#### FULL PAPER

WILEY Applied Organometallic Chemistry

## Reduction of furfural by Mn/2,4,6-Coll<sup>-</sup>HCl/H<sub>2</sub>O: Mechanistic aspects of this reaction

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## **1** | INTRODUCTION

Biomass, a renewable non-fossil carbon energy has gained worldwide attention as concerns grow over global warming, diminishing fossil fuel reserves and environmental problems caused by CO<sub>2</sub> emissions.<sup>[1]</sup> Therefore, biomass is one of the most encouraging options for a sustainable and green production of chemicals and fuels.

In this context, furfural (1), obtained from hemicellulose, is identified as one of most important building blocks, as well as a rich platform for value-added chemicals and lignocellulosic biofuels (Figure 1).<sup>[2]</sup>

Among these different chemical products, the furfuryl alcohol (FA) (2) is the most important. It has been estimated that approximately 65% of the furfural produced each year is turned into FA. FA is widely used in the production of initial building blocks for the preparation of other chemicals, fuels and resins.<sup>1a, 3</sup> For this reason, the selective hydrogenation of furfural has been extensively investigated using environmentally acceptable metal catalysis (Cu, Pd, Pt, Rh, Ru, Ni, Co and Zn).<sup>2a</sup> More recently, other methods such as the electrocatalytic

A simple, mild and safe reduction of furfural to furfuryl alcohol by the Mn/2,4,6-Coll<sup>·</sup>HCl/H<sub>2</sub>O system is described. An experimental study on the role played by each of the reagents involved in this reduction and DFT calculations are reported. With the aim to provide an explanation for the results obtained, a complete mechanism is proposed.

#### KEYWORDS

furfural, Furfuryl alcohol, green chemistry, manganese, reduction reaction

and Meerwein-Ponndorf-Verley reduction with alcohol as H-donor have been reported.<sup>2b, c</sup> However, many of these procedures are not affordable and usually hydrogen gas as reducing agent is used. These methods, based on the use of hydrogen gas as reducing reagent, often present problems because high-pressure equipment is needed to handle the gas. In this context, the development of a new procedure for the reduction of furfural that avoids the presence of hydrogen gas and uses an inexpensive, nontoxic and environmentally friendly metal, is desirable. Taking this into account, the Mn/2,4,6-Coll<sup>-</sup>HCl/H<sub>2</sub>O system is a safe, selective and mild procedure which promotes the chemoselective reduction of aldehydes.<sup>[4]</sup> A detailed knowledge of the mechanism involved in the reduction of aldehydes by the Mn/2,4,6-Coll<sup>-</sup>HCl/H<sub>2</sub>O system is necessary to provide a platform for the design of more and novel efficient processes. In this paper, we report on the experimental conditions and reagents necessarily required for the Mn/2,4,6-Coll<sup>·</sup>HCl/H<sub>2</sub>O-promoted reduction of furfural. Additionally, DFT calculations were carried out with the aim to verify the reduction mechanism.



FIGURE 1 Value-added chemicals obtained from furfural

## 2 | RESULTS AND DISCUSSIONS

Here, we describe a set of experiments to optimize the reduction of furfural by the Mn/2,4,6-Coll'HCl/H<sub>2</sub>O system. Their results provide solid experimental evidence of the mechanism of reduction. These results are summarized in Table 1.

Initially we studied the reduction of furfural (1), using the experimental conditions reported by Justicia et al. in the reduction of aldehydes<sup>[4]</sup> (entry 1). After 24 hr stirring 1 with Mn dust (8 equiv), 2,4,6-Coll<sup>·</sup>HCl (2 equiv), and water (10 equiv) in THF (20 ml), to our satisfaction, FA (2) and pinacol coupling products 3 were observed. The relative ratio of 2 and 3 was 56/23 (calculated by <sup>1</sup>H NMR). The ratio of *dl/meso* of the 1.2-diols was 1/1 (calculated by <sup>1</sup>H NMR). The most important observation to be made about this result is that pinacol coupling products were detected for first time when the Mn/2,4,6-Coll HCl/H2O system is used as a reducer. We subsequently investigated the role played by each reagent in a series of thirteen experiments (entries 2-13, 15). We decided to start studying the effect of concentration on conversion reduction (entries 2, 3). With 30 ml of THF per one mmol of fufural (1) a significant quantity of reduction product 2 (65%) was obtained (entry 3).

