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Manganese Catalysed Hydrogenation of Organic Carbonates to Methanol and Alcohols.

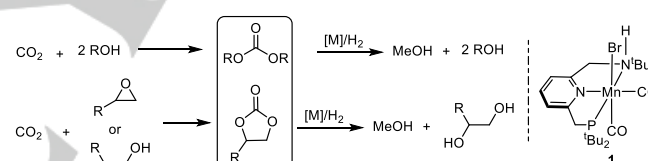
Amit Kumar, Trevor Janes, Noel Angel Espinosa-Jalapa and David Milstein.*

Abstract: The first example of a homogeneous catalyst based on an earth-abundant metal for the hydrogenation of organic carbonates to methanol and alcohols is reported. Based on the mechanistic investigation which indicates metal-ligand cooperation between the manganese center and the N-H group of the pincer ligand, we propose that the hydrogenation of organic carbonates to methanol occurs via formate and aldehyde intermediates. The reaction offers an indirect route for the conversion of CO₂ to methanol, which coupled with the use of an earth abundant catalyst, makes the overall process environmentally benign and sustainable.

Of all families of organic carbonyl compounds, carbonic acid derivatives are among the most difficult to hydrogenate.^[1] As a matter of fact, cyclic carbonates are used as solvents for hydrogenation reactions.^[2] This is because the reactivity of carbonyl groups towards hydrogenation depends on their polarizability; more electrophilic carbonyl groups exhibit higher reactivity towards hydrogenation. The common trend for the polarizability of carbonyl groups is: aldehyde > ketone > anhydride > imide > ester > acid > amide >> carbonate > carbamate > urea.^[3] In particular, hydrogenation of organic carbonates is a desirable reaction because of its relevance to the indirect synthesis of methanol, a versatile chemical and a potential fuel, from CO₂, a waste product and greenhouse gas (Scheme 1). Although the direct hydrogenation of CO₂ to methanol has been intensively explored, relatively harsh conditions and/or use of additives are required which present an opportunity for the indirect approach.^[4] A few years ago, we reported the first catalytic hydrogenation of organic carbonates and carbamates, which are readily available from CO₂, to methanol and alcohols using ruthenium pincer catalysts, thus providing a mild, low pressure two-step process for the conversion of CO₂ to methanol.^[5] We have also reported a process of CO₂ capture (at 1-3 bar) as a cyclic carbamate using ethanolamine, combined with its direct hydrogenation to form methanol.^[6] Ding also reported ruthenium catalysed hydrogenation of cyclic carbonates to methanol and diols.^[7] The process can be viewed as a modified *Omega process* in which an epoxide reacts with CO₂ to form a cyclic carbonate, which is hydrogenated to form ethylene glycol and methanol instead of ethylene glycol and CO₂. Despite the significance of this reaction, reports of hydrogenation of organic carbonates using homogeneous catalysts are limited to ruthenium.^[8] For cost effective production and availability, catalysts based on earth abundant metals are desirable.

Recently, there has been much interest in the

hydrogenation/dehydrogenation catalysis using earth abundant metals such as manganese, iron and cobalt.^[9] In particular, manganese pincer complexes have exhibited unique and unprecedented catalytic activities such as dehydrogenative formation of amide bonds.^{[9],[10]} We and others have previously reported on the hydrogenation of ketones, esters, acids, amides and nitriles using catalysts based on earth abundant metals.^[9] Hydrogenation of CO₂ to formic acid/formate catalysed by pincer complexes of earth-abundant metals has also been reported.^[11] Recently, Prakash has reported manganese catalysed conversion of CO₂ to methanol via the formation of formamide in presence of an amine.^[12] However, high pressure of CO₂ (>30 bar) is required for the formation of formamide, whereas organic carbonates can be formed at mild pressure of CO₂ and even at atmospheric pressure in some cases.^[13] Thus, hydrogenation of carbonates presents an attractive strategy for the conversion of low pressure CO₂ to methanol. To the best of our knowledge there is no report on the hydrogenation of organic carbonates by homogeneous catalysts based on an earth abundant metal. We present here the hydrogenation of carbonates catalysed by a complex of the earth abundant manganese.



Scheme 1. Synthesis of organic carbonates from CO₂ and subsequent hydrogenation to form methanol. Manganese complex **1** used in this report is shown on the right.

