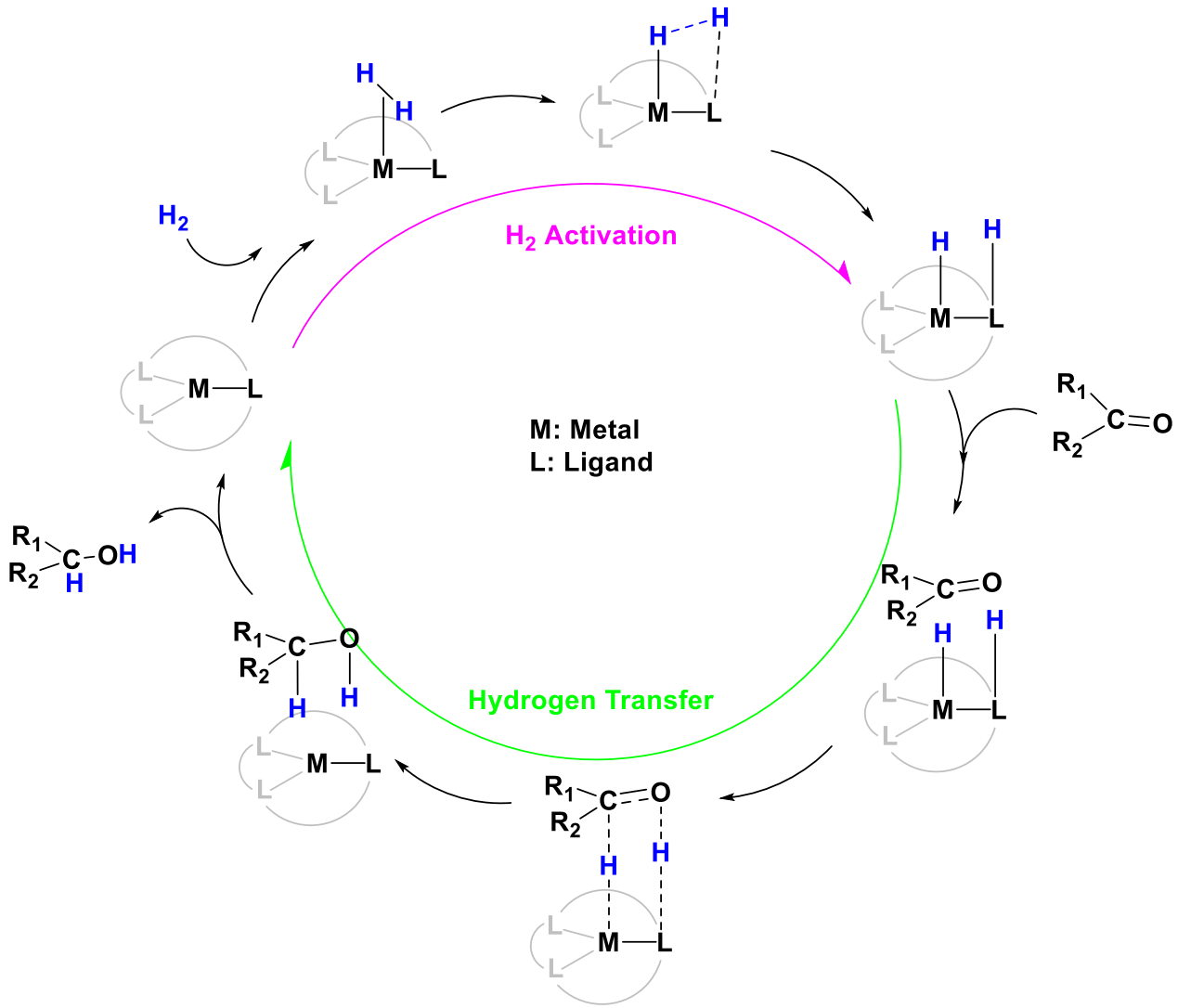
Figure 2. Preparation and tuning options of Mn^{I} pincer catalysts

The preparation of pincer manganese(I) hydrogenation catalysts is simple and can be done under mild conditions. The manganese source is usually the commercially available $Mn(CO)_5Br$, while the common solvent used is toluene (**Figure 2**). Characterizations of the product include conventional IR, ^{1}H-NMR, ^{31}P-NMR spectroscopy, mass spectrometry, and elemental analysis.

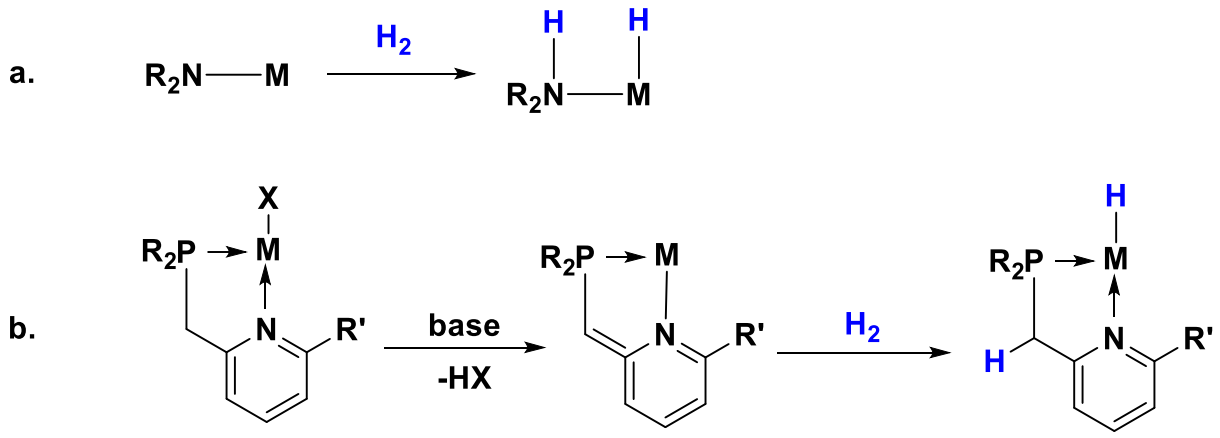
Mechanisms of hydrogenations of C=O and C=N bonds usually include (1) the hydride transferring to substrate and (2) the dihydrogen activation.[3,6,7] The most ubiquitous path of hydride transfer step seen in pincer catalysts is via the outer-sphere mode; and the H_2 activation step consists of a H_2 heterolytic cleavage process.[3,6] Studies of hydrogenations of C=O bonds catalyzed by pincer ligated transition metals also reveal the outer-sphere *metal–ligand*

cooperativity (MLC) mechanism, which occurs when both ligand and metal ion participate in substrate activation and, therefore, accelerates the rate of the catalytic cycle (**Scheme 1**).[6] The activation and hydrolytic cleavage of H_2 in catalytic hydrogenation can be supported by amide or amine, as seen in seminal works by Noyori et al. (**Scheme 1a**),[6] and N- and P- moieties in later works using pincer ligands (**Scheme 2b**).[14,16] For the latter case, the deprotonated species can activate H_2 that is mainly supported by the aromatization of the pyridine moiety.[16] The hydrogen transfer step is proposed to be either concerted (bond breaking and bond making occur in one step) or stepwise (bond breaking and bond making occur stepwise).