Then, we investigated the role played by 2,4,6collidinium hydrochloride (2,4,6-Coll HCl) in a series of four experiments with increasing amounts of this reagent (entries 3–6). We decided to start with a control experiment in the absence of 2,4,6-Coll HCl. After 24 hr of stirring, **1** was recovered unchanged (entry 4), showing that 2,4,6-Coll HCl is required for the reduction of aldehydes **1** to **2** to take place. These results indicate that 2,4,6-Coll HCl reactivates the manganese surface previously deactivated due to the dissociative adsorption between water and the manganese surface.<sup>[5]</sup> Nevertheless, with 2 equiv of 2,4,6-Coll HCl a significant level of **2** (65%) was obtained (entry 3). A similar amount of **2** was obtained using 3 or 4 equiv of 2,4,6-Coll HCl (entries 5–6). 

0	0	0	ОН	HO >-	_O⊦	I	
				0		0	
1		2		3			
	THF (ml/ mmol 1)	Mn (equiv)	2,4,6- coll·HCl (equiv)	H <sub>2</sub> O (equiv)	1 (%)	2 (%)	3 (%)
1	20	8	2	10	$21^{a}$	56 <sup>a</sup>	23 <sup>a</sup>
2	10	8	2	10	40 <sup>a</sup>	36 <sup>a</sup>	24 <sup>a</sup>
3	30	8	2	10	19 <sup>a</sup>	65 <sup>a</sup>	16 <sup>a</sup>
4	30	8	0	10	$100^{\mathrm{a}}$		
5	30	8	3	10		$81^{\mathrm{a}}$	19 <sup>a</sup>
6	30	8	4	10		86 <sup>a</sup>	14 <sup>a</sup>
7	30	0	3	10	$100^{\mathrm{a}}$		
8	30	6	3	10		80 <sup>a</sup>	20 <sup>a</sup>
9	30	4	3	10	53 <sup>a</sup>	39 <sup>a</sup>	8 <sup>a</sup>
10	30	8	3	0	17 <sup>a</sup>	65 <sup>a</sup>	$18^{a}$
11	30	8	3	2.5		$81^{\mathrm{a}}$	19 <sup>a</sup>
12	30	8	3	5		$81^{\mathrm{a}}$	19 <sup>a</sup>
13	30	8	3	15	$10^{a}$	72 <sup>a</sup>	$18^{a}$
14	30	6	4	5		87 <sup>b</sup>	$13^{b}$
$15^{\rm c}$	30	6	4	5		86 <sup>a</sup>	14 <sup>a</sup>

<sup>a</sup>Relative ratio determined on the basis of the <sup>1</sup>H NMR spectrum of the reaction crude.

<sup>b</sup>Relative ratio determined on the basis of the <sup>1</sup>H NMR spectrum after flash chromatography.

<sup>c</sup>Furfural was slowly added during 8 hr.

Then, we researched the role played by manganese. As above, we started with a control experiment in the absence of manganese (entry 7). Under these conditions, furfural (1) was recovered quantitatively. This confirms that manganese is essential for the reduction process. We determined the exact amount of manganese required to complete the reduction reaction by means of three experiments with increasing amounts of this metal (entries 5, 8–9). It was found that at least 6 equiv of manganese are required to complete the process and to obtain a good (80%) yield of FA (entry 8).

