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Magnesium-catalyzed hydroboration of organic carbonates, carbon dioxide and esters

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The low-valent magnesium(I) complex $[{^{XyI}Nacnac}Mg]_2$ was employed as a highly efficient precatalyst for the hydroboraton of a variety of cyclic and linear organic carbonates, polycarbonates, CO₂ and esters with HBpin under mild conditions. The resultant boronates can be used for the preparation of the corresponding value-added diols, triol or alcohols through hydrolysis.

Due to their high stability under ambient conditions, organic carbonates are frequently used as green solvents in synthesis and catalysis¹ and therefore the reduction of organic carbonates is a very challenging task. Recently, reduction of organic carbonates has attracted considerable attention because they can be readily prepared from CO₂ or CO etc renewable C1 feedstock, and further reduced to produce methanol derivatives.^{2,3} On the other hand, cyclic organic carbonates synthesized by the direct coupling between carbon dioxide and epoxides can be performed as protecting groups or synthetic precursors to obtain the corresponding diols which can be used in a wide range of chemicals and materials.⁴ These lead to a practical two-step route for the conversion of greenhouse gas CO₂ into methanol, value-added diols or their derivatives which is a promising solution to emerging global energy problem. Catalytic hydrogenation is an excellent method to reduce cyclic organic carbonates to form a variety of diols. However, it required highly pressurized and flammable hydrogen gas and high reaction temperature as well as using transition metals such as Ru, Mn, Fe complexes as catalysts commonly.^{2,3,5-10}

Recently, hydroboration of unsaturated organic compounds has gained increasing attention due to its high efficiency.¹¹⁻¹² For example, various magnesium complexes have been employed as efficient catalysts for the hydroboration of a series of unsaturated substrates such as aldehydes, ketones, isocyanates, imines, amides, pydidines, nitriles, and alkynes reported by Hill, Harder, Sadow, Okuda, Nembenna, Lin, Rueping et al., respectively.¹³ Moreover, boranes such as pinacolborane (HBpin) are relatively stable and easyto-handle thus circumventing the use of highly flammable and pressurized hydrogen gas or hazardous metal-hydride reducing agents. Hence catalytic hydroboration of organic carbonates is an interesting and possible alternative to the corresponding hydrogenation. However, only few examples of hydroboration of organic carbonates have been reported hitherto.^{14,15} Very recently Leitner et al. used transition metal manganese pincer complex [Mn(Ph₂PCH₂SiMe₂)₂NH(CO)₂Br] as a catalyst for the hydroboration of a variety of organic carbonates with HBpin as reducing agent. However, there are still significant limitations such as the requirement of additional base (NaO^tBu) and high reaction temperature (90 °C).^{14a} During the preparation of this manuscript, Rueping et al. reported dibutylmagnesium catalyzed hydroboration of carbonates guite recently. Nevertheless, it was still required to be carried out at relatively high reaction temperature (65-85 °C) and in toluene solvent.¹⁵ Meanwhile, hydroboration of esters is an efficient catalytic reduction process that avoids using traditional aggressive, functional-group intolerant reagents such as LiAlH₄ or LiBH₄ for the construction of complex molecules, preparation of materials and fine chemical production. To the best of our knowledge, few examples of esters hydroboration are reported because ester reduction is thermodynamically more challenging than aldehyde and ketone conversion.16-20

Compared to the transition metal, the main group metal magnesium is earth-abundant, cheap, and environmentally friendly. Since the first room temperate stable magnesium(I) complexes has been prepared by Jones et al.,²¹ considerable efforts have been made to study their reactivity,^{22,23} however, no catalytic application of magnesium(I) compounds have been reported except our two examples. Our group recently found that the magnesium(I) complex could be employed as an efficient precatalyst for the cyanosilylation and hydroboration of a variety of aldehydes, ketones, nitriles and alkynes under mild conditions.24 We wondered whether the lowvalent magnesium(I) catalyst could be extend to apply in the hydroboration of carbonates and esters. To our delight, we found that the highly efficient hydroboration of a wide range of cyclic and linear organic carbonates, carbon dioxide and esters catalyzed by various low-valent magnesium(I) complexes have been achieved under mild reaction condition. Herein, we reported these results.

