

Synthetic Methods

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Highly Selective Hydroboration of Alkenes, Ketones and Aldehydes Catalyzed by a Well-Defined Manganese Complex

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Abstract: Well-defined manganese complexes based on inexpensive, readily available ligands, 2,2':6',2''-terpyridine and its derivatives have been prepared and employed for the selective hydroboration of alkenes, ketones and aldehydes. Highly Markovnikov regioselective hydroboration of styrenes as well as excellent chemoselective hydroboration of ketones over alkenes were achieved, for the first time, by an earth-abundant manganese catalyst.

Boronate esters represent a class of crucial organic reagents in synthetic chemistry, as organoboronates are considered to be stable, easy-to-handle and versatile as building blocks for a variety of cross-coupling transformations.^[1] The hydroboration of alkenes offers a direct and effective method for the preparation of organoboronate compounds.^[2] Metal-catalyzed hydroboration of alkenes has proven to be an atom-economical and selective route to valuable alkylboronate esters, and hence the development of effective metal catalysts for this conversion in a regio- and/or stereo-selective manner has attracted considerable attention.^[3] While precious metals (Rh, Ru, or Ir) have been extensively explored for the selective hydroboration of alkenes,^[4] recent efforts have shown that earth-abundant metals such as Cu, Fe and Co could display equally high activity and selectivity through rational catalyst design, highlighting their great potential in replacing precious metal catalysts for alkene hydroboration. Recently the research groups of Chirik,^[5] Huang^[6] and others^[7] have reported several Co- or Fe-catalyzed alkene hydroboration catalysts which typically involve the use of pincer-type ligands. However, the catalytic hydroboration of terminal alkenes by these complexes showed exclusively anti-Markovnikov regioselectivity. The Markovnikov hydroboration of styrene derivatives was rarely achieved by using primarily Rh catalysts,^[4c,8] although two Cu^I catalysts based on phosphine ligands recently emerged, which were suitable

for the Markovnikov hydroboration of aryl or alkyl terminal alkenes, respectively.^[9a,b] Most recently, a cobalt-catalyzed alkyne hydrosilylation and sequential vinylsilane hydroboration with Markovnikov selectivity was reported by the Lu^[9c] and Huang^[9d] groups independently.

In addition to alkene hydroboration, the catalytic hydroboration of carbonyl compounds is also an important transformation in organic chemistry, giving facile and efficient access to alcohols.^[10] Although the majority of known catalysts for effective hydroboration of ketones and aldehydes are limited to late transition metal (Mo, Ru or Rh, etc.) complexes,^[11] the utilization of more abundant and less toxic metals (Ti, Co or Cu, etc.) for this conversion are becoming more attractive.^[12]

Despite all these advances, manganese, as one of the most abundant transition metals in the Earth's crust (the third most abundant after iron and titanium), is surprisingly unknown for catalytic hydroboration. Although catalysts based on manganese have been popular choices in oxidation processes,^[13] they were sparsely explored for catalytic reductions. Indeed, well-defined, homogeneous manganese catalysts were only known for special hydrosilylation and a few coupling reactions,^[14] and very recently, hydrogenation and dehydrogenation processes involving manganese PNP pincer catalysts were reported by Beller, Milstein and Kempe's groups, respectively.^[15] In addition, manganese-catalyzed borylation of alkyl chlorides has been realized in the presence of Grignard reagents.^[16]

Herein, we report for the first time a well-defined manganese-catalyzed hydroboration of alkenes, ketones and aldehydes. Significantly, the manganese catalyst described here can be readily prepared from an inexpensive, readily available ligand, 2,2':6',2''-terpyridine, and the catalytic hydroboration is highly efficient under mild conditions, displaying unusual Markovnikov selectivity for styrene derivatives. In addition, excellent chemoselectivity of this catalyst towards ketones over alkenes was achieved.

