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Efficient and chemoselective hydrogenation of aldehydes catalyzed by well-defined PN^3 -pincer manganese(II) catalyst precursors: an application in furfural conversion[†]

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Well-defined and air-stable PN^3 -pincer manganese(II) complexes were synthesized and used for the hydrogenation of aldehydes into alcohols under mild conditions using MeOH as a solvent. This protocol is applicable for a wide range of aldehydes containing various functional groups. Importantly, α,β -unsaturated aldehydes, including ynals, are hydrogenated with the $\text{C}=\text{C}$ double bond/ $\text{C}\equiv\text{C}$ triple bond intact. Our methodology was demonstrated for the conversion of biomass derived feedstocks such as furfural and 5-formylfurfural to furfuryl alcohol and 5-(hydroxymethyl)furfuryl alcohol respectively.

The conversion of carbonyl compounds to alcohols is a widely used synthetic tool in organic synthesis.^{1,2} The catalytic hydrogenation with hydrogen (H_2) is an attractive way to avoid waste formation due to the use of stoichiometric reductants such as lithium aluminum hydride, sodium borohydride and lithium borohydride, silanes, and boranes.³ Homogenous catalytic systems offer advantages in terms of selectivity and activity over their heterogeneous counterparts.⁴ While a number of complexes containing precious metals, such as Ru, Rh, and Ir, show excellent selectivity towards hydrogenation of aldehydes over other sensitive functionalities such as ketones and/or alkenes,⁵ the search for more economical and efficient methods by using catalysts derived from earth-abundant metals, for example, Fe, Mn and Co, is of great interest. In this regard, several Mn-based catalysts have been reported for the hydrogenation of aldehydes, ketones, and esters (Fig. 1);^{6,7} however, the catalyst preparation typically requires expensive Mn(I) precursors, such as $\text{Mn}(\text{CO})_5\text{Br}$, and harsh reaction conditions are often employed, such as high catalyst loadings, use of strong

bases as additives, and high temperature. In 2016, Beller and co-workers reported a well-defined PNP-Mn pincer complex for the hydrogenation of aldehydes and ketones.^{7a} Kempe *et al.* reported a triazine-based PN^3P -Mn pincer system for hydrogenation of ketones, showing quantitative conversion in a short reaction time.^{7b} Thereafter, Sortais, Beller, and Clark reported various Mn pincer complexes for the reduction of both ketones and aldehydes.^{7f-h} In 2018, Kirchner reported an efficient PN^3P -Mn(I) pincer complex for hydrogenation of aldehydes over ketone and alkene functionalities.⁷ⁿ More recently, Filonenko and Pidko demonstrated the use of Mn(I)-CNP precatalyst for the hydrogenation of ketones, aldehydes, esters and imines.^{7o} The further development of selective hydrogenation catalysts from readily available and abundant metal complexes offers a promising and cost-effective protocol for practical applications.

Upon reduction biomass-derived feedstocks, such as furfural (FAL) and 5-formylfurfural (FFAL) containing the aldehyde functionality, can be converted into several renewable commodities.⁸ FAL is widely available in the fine chemical industry,⁹ and the conversion of FAL to furfuryl alcohol (FOL) and other value-added chemicals is of great interest.¹⁰ The catalytic hydrogenation of FAL to FOL has been accomplished

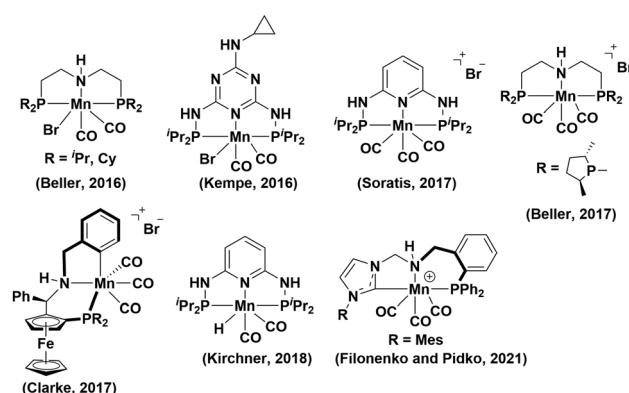


Fig. 1 Manganese(I) complexes studied for the hydrogenation of aldehydes.

