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PAPER

1-D manganese(II)-terpyridine coordination polymers as precatalysts for hydrofunctionalization of carbonyl compounds

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Reductive catalysis with earth-abundant metals is currently of increasing importance that shows potential in replacing precious metal catalysis. In this work, we revealed catalytic hydroboration and hydrosilylation of ketones and aldehydes achieved by a structurally defined manganese(II) coordination polymer (CP) as a precatalyst under mild conditions. The manganese-catalysed methodology can be applied to a range of functionalized aldehydes and ketones with turnover numbers (TON) of up to 990. Preliminary results on the regioselective catalytic hydrofunctionalization of styrenes by the Mn-CP catalyst are also presented.

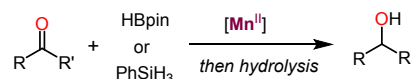
Introduction

The reduction of carbonyl compounds under mild, catalytic conditions is a paramount research topic in green and synthetic chemistry.¹ Compared to conventional stoichiometric methods for carbonyl reduction that utilize highly reactive and expensive hydride reagents, catalytic methods employ gentle, easy-to-handle and inexpensive hydride sources.² Moreover, catalytic reduction of carbonyl compounds often provides good chemoselectivity and ensures easy access to more challenging and functionalized substrates than stoichiometric methods.^{3,4} Hydrofunctionalization, involving mainly hydroboration and hydrosilylation, has been a popular choice for carbonyl reductions in the past two decades.⁵⁻⁷ Numerous catalytic and non-catalytic methods have been developed, with metal-catalysed reactions being the most promising in terms of efficiency and selectivity.⁸⁻¹² Considering the great advantage of earth-abundant metals in terms of low cost and environmental sustainability compared to noble metals, earth-abundant metal catalysts for highly efficient hydroboration and hydrosilylation of carbonyl compounds have experienced extensive development over the past decade.⁵⁻¹²

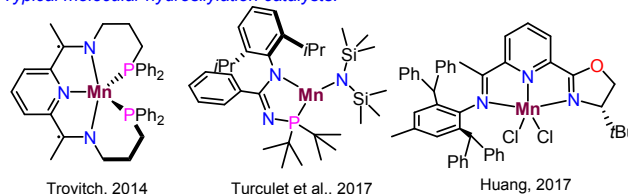
Despite great advances achieved by using earth-abundant metal complexes (e.g. Fe, Co, Ni, Cu, Zn, Al) for hydrofunctionalization of carbonyl compounds, manganese has been scarcely utilized for these transformations despite being the third most abundant transition metal and non-toxic.⁷

Previous work:

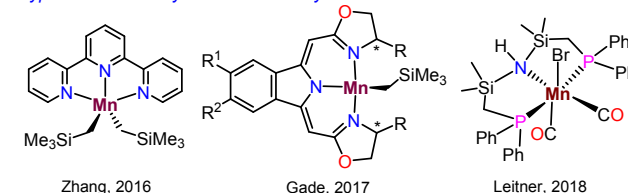
Mn-catalyzed hydroboration and hydrosilylation of carbonyl compounds



Typical molecular hydrosilylation catalysts:

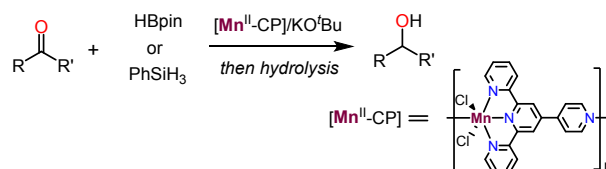


Typical molecular hydroboration catalysts:



This work:

Hydrofunctionalization of carbonyl compounds by Mn coordination polymer



Scheme 1. The state-of-the-art of Mn-catalysed hydrofunctionalisation of carbonyl compounds.

