Enantioselective Catalysis

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A Highly Active Manganese Catalyst for Enantioselective Ketone and Ester Hydrogenation

*Magnus B. Widegren, Gavin J. Harkness, Alexandra M. Z. Slawin, David B. Cordes, and Matthew L. Clarke**

Abstract: *A new hydrogenation catalyst based on a manganese complex of a chiral P,N,N ligand has been found to be especially active for the hydrogenation of esters down to 0.1 mol % catalyst loading, and gives up to 97 % ee in the hydrogenation of pro-chiral deactivated ketones at 30–50 °C.*

The hydrogenation of various carbonyl compounds with ruthenium catalysts is a very effective reduction that is applicable at commercial scale.[1] While the fine chemicals catalysis sector is unlikely to seriously deplete the worlds supply of ruthenium, replacing scarce metal catalysts with an essentially indefinitely sustainable metal source is desirable, elegant, and increases fundamental knowledge of catalytic hydrogenation. Moreover, some precious-metal-catalyzed hydrogenations can not be optimized to the very low catalyst loadings needed to make the cost of catalyst and metal removal from products economically viable; the use of a metal such as manganese could offer advantages in these cases (metal contamination limits in pharmaceutical compounds are 250 ppm compared to 10 ppm for Ru). There is an extensive global effort being expended on developing catalysts with more abundant metals. Fe and Co hydrogenation catalysts have probably been developed to the greatest degree,[2] but very recently catalysts based on abundant manganese[3,4] have appeared (e.g. compounds **1**[3a] and **2**[3c] in Figure 1). Further improvements in abundant metal catalysis are needed since only highly active catalysts will be used to replace Ru (or Rh and Ir).

The Noyori-type [$RuCl_2$(diphosphine)(diamine)] catalysts are widely used for ketone hydrogenation,[1] but our longstanding interest has been seeking to expand the scope of ketone and ester hydrogenation using ruthenium complexes of tridentate ligands.[5] While most of the ligands we have studied coordinate to ruthenium in a meridional fashion, we also identified a *P,N,N* ligand that would exhibit facial coordination.[6] The publication by the Beller group of a Mn catalyst based on a *P,N,P* ligand[3b] motivated us to examine the use of ligand **3** in Mn-catalyzed hydrogenation. Facially coordinating amino-phosphines have not been used to any great degree in bifunctional reduction catalysis, despite the importance of facially coordinating TRIPHOS ligands in hydrogenation catalysis.[7] Here we introduce, to our knowledge, the first enantioselective manganese-catalyzed ketone hydrogenation, which is based on a facially coordinating planar chiral *P,N,N* ligand. In addition to establishing asymmetric hydrogenation catalysis with manganese, these catalysts operate well below 100 °C and, in the context of abundant metal catalysts, at highly competitive catalyst loadings for the hydrogenation of both ketones and esters.

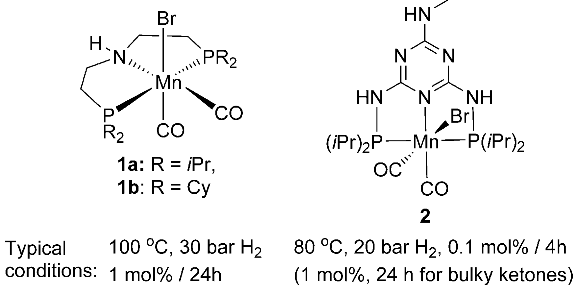

Figure 1. Ketone hydrogenation catalysts based on manganese.

Compared to many ligands used in hydrogenation studies, ligand (S_C,R_P)-**3** is easily prepared: it can be made in one step from a commercially available, well-known precursor that is prepared commercially at significant scale (or in a shorter time in a two-step process). This ligand is prone to facial coordination as evidenced by the crystal structure of the Ru complex **4** (Figure 2). Ligand **3** can be converted to the very sparingly soluble cationic Mn complex **5a** by reaction with convenient precursor $Mn(CO)_5Br$ in toluene at 110 °C for 2 hours in 60 % yield. In order to get more structural information on this type of Mn complex, ion exchange reactions were attempted with various anions in various solvents (see the Supporting Information (SI)). The complex containing a BARF anion, **5b** had good solubility, and crystals could be grown such that the complex was structurally characterized by X-ray crystallography.