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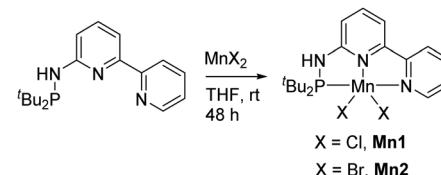
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mostly using heterogeneous catalyst systems such as Cu/Cr, Ni, Cu Co, Pt, and Pd supported catalysts;¹¹ however, these catalysts create some concerns about toxicity. On the other hand, the use of homogeneous catalysts for FAL conversion has been limited. For the first time, Paganelli *et al.* reported a reduction of FAL to FOL with H₂ using a recyclable dihydrothioacetic acid-modified Rh system.¹² Thereafter, Li and co-workers reported RuCl₂(PPh₃)₃/CH₃COOH catalyst to prepare FOL from FAL.¹³ Similarly, Ru-tris(2,2,6,6-tetramethyl-3,5-heptanedionate)₃ and NHC-based Ru-catalyst were demonstrated for the hydrogenation of FAL.¹⁴ Recently, Mika reported a bidentate phosphine modified Ru-based catalytic system for the efficient conversion of FAL to FOL,¹⁵ and more recently, Nielsen reported well-defined Ru and Ir PNP pincer complexes with low catalyst loadings for the hydrogenation of furanic aldehydes.¹⁶ However, the use of expensive catalysts has limited their practical applications. Thus far, non-noble homogenous catalyst systems for FAL to FOL have not been reported. In contrast to the significant achievements in the applications of novel Mn(i) pincer complexes as discussed earlier, the use of Mn(ii)-based pincer complexes in the organic transformation is limited,^{7c,17} even though MnX₂ (X = Cl, Br) (\$8.6 per mol_{Mn}) is considerably more economical than Mn(CO)₅Br (\$13 250 per mol_{Mn}) as a catalyst precursor.

Previously, our group developed a class of pincer complexes based on the phosphino aminobipyridine (PN³(P) pincer) ligand system and demonstrated the unique and enhanced reactivities in the direct coupling of amines to imines and ester hydrogenation.¹⁸ In this communication, we describe an experimental investigation of the chemoselective hydrogenation of aldehydes with hydrogen (H₂) using air-stable Mn(ii) PN³-pincer complexes (Scheme 1a). Extension of this protocol was applied to the selective conversion of FAL to FOL and FFAL to 5-(hydroxymethyl)furfuryl alcohol (HMFO), respectively.

The Mn(ii) based pincer complexes **Mn1** and **Mn2** were synthesized by the reaction of MnX₂ (X = Cl, Br) with the 'Bu₂PNH-BPy (bis-*tert*-butylphosphine-2,2'-bipyridine-6-amine) pincer ligand in THF at room temperature (Scheme 2). Upon crystallization in a solution of THF:acetonitrile (1:1), the crystals of **Mn1** and **Mn2** were fully characterized by single-crystal XRD analysis (Fig. 2) and elemental analysis (see the ESI[†]). The catalytic performance of **Mn1** and **Mn2** was first investigated for the hydrogenation of 3-methylbenzaldehyde as a model substrate to find the optimal hydrogenation reaction conditions (Table S1, ESI[†]). Changing the solvent to MeOH



Scheme 2 Synthesis of Mn(ii) PN³ pincer complexes **Mn1** and **Mn2**.