Nevertheless, a few manganese catalysts have emerged in the last few years, since the report of a penta-coordinate $\text{PN}_3\text{P-Mn}^{\text{II}}$ complex that catalyses hydrosilylation of ketones and esters with high turnover frequencies (TOF, up to $76,800 \text{ h}^{-1}$) by Trovitch's group (Scheme 1).^{13a} Later on, the same group

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developed similarly active Mn catalysts with structurally related bisimine-N₅ or PN₃P ligand sets that displayed comparable catalytic efficacy.^{13b,13c} In 2017, Turculet and coworkers reported a tri-coordinate PNN-Mn^{II} complex for mild hydrosilylation of ketones, aldehydes, esters and amides.¹⁴ An asymmetric version of ketone hydrosilylation was also revealed in the same year by the Huang group utilizing Mn^{II} dichloride complexes of a pincer-type N₃ ligand with NaHBET₃ as an activator (Scheme 1).¹⁵ Other contributions also include the development of Mn^I-carbonyl complexes bearing bis-N-heterocyclic carbene (NHC) ligands by the Sotias and Royo groups¹⁶ and Mn^I-carbonyl complexes of triazole-containing PNN ligands by Leitner and coworkers.¹⁷

Manganese hydroboration catalysts were first introduced by our group in 2016, where Mn^{II}-dialkyl complexes of simple terpyridine ligands were found to catalyse mild hydroboration of ketones, aldehydes and alkenes with pinacolborane (HBpin).¹⁸ Soon after, the Gade group developed the asymmetric version of ketone hydroboration using a Mn^{II}-monoalkyl catalyst with a bis(oxazoline)pyrrole ligand.^{19a} A comprehensive mechanistic examination was also performed by this group.^{19b} Recently, Leitner's group reported a pincer-type Mn-PNP carbonyl complex that catalysed the hydroboration of challenging carboxyl groups and CO₂ (Scheme 1).²⁰

All the above known Mn catalyst systems for ketone hydrofunctionalization utilized highly sensitive organometallic complexes and/or activators (e.g. NaHBET₃), and the ligand synthesis and purification processes were often non-trivial. To address this, we have recently developed air- and bench-stable cobalt and iron hydroboration catalysts based on readily available ditopic 4'-pyridyl-2,2';6',2''-terpyridine (pytpy) and 4,2';6',4''-terpyridine ligands, with relatively stable potassium *tert*-butoxide (KO^tBu) as an activator.²¹ These novel catalysts feature one- or two-dimensional (1- or 2-D) coordination polymers (CPs) instead of traditional small molecules and achieve high TOFs for carbonyl, alkene and alkyne hydroboration.²¹ The 2-D iron catalyst even carried out selective hydroboration of ketones and aldehydes in air, highlighting the potential of such polymeric catalysts for practical, green transformations.^{21b} To further pursue air-stable catalyst systems utilizing the underexplored metal Mn, we herein report the synthesis and characterization of 1-D Mn^{II} CPs based on pytpy, as well as their applications in catalytic hydrofunctionalization.

Results and discussion

Slow diffusion of a solution of MnCl₂ or MnBr₂ in MeOH into a CH₂Cl₂-MeOH solution (10 mL, 3:1, v/v) of pytpy over a one-month period led to the formation of yellow-orange crystals of **1** and **2**, respectively, that were suitable for single-crystal X-ray diffraction analysis. Their solid-state structures were unambiguously established by X-ray crystallography (see the ESI). **1** displays a linear coordination polymeric structure composed of alternate pytpy and MnCl₂ units with Mn sitting in

a pseudo-octahedral coordination environment. **2** is a similar 1-D polymer with Br in place of Cl. While **1** crystallises in the