We embarked on our investigation employing ethylene carbonate as a model substrate and HBpin as a reductant under neat condition at room temperature. Initially, the hydroboration of ethylene carbonate with 4 equiv. of HBpin was performed in the

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Table 1 Optimization of ethylene carbonate hydroboration

	+ n HBpin	$\frac{1 \text{ mol}\% \text{ Mg(I)}}{\text{rt}} \text{Bpin}^{C}$	2a	Bpin +	H ₃ C-OBpin
Entry	n	Cat	Т	Solvent	Yield
			(h)		(%) ^a
1	4	none	24	-	0
2	4	none	24	-	trace ^b
3	4	1	3	-	84
4	4	1	6	-	99
5	4	[(^{DippXyI} Nacnac)Mg] ₂	6	-	98
6	4	[(^{Mes} Nacnac)Mg] ₂	6	-	96
7	4	[(^{Dipp} Nacnac)Mg] ₂	6	-	83
8	4	1	6	THF	0
9	4	1	6	CHCl₃	34
10	4	1	6	Hexane	79
11	4	1	6	Et ₂ O	99
12	4	1	6	Benzene	99
13	4	1	6	Toluene	99
14	4	1	6	1,4- Dioxane	99
15	3	1	6	-	82
16	3	1	12	-	99
17	3.2	1	6	-	99
18	3.2	1	6	-	92 ^c
19	3.2	1	8	-	99 ^c
20	3.2	(^{XyI} Nacnac)MgI(OEt ₂)	6	-	85
				h	

 a The reaction was monitored by ^1H NMR spectroscopy. b 100 °C. c 0.1 mol%, 40 °C.

absence of any catalyst, no desired product was observed at room temperature after 24 h. Increasing the temperature to 100 °C, only trace yield was obtained even after 24 h which is similar to the result reported by Leitner et al. (Table 1, entries 1, 2).14a To our delight, when 1 mol% of magnesium(I) complex [(^{XyI}Nacnac)Mg]₂ (1, XyI = 2,6- $Me_2C_6H_3$) was added into the above reaction mixture, 84% yield was obtained after 3 h and ethylene carbonate was fully converted into the corresponding boronate ester ethylene glycol and methyl boronate only after 6 h at room temperature (Table 1, entries 3, 4). Methyl boronate is the actual reduction product from the central carbon of the ethylene carbonate group that originated from carbon dioxide. Subsequently, the catalytic performance of different sterically hindered magnesium(I) complexes [(ArNacnac)Mg]₂ (where Ar = DippXyl, Mes and Dipp; DippXyl = $2,6^{-i}Pr_2C_6H_3/2,6-Me_2C_6H_3$, Mes = 2,4,6-Me₃C₆H₂, Dipp = 2,6-ⁱPr₂C₆H₃) was examined. It can be seen that all these Mg(I) complexes can be used as efficient catalysts in the hydroboration of ethylene carbonate, however, the catalytic activity of Mg(I) complexes gradually decreased with increasing steric hindrance (Table 1, entries 5-7). Encouraged by these promising results, solvent effect was briefly screened. When tetrahydrofuran (THF) was used as a solvent, no hydroborated product was observed in 6 h (Table 1, entry 8). The reason could be that THF acted as a coordinated solvent to react with 1 to produce the corresponding magnesium adduct [(XyINacnac)Mg(THF)]2 and resulted in the deactivation of magnesium(I) complex. When chloroform or hexane was added, the corresponding hydroboration yield was 34% and 79% respectively (Table 1, entries 9, 10). However, to our surprise, when solvents such as diethyl ether, benzene, toluene, and 1,4-dioxane were employed, 99% yield was obtained in 6 h as neat conditions (Table 1, entries 11-14). Lowering the amount of HBpin to ideal 3 equivalents, a relatively lower yield (82%) was obtained in 6 h. Nevertheless, prolonging the reaction time to 12 h, 99% yield could be achieved as well (Table 1, entries 15, 16). When slightly increasing

the amount of HBpin to 3.2 equivalents, full conversion was achieved in 6 h at room temperature under neat condition too (Table 1) (entry 17). Decreasing the catalyst loading of 1 to 0.1 mol%, 99% yield was achieved in 8 h at 40 °C as well (Table 1, entries 18, 19). When the precursor of 1, (^{XyI}Nacnac)MgI(OEt₂), was tested under identical reaction conditions, a relatively low yield (85%) was obtained (Table 1, entry 20). Hence, the new main group Mg(I)-catalyzed protocol is much more efficient than the transition metal Mn-catalyzed hydroboration of carbonates (Mg: 40 °C, 0.1 mol%, 8h, 99% yield vs Mn: 90 °C, 0.1 mol% (with 0.3 mol% NaO'Bu), 8 h, 42-95% yield) and that of the divalent Mg(II) catalyst (Mg(I): rt, 1 mol%, 6 h, neat, 95-99% yield vs Mg(II): 65-85 °C, 1 mol%, 3-8 h, in toluene-d₈, 88-95% yield).^{14,15}

