

COMMUNICATION

Efficient and chemoselective hydrogenation of aldehydes catalyzed by a well-defined PN³-pincer manganese (II) catalyst precursor: an application in furfural conversionSandeep Suryabhan Gholap,^{a†} Abdullah Al Dakhil,^{a,b†} Priyanka Chakraborty,^a Huaifeng Li,^a Indranil Dutta,^a Pradip K. Das^a and Kuo-Wei Huang,^{*a}Received 00th January 20xx,
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Well-defined and air-stable PN³-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 C=C double bond/C \equiv C triple bond intact. Our methodology was demonstrated for biomass derived feedstock such as furfural and 2,5-diformyl furfural to furfuryl alcohol and 2-hydroxy 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 (H₂) is an attractive way to avoid waste formation from the use of stoichiometric reductants such as lithium aluminum hydride, sodium, and lithium borohydride, silanes, and boranes.³ Homogenous catalytic systems offer advantages in terms of selectivity and activity over the 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 Mn(CO)₅Br, and harsh reaction conditions are often employed, such as high catalyst loadings, use of a strong base

as additives, high temperature, etc. 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 PN³P-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, 7g, 7h} In 2018, Kirchner reported an efficient PN³P-Mn(I) pincer complex for hydrogenation of aldehyde over ketone and alkene functionalities.⁷ⁱ More recently, Filonenko and Pidko demonstrated the use of Mn(I)-CNP precatalyst for the hydrogenation of ketones, aldehydes, esters and imines.^{7o} Further development of selective hydrogenation catalysts from readily available and abundant metal complexes offers a promising and cost-effective protocol for practical applications.

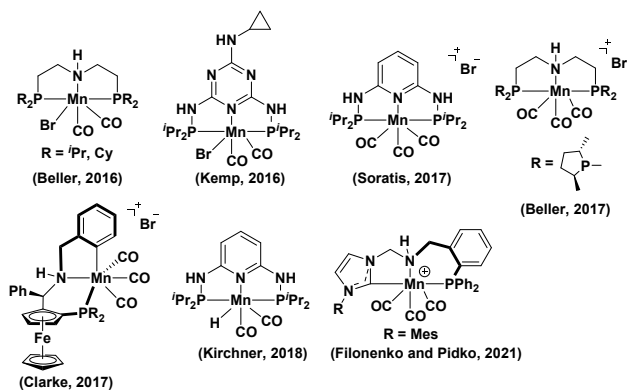


Fig. 1 Manganese(I) complexes studied for the hydrogenation of aldehydes.

A biomass-derived feedstock, such as furfural (FAL) and 2-formyl furfural (FFAL) containing aldehyde functionality allows the conversion into several renewable commodities upon reduction.⁸ FAL is widely available in fine chemical industries,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 mostly by

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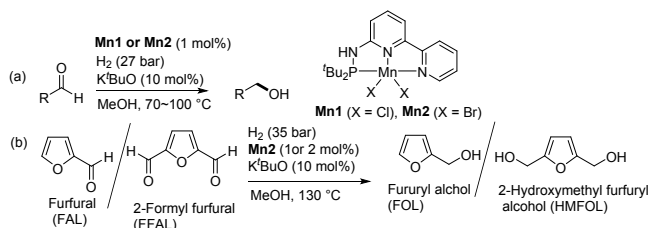
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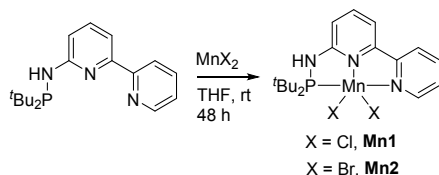


heterogeneous catalyst systems such as Cu/Cr, Ni, Cu Co, Pt, and Pd supported catalysts;¹¹ however, these catalysts create some concerns about toxicity. On the other hand, the use of homogeneous catalysts for FAL conversion has been limited. For the first time, Paganelli et al. reported a reduction of FAL to FOL with H₂ by 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 bidentate phosphine modified Ru-based catalytic system for the efficient conversion of FAL to FOL¹⁵ 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, the non-noble homogeneous 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/mol_{Mn}) is considerably more economical than Mn(CO)₅Br (\$13,250/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) by 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 2-hydroxymethylfurfuryl alcohol (HMFOL), respectively.