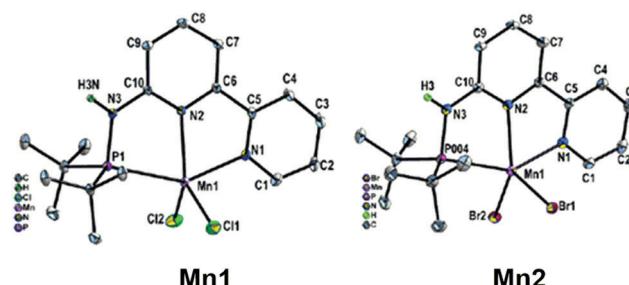
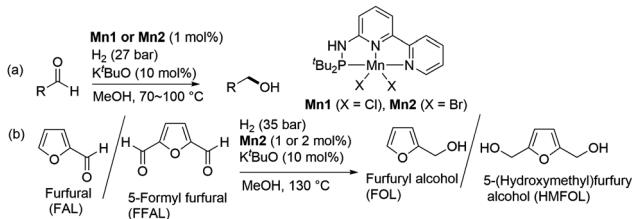


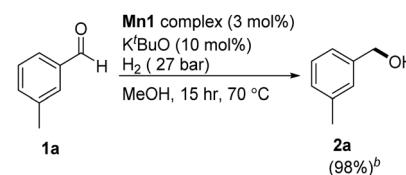
Fig. 2 Crystal structures of complexes **Mn1** and **Mn2**. All atoms have been shown with 30% probability ellipsoids. All hydrogen atoms except for N–H have been omitted for clarity. For **Mn1** and **Mn2**, details of selected bond distances (Å) and angles (degrees) are shown (Fig. S1 and S2, ESI[†]).

leads to an enhanced yield of product **2a** with full conversion (Table S1, ESI[†]). The performance of **Mn2** was tested, which showed its lower activity as compared to **Mn1** (Table S1, entries 4 and 5, ESI[†]). At 130 °C, **Mn2** exhibited a higher reactivity in MeOH (Table S1, entry 6, ESI[†]). MeOH was thus chosen as the optimal solvent for the conversion. Performing the reaction at 110 °C using **Mn1** resulted in full conversion to **2a** (Table S1, entry 7, ESI[†]). Decreasing the temperature to 70 °C still offered an excellent yield of **2a** (Table S1, entries 8–10). So, an excellent yield of 3-methylbenzyl alcohol was obtained using **Mn1** (3 mol%) and H₂ (27 bar) in MeOH (Scheme 3).

With the optimized reaction conditions in hand, various aldehyde substrates were examined. The aldehyde substrates bearing halogens such as fluorine (F) and bromine (Br) gave the alcohol products in excellent yields (Scheme 4, products **2b**–**2d**). Investigation of the aldehydes bearing different para substituents on the phenyl ring, such as isopropyl (iPr) and methoxy (OMe), showed higher yields of hydrogenation products (Scheme 4, products **2d** and **2e**). When terephthaldehyde was employed as a substrate, both aldehyde (–CHO) groups were reduced to afford 1,4-benzenedimethanol in 90% yield (Scheme 4, product **2g**). A dimethyl substituted aromatic aldehyde also underwent hydrogenation to give an excellent yield of

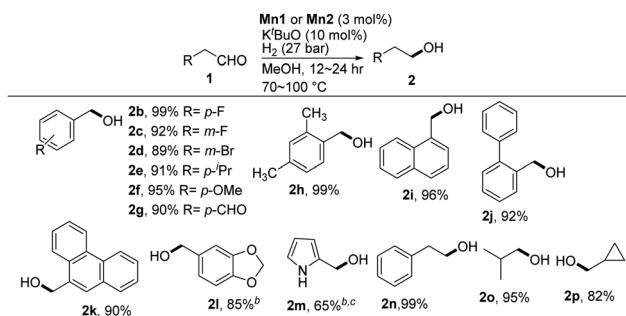


Scheme 1 In this work: (a) hydrogenation of aldehydes and (b) conversion of furfural (FAL) to furfuryl alcohol (FOL) and 5-(formylfurfural) (FFAL) to 5-(hydroxymethyl)furfuryl alcohol (HMFO).



