Letter

Manganese-Catalyzed Direct Deoxygenation of Primary Alcohols

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Manganese-Catalyzed Direct Deoxygenation of Primary Alcohols

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Supporting Information

ABSTRACT: Deoxygenation of alcohols is an important tool in the repertoire of defunctionalization methods in modern synthetic chemistry. We report the first example of a base- metal catalyzed direct deoxygenation of benzylic and aliphatic primary alcohols via oxidative dehydrogenation/Wolff-Kishner reduction. The reaction is catalyzed by a well-defined PNP pincer complex of earth-abundant manganese, evolving H2, N2, and water as the only by-products.

KEYWORDS: homogeneous catalysis, deoxygenation, alcohols, pincer complexes, manganese complex,

The exploration of efficient defunctionalization methods has become an important area of research in organic synthesis to ensure value chains not based on fossil fuels.[1] Non-selective deoxygenation of readily available alcohols, polyols, and organic feedstock materials has gained increased interest in order to provide sustainable platform chemicals and fuels beyond conventional petrochemistry-based technologies.[2] The synthesis of specialty chemicals and natural product-derived molecules, however, requires functional group tolerant synthetic methods which are also applicable to late-stage transformations.[3] To comply with the increasing complexity of organic syntheses, function-oriented and highly selective one-step deoxygenation processes are required.[4]

The common alcohol deoxygenation methods can be classified into single-step and two-step strategies.[5-9] Among the latter procedures, which generally involve intermediate conversion of the alcohols into reactive derivatives prior to reduction,[6] the Barton-McCombie radical pathway is probably the most important and widely practiced method.[7] Direct deoxygenation of alcohols is challenging due to the high C–O bond dissociation energy and a high kinetic barrier, which can be overcome by use of catalytic amounts of transition metal complexes, and Lewis- or Brønsted-acid activation of the hydroxyl function.[8,9] In most cases, silanes are used as hydride sources for the following reductive hydrogenation.[9]

Recently, Li reported a direct deoxygenation of primary benzylic and aliphatic alcohols by a combination of dehydrogenative oxidation and Wolff-Kishner reduction.[10] By using iridium- or ruthenium-based dehydrogenation catalysts, the initially formed aldehyde undergoes Wolff-Kishner reduction in the presence of hydrazine hydrate and base (Figure 1). This method has significant advantages compared to the aforementioned methods because of its high functional group tolerance and selectivity toward primary alcohols.[10] However, in terms of sustainability, low cost, and earth abundance, the replacement of expensive noble metals by first-row base metals like Mn, Fe, and Co is desirable.[11] In this respect, manganese offers an attractive replacement since it is the third most earth-abundant metal after iron and titanium.

In recent years, our group reported several unprecedented catalytic one-step reactions based on the concept of metal-ligand cooperation[12] in pincer-type transition metal complexes.[13] The acceptorless dehydrogenation of alcohols, avoiding stoichiometric amounts of oxidants and the formation of wasteful and toxic by-products has become an important future-oriented paradigm for the development of "green" synthetic methodologies and hydrogen storage systems.[14] At the beginning of 2016, our group reported the dehydrogenative coupling of alcohols and amines to form imines and dihydrogen catalyzed by a pyridine-based manganese PNP pincer complex.[15] Within the following months a remarkable number of intriguing developments in catalytic transformations with Mn pincer-type complexes has been achieved.[16-20] The groups of Kirchner and Kempe reported the dehydrogenative coupling of alcohols with amines and amidines to form pyrimidines, quinolines, and imines catalyzed by Mn-PNP pincer complexes.[16a,b,d] Beller et al. described the Mn-catalyzed dehydrogenation of methanol,[16c] and our group has recently reported the *N*-formylation of amines with methanol using the Mn complex **1** (Figure 2).[20] Mn pincer complexes have also been exploited for ester formation,[16e] the hydrogenation of nitriles,[17a] carbonyl compounds,[17a,b,e] and esters,[17c,d] as well as for (auto)transfer hydrogenation reactions.[18]

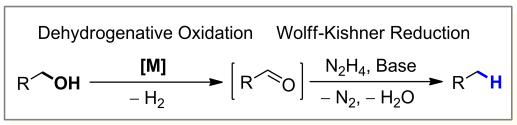


Figure 1. Direct metal-catalyzed deoxygenation of alcohols via a sequence of dehydrogenative oxidation/Wolff-Kishner reduction.