Catalyst **5a** was investigated in the hydrogenation of a range of pro-chiral ketones including those that have proven difficult to reduce with most common ruthenium catalysts. Pleasingly, **5a** was found to reduce ketone **6b** to complete conversion with 82 % *ee* at just 50 °C. As has been observed with ruthenium catalysts derived from *P,N,N* ligands, some steric bulk on the substrate[4b,g] is required to get the best enantioselectivity. In this case both secondary alkyl and (often challenging)[3c,5b] tertiary alkyl substitution gives good *ee* (Table 1 and Scheme 1).[5f]

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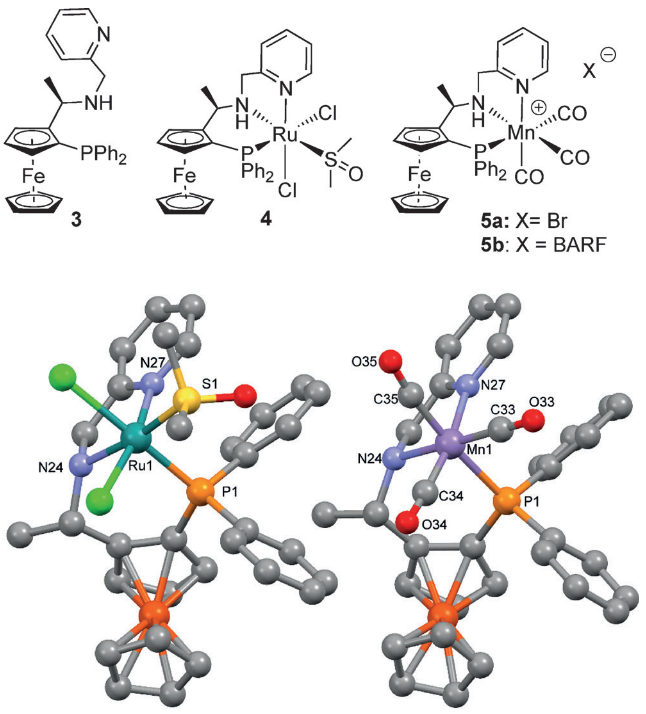
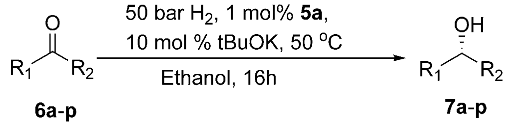


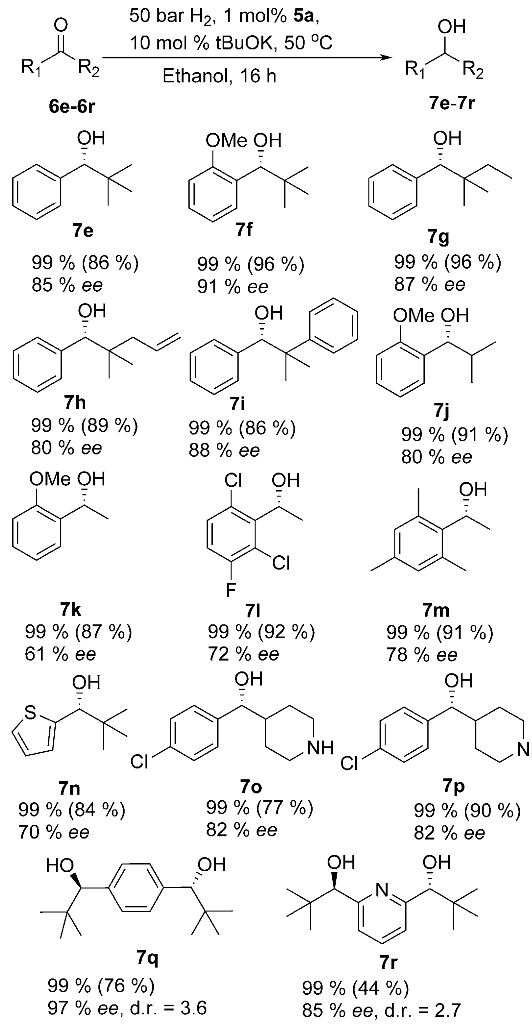
Figure 2. *fac*-Ru and *fac*-Mn complexes of ligand (S_c,R_p)-**3**; X-ray structure of complex **4** and **5b** with hydrogen atoms (and BARF counterion) omitted for clarity.[12] BARF = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