Scheme 1. The general outer-sphere MLC mechanism for C=O hydrogenation of pincer catalysts



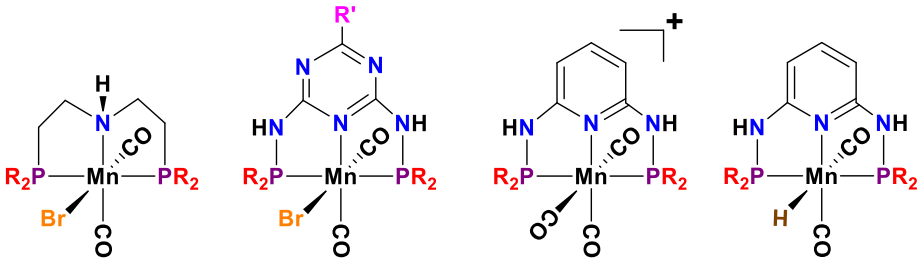
Scheme 2. H_2 activation pathways via MLC-assisted mechanism



II. B. Hydrogenation of Ketones and Aldehydes

In the past 5 years, different platforms of pincer ligands have been used to design catalysts for hydrogenation of ketones and aldehydes (**Chart 1**). Ketones and aldehydes are among the easiest to be hydrogenated; therefore, the challenge for hydrogenation reactions of these compounds is the reduction selectivity on the desired group. The first Mn-based hydrogenation catalysts reported by the Beller group (compound **1a** and **1b**) show great catalytic activities toward ketone and aldehyde group but tolerate lactam, ester, and alkene groups.[14] Compound **1a** and **1b**, ligated by **P_2N** pincer ligands (with 2 phosphorous and one nitrogen in the ligand system), show catalytic activity only with a presence of an additive base. Different solvents were also examined in the catalytic hydrogenation reactions using catalyst **1a**; the optimal yield was obtained when using toluene. Catalyst **1a** shows high efficiency for ketone hydrogenation; however, efficiency for aldehyde hydrogenation was inferior (**Figure 3**). Interestingly, the bromine in compound **1a** can be replaced by a hydrogen by adding H_2 and a base under pressure to make a hydride version of compound **1a**; however, this hydride version shows a lower catalytic activity than its bromide version.[14]

Chart 1. Manganese catalysts bearing pincer-type ligand for hydrogenation of ketones and aldehydes



Beller 2016[14]
1
a: R = ^{i}Pr
b: R = C_6H_5

Kempe 2016[15]
2
a: R = ^{i}Pr, R' = C_6H_5
b: R = ^{i}Pr, R' = HN-C_3H_5
c: R = ^{i}Pr, R' = CH_3
d: R = ^{i}Pr, R' = $N(C_2H_5)_2$

Sortais 2017[22]
3
R = ^{i}Pr

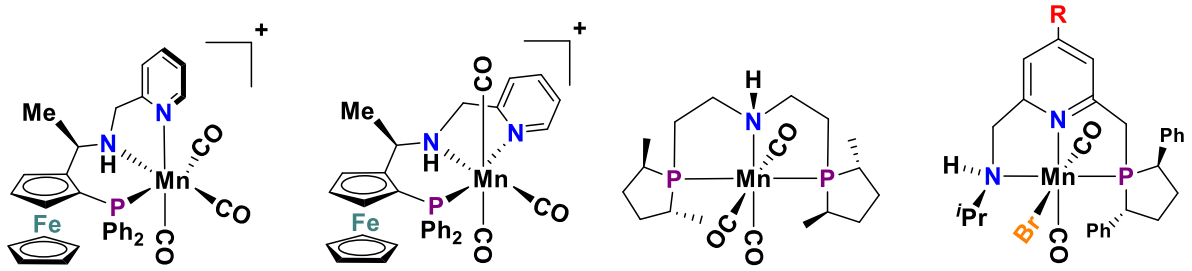
Kirchner 2018[23]
4
R = ^{i}Pr

Parallel to the Beller group's work, Kempe and coworkers chose the approach using the pincer **P_2N_5** to synthesize a series of hydrogenation catalysts (compound **2**).[15] This ligand and its related versions have been vastly used in designing iridium and cobalt catalysts in recent years.[19,20] This ligand is advantageous for hydrogenation reactions because there are two positions where adjustments can be made to tune the catalytic activity. More importantly, even when the catalytic reactions are operated under milder conditions with a smaller catalyst loading and in shorter reaction time, catalysts **2a-d** are up to 10 times more active than complex **1a**. This superior activity may be due to the electron-deficient 1,3,5-triazine ring on the **P_2N_5** pincer ligand. Since electron-poor ligands accelerate the reductive elimination reactions,[21] the ligand systems in compound **2a-d** likely promote the bromide loss, which is a critical step in the catalytic mechanism for hydrogenation. Among the four catalysts reported by the Kempe group, catalyst **2b** shows the highest catalytic activity toward linear as well as cyclic aliphatic ketones.

The **P_2N_3** pincer ligand can also be used for hydrogenation of ketones and aldehyde, which was reported Sortais and coworkers in 2017 (compound **3**).[22] Compound **3**, bearing the tridendate ligand with a 2,6-(diaminopyridinyl)diphosphine scaffold, shows good catalytic activity for ketone reductions. Unlike the previously reported manganese catalysts by the Beller and Kempe group, ketone hydrogenation catalyst **3** is a cationic complex and can also catalyze the

reverse reaction (oxidation) of alcohols. In contrast with Kempe's report and in agreement with Beller's report, stoichiometric ^{1}H-NMR experiment for complex **3** proved the presence of a manganese(I) hydride is the intermediate of the hydrogenation process. Compound **3** catalyzes ketone reactions less efficiently than **2b** and does not show activity toward aldehyde reductions. Kirchner and coworkers soon modified compound **3** to a neutral dicarbonyl hydride version of the manganese catalyst (compound **4**).[23] Compound **4** exhibits a great chemoselectivity toward aldehydes without any additive. With an impressively low catalyst loading (0.05 – 0.1 mol %), compound **4** can catalyze the reduction of a wide range of aldehydes and does not show any activity toward 4-fluoroacetophenone in both protic and aprotic solvents. More efficiency comparison of Mn^{I} pincer catalysts is shown in **Figure 3**.

Chart 2. Manganese catalysts bearing pincer-type ligand for asymmetric hydrogenation of ketones