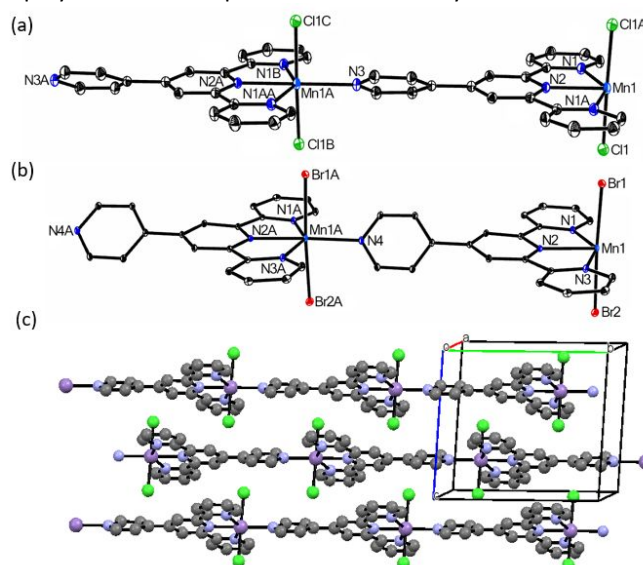


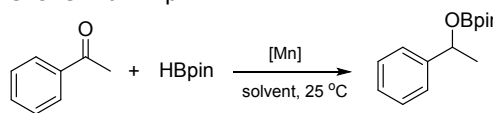
Fig. 1. Molecular structures of **1** (a) and **2** (b), with thermal ellipsoids drawn at the 30% probability level and H atoms omitted for clarity. Two repeat pytpyMnX₂ units are shown for each structure. Additionally, a ball-and-stick packing model of the 1-D chains in **1** is displayed (c).

monoclinic space group $P2_1/n$, **2** crystallises in the triclinic $P-1$ space group. The partial structures of polymers **1** and **2** are shown in Fig. 1, respectively. There exists one half independent pytpy ligand in the asymmetric unit of **1**, along with one independent Mn centre and Cl co-ligand, due to the C₂-symmetry. The Mn center of **1** is located in a N₄Cl₂ coordination environment between the N₃ chelating cavity and the 4'-pyridyl group of another symmetrically related ligand. The Mn-N bond lengths are between 2.242(4) and 2.274(4) Å, while the Mn-Cl distances are both 2.5157(11) Å (equivalent due to symmetry). The tpy backbone of the ligand is essentially co-planar (the deviation between planes of side and central pyridine rings is 3.28°), while the 4'-pyridine ring is out of the plane by 32.93°. As expected, the Mn-Br bonds in **2** [2.6563(3) and 2.7714(3) Å] are longer than the analogous Mn-Cl bonds. In comparison, in the structure of **2** the ligand adopt C₁-symmetry and one independent ligand molecule with a MnBr₂ unit is present in the asymmetric unit. The Mn-N bond lengths of **2** are between 2.2147(12) and 2.2577(13) Å, slightly shorter than those found in **1**. The tpy moiety in **2** is also very planar with the torsional angle being just 0.22°, while the 4'-pyridine ring has a deviation of 37.67° from this plane. The packing modes in both crystals are mainly driven by π...π stacking interactions between aromatic regions of discrete 1-D chains; the packing for **1** is shown in Fig. 1c.

With the bulk materials of CP **1** and **2** in hand, we first evaluated their catalytic performance for hydroboration of acetophenone with HBpin, which has previously been reported using Mn-based molecular complex catalysts.¹⁸⁻¹⁹ The results for the screening of catalytic reactivity are summarized in Table 1. It was found that the reaction of acetophenone with HBpin using CP **1** (0.1 mol% based on one Mn(pytpy)Cl₂ unit) in the presence of KO^tBu (1 mol%) led to complete conversion to the