Scheme 1 In this work: a) Hydrogenation of aldehydes. b) Conversion of furfural (FAL) to furfuryl alcohol (FOL) and 2-formyl furfural (FFAL) to 2-hydroxymethylfurfuryl alcohol (HMFOL).



Scheme 2 Synthesis of Mn(II) PN³ Pincer Complexes **Mn1** and **Mn2**.

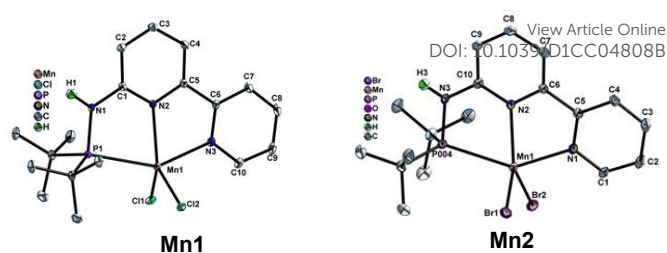
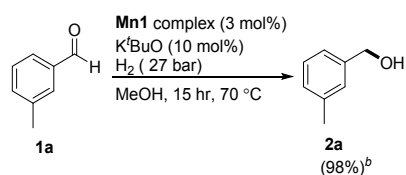


Fig. 2 Crystal structure of catalyst **Mn1** and **Mn2**. All atoms have been shown with 30% probability ellipsoid, All hydrogen atoms except N-H have been omitted for clarity. For **Mn1** and **Mn2**, details of selected bond distances (Å) angles (deg) shown (Fig. S1 and S2, ESI).

The Mn(II) based pincer complexes **Mn1** and **Mn2** were synthesized by the reaction of MnX₂ (X = Cl, Br) with the ^tBu₂PNH-BPy (bis-tertbutylphosphine-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 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 leads to an enhanced yield of product **2a** with full conversion (Table S1, ESI). The performance of **Mn2** was tested, which implies lower activity as compared to **Mn1** (Table S1, entries 4-5, 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** achieved full conversion to **2a** (Table S1, entry 7, ESI). Lowering the temperature to 70 °C still offered an excellent yield of **2a** (Table S1, entries 8-10). So, excellent yield of 3-methyl benzyl alcohol was obtained using Mn1 (3 mol%), H₂ (27 bar) in MeOH (Scheme 3).

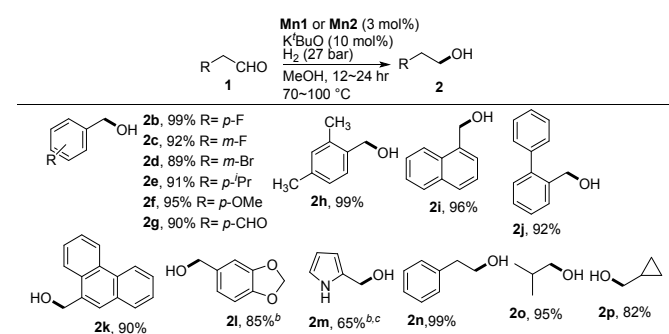


Scheme 3 Hydrogenation of 3-methylbenzaldehyde. ^aFor the reaction, 3-methylbenzaldehyde (0.83 mmol), **Mn1** (3 mol%, 0.024), K^tBuO (0.083 mmol) H₂ (27 bar). ^bIsolated yield.

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



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

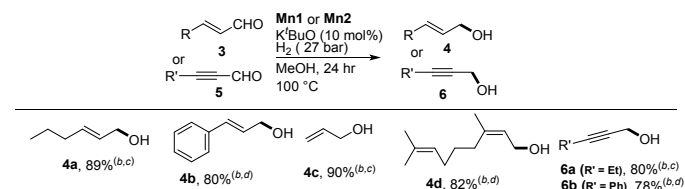


Scheme 4 The substrate scope of the hydrogenation of aldehydes. ^aFor the reaction, aldehyde (1.0 mmol), **Mn 1** (3 mol%), K^tBuO (10 mol%) H₂ (27 bar) in MeOH (1.0 mL). Isolated yields are in parenthesis. ^b**Mn2** ^c24 hr.