Clarke 2017[24] ***fac*-5**

Clarke 2019[25] ***mer*-5**

Beller 2017[26] **6**

Ding 2019[27] **7**

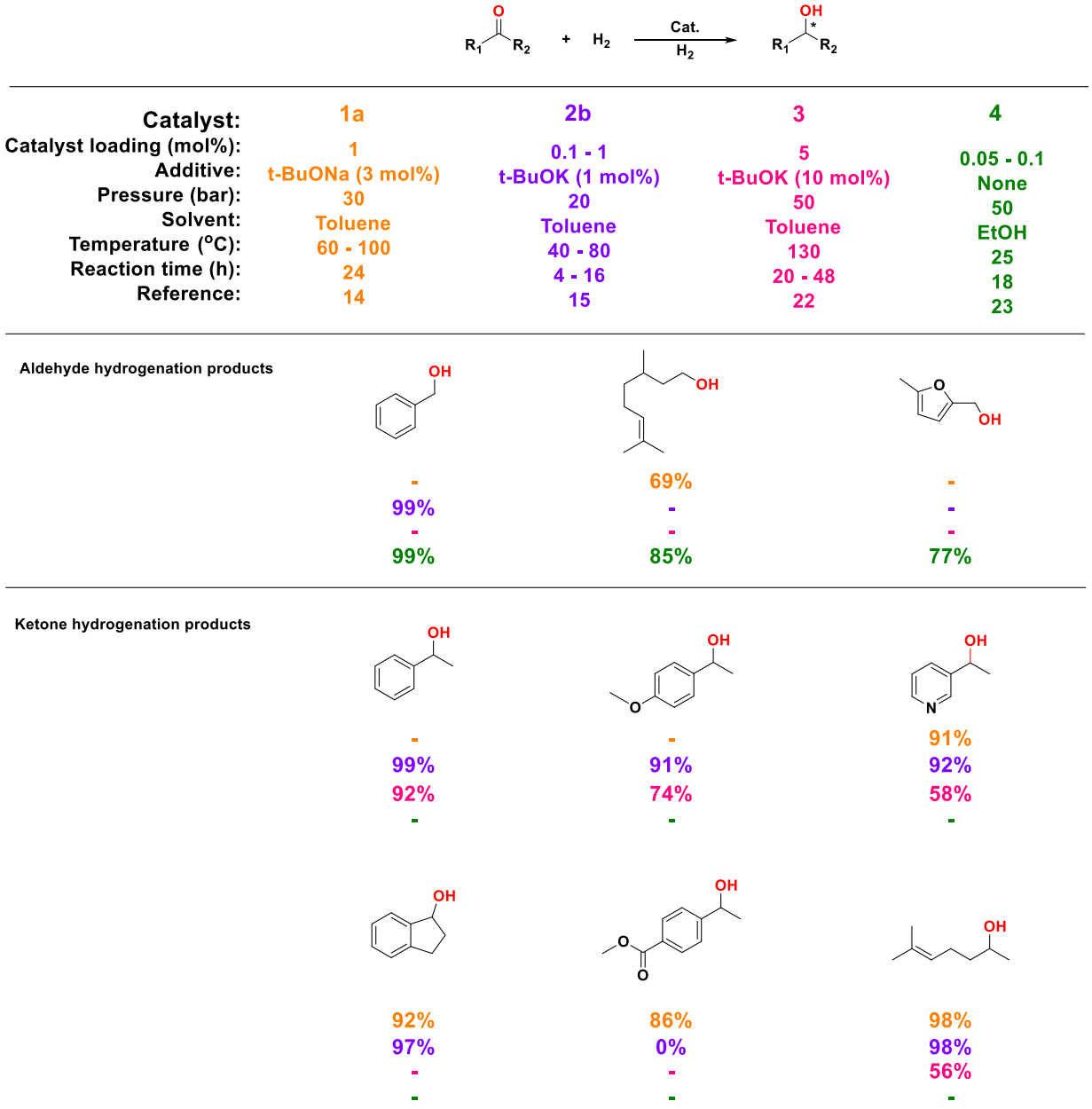


Figure 3. Efficiency of pincer Mn^{I} catalysts for hydrogenations of selected ketones and aldehydes

II. C. Hydrogenation of Asymmetric Ketones

Asymmetric hydrogenation for ketones using manganese-pincer catalysts has also been studied (**Chart 2**). The first asymmetric hydrogenation for ketones by a manganese-pincer pre-catalyst was introduced by Clarke and coworkers in 2017. Clarke's catalyst (compound ***fac*-5**) is a chiral, ferrocene- substituted, **PN_2** complex with facially coordinating amino-phosphines.[24]

Complex ***fac*-5** shows a high activity and moderate to excellent enantioselectivity for hydrogenations of a wide range of ketones, especially aromatic ketones. Hydrogenations of ketones by compound ***fac*-5** also tolerate double bonds and both electron-withdrawing and electron-donation aromatic substituents. More importantly, increase in steric hindrance at the alkyl chain of the aryl alkyl ketones greatly enhances the enantioselectivity of the asymmetric hydrogenations catalyzed by ***fac*-5**. In addition, the *mer*-configuration of ***fac*-5** was also reported spectroscopically, which explained the selectivity of the asymmetric hydrogenations.[25] As the CO loss results in a formation of the hydride species, which is the key step for hydrogenation of ketones,[14,24] the selectivity of the asymmetric hydrogenation by catalyst ***fac*-5** and ***mer*-5** is explained in **Figure 4**. For catalyst ***fac*-5**, the (R)-configuration of the product alcohol is preferred when the aromatic end of the ketone is aligned with the pyridine ligand (as shown in **Figure 4** left); while for complex ***mer*-5**, the enantioselectivity is lower because the aliphatic R of the ketone is strained by the phenol group of the phosphine (**Figure 4** right). The substitutions of the arylphosphine ligand impact the catalytic activity, but do not affect the enantioselectivity.

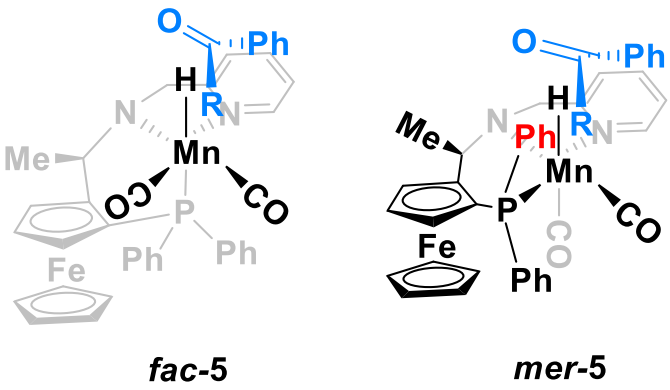


Figure 4. The fac- and mer-structure of complex **5** with an aromatic ketone

Soon after Clarke's discovery of compound ***fac*-5**, the Beller group reported a chiral manganese catalyst (complex **6**)[26] that features the same **P_2N** backbone as compounds **1**. Complex **6** can catalyze asymmetric hydrogenations of ketones under milder conditions (30 °C, 30 bar, and 4h) than catalyst ***fac*-5**. In contrast with ***fac*-5**, catalyst **6** shows a higher catalytic activity and better enantioselectivity toward aliphatic ketones (up to 84% ee[†]) than aromatic

[†] Enantiomers excess (the ratio between two enantiomers)

ketones. The author also included DFT calculations to support the proposal that the mechanism of this catalyst followed the outer-sphere mechanism, in which the CO dissociation leads to the formation of a manganese hydride species.