We began our design of manganese catalysts by using the well-known, inexpensive 2,2':6',2''-terpyridine (tpy) bearing a NNN chelating site. Treatment of the manganese dichloride complex of tpy with 2.0 equiv of LiCH₂SiMe₃ in Et₂O at room temperature gave a dark solution, from which good-quality dark-cyan crystals of **1** were isolated after 1 h in high yield (Figure 1 and Supporting Information). Likewise, derivatives **2** and **3** bearing phenyl or 4-chlorophenyl substituent on the 4'-position of tpy were prepared by the same procedure. The manganese alkyl complexes exhibit no significant NMR signals in C₆D₆, indicating the paramagnetic feature of Mn^{II}. While the samples are very sensitive to air and moisture, they were characterized by IR spectra, elemental analysis and X-

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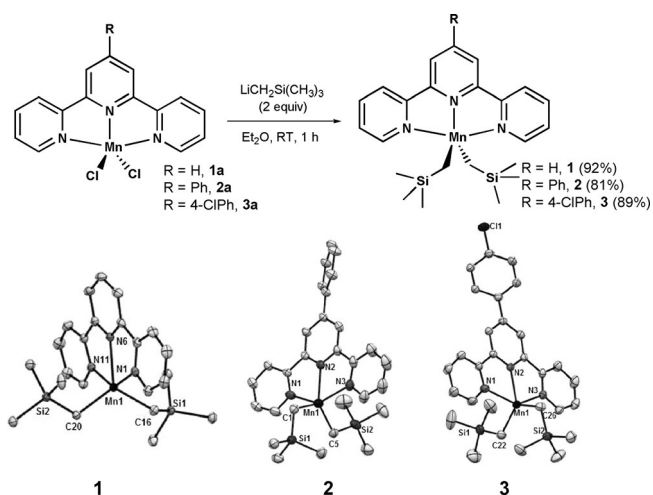


Figure 1. Synthesis of manganese(II) complexes **1**–**3** and their X-ray structures (ORTEP at 30% probability level).

ray structural analysis under inert atmosphere (see the Supporting Information). Crystal structures of **1**–**3** show almost identical coordination mode for the manganese center which is penta-coordinate with the N_3 cavity of tpy and two trimethylsilylmethylene ligands, except that the C–Mn–C angles are slightly different for three complexes ($116.62(11)^\circ$, $123.2(2)^\circ$ and $124.13(8)^\circ$ for **1**–**3**, respectively). It is worth mentioning that a square-planar cobalt(II) complex of tpy ($\text{Co}^{\text{II}}(\text{tpy})(\text{CH}_2\text{SiMe}_3)$) has been previously reported,^[5d] which, however, experienced one electron reduction on the tpy chelate upon coordinating to cobalt(II).

With new manganese catalysts in hand, we initially examined their catalytic activity towards the hydroboration of styrene with pinacolborane (HBPin), and the results are summarized in Table 1. Although the reaction of styrene with pinacolborane (1.1 equiv) in Et_2O in the absence of a catalyst gave no products, to our delight, Mn complex **1** was observed to be very active towards the hydroboration of styrene. Thus, stirring a Et_2O solution of styrene and pinacolborane in the presence of **1** (1 mol %) at room temperature resulted in complete conversion of styrene to hydroborated products **4** and **5** within 1 h. Interestingly, NMR and GC analysis identified **4**, a Markovnikov product as the major one in the mixture with a ratio of **4**:**5** as high as 95:5, indicating excellent regioselectivity (entry 2, Table 1). To investigate the influence of substituents in the manganese complex on the catalytic efficacy, we tested the same reactions by using **2** and **3** as catalysts. The results revealed that much poor yields of products **4** and **5** were obtained, although the regioselectivity kept high in both cases (entries 3 and 4). This suggests that the change of electronic properties of the tpy backbone could greatly impact the catalytic activity of manganese center. The solvent effect was then explored, and it was found that Et_2O performed better than other solvents such as THF, toluene and pentane. When the reaction was conducted under neat conditions, both low conversion and poor regioselectivity were observed (entries 5–9). Lowering down the catalytic loading to 0.1 mol % led to 65% conversion after 24 h (TON = 650), with a slight drop in regioselectivity (entry 10). In contrast, the catalyst precursor **1a** is not an

Table 1: Reactivity test for manganese-catalyzed hydroboration of styrene with pinacolborane.^[a]

