



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Hydrogenation of CO₂-Derived Carbonates and Polycarbonates to Methanol and Diols via Metal Ligand Cooperative Manganese Catalysis

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201805630
Angew. Chem. 10.1002/ange.201805630

Link to VoR: <http://dx.doi.org/10.1002/anie.201805630>
<http://dx.doi.org/10.1002/ange.201805630>

Hydrogenation of CO₂-Derived Carbonates and Polycarbonates to Methanol and Diols via Metal Ligand Cooperative Manganese Catalysis

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Abstract: The first example of base-metal catalysed hydrogenation of the CO₂-derived-carbonates to alcohols is presented. The reaction operates under mild conditions using a well-defined manganese complex with loading as low as 0.25 mol %. The nonprecious homogenous catalytic system provides an indirect route to convert CO₂ to methanol with the co-production of the value-added vicinal diols with yields up to 99%. Experimental and computational studies indicate a metal ligand cooperative catalysis mechanism.

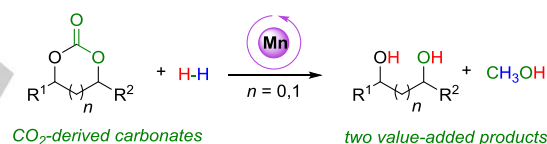
Transition metal catalysed hydrogenation of polar bonds is a key technology in modern industrial chemistry. So far most of these catalytic systems rely on the use of precious metal catalysts.^[1] However, the replacement of the rare-earth metal catalysis by the earth-abundant alternatives is a topic of current interest.^[2] Accordingly, significant advances have been made to the hydrogenation of aldehydes,^[3] ketones,^[3] esters,^[4] carboxylic acids^[4d] and amides^[5] using base-metal catalysts. On the other hand, the hydrogenation of the carbonic acid derivatives is significantly more difficult due to the resonance stabilisation effect of the adjacent alkoxy groups which lower the electrophilicity of the carbonyl group. To the best of our knowledge, catalytic hydrogenation of carbonic acid derivatives has never been reported using a homogenous non-precious metal catalyst.^[6]

Among the carbonic acid derivatives, the hydrogenation of cyclic organic carbonates (COCs) to alcohols is of particular interest, because COCs are industrially synthesised by the direct coupling between carbon dioxide and oxiranes or oxetanes. Hence, developing mild hydrogenation of the COCs would lead to a practical two-step route to convert CO₂ to methanol, in addition to the production of the value added diols (Scheme 1). More specifically, the industrial production of ethylene glycol (EG) involves the use of the so called “omega process” in which CO₂ is inserted into the ethylene oxide to produce ethylene carbonate, followed by catalytic hydrolysis of the former carbonate to (EG) and CO₂.^[7] The replacement of the catalytic hydrolysis by catalytic hydrogenation would lead to the formation of methanol instead of CO₂, thus giving a great advantage in terms of sustainability. The catalytic production of methanol from CO₂ is an elegant alternative option for the recycling of carbon and could lead to “methanol economy” which is a suggested

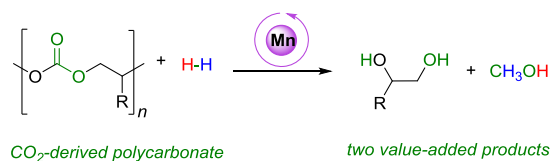
future in which methanol might play the central role as a hydrogen storage material and C1 building block.^[8] This reaction has been studied with heterogeneous catalysts. Nevertheless, these catalytic systems have to operate at elevated temperature (>200 °C) and suffer from the formation of several side-products.^[9] In contrast, well-defined homogenous catalysts are potentially more active and can be tuned by mechanistic studies. In that regard only recently, seminal reports outlined preliminary results on the direct^[10] and indirect^[6,11] hydrogenation of CO₂ to methanol.

However, an efficient catalytic system based on an earth-abundant metal remains an elusive goal. Thus a development of a base metal catalyst which could be used at low catalyst loadings for the reduction of CO₂ derived organic carbonates to value added alcohols would be an important advancement in achieving the requirements of an ecologically and economically benign process (Scheme 1a). Besides, the successful development of such a process may also be extended to the recycling of polycarbonates with the simultaneous formation of valuable diols and methanol (Scheme 1b).

a) indirect reduction of CO₂ to methanol



b) recycling of polycarbonates to valuable products



Scheme 1. Unprecedented base-metal catalysed hydrogenation of organic carbonates.

