

# Reduction of Cyclic and Linear Organic Carbonates Using a Readily **Available Magnesium Catalyst**

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Supporting Information

ABSTRACT: Efficient reduction of cyclic and linear organic carbonates catalyzed by a readily available earth alkaline catalyst has been achieved. The described homogenous reaction based on a ligand-free magnesium catalyst provides an indirect route for the conversion of CO<sub>2</sub> into valuable alcohols. The reaction proceeds with high yields under mild reaction conditions, with low catalyst loading and short



reaction times, and shows a broad applicability toward various linear and cyclic carbonates. Additionally, it can be applied for the depolymerization of polycarbonates.

KEYWORDS: magnesium, carbonates, hydroboration, carbon dioxide, alkaline base earth-abundant metal

ecent years have shown progress in the application of  $\mathbf{\Gamma}$  carbon dioxide as a  $C_1$  building block.<sup>1</sup> One of the industrially applied approaches for the reduction of atmospheric CO<sub>2</sub> emissions is the use of this greenhouse gas in reactions with alcohols or epoxides to form organic carbonates. Especially, the latter method is based on an economic and environmental rationale as it not only provides commercially important chemicals but also utilizes readily available epoxides.<sup>2</sup> The following reduction of organic carbonates results in a two-step route conversion of CO<sub>2</sub> into methanol and value-added diols or their derivatives.

However, reduction of organic carbonates is disfavored because of their high stability. Therefore, organic carbonates can be used as solvents, even in reductive transformations involving metal hydride species.<sup>3</sup> For this reason, only few examples of carbonate reductions have been reported to date.<sup>4,5</sup> Direct hydrogenation, the most common method for the reduction of carbonates has been studied in the past. However, all protocols are based on transition-metal catalysts and often require high pressures and temperatures.<sup>4</sup>

Boranes are often used as alternative reducing agents in order to circumvent high-pressure hydrogenations with the use of the flammable hydrogen gas. Thus, the hydroboration of carbonates is an interesting alternative. Recently, Leitner and co-workers reported an interesting transition metal-catalyzed reduction of organic carbonates using pinacolborane as a reducing agent.<sup>5</sup> However, efficient transition metal-free protocols based on earth alkaline metals remain an elusive goal. Thus, the use of a readily available magnesium catalyst which could be used in 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 1).

Scheme 1. MgBu<sub>2</sub>-Catalyzed Hydroboration of Carbonates This work: Earth alkaline metal catalysis



Furthermore, 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. Based on our interest in earth alkaline metal catalysis and in particular magnesium catalysis, we wondered whether a readily available magnesium catalyst could be applied in the reduction of CO<sub>2</sub>-derived carbonates.

Although magnesium is one of the most abundant metals on earth, the application of magnesium-based catalysts for organic reactions is still relatively unexplored compared with other

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metals.<sup>6–8</sup> Recently, magnesium complexes, such as  $\beta$ -diketiminato-magnesium complexes,<sup>9,10</sup> have been employed for the hydroboration of unsaturated polarized bonds, including aldehydes, ketones, and esters.<sup>11–13</sup> Our group reported a protocol for the selective hydroboration of terminal and internal alkynes catalyzed by commercially available MgBu<sub>2</sub>.<sup>11a</sup> Mechanistic studies revealed that in the presence of the reductant HBpin, an active BuMgH species is formed in situ.<sup>14</sup> Given the growing interest in earth alkaline metal-catalyzed organic transformations and the valorization of CO<sub>2</sub> and its derivatives, we decided to examine Mg-catalyzed reduction of carbonates as well as the extension to the recycling of polycarbonates with simultaneous generation of valuable diols and methanol (Scheme 1).

To develop a practical reduction protocol for the rather stable and challenging cyclic carbonates, we started to explore a magnesium-catalyzed protocol which should proceed with low catalyst loading and under mild reaction conditions. Hence, we chose cyclic carbonate 1a as our model substrate and run initial screening of solvents, as well as the reaction under solvent-free conditions, at ambient temperature (Table 1, entries 1-4).

Table 1. Optimization of MgBu<sub>2</sub>-Catalyzed Hydroboration of Carbonate  $1a^a$ 

0	MgE HBPin	<sup>3</sup> u <sub>2</sub> (cat.) (3.1 equiv.)	PinBO	OBPin	Pin + CH₃OBPin	
Ph	_/ s	olvent	Ph	·		
	1a		I			
entry	solvent	cat. (%)	temp. ( $^{\circ}C$ )	time (h)	yield (%) <sup>b</sup>	
1	toluene-d <sub>8</sub>	5	23	4	78	
2	$THF-d_8$	5	23	4	52	
3	benzene-d <sub>6</sub>	5	23	4	81	
4	neat	5	23	4	71	
5	toluene- $d_8$	5	65	3	>95	
6	toluene-d <sub>8</sub>	3	65	3	>95	
7	toluene- $d_8$	2	65	3	88	
8	toluene- $d_8$	3	65	2	92	
9 <sup>c</sup>	toluene- $d_8$	3	65	2	82	
10	toluene- $d_8$	-	65	3	<5	

<sup>*a*</sup>**1a** (1 mmol), HBpin (3.1 equiv), MgBu<sub>2</sub> (2–5 mol %, 0.5 M in heptane), solvent [1 M] at a given temperature. <sup>*b*</sup>Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup>With  $\beta$ -diketiminate–MgBu **I**.