Entry	Catalyst	Solvent	Yield (%) ^[b] (4 + 5)	Ratio (4 / 5) ^[c]
1	none	Et_2O	0	–
2	1	Et_2O	> 99	95:5
3	2	Et_2O	31	94:6
4	3	Et_2O	12	95:5
5	1	THF	76	94:6
6	1	toluene	54	89:11
7	1	pentane	60	98:2
8 ^[d]	1	pentane	72	95:5
9	1	neat	35	48:52
10 ^[e]	1	Et_2O	65	90:10
11 ^[f]	1a	Et_2O	0	–

[a] Conditions: styrene (1.0 mmol), pinacolborane (1.1 mmol), catalyst (1 mol %) and solvent (1 mL), 25°C , 1 h, N_2 . [b] Determined by GC analysis with hexamethylbenzene as an internal standard. [c] Determined by GC analysis. [d] Reaction was run for 24 h. [e] Reaction was run using 0.1 mol % of **1** for 24 h. [f] Reaction was run using 5 mol % of **1a** or 24 h.

active catalyst (entry 11), highlighting the important role of alkylated Mn active sites in initiating the catalytic cycle.

Next, the applicability of catalyst **1** to various alkenes was explored (Table 2). Reactions were carried out in a 1 mmol scale using 1 mol % of **1** as catalyst and the products were analysed by GC-MS and purified by column chromatography. It was revealed that styrenes bearing methyl or halo groups on the *para*- or *meta*-position were suitable substrates, furnishing the reactions with the isolation of Markovnikov products **4b**–**e** in good to high yields and excellent regioselectivities (entries 2–6). However, the reaction with *o*-chlorostyrene requires elevated temperature and longer time to be complete and the regioselectivity slightly dropped to 90:10 (entry 6). Styrenes with either electron-donating or electron-withdrawing groups are all compatible substrates, affording products **4h**–**j** in good yield and high regioselectivities. It was noted that α -methylstyrene and 1*H*-indene were challenging substrates under the optimized reactions conditions (entries 11 and 12), and nitro, cyano and alkenyl groups were not tolerated and were partially reduced leading to complex reaction mixtures. In addition, several aliphatic alkenes were examined for manganese-catalyzed hydroboration with pinacolborane. It was surprising to observe that even though reactions of alkenes including 1-hexene (entries 13–16, Table 2) with pinacolborane using 1 mol % of **1** proceeded well, anti-Markovnikov hydroborated products **5** were confirmed to be the major products and isolated in moderate to good yields. Meanwhile, the regioselectivity was generally inferior to those for aromatic alkenes.

Furthermore, the manganese-catalyzed hydroboration has been expanded to carbonyl compounds such as ketones and aldehydes. Although a number of metal catalysts have been reported for the hydroboration of various carbonyl compounds, catalysts suitable for both alkenes and carbonyl compounds are scarce.^[17] It was observed that **1** also catalyzed

Table 2: The manganese-catalyzed hydroboration of alkenes.^[a]

$\text{R}^1\text{CH=CH}_2 + \text{HB} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \xrightarrow[\text{Et}_2\text{O}, 25^\circ\text{C}]{\text{1 (1 mol\%)}} \text{R}^1\text{CH}_2\text{CH}_2\text{BPin} \quad \text{4} \quad \text{5}$					
Entry	Substrate	Product (4 or 5)	t [h]	Yield [%] ^[b]	Ratio (4/5) ^[c]
1			1	90 (4a)	95:5
2			2	89 (4b)	93:7
3			16	86 (4c)	94:6
4			16	87 (4d)	98:2
5			4	93 (4e)	97:3
6			24	65 (4f)	96:4
7 ^[d]			24	75 (4g)	90:10
8			16	73 (4h)	98:2
9 ^[d]			24	70 (4i)	91:9
10 ^[d]			24	72 (4j)	97:3
11 ^[d]			24	< 5	—
12 ^[d]			24	n.r.	—
13			16	59 (5a)	33:67
14			16	73 (5b)	20:80
15 ^[d]			16	80 (5c)	7:93
16 ^[d]			24	66 (5d)	21:79