Lutidine-based **PN_2** pincer ligand, reported by Ding and coworkers,[27] was also utilized for asymmetric hydrogenations of ketones (compound **7)**. This catalyst shows an outstanding catalytic activity (isolated yield >90%) and enantioselectivity (>85% ee) for different substrates. The advance of catalyst **7** is that the R group can be modified to tune the activity of the catalysis. Different R-group substituents including H, Cl, ^{t}Bu, OMe were examined; the optimal catalyst is obtained when ^{t}Bu is used. Substitution of NH by the N-methylated group showed that when N-methyl was used, the conversion percentage dropped to 5% (from 99%) and the ee value dropped to 58 (from 90). This result showed that the NH moiety is important for the catalysis of compound **7**. More comparisons of asymmetric ketones hydrogenation catalyzed by Mn^I pincer complexes are shown in **Figure 5.**

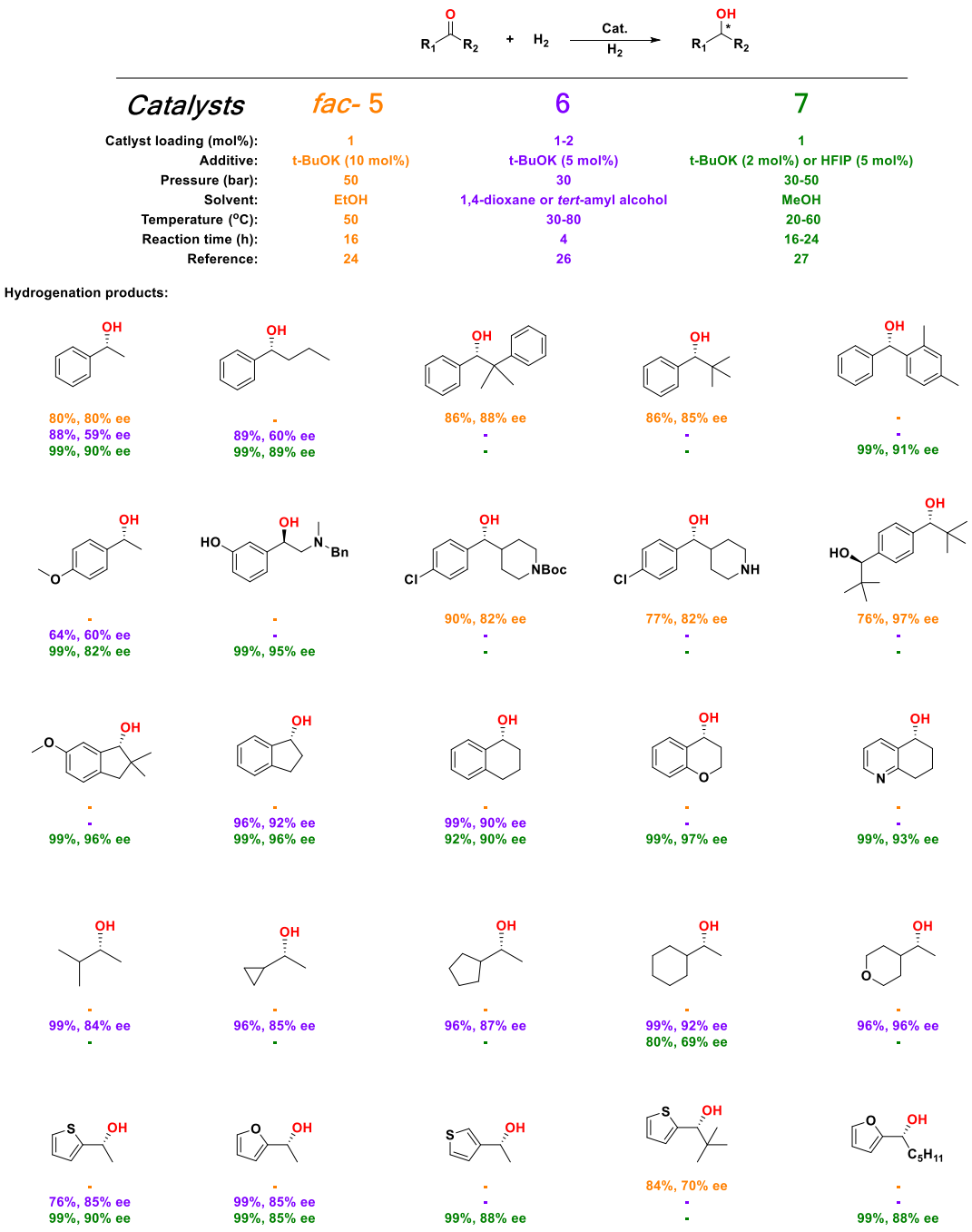


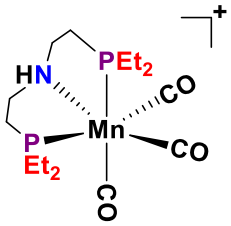
Figure 5. Isolated yield and enantioselectivity for selected asymmetric hydrogenations of ketones with Mn-based pincer catalysts

II. D. Hydrogenation of Esters

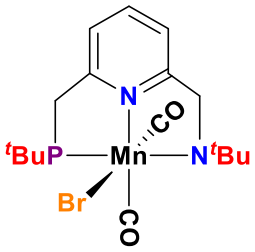
The manganese pincer catalyzed hydrogenation of esters was first reported by Beller and coworkers (compound **8**, Chart 3).[28] The author initially tested the efficiency of compounds

1a and **1b**, but these compounds, which exhibit high activities toward ketones and aldehydes, did not show good yields for the conversion of methyl benzoate to an alcohol. The less hindered cationic tricarbonyl manganese catalyst **8** was then used for this catalysis. Interestingly, the synthesis of **8** resulted in a mixture of the *fac*- and *mer*-configurations, in which the *fac*-coordinated product dominated the yield; however, conversion from one coordination to the other was possible via treating the reaction in toluene at high temperature. Catalytic activities of the two configurations were experimentally shown to be similar. Compound **8** gave good yields (78-95%) for hydrogenations of a broad range of ester compounds including both aliphatic, aromatic, and lactones while retaining double bonds. Moreover, unsaturated esters were hydrogenated to saturated alcohol with the presence of **8**. Similar to ketone and aldehyde hydrogenations catalyzed by **1**,[14] the outer-sphere mechanism was also proposed for the case of compound **8**. This mechanism, again, suggested the formation of the amido hydride dicarbonyl manganese species.

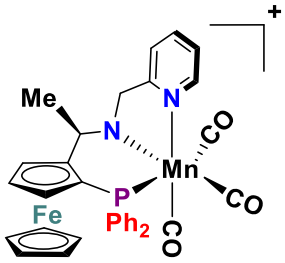
Chart 3. Manganese catalysts bearing pincer-type ligand for hydrogenations of esters



Beller 2016[28]
8



Milstein 2017[29]
9



Clarke 2017[22]
***fac*-5**

The Milstein group has also demonstrated the lutidine-based **PNN** pincer ligated manganese catalyst (compound **9**).[29] The reactions were run under mild conditions (20 ^{o}C and 20 bar) and the catalyst was activated by an uncommon base, KH. The yields of the conversions of esters to alcohol were relatively high (up to 98%). The authors were also successful in characterizing the intermediates (amido dicarbonyl and hydride dicarbonyl species) when KO^{t}Bu and H_2 were applied; these observations support the proposed outer-sphere mechanism for the catalysis.

In addition, compound ***fac*-5** can also catalyze the hydrogenations of a variety of esters, even esters containing a free amido group.[24] The catalytic reactions were operated under mild conditions (75 °C and 50 bar) and surprisingly the hydrogenation of butyl butyrate was achieved with only 0.1 mol% of the catalyst. The conversion of *para*-nitro derivative was not successful and the conversions of aliphatic esters gave lower yields when catalyst ***fac*-5** was used. More efficiency comparisons of current pincer Mn^{I} catalysts for ester hydrogenation are included in **Figure 6**.