We recently reported the catalytic hydrogenation of esters using the manganese pincer complex **1** in which the N-H group of the pincer ligand is crucial for the catalytic process, involving metal-ligand cooperation.^[14] Complex **1** was also used by us for the direct synthesis of cyclic imides by dehydrogenative coupling of diols and amines.^[10] Using 1-2 equivalents of base (KH or KO^tBu), complex **1** is deprotonated to form the corresponding amido complex that has been proposed to be the catalytically active species. In pursuit of efficient base-metal catalysts for the hydrogenation of organic carbonates, we tested the catalytic utility of complex **1**. Interestingly, heating a toluene solution of complex **1** (2 mol%), KH (2 mol%) and dimethyl carbonate at 110°C under 30 bar H₂ for 16 h resulted in 60% conversion of dimethyl carbonate to the corresponding amount of methanol, as detected by GC-MS and ¹H NMR spectroscopy. Increasing the reaction time to 30 h and the amount of base to 4 mol% resulted in approximately quantitative conversion of dimethyl carbonate to methanol, which was detected in 90% yield by ¹H NMR spectroscopy. Encouraged by this result, we explored the hydrogenation of other types of carbonates. Under the same catalytic conditions, hydrogenation of diethyl carbonate resulted in the formation of ethanol and methanol in 97% and 95% yields, respectively. Dibenzyl carbonate, diphenyl carbonate and unsymmetrical methyl carbonates

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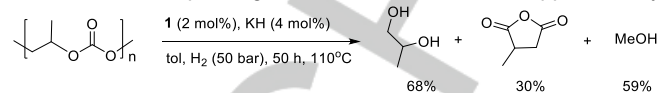
Table 1. Manganese catalysed hydrogenation of carbonates.

Entry	carbonate	conversion	alcohol/diol yield	methanol yield
		$\xrightarrow[\text{tol, H}_2 \text{ (30 - 50bar), 30 - 50 h, 110}^\circ\text{C}]{\text{1 (2 mol\%), KH (4 mol\%)}}$ $2 \text{ ROH} + \text{MeOH}$		
1 ^a		99%	-	90%
2 ^a		99%	97%	95%
3 ^a		99%	98%	72%
4 ^a		85%	84%	62%
5 ^a		99%	99%	92%
6 ^a		99%	92%	88%
7 ^a		99%	99%	92%
8 ^a		92%	85%	77%
9 ^a		99%	99%	74%
10 ^a		99%	99%	74%
11 ^a		99%	99%	66%
12 ^b		94%	92%	76%
13 ^b		99%	99%	99%
14 ^b		99%	99%	92%

^aReaction conditions: carbonate (3 mmol), complex **1** (0.06 mmol), KH (0.12 mmol), toluene (2 mL), 110°C, H₂ (30 bar), 30 h. Products were determined by GC-MS using mesitylene as an internal standard. Conversion of carbonates and yields of methanol/alcohols are based on ¹H NMR spectroscopy using mesitylene as an internal standard. ^bReaction conditions: carbonate (3 mmol), complex **1** (0.06 mmol), KH (0.12 mmol), toluene (2 mL), 110°C, H₂ (50 bar), 50 h. Conversion of carbonate and yields of methanol and diols are based on ¹H NMR spectroscopy using mesitylene as an internal standard.

(Table 1, entries 5-11) were also hydrogenated to afford the corresponding alcohol and methanol in good to excellent yields. We then used complex **1** for the hydrogenation of the more challenging cyclic carbonates. Under the optimized conditions used for the

hydrogenation of acyclic carbonates, only 60% conversion of propylene carbonate was observed, forming propylene glycol and methanol in ~60% and 45% yields, respectively. Increasing the hydrogen pressure to 50 bar and reaction time to 48 h resulted in the quantitative conversion of propylene carbonate to propylene glycol and methanol. Ethylene carbonate and styrene carbonate were also successfully hydrogenated under the optimized catalytic conditions to afford the corresponding diols and methanol in approximately

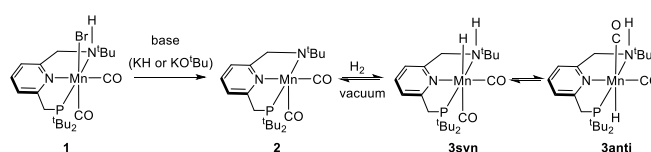


quantitative yields.

Scheme 2. Catalytic hydrogenative depolymerization of poly(propylene carbonate).

After successfully hydrogenating a broad scope of carbonates to methanol and alcohols, we tested the catalytic activity of complex **1** towards the hydrogenative depolymerization of poly(propylene carbonate) which is a thermoplastic material prepared from the copolymerization of CO₂ with propylene oxide or propylenediol.^[15] Hydrogenation of poly(propylene carbonate) was attempted using the catalytic conditions optimized for the cyclic carbonates. Analysis of the product mixture by GC-MS and the ¹H NMR spectroscopy revealed the formation of methanol and propylenediol in 59% and 68% yields, respectively. The remaining product was propylene carbonate in approximately 30% yield (Scheme 2). This provides a route for treatment of waste polycarbonates to useful chemicals using an earth abundant Mn-based catalyst, which has been reported before using ruthenium.^[16]