Later, we investigated the role played by water in a series of five experiments with increasing amounts of this reagent (5, 10–13). As above, we started with a control experiment in absence of water (dry TFH, entry 10). This system (Coll<sup>+</sup>HCl/Mn) was previously introduced by Gansäuer *et al.* in the radical chemistry catalyzed by titanocenes.<sup>[6]</sup> In order to check the degree of conversion

of this reduction in comparison to that obtained in the experiment collected in entry 5, the reaction was quenched just after the fixed reaction time (24 hr). Under these conditions, **2** (65%) was the main product. This result reflects that the hydrogen atom needed in the reduction process does not necessarily come from water, as previously was reported.<sup>[4]</sup> The optimum yield of **2** (81%) was obtained with 2.5 or 5 equiv of water (entry 11 and 12). An increase in the amount of water (entry 13) results in a lower yield of **2** possibly due to a dissociative adsorption between water and the manganese surface and the consequent inactivation of this metal.

After optimizing all the reagents involved in the reduction reaction, the treatment of furfural (1) with Mn dust (6 equiv), 2,4,6-Coll<sup>+</sup>HCl (4 equiv), and water (5 equiv) in THF (30 ml) afforded a mixture of FA (2) and 3 (92 mg, 95%). The relative ratio of 2 (87%) and 3 (13%) (entry 14) was determined on the basis of their <sup>1</sup>H NMR spectra.

Finally, in order to discard or confirm the presence of free radicals, furfural (1) was added dropwise to the reaction medium (entry 15). Under these conditions, the same ratio of coupling products **3** was found in this reaction (entry 15) and in that of entry 14. This result confirms that free ketyl radicals are not involved in this reduction. This conclusion was previously reported by Justicia *et al.*<sup>[4]</sup>

After all the optimization reactions were carried out, the formation of pinacol coupling products **3** was not avoided. However, different material transfer operations, such as rectification, have been used for the purification of furfuryl alcohol (**2**).<sup>[7]</sup>

The observations mentioned above cannot be fully explained by the mechanism previously reported.<sup>[4]</sup> Instead, the mechanism tentatively proposed in Scheme 1 adequately accommodates the new experimental observations collected in Table 1. The coordination between **1** and manganese would provide the intermediate **4** in solution. This type of metallaoxiranes (in free solution) is well-known. In fact, both titanaoxiranes and zirconaoxiranes closely related to **4** have been reported.<sup>[8]</sup>



**SCHEME 1** Mechanism for the Mn/2,4,6-Coll'HCl/H<sub>2</sub>Opromoted reduction of furfural

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In the original work it was proposed that the metalloxirane was generated by  $\eta^2$ -interaction between the carbonyl group and the Mn surface.<sup>[4]</sup> In absence of a water-compatible regenerating agent (2,4,6-Coll'HCl), the manganese surface is inactivated and the key intermediate 4 is not generated, and consequently, neither reduction nor pinacol coupling products are obtained (entry 4). In presence of 2,4,6-Coll HCl, the metal surface is reactivated, and the intermediate 4 is formed. The presence of a donor source of hydrogen (water and/or 2,4,6-Coll<sup>·</sup>HCl) could promote the hydrolysis of 4 to 2. Also, the subsequent coordination of 4 to a second molecule of furfural (1) could lead to pinacol coupling products such as 3 via five-membered intermediate 5. The higher ratio of 2 with respect to 3 in all experiments listed in Table 1 may be due to the fact that 2 is more favorable energetically.To corroborate Scheme 1, geometry optimizations and energy calculations were performed with Gaussian16<sup>[9]</sup> using DFT at the B3LYP-D3/6-31g(d) level of theory in vacuo. We have verified that this level of theory yields the lowest energy for multiplicity 6. The D3 scheme,<sup>[10]</sup> dispersion-correction applying the Becke–Johnson damping,<sup>[11]</sup> was included for all calculations. Intermediates, products and transition states were located by means of the GRRM<sup>[12]</sup> (Global Reaction Route Mapping) program, linked to Gaussian16. Transition state structures were optimized as saddle points at the B3LYP-D3/6-31g(d) level of calculation. To verify that they correspond to the expected reactant and product, intrinsic reaction coordinate (IRC) calculations were performed at the same level. To obtain the Gibbs Free Energy correction, a vibrational analysis was performed at the same level of theory, using the SMD continuum model<sup>[13]</sup> for the solvent (tetrahydrofuran) and the experimental temperature.