Lately, we reported the first base-free direct synthesis of symmetrical azines by dehydrogenative coupling of alcohols and hydrazine catalyzed by a ruthenium PNP pincer complex.[21] By combining with base-metal pincer chemistry, we applied this hydrazine-based methodology for environmen-

tally benign and atom-economical defunctionalization of alcohols. Herein, we present direct deoxygenation of primary benzylic and aliphatic alcohols, catalyzed for the first time by a base metal complex (Figure 1). The reaction is based on metal-ligand cooperation[12] using a manganese PNP pincer-complex (Figure 2), which involves the acceptorless dehydrogenation of an alcohol and subsequent Wolff-Kishner reduction with hydrazine hydrate and base. The reaction generates dihydrogen, valuable by itself, together with N_2 and water as the only by-products.

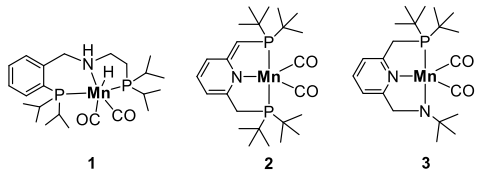
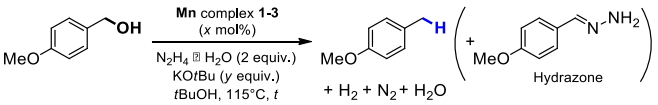


Figure 2. Manganese pincer complexes studied for the direct deoxygenation of alcohols.

Initially, we explored the catalytic activity of the manganese PNP pincer complexes **1-3** (Figure 2) in the direct deoxygenation of alcohols using 4-methoxybenzyl alcohol as a model system (Table 1). Complex **1** was previously described by our group.[20] Heating a solution of 4-methoxybenzyl alcohol with two equivalents hydrazine hydrate in the presence of 0.2 equiv. KO*t*Bu and 3 mol% **1** in *tert*-butanol at reflux for 48 h resulted in full conversion of the alcohol and formation of 4-methylanisole in 30% yield along with 62% hydrazone (Table 1, entry 1). The latter is considered a key intermediate in the deoxygenation process, formed by dehydrogenative coupling of the alcohol and hydrazine. Performing the same reaction with no base also led to full conversion, forming the desired deoxygenation product in 44% yield along with considerable amounts of the hydrazone (52%, entry 2). Thus, the manganese complex **1** seems active in dehydrogenation of the alcohol even in absence of added base. Significantly, by increasing the amount of base to 1 equiv. under otherwise the same conditions (entry 3), the formation of the deoxygenation product became more dominant (54%), with the hydrazone being obtained in 45% yield. Upon addition of 2 equiv. KO*t*Bu to the reaction catalyzed by the Mn complex **1** (3 mol%) the deoxygenation process proceeded smoothly with full conversion after 48 h, forming 4-methylanisole as the only product (entry 4). After 24 h reaction time, the deoxygenation product was also obtained with good selectivity, albeit in lower conversion (80%) and yield (74%, entry 5). Carrying out the reaction under the optimized conditions in a *closed* Teflon Schlenk tube for 48 h had no effect on conversion and yield despite the formation of gaseous by-products (compare entries 4 and 6 in Table 1), indicating favorable release of dihydrogen from the manganese complex **1** in the catalytic cycle (see Scheme 1, below). Using benzene instead of polar *tert*-butanol as solvent, the conversion of 4-methoxybenzyl alcohol was lower (64%) after 24 h, with 4-methylanisole being formed in 54% yield (compare entries 5 and 7 in Table 1). Experiments using only 1 mol% of the Mn catalyst **1** also demonstrate the significant effect of the amount of base on the selectivity toward the deoxygenation product, while it had only little effect on the total conversion (entries 8-10). However, even when using 2 equiv. KO*t*Bu in the reaction with 1 mol% **1**, the conversion was incomplete (78%) after 48 h, but the deoxygenation product was selectively obtained in good yield (76%, entry 10). As shown in entries 11 and 12 in Table 1, we also studied the catalytic activity of the manganese complexes **2** and **3** (Figure 2) in the direct deoxygenation of 4-methoxybenzyl alcohol. Using the dearomatized complex **2**[15,22] (3 mol%) and 2 equiv. base, 4-methylanisole was selectively obtained, although less efficiently (20% conversion, entry 11). Reaction of 4-methoxybenzyl alcohol with 3 mol% of the Mn-PNN complex **3**[17d] and two equiv. KO*t*Bu for 48 h led to high conversion (80%) but only 53% of the deoxygenation product, along with 14% hydrazone, were obtained (Table 1, entry 12).