Table 1: Enantioselective reduction of ketones.[a]



Entry	No.	R_1	R_2	Conversion [%][b]	*ee* [%][c]
1	**6a**	Ph	CH_3	99 (80)	20 (*R*)
2	**6b**	Ph	$CH(CH_3)_2$	99 (87)	82 (*R*)
3[d]	**6b**	Ph	$CH(CH_3)_2$	99 (n.d.)	84 (*R*)
4[e]	**6b**	Ph	$CH(CH_3)_2$	99 (89)	80 (*R*)
5[f]	**6b**	Ph	$CH(CH_3)_2$	99 (91)	85 (*R*)
6	**6c**	4-Cl-Ph	CH_3	99 (90)	23 (*R*)
7[d]	**6c**	4-Cl-Ph	CH_3	99 (n.d.)	27 (*R*)
8	**6d**	2-Cl-Ph	CH_3	99 (85)	58 (*R*)
9[e]	**6d**	2-Cl-Ph	CH_3	99 (n.d.)	58 (*R*)
10[g]	**6d**	2-Cl-Ph	CH_3	99 (n.d.)	58 (*R*)
11[d]	**6d**	2-Cl-Ph	CH_3	99 (n.d.)	57 (*R*)
12[h]	**6d**	2-Cl-Ph	CH_3	99 (87)	53 (*R*)

[a] Typical reaction conditions: 0.34 mmol substrate, 0.003 mmol catalyst, 0.034 mmol base and internal standard (0.06 mmol) in 1.6 mL ethanol (0.2 M) under 50 bar of H_2 at 50 °C for 16 h. [b] Conversion was estimated by ^1H-NMR using 1-methylnaphthalene as internal standard (8–10 μL). Isolated yield in brackets. [c] *ee* was measured using chiral HPLC, known absolute configuration in brackets. [d] Reaction run at 30 °C for 65 h. [e] 0.034 mmol K_3PO_4 as base. [f] Reaction run using 30 bar H_2, reaction time 4 h. [g] 0.034 mmol K_2CO_3 as base. [h] 0.1 mol% **5a**, 16 h reaction time; n.d. = not determined.



Scheme 1. A range of functionalized ketones hydrogenated in presence of the chiral Mn catalyst **5a**. Typical reaction conditions: 0.34 mmol substrate, 0.003 mmol catalyst, 0.034 mmol base and internal standard (0.06 mmol) in 1.6 mL ethanol (0.2 M) under 50 bar of H_2 at 50 °C for 16 h.

In the context of establishing the best ligand classes to further develop Mn-catalyzed hydrogenation, we carried out one experiment at low catalyst loading of 0.1 mol%, and were pleased to find complete conversion of the *ortho*-substituted ketone **6d** within 16 hours at just 50 °C. Given that bulky ketones can also be reduced within 16 hours at 50 °C, (and are still reduced at 30 °C), it seems very likely that this type of catalyst is more active than the previous benchmarks (Figure 1). Table S4 (SI) shows that at least 30 bar hydrogen pressure is desired; A reaction run without hydrogen using ethanol as potential reductant[8] only gave 16% yield under otherwise standard conditions. Transfer hydrogenation using isopropanol as solvent and hydrogen source *is* possible with complete conversion, but not with good enantioselectivity.

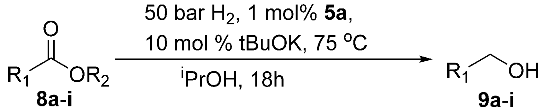
Stable pre-catalysts that can reduce carbonyls with cheap weak bases are desired and rare. Preliminary experiments using catalyst **5a** show that the weak bases K_3PO_4 or K_2CO_3 can be used and, where examined, give similar results under otherwise standard conditions (see SI and Table 1, entries 4 and 10).