boronic ester product in 2 h, corresponding to a TON of 990 and turnover frequency (TOF) of 495 h⁻¹ (entry 1, Table 1). In contrast, the use of CP 2 under the same conditions afforded the hydroborated product in only 59% GC yield (entry 2), indicating that the effect of the halogen co-ligand of the CPs is significant. In addition, the choice of KO^tBu as an additive is a key to high efficiency, as replacing it with KOH, K₂CO₃ or NaBH₄ resulted in inferior results (entries 3-5). Control experiments revealed that both **1** and an additive (1 mol%) are required for the desired catalytic activity (entries 6-9). It is worth mentioning that although the attainment of X-ray quality crystals of **1** requires a long crystallization period (over 1 month), a rapid, large-scale synthesis of microcrystalline material of **1** can be approached in minutes (see the ESI). Notably, the use of this microcrystalline sample as a precatalyst for the hydroboration of acetophenone with HBpin achieved equally high efficiency (entry 10). Finally, the solvent effect was found to be insignificant. Though the yield was slightly lower in benzene, the reactions in other solvents such as Et₂O, toluene, pentane, or under neat conditions were all effective with 95-99% yields (entries 11-15).

Table 1. Catalytic test for Mn^{II}-CP-catalysed hydroboration of acetophenone with HBpin.^a



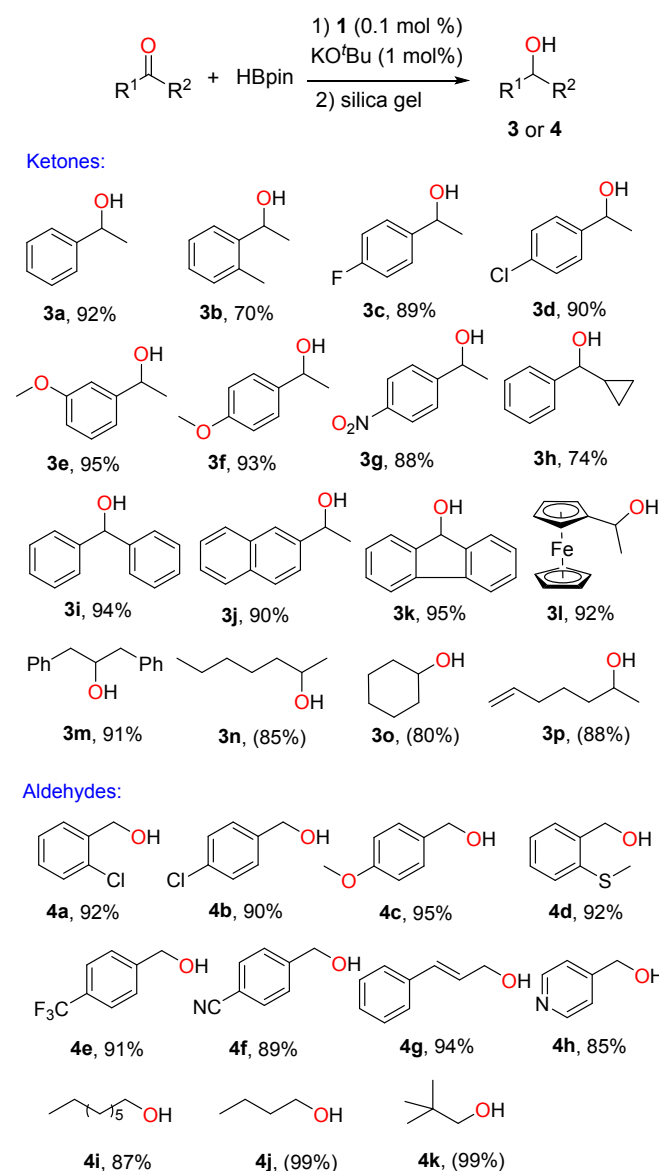
Entry	Catalyst	Activator	Solvent	Yield /% ^b
1	1	KO ^t Bu	THF	99
2 ^c	2	KO ^t Bu	THF	59
3	1	KOH	THF	95
4	1	K ₂ CO ₃	THF	60
5	1	NaBH ₄	THF	72 ^d
6	1	-	THF	<5
7	-	KO ^t Bu	THF	<5
8	-	KO ^t Bu	neat	21
9 ^e	1	KO ^t Bu	THF	95
10 ^f	MnCl ₂ /L	KO ^t Bu	THF	99
11	1	KO ^t Bu	Et ₂ O	99
12	1	KO ^t Bu	toluene	95
13	1	KO ^t Bu	benzene	88
14	1	KO ^t Bu	pentane	96
15	1	KO ^t Bu	neat	99