Table 1. Optimization of the reaction conditions for the direct deoxygenation of alcohols.[a]

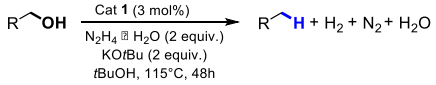


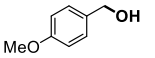
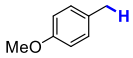
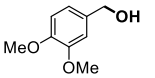
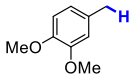
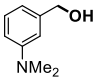
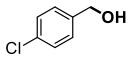
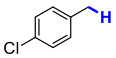
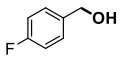
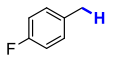
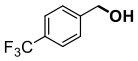
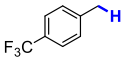
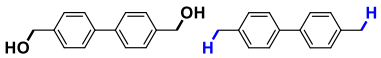
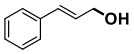
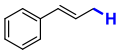
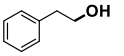
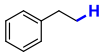
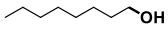
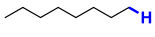
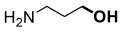
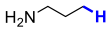
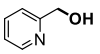
Entry	**1-3** (*x* mol%)	*t* [h]	KO*t*Bu (*y* equiv.)	Conv. of alcohol [%][b]	Yield [%][b]	Hydrazone [%][b]
1	**1** (3)	48	0.2	99	30	62
2	**1** (3)	48	-	99	44	52
3	**1** (3)	48	1	99	54	45
4	**1** (3)	48	2	99	99	-
5	**1** (3)	24	2	80	74	6
6[c]	**1** (3)	48	2	99	99	-
7[d]	**1** (3)	24	2	64	54	10
8	**1** (1)	48	0.2	68	6	57[e]
9	**1** (1)	48	1	69	31	26[f]
10	**1** (1)	48	2	78	76	-
11	**2** (3)	48	2	20	20	-
12	**3** (3)	48	2	80	53	14

[a]Reaction conditions: Mn complex **1-3** (*x* mol%), alcohol (0.5 mmol), hydrazine hydrate (2 equiv., 1.0 mmol), KO*t*Bu (*y* equiv.), *N*,*N*-dimethylaniline (internal standard, 0.5 mmol), and *tert*-butanol (1.5 ml) were heated at reflux in a Schlenk flask (oil bath temperature: 115 °C) for 24 or 48 h. [b]Conversion of alcohol and yields of products were determined by ^{1}H NMR spectroscopy using *N*,*N*-dimethylaniline as internal standard, supported by GC/MS analysis. [c]The reaction was carried out in a closed 50 ml Teflon Schlenk tube. [d]The reaction was carried out using benzene (3 ml) as solvent. [e]Azine formation (4%) determined by ^{1}H NMR spectroscopy. [f]Azine formation (12%) determined by ^{1}H NMR spectroscopy.

Table 2 shows the substrate scope of the new Mn-catalyzed direct deoxygenation of alcohols using catalyst **1** (3 mol%) and KO*t*Bu (2 equiv.) under the optimized conditions. The reaction with primary benzylic alcohols proceeds with excellent yields, tolerating a variety of functional groups (entries 1-8). Interestingly, the reaction can even be applied to the deoxygenation of primary benzylic alcohols bearing strong electron-withdrawing groups (Table 2, entries 5 and 6). 4-Fluoro- and 4-(trifluoromethyl)benzyl alcohols were smoothly deoxygenated in very good yields (F: 91%, CF_3: 97%). Easy removal of both hydroxyl groups in 4,4`-bis(hydroxymethyl)biphenyl was achieved, leading to 4,4`-dimethylbiphenyl in 99% yield (entry 8). Deoxygenation of cinnamyl alcohol proceeded with full conversion, although formation of the deoxygenation product (46% yield) was accompanied by 53% yield of 1-phenylpropane by hydrogenation of the C=C double bond (entry 9). The applicability of our strategy to primary aliphatic alcohols was also demonstrated (Table 1, entries 10-12). 2-Phenylethanol and 1-octanol were readily deoxygenated in high yields (entries 10 and 11). Remarkably,

Table 2. Deoxygenation of alcohols catalyzed by the manganese complex 1.[a] [P] = P(*i*Pr)$_2$.



Entry	Substrate	Product	Yield [%][b]
1			99
2			99
3[c]			99
4[d]			99
5[d]			91
6			97
7			83
8[d]			99
9			46[e]
10[d]			92
11			84
12[d]			93
13[d]			26
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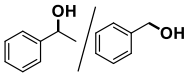
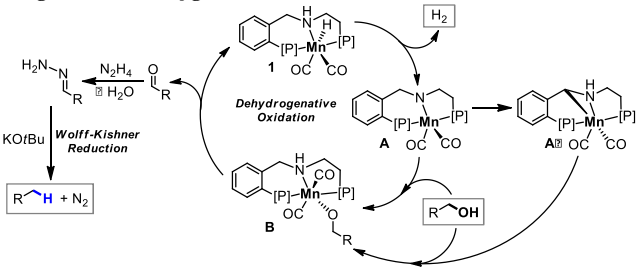
15[d,f]			93[g]