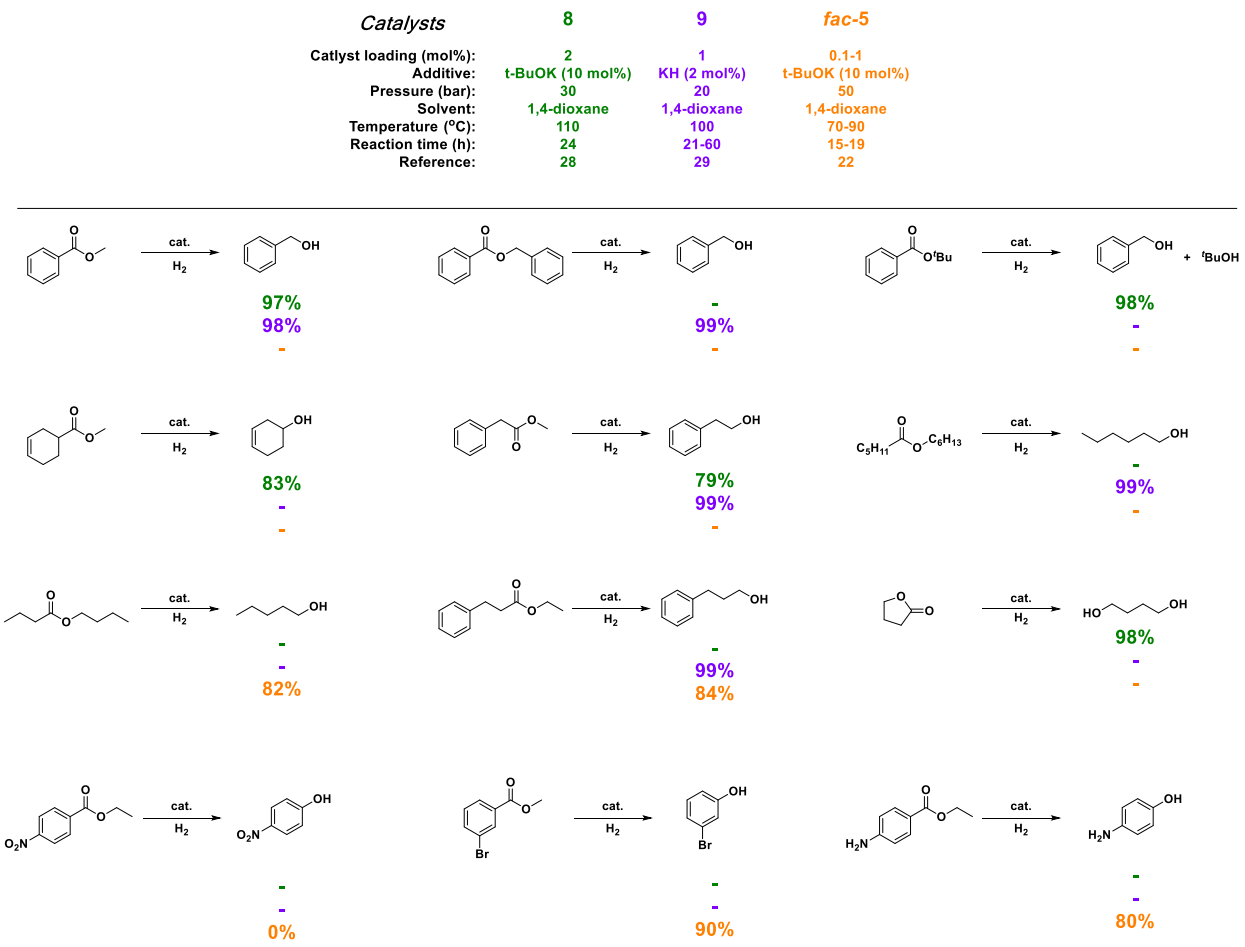


Figure 6. Efficiency of pincer Mn^{I} catalysts for selected esters

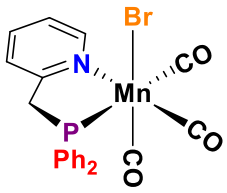
III. Manganese Catalysts with Non-Pincer Ligands

III. A. Overview and Mechanism

Disadvantageous stability and lack of suitable ligand platforms are core reasons that have restricted the development of efficient non-pincer catalysts for hydrogenations.

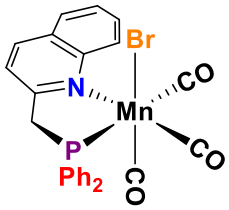
Consequently, the substrates scope for these catalysts is also limited. Progress in using non-pincer ligands for hydrogenation catalysis of Mn^{I} has been reported mainly by the Sortais group,[30,31] the Beller & Pidko groups,[32,33] and the Kircher group,[34] in which phosphine ligands are often used to assist the catalytic bond activation (**Chart 4**). Challenges for using non-pincer ligands for catalytic hydrogenation of C=O bonds can arise from the lack of understanding about the mechanism. Mechanistic study is not usually included because the MLC is not possible in some catalysts such as Kirchner's bisphosphine Mn^{I} catalyst.[30,34]

Chart 4. Selected non-pincer Mn^{I} hydrogenation catalysts



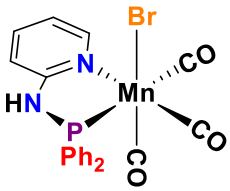
Sortais 2018[30]

10



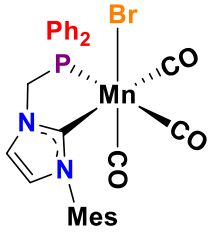
Sortais 2018[30]

11



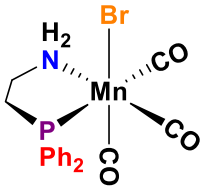
Sortais 2018[30]

12



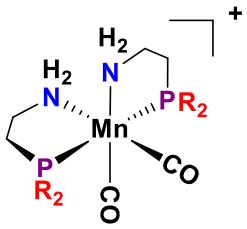
Sortais 2019[31]

13



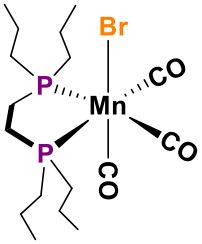
Beller & Pidko 2017[33]

14



Beller & Pidko 2017[33]

15

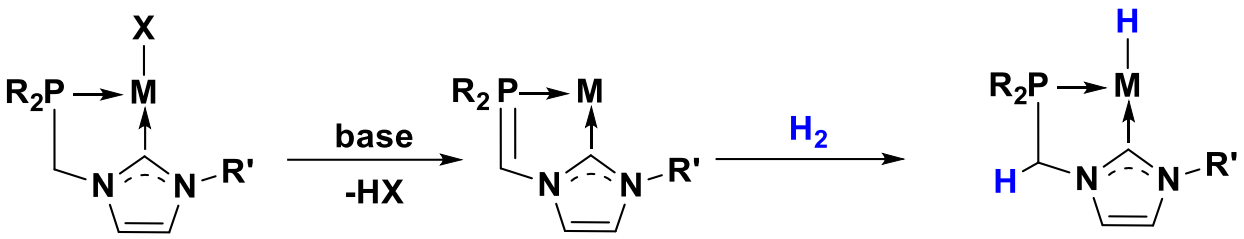


Kircher 2018[34]

16

Recently, Sortais and coworkers introduced an interesting Mn^{I} catalyst **13** in a NHC-phosphine ligand system that displays an unprecedented H_2 activation through MLC-assisted mechanism.[31] The deprotonation step of the complex resulted in metal-substituted phosphonium ylide that is able to easily activate H_2 (**Scheme 3**). Catalyst **13** is one of the most efficient Mn^{I} catalysts for ketones hydrogenation up to date.