^a Conditions: benzaldehyde (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%), activator (1 mol%) and solvent (1 mL), 25 °C, 2 h, in air. ^b Determined by GC-MS analysis with hexamethylbenzene as an internal standard. ^c Reaction run for 16 h. ^d 1-phenylethanol was also detected in 22% yield. ^e 0.5 mol% KO^tBu was used. ^f Microcrystalline catalyst prepared in a large scale was used.

Next, we investigated the applicability of CP precatalyst **1** towards hydroboration of different aromatic and aliphatic ketones and aldehydes. The results for a range of substrates tested are summarized in Table 2. The products of boronate esters have been detected by GC-MS, and the corresponding alcohols (**3** and **4**) were then readily isolated by column chromatography, according to the known silica-promoted hydrolysis of boronate precursors.¹⁶ It was found that a range of different aryl ketones have been smoothly hydroborated.

Methyl phenyl ketones bearing halo and electron-donating or -withdrawing groups furnished the reaction with generally high isolated yields of alcohols (**3a-h**), although in the cases of **3b** and **3h**, a steric effect was observed that led to relatively lower yields. In addition, ketones with diaryl, naphthyl, or ferrocenyl groups are excellent substrates, leading to complete conversion and high yields of the corresponding alcohols (**3i-l**). Aliphatic and cyclic ketones were also suitable substrates for hydroboration (**3m-p**). It was further observed that the same method could be applied to aldehyde hydroboration. A series of functionalized aldehyde substrates were examined, and good to excellent yields of the corresponding primary alcohols (**4a-i**) were obtained. It is worth mentioning that although the reaction proceeded equally well with acetophenone under neat conditions, to ensure the highest conversion for all substrates including some solid ketones and aldehydes, all reactions have been performed in a THF solution.

Scheme 2. Substrate scope for the hydroboration of ketones and aldehydes using CP **1**.^a

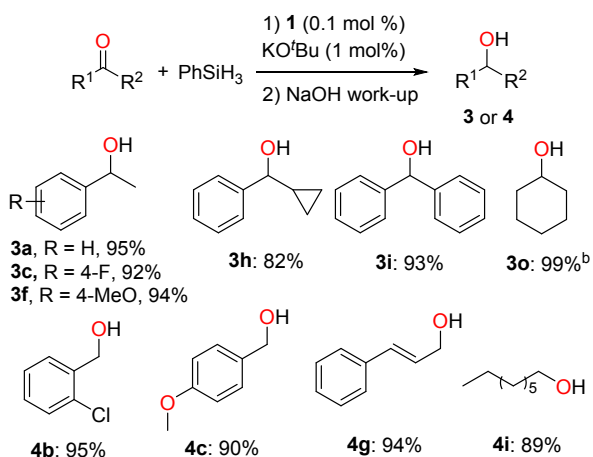


^a Conditions: **1** (0.1 mol% based on Mn), KO^tBu (1 mol%), ketone or aldehyde (1.0 mmol), HBpin (1.1 mmol) and THF (1 mL), 25 °C, 2 h, N₂.

Yields of isolated alcohols (GC yields of borate ester precursors are shown in parentheses).

