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Reduction of Cyclic and Linear Organic Carbonates using a Readily Available Magnesium Catalyst

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ABSTRACT: The 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 CO₂ into valuable alcohols. The reaction proceeds with high yields under mild reactions conditions, with low catalyst loading, short reaction times and shows a broad applicability towards various linear and cyclic carbonates and can additionally be applied for the depolymerization of polycarbonates.

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

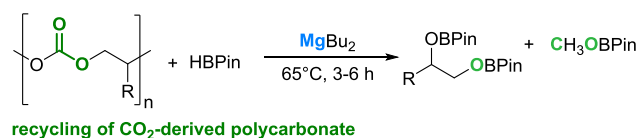
Recent years have shown progress in the application of carbon dioxide as a C₁ building block.^[1] One of the industrially applied approaches for reduction of atmospheric CO₂ emissions is the use of this Greenhouse gas in reactions with alcohols or epoxides to form organic carbonates. Especially the latter method is based on an economic and environmental rationale as not only it provides commercially important chemicals but also utilizes readily available epoxides.^[2] The following reduction of organic carbonates results a two-step route conversion of CO₂ into methanol and value-added diols or their derivatives.

However, reduction of organic carbonates is disfavored due to their high stability. Therefore, organic carbonates can be used as solvents, even in reductive transformations involving metal hydride species.^[3] For this reason only few examples of carbonate reductions have been reported to date.^[4,5] 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.^[4]

Boranes are often used as alternative reducing agents in order to circumvent high-pressure hydrogenations with 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 reducing agent.^[5] However, an 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).

This work: Earth alkaline metal catalysis

Commercially available magnesium catalyst



Scheme 1. MgBu₂-catalyzed chemoselective hydroboration of ketones.

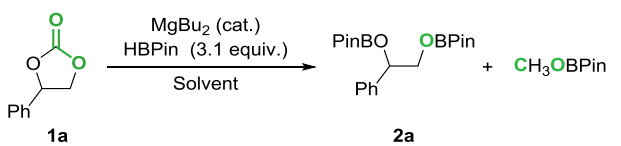
Furthermore, the successful development of such a process may also be extended to the recycling of polycarbonates with the simultaneous formation of valuable diols and methanol. Based on our interest in earth alkaline metal catalysis and in particular magnesium catalysis we wondered whether a readily available magnesium catalyst could be applied in the reduction of CO₂ 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 metals.^[6-8] Recently, magnesium complexes, such as β-diketiminato-magnesium complexes,^[9,10] have been employed for the hydroboration of unsaturated polarized bonds, including aldehydes, ketones and esters.^[11-13] Our group reported a protocol for the selective hydroboration of terminal and internal alkynes catalyzed by commercially available MgBu₂.^[11a] Mechanistic studies revealed that in the presence of the reductant HBPIn, an active BuMgH species is formed in situ.^[14] Giv-

en the growing interest in earth alkaline metal-catalyzed organic transformations and the valorization of CO₂ and its derivatives, we decided to examine a 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 in solvent-free conditions, at ambient temperature (Table 1, entries 1–4). Analysis of the crude reaction mixture by ¹H 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 hours 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 to achieve 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 to mention that use of a β-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).

Table 1. Optimization of MgBu₂-catalyzed hydroboration of carbonate **1a.**^[a]



Entry	Solvent	Cat. (%)	Temp. (°C)	Time (h)	Yield (%) ^[b]
1	Toluene-d ₈	5	23	4	78
2	THF-d ₈	5	23	4	52
3	Benzene-d ₆	5	23	4	81
4	Neat	5	23	4	71
5	Toluene-d ₈	5	65	3	>95
6	Toluene-d₈	3	65	3	>95
7	Toluene-d ₈	2	65	3	88
8	Toluene-d ₈	3	65	2	92
9 ^[c]	Toluene-d ₈	3	65	2	82
10	Toluene-d ₈	-	65	3	<5

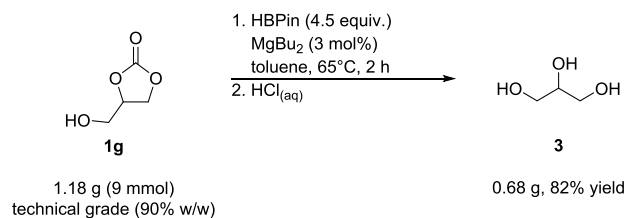
[a] **1a** (1 mmol), HBPin (3.1 equiv), MgBu₂ (2–5 mol%), 0.5 M in heptane), solvent [1 M] at given temperature. [b] Determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] With β-diketiminate-MgBu **I**.