The energies have been refined by single-point calculations at the B3LYP-D3/def2tzvpp level on the previously optimized structures. The reported energies are given in Hartrees. In the Scheme 2, these energies are in kcal/mol relative to intermediate **4**.

As we can see in Scheme 2, the energy barriers associated with the reduction of **4** or the coupling of **4** with **2** are similar. However, FA (**2**) is energetically more favorable than the coupling products **3**, which is translated into a greater proportion of **2** with respect to **3**. In addition, we have verified that the initial barrier of path (c) is practically the same for both coupling products, using the SCW<sup>[14]</sup> algorithm, included in the GRRM package, that provides quick, rough estimates of minimum energy reaction pathways between two minima. These calculations corroborate the 1:1 ratio found experimentally for coupling products **3**. Cartesian coordinates and energies of the computed structures are given in the supporting information.

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#### SCHEME 2 Free energy profile

## 3 | CONCLUSIONS

In summary, a safe, chemoselective, mild, affordable method for the reduction of furfural (1) to furfuryl alcohol (2) based on the Mn/2,4,6-Coll·HCl/H<sub>2</sub>O system, is described. Moreover, a detailed experimental study of the role played by effect of the concentration and reagent involved in the reduction process is reported. Additionally, a computational investigation confirmed low barriers from metallaoxirane intermediate **4** to furfuryl alcohol **2** and coupling products **3**, and that **2** is the most energetically favorable product. At the moment, we are working in the semipreparative production of **2** from **1** using the described method.

### 4 | EXPERIMENTAL

### 4.1 | General methods

All the reactions were carried out under argon using standard Schlenk. THF was distilled from Na/benzophenone under argon and was deoxygenated prior to use. THF was deoxygenated by bubbling argon. <sup>1</sup>H NMR spectra were recorded at 300 MHz. All reactions were monitored by thin-layer chromatography (TLC). The TLC plates were visualized with UV light and 7% phosphomolybdic acid. Flash chromatography was performed on silica gel 60 (0.04–0.06 mm). Reagents and solvents were purchased from commercial sources. Compounds **2** and **3** are commercial.

## 4.2 | General procedure for Mn/2,4,6-Coll<sup>·</sup> HCl/H<sub>2</sub>O-mediated reduction of furfural (1)

Effect of concentration (entries 1–3).

Deoxygenated THF (10 mL, entry 2); (20 ml, entry 1) or (30 ml, entry 3) was added to a mixture of Mn (437.6 mg, 8 mmol) and 2,4,6-Coll HCl (307.2 mg, 2 mmol) under an Ar atmosphere. Then, a solution of furfural (1) (96.0 mg, 1 mmol) and water (180 mg, 10 mmol) in 1 ml of THF was added, and the solution was stirred for 24 h at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed to afford the compounds indicated in entries 1–3 in Table 1. The relative ratio (see entries 1–3 in Table 1) was determined on the basis of their <sup>1</sup>H NMR spectra.

# 4.3 | Role played by 2,4,6-Coll<sup>·</sup>HCl (entries 3–6)

Deoxygenated THF (30 ml) was added to Mn (437.6 mg, 8 mmol) (entry 4) or a mixture of Mn (437.6 mg, 8 mmol) and 2,4,6-Coll<sup>+</sup>HCl (307.2 mg, 2 mmol, entry 3); (460.9 mg, 3 mmol, entry 5) or (614.5 mg, 4 mmol entry 6) under an Ar atmosphere. Then, a solution of furfural (1) (96.0 mg, 1 mmol) and water (180 mg, 10 mmol) in 1 ml of THF was added, and the solution was stirred for 24 h at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 ml;) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed to afford the compounds indicated in entries 3–6 in Table 1. The relative ratio (see entries 3–6 in Table 1) was determined on the basis of their <sup>1</sup>H NMR spectra.