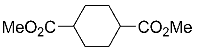
Further examples of ketones that can be reduced with good enantioselectivity are shown in Scheme 1. The level of enantioselectivity observed for the hydrogenation of **6f**, **6h**, and **6i** exceeds previous best reports in the literature for these substrates using precious-metal-catalyzed hydrogenations.[5b,c,f] Methylketones containing aromatic rings with *ortho*-substituents give higher selectivity, which allowed promising levels of selectivity for producing the drug intermediate **7l**.[9]

The results described above suggest this catalyst is unusually reactive in the hydrogenation of carbonyl derivatives. We therefore examined the hydrogenation of esters[5e,10] using catalyst **5a**, and found considerable success.

While this work was in progress, the first examples of Mn-catalyzed ester hydrogenation were reported: typical conditions were 110–120 °C for 24 hours using 2 mol% of Mn catalyst.[3b] The use of 1 mol% of catalyst **5a** at just 75 °C to deliver similar yields of products in slightly shorter reaction times suggests that this type of ligand may be more promising to develop Mn-catalyzed ester hydrogenation further (Table 2). A variety of esters were reduced with good yield under these milder conditions, including **8d**, containing an often problematic[5d] free amino group. We also carried out a single example of an ester hydrogenation using just 0.1 mol% catalyst, giving good conversion at 90 °C (Table 2, entry 8).

Table 2: Hydrogenation of esters.[a]



Entry		R_1	R_2	Conversion[b] [%]
1	**8a**	4-F-Ph	CH_3	99 (86)
2	**8b**	2-Br-Ph	CH_3	99 (90)
3	**8c**	$Ph(CH_2)_2$-	CH_2CH_3	99 (84)
4	**8d**	4-H_2N-Ph	CH_3	91 (80)
5	**8e**	4-O_2N-Ph	CH_2CH_3	0
6	**8f**	2-Naphth	CH_3	99 (87)
7	**8g**	4-(Ph-C≡C)-C_6H_4	CH_3	99 (n.d)[c]
8	**8h**	nPr	nBu	82[d]
9	**8i**			99 (86)[e]

[a] Typical reaction conditions: 0.34 mmol substrate, 0.003 mmol catalyst, 0.034 mmol base and internal standard (0.06 mmol) in 1.6 mL isopropanol (0.2 M) under 50 bar of H_2 at 75 °C for 16 h. [b] Conversion was estimated by ^1H-NMR using 1-methylnaphthalene as internal standard (8–10 μL). Isolated yield in brackets. [c] ^1H-NMR analysis showed the presence of ≈20% alkene. [d] Reaction run neat with 0.1 mol% **5a** and 2 mol% base at 90 °C for 15 h. [e] A 50:50 mixture of *cis* and *trans* isomers.

In conclusion, we have shown that enantioselective ketone hydrogenation is possible using manganese. The catalyst seems to display enhanced activity relative to recent important benchmarks for achiral Mn catalysts (Figure 1). The mechanism of Mn catalysis is beginning to attract attention,[3b,4f,o,p] and in achiral Mn PNP systems, a neutral Mn-hydride is proposed that can be formed after CO loss; while we have not been able to isolate such a species, we assume that an analagous complex reduces the substrates, with the NH group likely to be involved in hydrogen splitting and control of stereochemistry in some way.[11] The tuning of this ligand structure to further lower catalyst cost and enhance activity for achiral processes, or to tune catalyst structure to deliver broad scope or improved enantioselectivity in asymmetric hydrogenation, is underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: enantioselective catalysis · ester hydrogenation · ferrocene · manganese · reduction

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[12] CCDC 1517612 (**4**) and 1531517 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Communications

Enantioselective Catalysis

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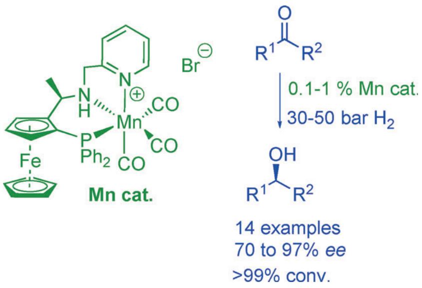
A Highly Active Manganese Catalyst for Enantioselective Ketone and Ester Hydrogenation



Non-precious metal for valuable catalysis: A new manganese catalyst for enantioselective ketone hydrogenation has been developed (see scheme). This catalyst also hydrogenates esters at low catalyst loadings for an earth-abundant metal system.