Encouraged by the excellent results 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, product **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-phenylpropionaldehyde gave the pent-2-yn-1-ol and 3-phenylprop-2-ynol in 80% and 78% yields, respectively, without affecting alkyne functionality (Scheme 5, **6b** and **6b**).

After successfully studying the wide range of aldehydes substrates, we turned our attention to explore the hydrogenation of aldehydes that are used as feedstocks for FAL to FOL and FFAL to HMFOL. The effect of **Mn2** catalyst loading on the hydrogenation of FAL shows that 2.0 mol% catalyst loading gave full conversion (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). Increasing the reaction temperature from 120 °C to 130 °C, the full conversion of FAL was achieved within 16h with excellent yields (Table 1, entries 2–3). However, when the reaction was conducted in the absence of solvent, the conversion of product and selectivity were both dropped. 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). Increasing the pressure from 5 bar to 35 bar, the conversion of FOL was increased to 99%. While 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.



Scheme 5 Hydrogenation of α,β -unsaturated aldehydes and ynals. ^aReaction condition: aldehyde (1.0 mmol), **Mn1** or **Mn2** (3 mol%), K^tBuO (10 mol%) H₂ (27 bar) in MeOH (1.0 mL). Isolated yields are shown in parenthesis. ^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 (%)
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

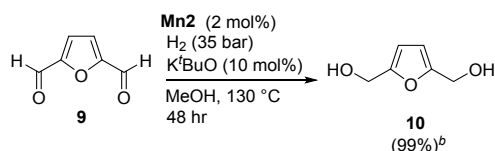
^aFurfural (1.04 mmol), **Mn2** (5.5 mg, 0.010 mmol), K^tBuO (11.6 mg, 0.103 mmol) in methanol for 16 h. ^bIsolated yields. ^cNeat condition.

After the excellent selectivity was achieved for the conversion of FAL to FOL, it was interesting to study the hydrogenation of feedstock bearing two aldehyde groups such as 2-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% of **Mn2** with H₂ (20 bar) at 130 °C, the mixture of 2-hydroxy methyl furfural (HMFAL) **10** and HMFOL **11** was obtained with high selectivity of **11** (Table S3, entry 1, ESI). Catalyst loading to 2.0 mol% under H₂ (30 bar), improved conversion and selectivity of **11** (Table S3, entry 2, ESI). When prolonging the reaction time to 24h, both aldehyde groups were hydrogenated to afford HMFOL exclusively with high conversion (Table S3, entry 3, ESI). At 48h, under 35 bar pressure of H₂, full conversion and excellent yield of product **11** was obtained (Scheme 6). Finally, we studied the hydrogenation of ester and ketone substrates (see ESI). For both reactions, hydrogenation products were not observed, implying that this protocol is selective towards the hydrogenation of aldehyde substrate only.

In conclusion, we have 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 are hydrogenated without affecting double and triple bonds with excellent selectivity. The present



methodology was applied for the selective biomass-derived chemicals conversion, such as FAL into FOL. Notably, by increasing the pressure of H₂ to 35 bar and temperature to 130 °C, 5-Formylfurfural was fully converted into 2-hydroxy methyl furfuryl alcohol in a quantitative yield. The fact that ester and ketone substrates resulted in no reaction indicated the excellent chemoselectivity towards aldehyde substrates. The inexpensive, air-stable, and robustness of the presented catalyst system may offer an opportunity for large scale applications.



Scheme 6 Hydrogenation of 2-formyl furfural (FFAL): ^a2-formyl furfural (0.80 mmol), **Mn2** (8.5 mg, 0.016 mmol), K^tBuO (9.0 mg, 0.080 mmol) in methanol for 24 h. ^bIsolated yields.

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Conflicts of interest

The authors declare no competing financial interest.

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