Scheme 3. H_2 activation by catalyst **13**



Significantly, Hu and coworkers reported a catalytically active Mn^{I} model of the biological [Fe]-hydrogenase (compound **17**).[35] This complex is the first example of a non-native metal biomimetic model of [Fe]-hydrogenase enzyme (**Figure 7a**). Because of its unique ligand system, catalyst **17** was proposed to have a different mechanism from the Mn^{I} catalysts mentioned above. The proposed hydrogenation mechanism of **17**, akin to the semisynthetic enzyme [Fe]-hydrogenase,[36] relies on the deprotonation of the hydroxide group on the ligand. In the presence of a base, KH, at room temperature, the deprotonation of **17** resulted in the deprotonated product **17***, which was confirmed by infrared, ^{1}H-NMR spectroscopy and X-ray crystallography (**Figure 7b**). Both **17** and **17*** are hydrogenation catalysts. Density functional theory study suggested that under pressure, H_2 substitutes the CO at the *trans*- position to the acyl ligand to give intermediate **17a**, which then undergoes a heterolytic H_2 cleavage to produce the hydride intermediate **17b**. The hydrogenation substrate interacts with **17b**, leading to the hydrogenated alcohol product and the reformation of catalyst (**Scheme 4**).

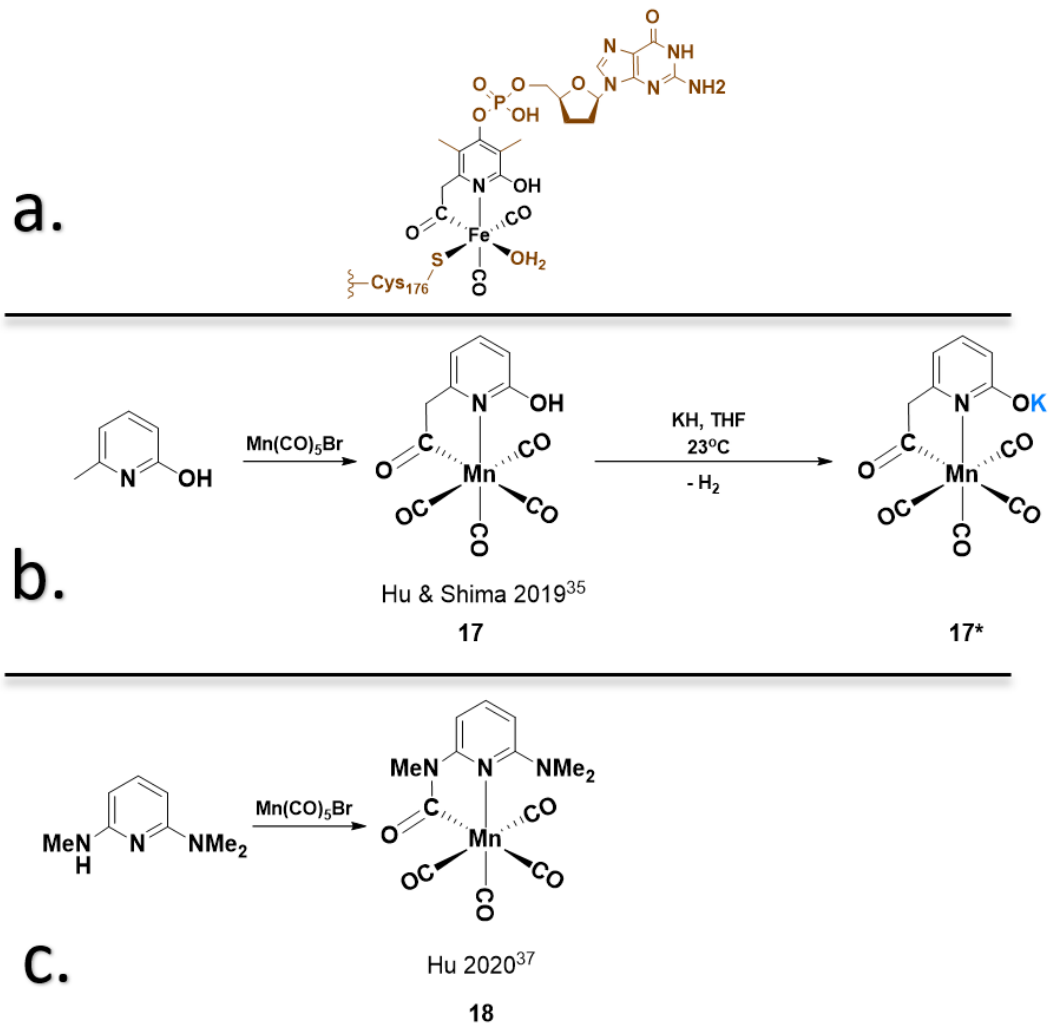
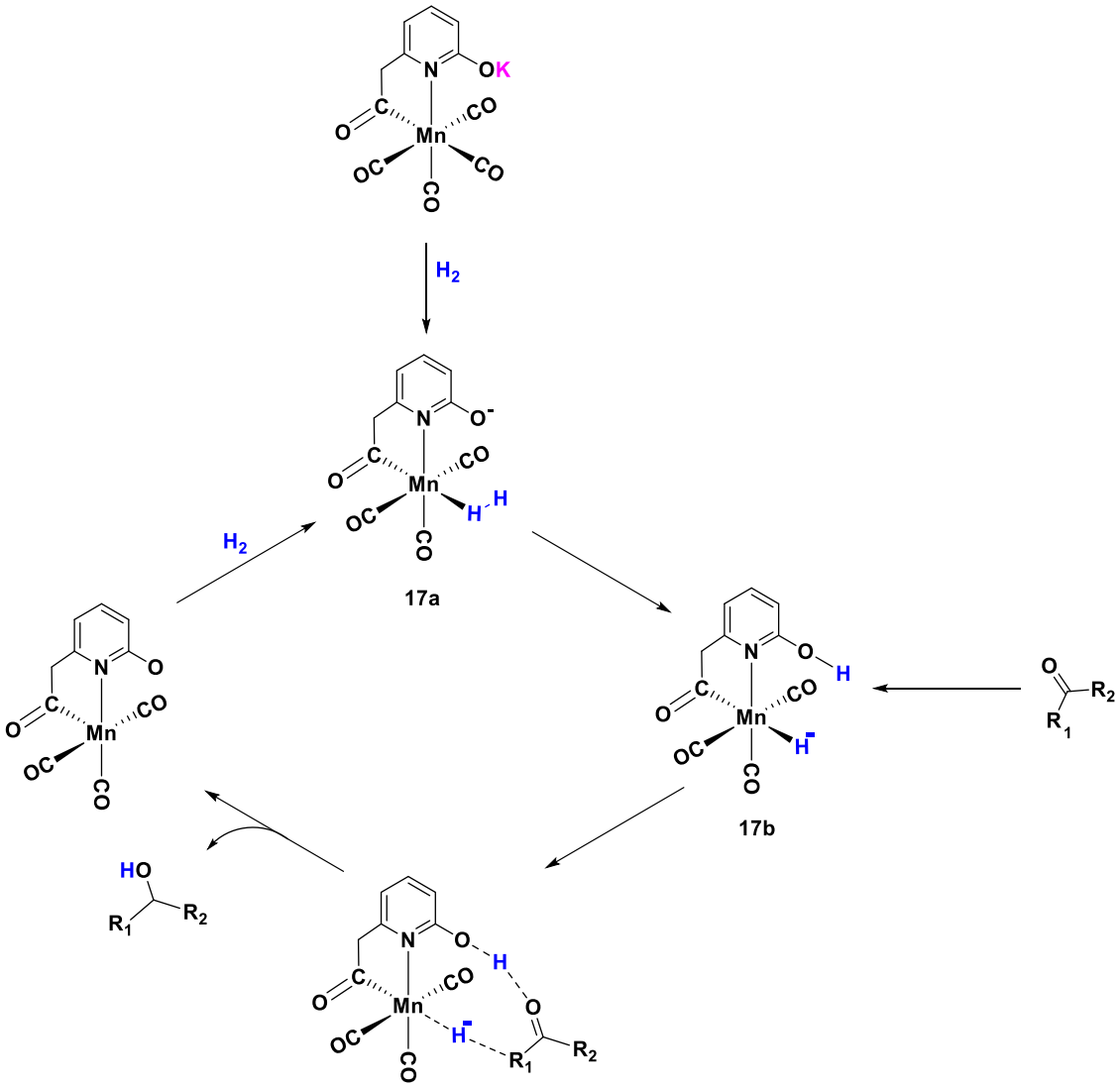