In order to understand the mechanism of the hydrogenation of carbonates catalyzed by complex **1** we performed some stoichiometric experiments. We have previously reported that complex **1** in the presence of base forms the deprotonated amido complex **2** that reversibly adds H₂ to form the manganese hydride complexes **3syn** and **3anti** which are in equilibrium (Scheme 3).^[14] The hydride complex **3syn** can be independently prepared *in-situ* by the reaction of complex **1** with NaBEt₃H.^[14]

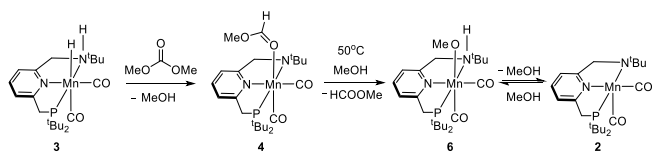


Scheme 3. Reaction of complex **1** with base to form **2** and its further reaction with H₂.

The reaction of the *in-situ* prepared complex **3** with 2-3 equivalents of dimethylcarbonate in toluene-*d*₈ was studied. After 5 minutes at room temperature, ³¹P NMR spectroscopy showed complete consumption of complex **3** and appearance of two sharp singlets at δ 142.9 and δ 114.8 and a broad signal at δ 134.5 due to complex **2**. ¹H NMR spectroscopy showed a broad signal at δ 10.9, tentatively assigned to the methyl formate complex **4**. Heating the reaction mixture at 50°C for 4 h resulted in the complete consumption of **4**. Additionally, the broad signal of complex **2** (δ 134.5) became sharp, whereas the sharp singlet at δ 114.8 became broad. We suggest that the signal at δ 114.8 is due to the methoxide complex **6** and that it exists in equilibrium with complex **2** and free methanol (*vide infra*). Reaction of independently prepared complex **2** with 2 equivalents of methyl formate also resulted

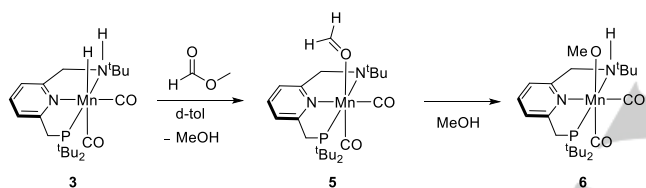
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in the signal at δ 10.9 in the ^1H NMR spectrum, consistent with the identity of complex **4**.



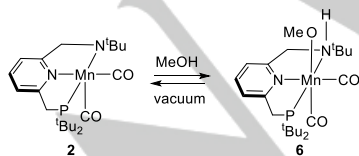
Scheme 4. Reaction of *in-situ* prepared complex **3** with dimethyl carbonate.

In support of our hypothesis that the hydrogenation of carbonates to alcohols proceeds via a formate intermediate, the hydrogenation of methyl formate under the catalytic conditions described in Table 1 (condition a) was performed which resulted in the formation of methanol in 85% yield. Additionally, we performed the reaction of the *in-situ* prepared complex **3** with 2-3 equivalents of methyl formate in toluene- d_6 . $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after 30 minutes at room temperature showed complete consumption of complex **3** with the concomitant formation of the methoxide complex **6** (*vide infra*) and the appearance of a new signal at δ 135.7 which was tentatively assigned to a formaldehyde bound manganese complex **5** (Scheme 5). ^1H NMR spectroscopy showed a broad signal at δ 9.68, shifted downfield from free formaldehyde (δ 8.73 in toluene- d_6) indicating the formation of complex **5**.



Scheme 5. Reaction of *in-situ* prepared complex **3** with methyl formate.

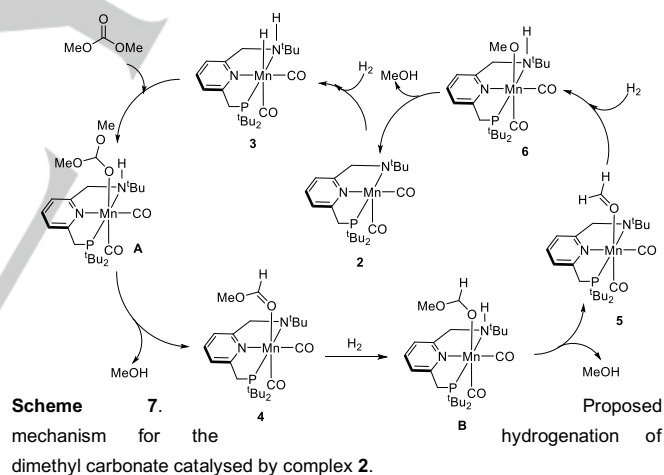
In order to confirm the identity of complex **6**, we attempted to independently synthesize it by the reaction of complex **2** with methanol. Addition of ~ 30 equivalents of methanol to the toluene- d_6 solution of complex **2** resulted in an immediate colour change from dark blue to orange. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a clean signal at δ 116.04 similar to the one observed for an analogous manganese alkoxide complex previously reported by us.^[10] Interestingly, evaporating the orange solution resulted in a blue solid. A solution of this solid in toluene- d_6 exhibited in the $^{31}\text{P}\{^1\text{H}\}$ spectrum a broad signal at δ 123.6 which upon cooling to 250 K split into two sharp singlets at δ 134.0 and δ 116.0 corresponding to complexes **2** and **6**, respectively. This indicates that complexes **2** and **6** exist in equilibrium in solution (Scheme 6). Attempts to grow single crystals of complexes **4-6** were not successful.