Scheme 3 Hydrogenation of 3-methylbenzaldehyde. ^a For the reaction, 3-methylbenzaldehyde (0.83 mmol), **Mn1** (3 mol%, 0.024), K₃BuO (0.083 mmol) and H₂ (27 bar) were used. ^b Isolated yield.



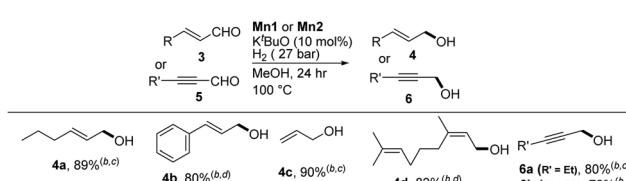


Scheme 4 The substrate scope of the hydrogenation of aldehydes. ^a For the reaction, aldehyde (1.0 mmol), **Mn1** (3 mol%), K'BuO (10 mol%), and H₂ (27 bar) in MeOH (1.0 mL) were used. Isolated yields are provided. ^b **Mn2.** ^c 24 h.

the alcohol product (Scheme 4, product **2h**). Biphenyl and naphthalene containing aldehydes were also converted to alcohol products in high yields (Scheme 4, products **2i** and **2j**). Heteroaromatic rings did not interfere with the hydrogenation reactions (Scheme 4, products **2l** and **2m**). Both acyclic and cyclic aldehydes worked efficiently to give alcohol products in high yields (Scheme 4, products **2o** and **2p**).

Encouraged by the excellent results obtained with aromatic aldehydes, we further examined more challenging α,β -unsaturated substrates. Selective hydrogenation of such aldehydes is important because double bonds are often reduced along with the aldehyde functionality.¹⁵ Using our PN³ Mn(II) catalytic system, only the aldehyde group was hydrogenated selectively, with conjugated and nonconjugated C=C double bonds untouched (Scheme 5, products **4a**–**4c**). The aldehyde substrate containing two double bonds, for example, 3,7-dimethyl-2,6-octadienal (ethyl citral), was hydrogenated smoothly to give the alcohol product in good yield without affecting the double bonds (Scheme 5, **4d**). We also examined alkyne conjugated aldehydes (ynals). Previously, PNP Mn(II) pincer complex catalyzed semi-hydrogenation of alkynes with ammonia borane was reported.^{17a} Surprisingly, the hydrogenation of pent-2-ynal and 3-phenylpropiolaldehyde gave pent-2-yn-1-ol and 3-phenylprop-2-ynol in 80% and 78% yields, respectively, without affecting the alkyne functionality (Scheme 5, **6a** and **6b**).

After successfully studying a wide range of aldehyde substrates, we turned our attention to exploring the hydrogenation of aldehydes that are used as feedstocks, for example, conversion of FAL to FOL and FFAL to HMFOL. The study of the effect of the **Mn2** catalyst loading on the hydrogenation of FAL showed that 2.0 mol% catalyst loading gave full conversion



Scheme 5 Hydrogenation of α,β -unsaturated aldehydes and ynals. ^a Reaction conditions: aldehyde (1.0 mmol), **Mn1** or **Mn2** (3 mol%), K'BuO (10 mol%), H₂ (27 bar) in MeOH (1.0 mL). ^b Isolated yield. ^c **Mn1.** ^d **Mn2.**

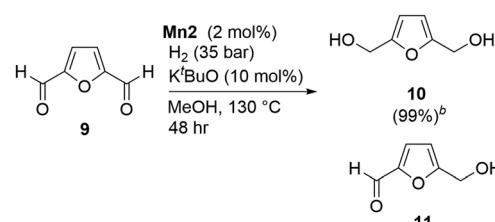
Table 1 Optimization of the reaction conditions for hydrogenation of furfural (FAL)^a

| Entry | X (bar) | Temp. (°C) | Conv. (%) | Yield ^b (%) | Selectivity (%) | 7 | | 8 | |
|----------------|---------|------------|-----------|------------------------|-----------------|------------------------|--|-----------------------|--|
| | | | | | | H ₂ (X bar) | | Mn2 (2.0 mol%) | |
| | | | | | | K'BuO (10 mol%) | | MeOH, 16 h | |
| | | | | | | | | | |
| 1 | 35 | 100 | 85 | 82 | 96 | | | | |
| 2 | 35 | 120 | 90 | 88 | 98 | | | | |
| 3 | 35 | 130 | 100 | 99 | 99 | | | | |
| 4 ^c | 35 | 100 | 75 | 70 | 93 | | | | |