Figure 7. The active site of [Fe]-hydrogenase enzyme (a); Synthesis of catalysts **17** (b) and **18** (c)

Because the catalytic activity of **17** for hydrogenation was moderate compared with highly active pincer Mn^{I} catalyst, the author later introduced a structurally modified catalyst **18** with both enhanced activity and substrates scope.[37] Catalyst **18** is ligated by the robust carbamoyl donor instead of the acyl donor, giving a more stable structure. Although the authors did not give a catalytic mechanism study for **18**, they expected similar H_2 activation and cleavage as catalyst **17**.

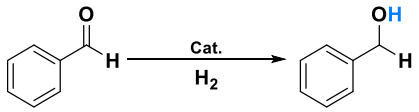
Scheme 4. Catalytic cycle for hydrogenation catalyzed by **17** and **17***



III. B. Hydrogenation of Aldehydes

Non-pincer Mn(I) complexes have rarely been reported in hydrogenation of aldehydes. Among the mentioned non-pincer complexes, the models of Hu et al. are the only catalysts that are active toward aldehyde hydrogenations. Both catalysts **17** and **18** show excellent activity toward the hydrogenation of benzaldehyde (>99% isolated yield); however, the reaction conditions for these catalysts are harsher and require more toxic additive base than highly active pincer catalysts **2b** and **4** (**Table 1**). While catalyst **17** can only catalyze one aldehyde, the more robust catalyst **18** showed a wider substrates scope albeit more severe reaction conditions.

Table 1. Benzaldehyde hydrogenation efficiency comparison of different catalysts



Catalysts	Cat. loading (mol%)	Pressure (bar)	Temperature (°C)	Reaction time (h)	Additive	Isolated yield (%)	Ref.
17	1	50	80	16	MP 20 mol%	99	35
18	2	50	100	24	MP 50mol%	99	37
2b	0.1	20	80	4	^{t}BuOK 1 mol%	99	15
4	0.05	50	25	18	None	99	23

MP = 1-methyl-2-pyrrolidinone

III. C. Hydrogenation of Ketones

In contrast with aldehydes, ketones hydrogenation using Mn^{I} non-pincer catalysts have been more developed. The series of catalysts (**10**, **11**, **12**) introduced by Sortais and coworkers unveiled more insight on the role of the ligand environment.[30] Different phosphino-pyridinyl PN bidentate ligands were examined for the hydrogenations. The catalytic activity was dramatically lowered when methylene-bridged PN ligands (**10** and **11**) were used in replacement of the amino-bridge **PN** ligand (**12**). Here, the much lower electron activating effect of the methylene bridge compared with the amino bridge might be the origin of the subdued activity; however, mechanistic study to support this hypothesis is still under investigation. Catalyst **12** is also active toward 24 ketones and tolerates other functional groups.

Even more active than **12**, Kirchner's biphosphine Mn^{I} complex **16** and Sortais's complex **13** are also excellent ketone hydrogenation catalysts, which are comparable to the highly active Mn^{I} pincer catalysts (**Figure 8**). In general, halide, methyl, and methoxide substituents do not affect the activity of these catalysts. Semisynthetic [Mn]-hydrogenase, complex **17**, showed a modest activity toward acetophenone (40% yield),[35] while the more developed catalyst **18**

exhibits a superior activity (91% yield).[37] The low catalytic activity of **17** is mostly due to the less electron-donating ligand environment, resulting in a less-hydridic Mn–H intermediate in the catalytic cycle (See mechanism discussions). In summary, ketones hydrogenations by non-pincer Mn^{I} catalysts have been advanced and shown as high activity as Mn pincer catalysts.