Inspired by the recent progress on manganese catalysis^[12] and our interest on developing sustainable transformations using inexpensive base-metals stabilised by stable non-innocent ligands,^[13-14] we herein present a new manganese complex that reduces COCs as well as recycles polycarbonates into methanol and vicinal diols under mild reaction conditions. For the first time, a combined experimental and computational study provides insight into the reaction mechanism and explains the role of the non-innocent ligand in the cascade hydrogenation of the CO₂-derived COCs.

In order to accomplish a practical reduction method for the rather challenging cyclic carbonates, we started our studies with the synthesis of a new bench stable ^{Ph}PNN-Mn complex **Mn-1**,

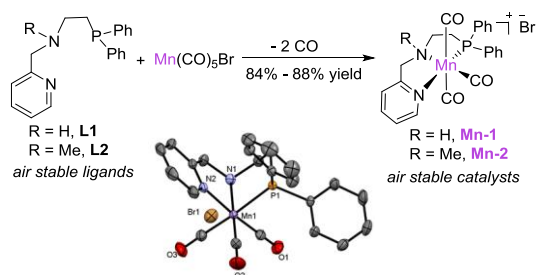
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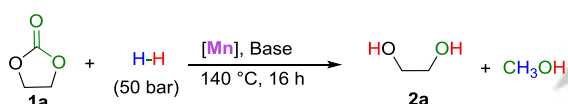
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which is supported by an air and moisture stable Ph_2PNN ligand **L1**.^[15] Following the typical route for the synthesis of the pincer manganese carbonyl complexes,^[12] **Mn-1** was readily prepared by treatment of **L1** with 1 eq. of $\text{Mn}(\text{CO})_5\text{Br}$ as metal precursor in THF at 80 °C for 16 h. The pale yellow complex was isolated in 84% yield and characterised by multinuclear NMR, IR, and mass spectrometry as well as single crystal X-ray diffraction study. In order to study the role of the N-H group, we also synthesized and the corresponding N-methylated ligand and complex **Mn-2** in 88% yield (Scheme 2)



Scheme 2. Synthesis of two Mn-complexes and the single crystal X-ray structure of **Mn-1** at 50% probability level.

Table 1. Optimisation of the reaction conditions.^[a]



entry	[Mn] (mol%)	base (mol%)	solvent (conc.)	yield of EG	yield of MeOH
1	Mn-1 (1)	KOtBu (2.5)	1,4-dioxane	>99	92
2	Mn-2 (1)	KOtBu (2.5)	1,4-dioxane	14	0
3	Mn-1 (1)	K ₂ CO ₃ (2.5)	1,4-dioxane	>99	86
4	Mn-1 (1)	Cs ₂ CO ₃ (2.5)	1,4-dioxane	>99	92
5	Mn-1 (1)	KOtBu (2.5)	THF	>99	77
6	Mn-1 (1)	KOtBu (2.5)	2-Me-THF	90	80
7	Mn-1 (1)	KOtBu (2.5)	Toluene	61	52
8	Mn-1 (0.5)	KOtBu (1.25)	1,4-dioxane	>99	89
9	Mn-1 (0.25)	KOtBu (0.63)	1,4-dioxane	54	36
10 ^[c]	Mn-1 (0.25)	KOtBu (0.63)	1,4-dioxane	99	92
11 ^[c]	Mn-1 (0.1)	KOtBu (0.25)	1,4-dioxane	40	20

[a] Reaction conditions: **1a** (1 mmol), **Mn-1**, base, solvent (0.25 M) at 140 °C under 50 bar of hydrogen for 16 h. [b] Determined by the GC analysis using m-xylene as internal standard. [c] **1a** (5.7 mmol, 500 mg) in 1,4-dioxane (1.46 M), .