The ability of CP **1** to promote effective hydroboration of various carbonyl compounds encouraged us to further explore its performance in hydrosilylation catalysis. To our delight, the hydrosilylation of ketones and aldehydes under the standard conditions (in THF solution) using **1**/KO^tBu as a catalyst and phenylsilane as a Si-H source was also successful based on the results obtained from selected substrates examples shown in Scheme 3. Full conversions of the carbonyl groups were found based on GC analyses, and the alcohol products were isolated after NaOH workup. Both aromatic and aliphatic substituted carbonyl groups have experienced effective hydrosilylation, indicating the good applicability of this method for a broad scope of substrates. It was observed that the hydrosilylation of acetophenone under neat conditions was equally efficient, giving siloxane product with 99% GC yield. It is worth noting that although molecular Mn catalysts for either hydroboration or hydrosilylation of carbonyl compounds were reported as we introduced above, a catalyst that is suitable for both reactions is unknown.^{13–20}

Scheme 3. Hydrosilylation of selected ketones and aldehydes using CP **1**.^a

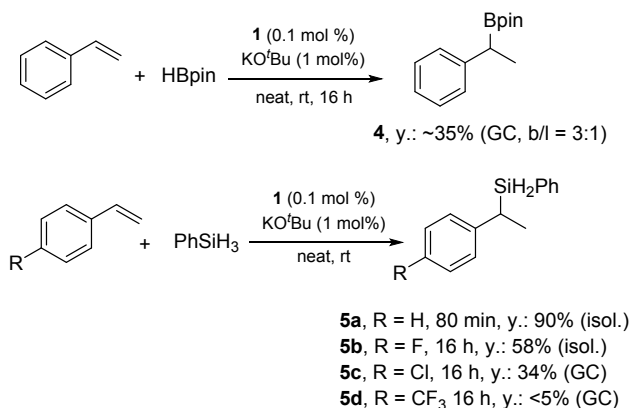


^aConditions: **1** (0.1 mol% based on Mn), KO^tBu (1 mol%), ketone or aldehyde (1.0 mmol), PhSiH₃ (1.2 mmol) and THF (1 mL), 25 °C, 2 h, N₂. Yields of isolated alcohols. ^bGC conversion of its siloxane precursor.

To further explore the catalytic ability of our Mn-CP system for hydrofunctionalization, we performed additional catalytic reactions using nonpolar alkenes as substrates (Scheme 4). While the hydroboration of styrene under neat conditions proceeded sluggishly, affording alkylboronate **4** with approximately 35% yield and 3:1 branched-to-linear ratio of the products, the hydrosilylation of styrene was found to be very effective and regioselective, giving the branched product **5a** as the only product in 90% isolated yield after 80 min. However, attempts to apply this method for other functionalized styrenes proved to be not as successful as styrene. While 4-fluorostyrene can be hydrosilylated with appreciable yield (58%) and complete regioselectivity, 4-chloro or 4-trifluoromethyl styrenes (**5c** and **5d**) showed poor reactivity. It is worth noting that Mn-catalysed Markovnikov hydrosilylation of terminal alkenes was only recently realized by a dimeric Mn-H complex by the Trovitch group.²² Our results indicate the potential of the

Mn-CP catalyst system for catalytic hydrofunctionalization of multiple types of substrates. A better substrate tolerance can be anticipated should appropriate structural modification on both the ligand and metal center be carried out.

Scheme 4. Preliminary experiments for hydroboration and hydrosilylation of styrenes catalysed by CP **1**.^a



Conclusions

In conclusion, we have synthesized and characterized 1-D Mn CPs built on a ditopic terpyridine ligand and studied their catalytic performance on the reduction of carbonyl compounds via hydroboration and hydrosilylation. The polymeric structures of the Mn^{II} precatalysts are elucidated by X-ray crystallography. This represents the first example of hydroboration/hydrosilylation reactions using a Mn^{II}-CP catalyst. The Mn^{II} catalyst is tolerant of a wide range of carbonyl substrates under mild conditions. We also revealed that the Mn^{II} CP catalyst could be a promising candidate for alkene hydrosilylation. Further efforts on the structural modification of the current CP catalysts for improved performance in alkene hydroboration and/or hydrosilylation, as well as mechanistic studies, are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table of Contents

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