[a] Conditions: alkene (1.0 mmol), pinacolborane (1.1 mmol), catalyst **1** (1 mol%) and Et₂O (1 mL), room temperature, N₂, n.r.: no reaction.
 [b] Yields of isolated products of **4** or **5**. [c] Determined by GC analysis.
 [d] Reaction was run at 50°C in a sealed tube.

efficient hydroboration of a variety of ketones and aldehydes (Table 3) under standard conditions, and the hydroborated products were analyzed by GC-MS. Purification of products by SiO₂ column chromatography led exclusively to the isolation of alcohols **6** in good to excellent yields, according to a silica-promoted hydrolysis of alkoxy-pinacolboronate esters.^{12b} Methyl phenyl ketones containing halo substituents, electron-donating or -withdrawing groups have been hydroborated effectively, affording the corresponding alcohols in good to excellent yields (Table 3). Cyclopropyl phenyl ketone was smoothly converted to the desired product (**6h**) without the observation of any ring-opening products, indicating that a radical intermediate was not involved. In addition, alde-

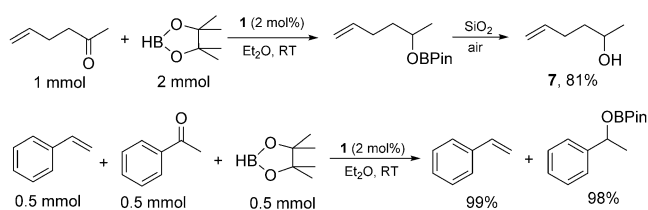
Table 3: The manganese-catalyzed hydroboration of ketones and aldehydes.^[a]

$\text{R}^1\text{C(=O)R}^2 + \text{HB} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \xrightarrow[\text{Et}_2\text{O}, 25^\circ\text{C}]{\text{1 (1 mol\%)}} \text{R}^1\text{CH}_2\text{CH}_2\text{OBPin} \xrightarrow[\text{air}]{\text{SiO}_2} \text{R}^1\text{CH}_2\text{CH}_2\text{OH} \quad \text{6}$					
	6a , 96%		6b , 98%		6c , 84%
	6d , 95%		6e , 95%		6f , 99%
	6g , 98%		6h , 96%		6i , 62%
	6j , 82%		6k , 92%		6l , 90%
	6m , 99%		6n , 96%		6o , 79% ^[b]

[a] Conditions: alkene (1.0 mmol), pinacolborane (1.1 mmol), catalyst **1** (1 mol%) and Et₂O (1 mL), room temperature, N₂, 16 h. Yields shown are of isolated products of **6**. [b] 2.0 mmol pinacolborane was used.

hydes were also studied under the same conditions. Generally, good to high yields of isolated primary alcohols were obtained for benzaldehydes bearing various substituents and heteroaryl aldehydes (**6j–n**). Interestingly, *trans*-cinnamaldehyde containing both C=C and C=O bonds was selectively hydroborated on the C=O bond, even in the presence of 2.0 equiv of pinacolborane.

To further evaluate the chemoselective hydroboration of alkenes vs. ketones, two additional experiments were conducted (Scheme 1). First, unlike the Männig and Nöth results,^{11a} 5-hexen-2-one was reacted with pinacolborane (2.0 equiv) in the presence of **1** (2 mol%) to give 5-hexen-2-ol as the only product in 81% yield after purification, remaining the alkene intact. Second, the competing experiment involving a mixture of acetophenone and styrene resulted in almost quantitative hydroboration of ketone and complete recycle of styrene. These results show excellent chemoselectivity of ketones over alkenes for manganese-catalyzed hydroboration, which is similar to the selective hydrogenation of C=O using a manganese catalyst reported by Kempe.^{115c}

**Scheme 1.** The selective hydroboration by catalyst **1**.

In summary, we have reported on the facile synthesis of well-defined manganese alkyl complexes from inexpensive, readily available ligands, 2,2':6',2''-terpyridine and its derivatives. Effective, and highly regio- and chemo-selective hydroboration of a range of alkenes, ketones and aldehydes was revealed by using **1** (1 mol%) under mild, homogeneous conditions. This represents the first example of metal-

catalyzed hydroboration by using a well-defined manganese complex. The results shall provide significant implication for future catalyst design based upon earth-abundant elements, in particular the underexplored manganese.

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