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

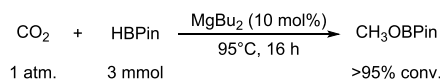
general, excellent yields were obtained (Table 2). Ethylene carbonate (**1b**) and its derivatives bearing aliphatic substituents, such as Me (**1c**), Et (**1d**), *n*-Hex (**1e**) and even sterically hindered *t*-Bu (**1f**), were efficiently reduced with excellent yields within 3 hours. Hydroboration 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. 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. Six-membered 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.^[5] To our delight, by simply prolonging the reaction time to 4 hours, 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 elevated temperature to yield the corresponding products in 90–92% yield. Further exploration focused on the depolymerization of polycarbonates. Polypropylene carbonate (PPC, **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 MgBu₂ competes favorably with 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.^[16]

The MgBu₂–HBpin catalytic system has been also tested for the reduction of CO₂ (Scheme 3). In this case, elevated temperature and 10 mol% of the catalyst were necessary for the full consumption of HBPin, leading exclusively to BPin-protected methanol derivative.^[16,17]

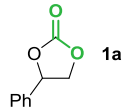
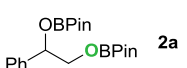
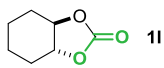
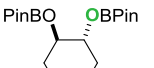
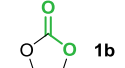
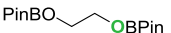

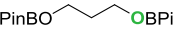
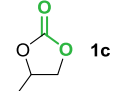


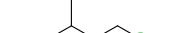
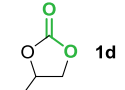
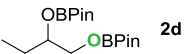

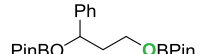
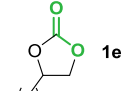
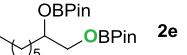

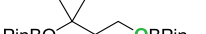
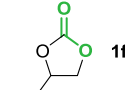
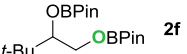

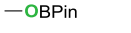
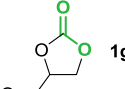
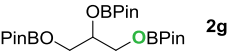
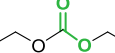

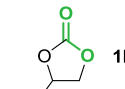
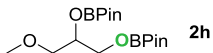
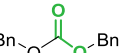
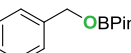
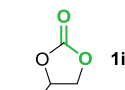


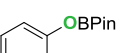
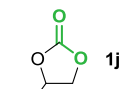

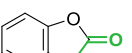
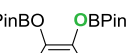
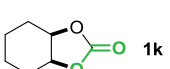
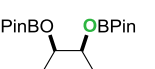
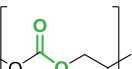



Scheme 2. Large-scale transformation.



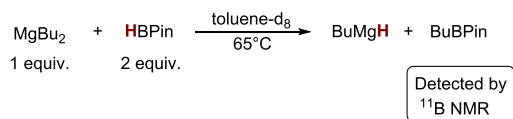
Scheme 3. MgBu₂-catalyzed hydroboration of CO₂.

Table 2. Magnesium-catalyzed hydroboration of CO₂-derived carbonates.^[a]

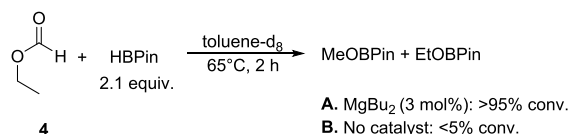
Entry	Carbonate (1)	Product (2)	Yield (%) ^[b]	Entry	Carbonate (1)	Product (2)	Yield (%) ^[b]
1			>95	12			>95
2			88	13 ^[f]			>95
3			92	14			>95
4			>95	15 ^[g]			>95
5			94	16			88
6			93	17 ^[h]			93
7 ^[c]			93	18 ^[h]			94
8 ^[d]			>95	19 ^[h]			>95
9 ^[d,e]			>95	20 ^[f]			92
10			>95	21 ^[f]			90
11			>95	22 ^[i]			91

[a] **1** (1 mmol), HBPin (3.1 equiv), MgBu₂ (3 mol%, 0.5 M in heptane), solvent [1 M] at 65°C for 3 h. [b] Determined by ¹H NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 4 equiv. of HBPin were used. [d] Mesitylene was used as an internal standard. [e] Reaction time 8 h. [f] Reaction time 6 h at 85°C. [g] C₆D₆ was used as a solvent. [h] Reaction time 4 h. [i] Average M_n of starting material: ~50,000.