## 4.4 | Role played by Mn (entries 5, 7–9)

Deoxygenated THF (30 ml) was added to 2,4,6-Coll<sup>·</sup>HCl (460.9 mg, 3 mmol, entry 7) or a mixture of 2,4,6-Coll<sup>·</sup>

HCl (460.9 mg, 3 mmol) and Mn (218.8 mg, 4 mmol, entry 9); (328.2 mg, 6 mmol, entry 8) or (437.6 mg, 8 mmol, entry 5) under an Ar atmosphere. Then, a solution of furfural (1) (96.0 mg, 1 mmol) and water (180 mg, 10 mmol) in 1 ml of THF was added, and the solution was stirred for 24 h at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed to afford the compounds indicated in entries 5, 7–9 in Table 1. The relative ratio (see entries 5, 7–9 in Table 1) was determined on the basis of their <sup>1</sup>H NMR spectra.

## 4.5 | Role played by water (entries 5, 10–13)

Deoxygenated THF (30 ml) was added to a mixture of Mn (437.6 mg, 8 mmol) and 2,4,6-Coll<sup>+</sup>HCl (460.9 mg, 3 mmol) under an Ar atmosphere. Then, furfural (1) (96.0 mg, 1 mmol, entry 10) in 1 mL of THF or a solution of furfural (1) (96.0 mg, 1 mmol) and water (45 mg, 2.5 mmol, entry 11); (90 mg, 5 mmol, entry 12); (180 mg, 10 mmol, entry 5) or (270 mg, 15 mmol, entry 13) in 1 ml of THF was added, and the solution was stirred for 24 hr at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed to afford the compounds indicated in entries 5,10–13 in Table 1. The relative ratio (see entries 5,10–13 in Table 1) was determined on the basis of their <sup>1</sup>H NMR spectra.

## 4.6 | Reduction using the optimized reagents (entry 14)

Deoxygenated THF (30 ml) was added to a mixture of Mn (328.2 mg, 6 mmol) and 2,4,6-Coll<sup>-</sup>HCl (614.5 mg, 4 mmol) under an Ar atmosphere. Then, a solution of furfural (1) (96.0 mg, 1 mmol) and water (90 mg, 5 mmol) in 1 mL of THF was added, and the solution was stirred for 24 hr at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried (anhyd Na<sub>2</sub>SO<sub>4</sub>) and the solvent removed. The crude of reaction was submitted to flash chromatography (hexane/AcOEt 1:1) to yield a mixture of 2 and 3 (92 mg, 95%). The relative ratio of 2 (87%) and 3 (13%) was determined on the basis of their <sup>1</sup>H NMR spectra. The ratio of dl/meso of the 1,3-diols is 1/1 (calculated by <sup>1</sup>H NMR). <sup>1</sup>H NMR of **2** and **3** is given in the supporting information. <sup>1</sup>H of **3** correspond to literature data.<sup>[15]</sup>

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## 4.7 | Slow addition of furfural (1) (entry 15)

Deoxygenated THF (30 ml) was added to a mixture of Mn (328.2 mg, 6 mmol) and 2,4,6-Coll HCl (614.5 mg, 4 mmol) under an Ar atmosphere. Then, a solution of furfural (1) (96.0 mg, 1 mmol) and water (90 mg, 5 mmol) in 2 mL of THF was slowly added during 8 hr and the solution was stirred for 24 hr at 27 °C. THF was removed under vacuum and the reaction was then quenched with 0.5 N HCl (15 ml) and extracted with  $CH_2Cl_2$ . The organic layer was dried (anhyd  $Na_2SO_4$ ) and the solvent removed. The organic layer was dried (anhyd  $Na_2SO_4$ ) and the solvent removed to afford the compounds indicated in entries 15 in Table 1. The relative ratio (see entry 15 in Table 1) was determined on the basis of their <sup>1</sup>H NMR spectra.

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