Scheme 6. Equilibrium between complex **2** and **6**.

Based on these experiments we propose a mechanism for the catalytic hydrogenation of carbonates as outlined in Scheme 7. This mechanism is similar to the one previously proposed by us for the hydrogenation of carbonates catalysed by ruthenium-based pincer complexes involving metal-ligand cooperation via

aromatization/dearomatization of the lutidine-based ligand backbone.^[5] Complex **1** in the presence of base generates the amido complex **2** by deprotonation of the N-H proton. We have previously shown that complex **2** is an active catalyst for the hydrogenation of esters.^[14] When a catalytic reaction was performed under the conditions described for entry 2 (Table 1) using the independently isolated complex **2**, complete conversion of diethyl carbonate to ethanol and methanol in more than 90% yield was observed, indicating that complex **2** is an active catalytic species in the hydrogenation of carbonates. In presence of H_2 , complex **2** immediately forms the hydride complex **3** as previously reported by us.^[14] Hydride transfer from complex **3** to the carbonyl group of the carbonate (shown in Scheme 7 as dimethyl carbonate) results in the formation of the intermediate **A** which then releases methanol through abstraction of N-H proton by the methoxide moiety, leading to formation of the formate complex **4**. Addition of hydrogen to complex **4** followed by subsequent hydride transfer to the bound methyl formate can result in the formation of intermediate **B**. Deprotonation of the N-H proton by the adjacent methoxide group releases the free methanol and forms the bound formaldehyde complex **5**. Complex **5** can undergo a similar hydrogenation step to form the methoxide complex **6** which upon proton abstraction can liberate methanol and regenerate the active catalyst **2**. Although dissociation of a CO ligand from the proposed catalytically active species **2** could offer a more active species for the H_2 activation, we believe that this is unlikely; the IR stretching frequency for the CO ligands in complex **2** are 1797 and 1874 cm^{-1} as previously reported by us^[14], indicating very strongly bound CO ligands.



Scheme 7. Proposed mechanism for the hydrogenation of dimethyl carbonate catalysed by complex **2**.

In conclusion, we have demonstrated the first example of an earth-abundant metal complex catalyst for the efficient hydrogenation of carbonates to the corresponding alcohols and methanol. The reaction is catalysed by the precatalyst **1** in presence of catalytic base, and it can also take place *under base-free conditions* using the actual catalyst, the amido catalyst **2**. A wide variety of carbonates, including symmetrical and unsymmetrical acyclic carbonates and cyclic carbonates were hydrogenated under moderate catalytic conditions. Moreover, hydrogenation of poly(propylene carbonate) was also demonstrated, providing a route for treatment of waste plastic based on this polymer using an earth-abundant complex. A plausible mechanism that involves metal-ligand cooperation between the manganese center and the N-H bond of the ligand is proposed. Overall, the process offers an indirect but efficient and sustainable route for the conversion of CO_2 to methanol.

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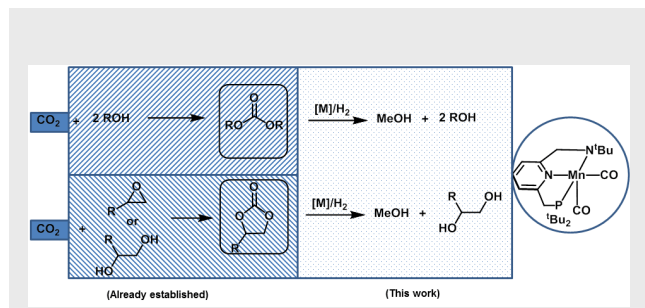
This research was supported by the European Research Council (ERC AdG 692775). D. M. holds the Israel Matz Professorial Chair of Organic Chemistry. A.K. is thankful to the Israel Planning and Budgeting Commission (PBC) for a fellowship. T.J. thanks the Azrieli Foundation for a postdoctoral fellowship. N. A. E.-J. thanks Mr. Armando Jinich for a postdoctoral fellowship.

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The first example of a homogeneous catalyst based on an earth-abundant metal for the hydrogenation of organic carbonates to methanol is reported. The reaction is catalyzed by a manganese pincer complex and offers an indirect route to convert CO₂ to methanol, making the overall process environmentally benign and sustainable.