^a Furfural (1.04 mmol), **Mn2** (5.5 mg, 0.010 mmol), K'BuO (11.6 mg, 0.103 mmol) in methanol for 16 h. ^b Isolated yields. ^c Neat conditions.

(Table S2, ESI[†]). When the reaction was carried out using H₂ (35 bar) at 100 °C, the product was obtained with 85% conversion with high selectivity (Table 1, entry 1). Upon increasing the reaction temperature from 120 °C to 130 °C, the full conversion of FAL was achieved within 16 h with excellent yields (Table 1, entries 2 and 3). However, when the reaction was conducted in the absence of solvent, the product conversion and selectivity both decreased. This observation suggested that methanol is necessary to achieve the full conversion of furfural (Table 1, entry 4). The effect of H₂ pressure during the reaction was studied (Fig. S1, ESI[†]). Upon increasing the pressure from 5 bar to 35 bar, the conversion of FOL was increased to 99%. On the other hand, at H₂ (50 bar), the yield was not much improved. These results suggested that 35 bar pressure of H₂ is an optimum pressure for the excellent conversion of FAL to FOL.

After the excellent selectivity was achieved for the conversion of FAL to FOL, it was interesting to study the hydrogenation of feedstocks bearing two aldehyde groups such as 5-formylfurfural (FFAL). The conversion of FFAL to value-added HMFOL in one pot is an interesting approach.^{18b} When the reaction was performed with 1.0 mol% **Mn2** with H₂ (20 bar) at 130 °C, a mixture of HMFOL **10** and 5-(hydroxymethyl)furfural (**11**) was obtained with a high selectivity of **10** (Table S3, entry 1, ESI[†]). Upon increasing the catalyst loading to 2.0 mol% under H₂ (30 bar), the conversion and selectivity of **10** improved (Table S3, entry 2, ESI[†]). When prolonging the reaction time to 24 h, both aldehyde groups were hydrogenated to afford HMFOL exclusively with high conversion (Table S3, entry 3, ESI[†]). At 48 h,



Scheme 6 Hydrogenation of 5-formylfurfural (FFAL). ^a Reaction condition: 5-formylfurfural (0.80 mmol), **Mn2** (8.5 mg, 0.016 mmol), K'BuO (9.0 mg, 0.080 mmol) in methanol for 24 h. ^b Isolated yield.

under 35 bar pressure of H_2 , full conversion and thus an excellent yield of product **10** was obtained (Scheme 6). Finally, we studied the hydrogenation of ester and ketone substrates (see the ESI[†]). For both reactions, hydrogenation products were not observed, implying that this protocol is selective towards the hydrogenation of aldehyde substrates only.

In conclusion, we developed well-defined PN³ pincer Mn(II) complexes as catalyst precursors for the hydrogenation of various aldehydes into corresponding alcohols under mild reaction conditions. More importantly, α,β -unsaturated aldehydes including ynals were hydrogenated without affecting double and triple bonds with excellent selectivity. The present methodology was applied for the selective conversion of biomass-derived chemicals, such as that of FAL into FOL. Notably, by increasing the pressure of H_2 to 35 bar and temperature to 130 °C, 5-formylfurfural was fully converted into 5-(hydroxymethyl)furfuryl alcohol in a quantitative yield. The fact that ester and ketone substrates resulted in no reaction indicated their excellent chemoselectivity towards aldehyde substrates. The inexpensive nature, air-stability, and robustness of the presented catalyst system may offer an opportunity for large scale applications.

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Conflicts of interest

The authors declare no competing financial interest.

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