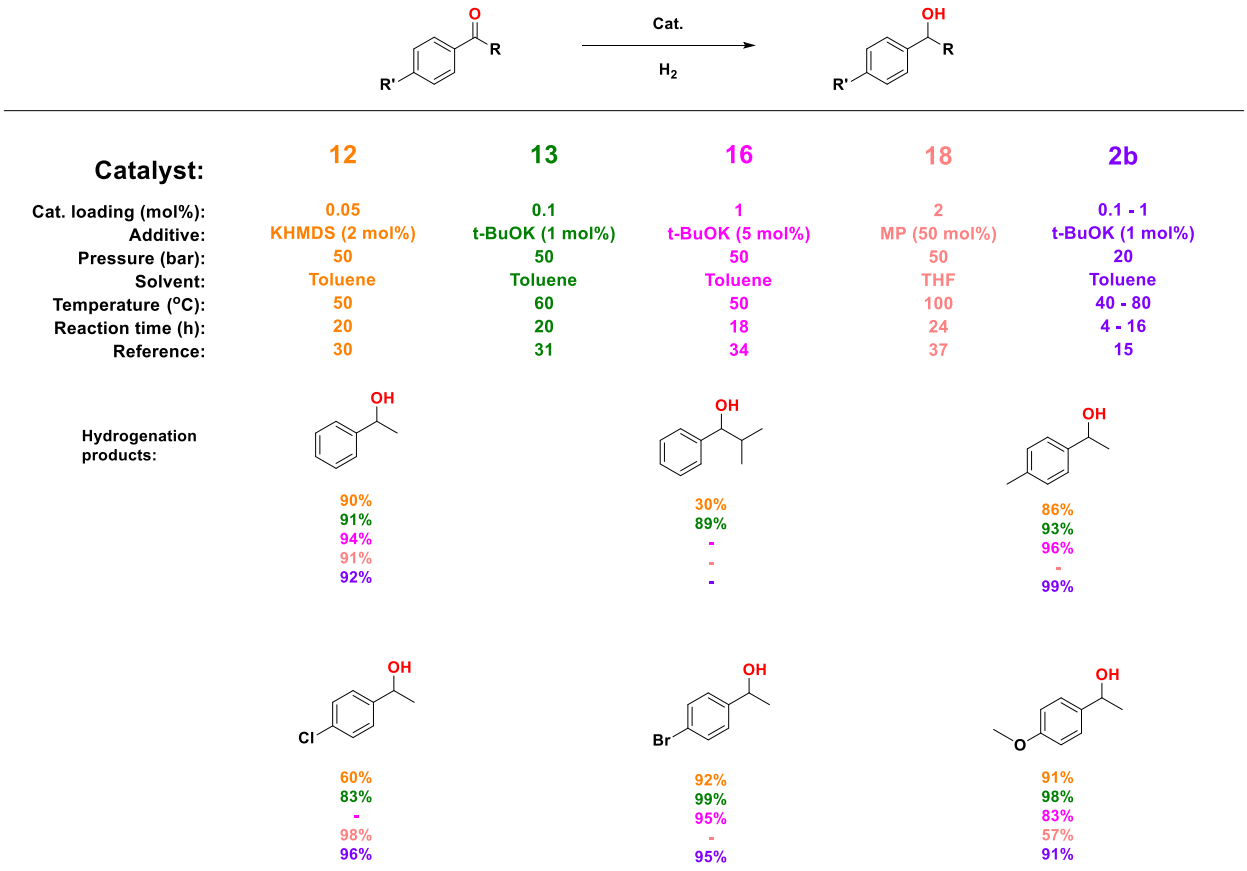


Figure 8. Efficiency of Mn^{I} catalysts for hydrogenations of selected ketones

III. D. Hydrogenation of Esters

Complexes **14** and **15**, introduced by the collaboration of the Pidko and the Beller groups, were the only non-pincer Mn^{I} complexes that can efficiently catalyze ester hydrogenations.[33] Hydrogenation of methyl benzoate was utilized for **14** and **15**, leading to the conclusion that monoligated catalyst **14** showed much higher activity than bi-ligated catalyst **15**. Such higher activity for **14** arises from the *cis* position between the bromide and amine, which promotes the bromide dissociation, hence favors the H_2 activation. Computational study of the mechanism of **14** suggested that the additive base also plays an important role in the catalytic

cycle. Both aromatic and aliphatic esters were able to be hydrogenated by catalyst **14** to give moderate-to-excellent yields. Interestingly, hydrogenations of more sterically hindered esters, which are typically harder to reduce, gave better yields (**Figure 9**). The future of ester hydrogenation by non-pincer Mn^{I} catalysts might rely heavily on the ligand platform of complex **14** that enables for a nonclassical MLC-assisted mechanism with the accessible bidentate aminophosphine ligand.

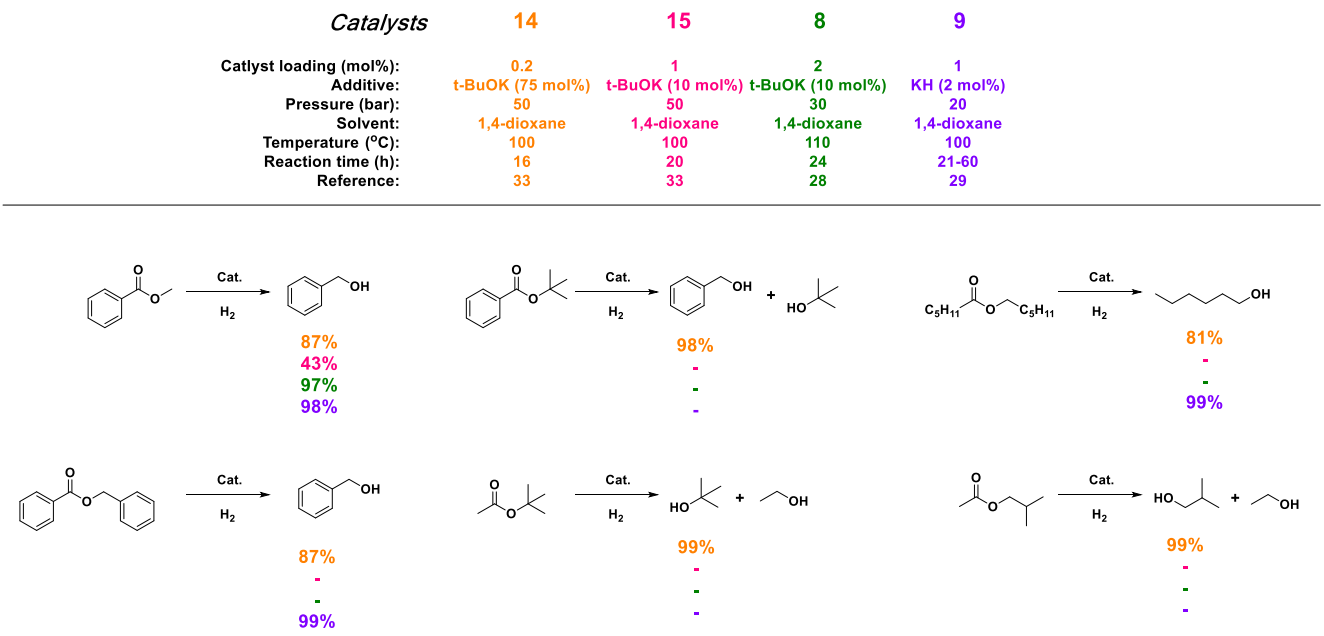


Figure 9. Efficiency of Mn^{I} catalysts for hydrogenations of selected ketones

IV. Conclusion and Outlook

In summary, with the motivation of making more sustainable catalysts for chemical industries, Mn has shown its potential to replace precious metals in catalysis. While pincer Mn^{I} catalysts have been highly developed in the past five years for hydrogenations, non-pincer Mn^{I} catalysts hold a great promise and display unconventional mechanism and catalytic effects. Catalytic hydrogenations of aldehyde, ketones, and esters by pincer Mn catalysts rely heavily on the ability to adjust electronic properties that have been ubiquitously seen in other pincer catalysts of transition metals, especially Ru.[3,6] Indeed, well-understood pincer precious metal catalysts and current effective pincer Fe catalysts are obviously good models and directions for

further development of Mn^{I} catalysts. From this aspect, other ligand platforms could bring new insight to not only catalysis and organometallics, but also biological chemistry.

Metal-ligand cooperativity, being the inspiration for most mechanistic studies, has been key for exploring more effective catalysts. The NH functionality in PN ligands has been seen to show a molecular Mn/NH bifunctional nature through metal–ligand cooperation, which is key for mechanistic study. Furthermore, recent investigations of CH and PH functionality have broadened understanding of catalytic mechanism and the metal-ligand relationship.

It is controversial to debate that the future of Mn^{I} catalysts can be futile to make them practically applicable because the activities of all Mn catalysts are still much lower than Ru catalysts. Regardless of the motivation for exploring new Mn^{I} catalysts, learning more about ligand effect on catalytic activity, metal-ligand bonding, and chemistry of inexpensive Mn compounds can undoubtedly bring us to a more sustainable world. For the most foreseeable future, the current hydrogenation substrates scope for Mn^{I} catalysts is also expected to expand to more challenging transformations such as CO_2 to formate or CO_2 to methanol. This development could add more to the ambitious of making useful fuels from CO_2.

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