With the aim to find the right reaction conditions, ethylene carbonate was selected as a benchmark substrate for catalytic hydrogenation of COCs. To our delight, the our complex **Mn-1** showed excellent reactivity and provided EG in >99% yield and methanol in 92% yield when the reaction was performed under 50 bar hydrogen pressure in 1,4-dioxane (Table 1, entry 1). Importantly, the application of **Mn-2** resulted in the formation of only 14% of EG and no methanol was detected (Table 1, entry

2). This result highlights the crucial role of the free N-H group in the pincer ligand. Further screening of different manganese complexes lead to unsatisfactory results (see Table S4 for details). Subsequently, the influence of different solvents and bases was investigated. Employing K₂CO₃ as a base did not provide improve the results while Cs₂CO₃ was similar effective as KOtBu (Table 1, entries 3, 4). Furthermore, testing various solvents such as THF, 2-methyl-THF and toluene did not lead to better results (Table 1, entries 5-7). Hence, 1,4-dioxane was chosen as appropriate solvent. The reduction of the catalyst loading to 0.5 mol % resulted in >99% of EG and 89% of methanol (Table 1, entry 8). Pleasingly, the reaction proceeded equally well when the catalyst loading was reduced 0.25 mol% and the substrate concentration was increased to 1.46 M (Table 1, entries 9-11).

In order to demonstrate the potential and applicability of the newly developed method, a range of COCs **1a-1m** were tested under the optimised reaction conditions (Table 2). An array of mono-substituted 5-membered 1,3-dioxolan-2-one bearing different alkyl and aryl substituents such as Me, Et, *n*-Bu, Pent, *t*-Bu and Ph could be efficiently and selectively hydrogenated to the corresponding vicinal 1,2-diol and methanol in very good yields (Table 2, entries 1-6). The reaction tolerates the benzyloxymethyl and methoxymethyl derivatives **1h** and **1i** and the desired alcohols were produced in excellent yields (Table 2, entries 7,8). Noteworthy, the disubstituted cyclic carbonate **1j** was successfully converted to methanol and 2,3-butylene glycol (**2j**) in very good yields (Table 2, entries 9). Under the same reaction conditions, different unsubstituted and substituted 6-membered COCs **1k-1m** were reacted in excellent yields to give methanol and the corresponding vicinal 1,3-diols (table 2, entries 10-12).

Additionally, our catalytic system was found to catalyse the hydrogenative depolymerisation of polycarbonates to the corresponding diol and methanol. An example is shown in Table 2, entry 13, poly(propylene carbonate) which can be prepared by copolymerisation of propylene oxide and CO₂,^[17] was hydrogenated using 1 mol% of **Mn-1** to produce methanol (87% yield) and 1,2-propyleneglycol (**2b**, 99% yield). This result might open new avenues for developing efficient base metal catalysts for the recycling of widely used polycarbonate plastic materials.

In order to gain more insight into the reaction mechanism, we performed deuterium-labelling studies by using D₂ instead of H₂ (see SI for details). The manganese catalysed deuteration of ethylene carbonate results in the production of methanol with >95% deuterium incorporation in the methyl group, whereas the ethylene glycol was produced with no deuterium incorporation. Thus, the deuteration of ethylene carbonate is much faster than the dehydrogenation-deuteration of EG. This result provides a practical alternative method for the production of the widely used deuterated methanol. On the other hand, the treatment of EG with deuterium at 140 °C caused significant deuterium substitution in the carbon atoms which indicates the potential of the manganese catalyst in the dehydrogenative deuteration reactions.

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Table 2. Manganese-catalysed hydrogenation of COCs.^[a]

entry	substrate	yield of diol (%) ^[b]	yield of methanol (%) ^[c]
1	1b	99 ^[c]	85
2	1c	94 ^[c]	92
3	1d	96	88
4	1e	99	95
5	1f	99	94
6	1g	99	95
7	1h	99	90
8	1i	99	94
9	1j	99	85
10	1k	99 ^[c]	95
11	1l	99	80
12 ^[d]	1m	99	99
13	1n	91	84

[a] Reaction conditions: **1** (1 mmol), **Mn-1** (0.01 mmol) and KO^tBu (0.025 mmol) in dioxane (4 mL) at 140 °C under 50 bar of hydrogen for 16 h. [b] Isolated yields [c] Determined by the GC analysis using m-xylene as internal standard. [d] **Mn-1** (0.012 mmol) and KO^tBu (0.03 mmol).

The mechanism of the Mn(I)-PNN-catalysed hydrogenation of COCs substrates was also investigated by DFT calculations.^[17] The overall hydrogenation of ethylene carbonate to EG and methanol can be separated into three independent C=O hydrogenation events, each with a corresponding catalytic cycle, see Figure 1.

The first is the hydrogenation of ethylene carbonate (**1a**) into 2-hydroxyethyl formate (**3**); the second is the hydrogenation of **3** into EG (**2a**) plus formaldehyde (**4**); and the third is the hydrogenation of **4** into CH₃OH. In the following, we discuss the first hydrogenation cycle only, **1a** to **3** (Figure 1). The other two catalytic cycles, composed of similar steps, are shown in the Supporting Information (Figure S3). Calculations were performed using the most active **Mn-1** catalyst.