Analysis of the crude reaction mixture by <sup>1</sup>H NMR spectroscopy revealed that **2a** and MeOBpin were the only products formed during the reaction. However, under these conditions, the reactions were not complete within 4 h and significant amounts of carbonate were still present in the crude mixtures. Further optimization was carried out with toluene as a solvent. Increasing the reaction temperature allowed the achievement of full conversion (Table 1, entry 5). Furthermore, we decided to lower the amount of the catalyst (Table 1, entries 6–7), and thus the optimal catalyst loading of 3 mol % was established. It is worth mentioning that use of  $\beta$ -diketiminate—MgBu complex I also provided the product; however, lower yield was observed (entry 8 vs 9). In the absence of the catalyst, no conversion of 1a was observed (Table 1, entry 10).

Under the optimized reaction conditions, we investigated the scope and limitations of this transformation. In general,

excellent yields were obtained (Table 2). Ethylene carbonate (1b) and its derivatives bearing aliphatic substituents, such as Me (1c), Et (1d), n-Hex (1e), and even sterically hindered t-Bu (1f), were efficiently reduced with excellent yields within 3 h. Hydroboration of glycerol derivatives with methyl (1h) and benzyl (1i) as protecting groups, as well as free OH group (1g) resulted in the formation of the desired products in excellent yields. Chemoselective reduction of unsaturated carbonate (1j) was also possible, and no product of reduction of C-C double bond was observed. Cyclic cis- and trans-diol derivatives (2k and 2l, respectively) were obtained with excellent yields regardless of the stereochemistry of the starting material. Sixmembered ring organic carbonates also underwent efficient hydroboration, affording the corresponding 1,3-diol derivatives (2m-2p) bearing various alkyl and aryl substituents. The lower activity observed in the case of 1,3-dioxan-2-one (1m) can be attributed to the lower solubility of the starting material.

Linear carbonates, especially aliphatic ones, usually require harsher conditions in order to achieve good conversions.<sup>15</sup> To our delight, by simply prolonging the reaction time to 4 h, we were able to reduce methyl, ethyl, and benzyl carbonates (1q-1s) with full conversions and excellent yields. Phenol-derived carbonates, both cyclic and linear (1t, 1u), required an elevated temperature to yield the corresponding products in 90-92% yield. Further exploration focused on the depolymerization of polycarbonates. Polypropylene carbonate (1v) which can be made from propylene and CO2, smoothly underwent hydroboration in the presence of the magnesium catalyst. In general, we were delighted to see that our earth alkaline metal catalyst based on low-cost and commercially available MgBu<sub>2</sub> competes favorably with the existing protocols in terms of broader substrate scope and milder reaction conditions. To demonstrate the practical applicability of the developed reaction, a gram-scale reduction of carbonate 1g was carried out (Scheme 2). After hydrolysis in acidic conditions, we obtained the deprotected alcohol 3 in 82% yield.<sup>16</sup>

The MgBu<sub>2</sub>–HBpin catalytic system has been also tested for the reduction of  $CO_2$  (Scheme 3). In this case, elevated temperature and 10 mol % of the catalyst were necessary for the full consumption of HBpin, leading exclusively to the Bpinprotected methanol derivative.<sup>16,17</sup>

In agreement with the previous study, reaction of MgBu<sub>2</sub> with HBpin gives the active species BuMgH, alongside with BuBpin (Scheme 4a).<sup>11a</sup> For better understanding of the reaction mechanism, we conducted several additional control experiments. We reasoned that the hydroboration of carbonates proceeds in three separated catalytic cycles with the corresponding formate and formaldehyde as intermediates. When the reaction with the plausible intermediate formate 4 was carried out (Scheme 4b), we found that only in the presence of the Mg catalyst, the reduction was possible, meaning that each catalytic step requires the presence of the magnesium catalyst. Finally, when an equimolar mixture of carbonate 1s and formate 5 was tested in a competitive reaction, we found out that only formate 5 was reduced quantitatively, whereas the carbonate 1s remained unreacted (Scheme 4c). With this finding, we reasoned that the ratelimiting step is the first Mg-H addition to the carbonate.