[a]Reaction conditions: Mn complex **1** (3 mol%), alcohol (0.5 mmol), hydrazine hydrate (2 equiv., 1.0 mmol), KO*t*Bu (2 equiv., 1.0 mmol), *N*,*N*-dimethylaniline (internal standard, 0.5 mmol), and *tert*-butanol (1.5 ml) were heated at reflux in a Schlenk flask (oil bath temperature: 115 °C) for 48 h. [b]Yields of products were determined by ^{1}H NMR spectroscopy using *N*,*N*-dimethylaniline as internal standard, supported by GC/MS analysis. [c]1,3,5-Trimethoxybenzene (0.5 mmol) was used as internal standard. [d]The reaction was carried out in a closed 50 ml Teflon Schlenk tube. [e]Additional formation of 1-phenylpropane (53%) by partial hydrogenation of the C=C double bond. [f]The reaction was carried out using a mixture of benzyl alcohol (0.5 mmol) and 1-phenylethane (0.5 mmol). [g]Formation of phenylethane (19%) determined by ^{1}H NMR spectroscopy.

the NH$_2$ functionality remains totally untouched during the Mn-catalyzed deoxygenation process as shown for 3-amino-1-propanol, which was converted to 1-aminopropane in 93% yield (entry 12). The deoxygenation can be applied also to 2-pyridinemethanol, although in low yield (26%, entry 13). Secondary alcohols are insufficiently deoxygenated(entry 14), which opens the possibility of chemoselective transformation of mixtures of primary and secondary alcohols. Thus, reaction of a mixture of benzyl alcohol and 1-phenylethanol (0.5 mmol each) with 1 mmol of hydrazine hydrate was converted to 93% toluene and only 19% phenylethane (entry 15). A competitive experiment using only 0.5 mmol of hydrazine resulted in 96% yield of toluene and only traces of phenylethane. (see SI).

In order to gain insight into the mechanism of the manganese catalyzed alcohol deoxygenation reaction, the amido complex **A** (Scheme 1) was freshly prepared according to a previously reported procedure,[20] and reacted with 5 equiv. of 4-methoxybenzyl alcohol in [D$_8$]-toluene at room temperature. After 15 min at room temperature, the ^{31}P NMR spectrum showed new broad signals at δ = 56 and 85 ppm, attributed to an alkoxo complex (**B**, Scheme 1). Formation of the hydride complex **1** was also observed. The ^{1}H NMR spectrum displayed singlet signals at δ = 9.60 and 3.17 ppm in [D$_8$]-toluene for the aldehyde formyl proton and the methoxy protons, respectively, indicating formation of 4-methoxybenzaldehyde via β-hydride elimination from the alkoxo complex **B**, regenerating complex **1** (see SI, Figures S19 and S20). Considering our experimental findings, and on the basis of recent mechanistic investigations in the Mn-catalyzed dehydrogenative coupling of amines and methanol using complex **1**,[20] the following catalytic cycle is postulated (Scheme 1). Initial dihydrogen liberation from complex **1** leads to the amido complex **A**. This step might be kinetically favored by using *tert*-butanol as solvent, which can serve as proton shuttle in the H$_2$ elimination process. Formation of dihydrogen during the reaction was verified by GC. Complex **A** likely undergoes intramolecular C–H activation to form the thermodynamically more stable *C*-metallated complex **A'** (for details, see also Ref. 20). O–H activation of the alcohol by complex **A** or **A'** via proton transfer either to the amido nitrogen or benzylic carbon atom results in the formation of the alkoxo complex **B**. The following β-hydride elimination step releases the aldehyde that undergoes condensation with hydrazine to form a hydrazone. Base-mediated Wolff-Kishner reduction with release of N$_2$ finally leads to the deoxygenated product (Scheme 1). A reduction process via N–H activation of the hydrazone by complex **A** or **A'** and Mn-catalyzed decomposition toward the deoxygenation product without the need of added base is also possible (for details, see SI), since deoxygenation occurs also in the absence of added base, albeit with lower yield (see Table 1, entry 2).

Scheme 1. Proposed mechanism for the Mn-catalyzed dehydrogenative deoxygenation of alcohols. [P] = P(*i*Pr)$_2$.



In summary, we have demonstrated for the first time a base metal-catalyzed direct deoxygenation of primary alcohols with liberation of dihydrogen. The reaction, catalyzed by a

robust Mn pincer complex, involves acceptorless dehydrogenative coupling of an alcohol with hydrazine, followed by base-mediated Wolff-Kishner reduction of the intermediate hydrazone. This Mn-catalyzed protocol is functional group tolerant and selective for different kinds of primary benzylic and aliphatic alcohols leading to moderate to excellent yields, even in the presence of electron-withdrawing functionalities and the NH_2 group. Moreover, the reaction is selective to *primary* alcohols. Further developments aimed at base-free direct deoxygenation methods using non-noble metal catalysts are in progress.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic and mechanistic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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