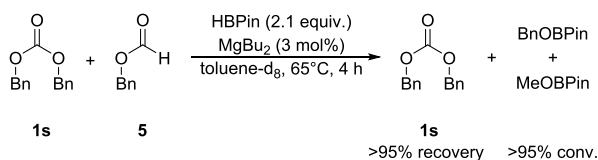
a) Formation of BuMgH active species



b) Reduction of plausible intermediate



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



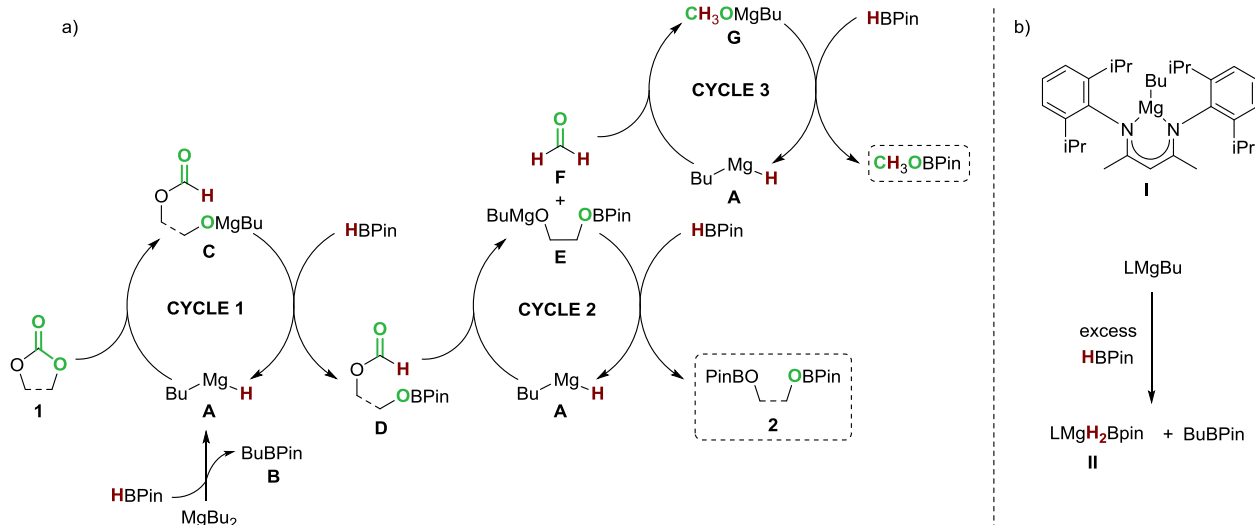
Scheme 4. Control experiments for mechanistic studies.

In agreement with the previous study, reaction of MgBu_2 with HBPIn gives the active species BuMgH , alongside with BuBPIn (Scheme 4a).^[11a] For the 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** were tested in a competitive reaction, we found out that only the formate **5** was reduced quantitatively, whereas the carbonate **1s** remained unreacted (Scheme 4c). With this finding, we reasoned

that the rate-limiting 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_2 with pinacolborane gives the active magnesium hydride species **A**. Carbonate **1** first reacts with magnesium hydride to form reactive 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 formation of formaldehyde **F** and the corresponding intermediate **E**. The 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 β -diketiminato- MgBu **I** catalyzes the reaction (Table 1, Entry 9), the formation of LMgH_2Bpin **II** in the reaction^[12b] (Scheme 5b) cannot be fully excluded.

In summary, we report the first earth alkaline metal-catalyzed 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, 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 reducing catalyst and is involved in three sequential reduction cycles.



Scheme 5. a) Proposed mechanism for MgBu_2 -catalyzed hydroboration of carbonates involving three sequential steps which require the Mg-H species. b) Formation of the alternative MgH species when β -diketiminato-magnesium complex is used.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization and NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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