During the initialisation process concerning the H₂ addition to the Mn active site (steps **A** to **C**, where **A** is a 16-electron species), H₂ coordination to Mn is a non-spontaneous process demanding 14.6 kcal mol⁻¹ at M06/TZVP//ωB97XD/SVP(H,C,N,O,P)-TZVP(Mn) computational level in 1,4-dioxane as solvent and relative to **A**. The heterolytic cleavage of H₂, *via* transition state **B-C** (at 21.3 kcal mol⁻¹ relative to **A**), leads to the hydrogenation of the catalytic species by hydridation of the Mn centre and protonation of the non-pyridinic N atom.

The resulting [Mn]-H₂ species **C** (zero energy reference) promotes the reduction of the C=O bond of the substrates (**1a**, **3** and **4**) in the three catalytic cycles. The C=O hydrogenation step is characterised by two main mechanistic events. On the one hand, the nucleophilic character of the hydride on Mn promotes the hydride transfer from Mn to the sp² C atom of the substrate (steps **D** to **E**). On the other hand, in agreement with literature proton transfer is achieved through cleavage of the H-H bond of a H₂ molecule η²-coordinated to the metal (steps **F** to **H**).^[18] This prevents formation of the 16-electron species **A** *via* deprotonation of the N-H functionality.

In more detail, the first step is the hydride transfer from the catalyst to the substrate *via* transition state **D-E** at 16.4 kcal mol⁻¹, leading to the Mn-alkoxide intermediate **E**, laying at -3.9 kcal mol⁻¹. It can be seen that, as consequence of such hydride transfer, 1,3-dioxolan-2-olate is transformed into 2-(formyloxy)ethan-1-olate by charge reorganisation in the substrate. The second step is proton transfer from a coordinated H₂ molecule, releasing the product. In excess of methanol, which is expected as the reaction evolves, metathesis of **E** with CH₃OH can lead to the methoxide species **F**. Coordination of H₂ leads to **G** and triggers rehydration of the Mn active site and proton transfer to methanolate *via* transition state **G-H**, 22.1 kcal mol⁻¹. This entails the regeneration of CH₃OH as well as the catalytic species. Based on calculations, the rate-determining TS along the cycle is this proton transfer, with an overall activation barrier of 25.0 kcal mol⁻¹ from **E** to **G-H**. Of course, this proton transfer can also occur without involving initial metathesis of CH₃OH with **E**, with very similar reaction steps involving the Mn-alkoxide bond of **E**.

The impact of the phosphine substituents was analysed by comparing **Mn-1** with catalysts presenting aliphatic and bulky *t*Bu substituents on the P atom and the less-sterically impeded *i*Pr.