Based on the results and control experiments, we propose a mechanism for the magnesium-catalyzed hydroboration of carbonates (Scheme 5a). Reaction of MgBu<sub>2</sub> with pinacolborane gives the active magnesium hydride species A. Carbonate 1 first reacts with magnesium hydride to form reactive

# Table 2. Magnesium-Catalyzed Hydroboration of CO<sub>2</sub>-Derived Carbonates<sup>a</sup>

Entry	Carbonate (1)	Product (2)	Yield (%) <sup>[b]</sup>	Entry	Carbonate (1)	Product ( <b>2</b> )	Yield (%) <sup>[b]</sup>
1	Ph 1a	OBPin Ph OBPin <b>2a</b>	>95	12	0 1I	PinBO OBPin	>95
2	0 0 1b	PinBOOBPin <b>2b</b>	88	13 <sup>[f]</sup>	0 0 0 1m	PinBO OBPin 2m	>95
3	0 1c	OBPin 2c	92	14	0 0 0 1n	PinBO OBPin <sup>2</sup> n	>95
4	0 1d	OBPin 2d	>95	15 <sup>[g]</sup>	Ph 10	Ph PinBO OBPin 20	>95
5		OBPin USPin 2e	94	16	0 0 0 1p	PinBO OBPin 2p	88
6	t-Bu	OBPin t-Bu OBPin 2f	93	17 <sup>[h]</sup>	0 1q	—OBPin 2q	93
7 <sup>[c]</sup>	0 1g	OBPin 2g PinBO OBPin 2g	93	18 <sup>[h]</sup>	~_0 <sup>0</sup> _0^ 1r	∕OBPin 2r	94
8 <sup>[d]</sup>	0 0 1h	OBPin OUOBPin 2h	>95	19 <sup>[h]</sup>	Bn <sub>o</sub> Bn 1s	OBPin 2s	>95
9 <sup>[d,e]</sup>	Bn Bn	OBPin <b>2i</b> Bn <sup>-0</sup>	>95	20 <sup>[f]</sup>	Ph <sub>O</sub> Ph 1t	OBPin 2t	92
10	o 1j	OBPin <b>2j</b>	>95	21 <sup>[f]</sup>	0 0 1u	PinBO OBPin	90
11		PinBO OBPin 2k	>95	22 <sup>[i]</sup>		OBPin 2c	91

<sup>*a*</sup>**1** (1 mmol), HBpin (3.1 equiv), MgBu<sub>2</sub> (3 mol %, 0.5 M in heptane), solvent [1 M] at 65 °C for 3 h. <sup>*b*</sup>Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup>4 equiv of HBpin was used. <sup>*d*</sup>Mesitylene was used as an internal standard. <sup>*c*</sup>Reaction time 8 h. <sup>*f*</sup>Reaction time 6 h at 85 °C. <sup>*g*</sup>C<sub>6</sub>D<sub>6</sub> was used as a solvent. <sup>*h*</sup>Reaction time 4 h. <sup>*i*</sup>Average  $M_n$  of starting material: ~50 000.

magnesium alkoxide intermediate C, which subsequently undergoes boron exchange with HBpin, regenerating the active species A. Thus, formed formate D enters the second catalytic cycle and reacts with the recovered active species A, leading to the reduction of ester bond and the formation of formaldehyde F and the corresponding intermediate E. The





## Scheme 3. MgBu<sub>2</sub>-Catalyzed Hydroboration of CO<sub>2</sub>



Scheme 4. Control Experiments for Mechanistic Studies (a) Formation of BuMgH Active Species; (b) Reduction of Plausible Intermediate; (c) Competing Reaction Rate of Equimolar Mixture of Carbonate and Formate

a) Formation of BuMgH active species



A. MgBu<sub>2</sub> (3 mol%): >95% conv.
 B. No catalyst: <5% conv.</li>

c) Competing reaction rate of equimolar mixture of carbonate and formate



second molecule of HBpin consumed in the reaction is necessary for the formation the final product **2** and the recovery of the active magnesium hydride species **A**, which closes the catalytic cycle. Finally, formaldehyde **F** is reduced to form magnesium methoxide **G**, which reacts with the third molecule of HBpin liberating MeOBpin. Given that  $\beta$ diketiminate–MgBu I catalyzes the reaction (Table 1, entry 9), the formation of LMgH<sub>2</sub>Bpin II in the reaction<sup>12b</sup> (Scheme 5b) cannot be fully excluded.

In summary, we report the first earth alkaline metalcatalyzed reduction of carbonates using a readily available magnesium catalyst. The new protocol shows a broad substrate scope, including various cyclic and linear carbonates. Furthermore, polycarbonates can be successfully recycled with the formation of the valuable diols and methanol. The procedure is characterized by its mild reaction conditions, fast reaction times, low catalyst loading, use of a readily available catalyst based on earth abundant magnesium, and avoidance of costly ligands as well as broad scope and competes favorably with the transition metal-catalyzed protocols. Mechanistic studies showed the formation of active BuMgH, which acts as a reducing catalyst and is involved in three sequential reduction cycles.

### ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b04086.

Experimental procedures, characterization, and NMR spectra (PDF)

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#### Notes

The authors declare no competing financial interest.





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(15) In some protocols for the transition metal-catalyzed direct hydrogenation of organic carbonates, the scope is limited only to cyclic carbonates. See for instance: refs.<sup>4a,e,g</sup>

(16) For the detailed experimental procedures, see Supporting Information.

(17) Magnesium complexes have been successfully employed for hydroboration of  $CO_2$ . For more detailed information, see: refs. 12c, 13a