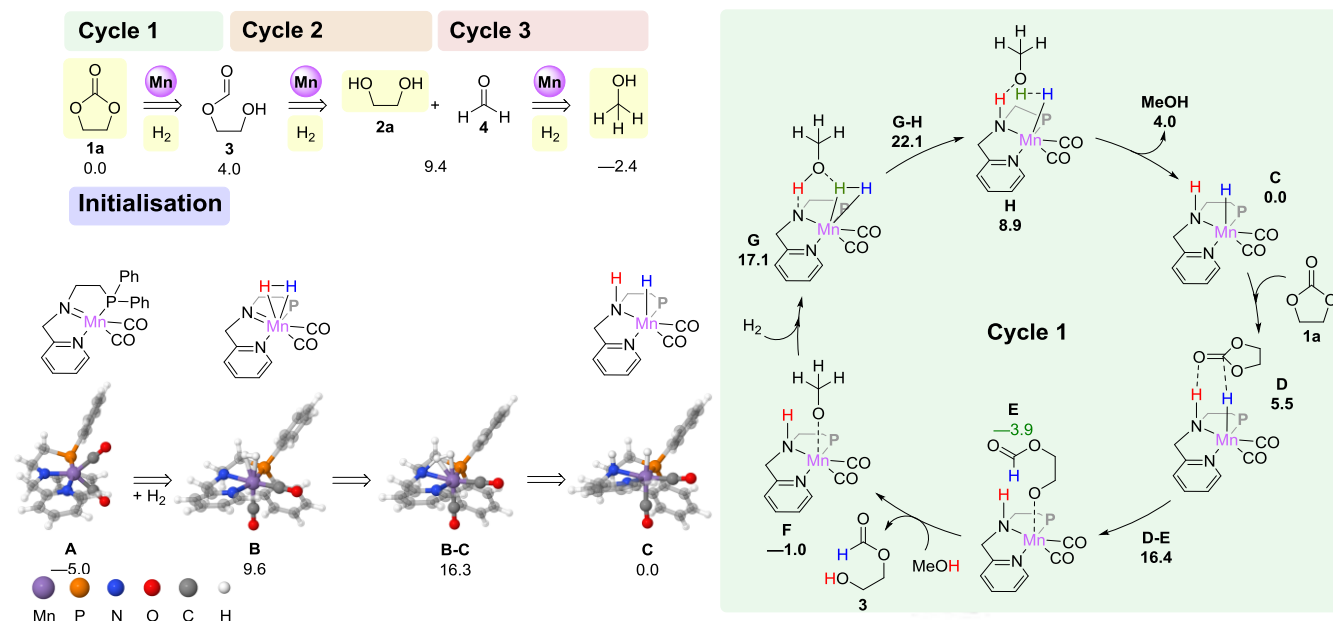


Figure 1. Proposed reaction mechanism for the three-cascade hydrogenation of ethylene carbonate into methanol plus EG catalysed by **Mn-1** (**P** = PPh_2). Steps **A** to **C** refer to the initialisation by catalyst hydrogenation, while steps **D** to **H** concern the substrate hydrogenation and catalyst regeneration by H_2 assistance. Calculated Gibbs free reaction and activation energies, at 140 °C and 50 bar reaction conditions, are shown in kcal mol^{-1} at the M06/TZVP// ω B97XD/SVP(H,C,N,O,P)-TZVP(Mn) computational level in 1,4-dioxane as solvent. Note: H–N–Mn–H species (**C**, Cycle 1) is relative zero in energy.

Hydrogenation during the initialisation process of both the alkyl substituted catalysts, *via* transition state **B-C**, exhibits larger barriers, 25.3 and 23.7 kcal mol^{-1} , compared to **Mn-1**, 21.3 kcal mol^{-1} and relative to **A**. In this sense, our DFT predictions are in agreement with experiments suggesting that the P^{Ph} PNN ligand confers to the manganese catalyst superior behaviour over those functionalised with aliphatic phosphines.

In conclusion, a new hydrogenation of the CO_2 -derived COCs to alcohols using a homogenous base metal complex is reported.^[19] The reaction is catalysed by a new bench stable Mn-PNN complex, proceeds with high selectivity under mild conditions, without generation of any waste or side products. A variety of 5- and 6-membered COCs were employed to furnish methanol and vicinal diols in very good to quantitative yields, providing a milder and indirect route for the production of methanol from CO_2 . Besides, the successful development of the recycling of polycarbonates with the simultaneous formation of valuable diols and methanol has been achieved. These preliminary results might lead to further development of more cost-effective catalytic hydrogenation systems which could offer a sustainable alternative for the ethylene carbonate hydrolysis as well as the existing waste recycling methods. The reaction mechanism was studied using D-labelling experiments and density functional theory. The process is characterised by three catalytic cycles of heterolytic cleavage of three dihydrogen molecules by metal-ligand cooperation.

Acknowledgements

L.M.A. and L.C. acknowledge King Abdullah University of Science and Technology (KAUST) for support. Gratitude is also due to the KAUST Supercomputing Laboratory using the supercomputer Shaheen II for providing the computational resources.

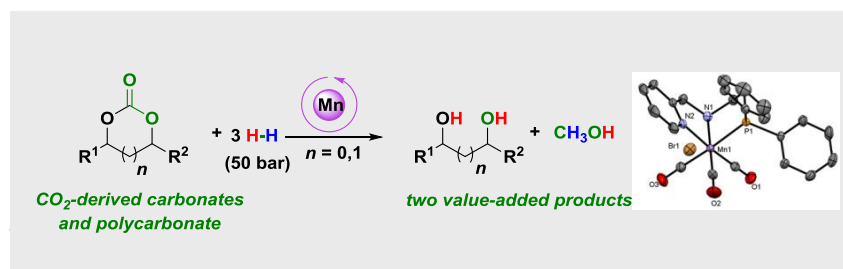
Keywords: manganese • reduction • CO_2 • carbonates • methanol

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