Table 2 Hydroboration of carbonates catalyzed by 1

$\begin{array}{c} O \\ O \\ O \\ O \\ O \\ O \\ R \\ O \\ C \\ O \\ C \\ O \\ R \end{array}$	3.2 HBpin $\frac{1 \mod \% Mg(I) 1}{\text{neat, rt, 6h}}$	pinBO_OBpin or + H ₃ C-OBpin 2 R-OBpin 2	$\left \begin{array}{c} Xyl \\ N \\ N \\ N \\ N \\ N \\ Xyl \end{array} \right $	$\begin{array}{c} Xyl \\ \downarrow \\ N = 0 \\ N = 0 \\ N = 0 \\ N = 0 \\ 1 \\ (1) \\ Xyl \end{array}$
Entry	Carbonates	Products		Yield (%)ª
1		BpinOOBpin	2a	99
2		BpinO OBpin	2b	97
3		BpinOOBpin	2c	96
4		BpinO OBpin	2d	99
5		BpinO OBpin	2e	99
6		BpinO OBpin	2f	99 ^b
7		BpinO OBpin	2g	99
8	Ph O o	BpinO Ph	2h	99
9		BpinOOBpin	2i	99
10		BpinO	2j	96
11		BpinOOBpin	2k	99
12		PhroBpin	21	99
13	Ph O Ph	PhOBpin	2m	98
14	$\sim_0 \stackrel{\forall}{\downarrow}_0 \sim$	EtOBpin	2n	99
15		EtOBpin + MeOBpin	20	98
16		MeOBpin (3 equiv.)	2р	99
17		OBpin	2q	95
18		BpinO OBpin	2c	96 ^c

^aThe reaction was monitored by ¹H NMR spectroscopy. ^b 4.2 HBpin. ^c0.5 ml C_6D_6 .

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With the optimized reaction conditions in hand, we explored the substrate scope of hydroboration reaction with various cyclic and linear structures carbonates (Table 2). All reactions underwent successful hydroboration using 1 mol% catalyst loading of 1 at room temperature under neat condition within 6 h. Five-membered ring carbonates with methyl and ethyl group gave very high yields similar to ethylene carbonate (Table 2, entries 2,3). Hydroboration of glycerol derivatives with methyl and benzyl and free OH group also produced the desired boronate products in excellent yield (Table 2, entries 4-6). It needs to be noted that when 4-vinyl-1,3-dioxolan-2one was used, hydroboration occurred at the carbonate functional group instead of terminal olefin group (Table 2, entry 7). Ethylene carbonate bearing aromatic substituent such as phenyl was efficiently reduced with high yield in 6h as well (Table 2, entry 8). Sixmembered ring carbonates also gave excellent yields of products (Table 2, entries 9-11). Surprisingly, in the aforementioned report by Leitner et al., the substrate 5,5-dimethyl-1,3-dioxan-2-one gave significantly lower yield of product (only 39%) due to its low solubility in pinacolborane.14 Gratifyingly, similar phenomenon did not occur in our subvalent Mg-catalyzed system, 96% yield was observed (Table 2, entry 10). In contrast to the lower conversion of linear carbonates hydroboration catalyzed by Mn catalyst,¹⁴ the Mg catalysts showed high reaction activities as their cyclic congeners. To our delight, both dibenzyl carbonate and diphenyl carbonate proceeded smoothly in quantitative yield (Table 2, entries 12,13). In the Mn-catalytic system, the hydroboration of ethyl methyl and dimethyl carbonate only offered 42% and 54% yield, respectively.¹² However, hydroboration of the corresponding linear carbonates catalyzed by magnesium 1 gave up to 99% yield (Table 2, entries 14-17). Additionally, our catalytic system was found to catalyze the hydroboration depolymerization of polycarbonates to the corresponding diboronate ester and methyl boronate. For example, polypropylene carbonate, which can be prepared from propylene and CO_2 , underwent hydroboration in the presence of **1** to produce boronate ester propylene glycol and methyl boronate in 96% yield (Table 2, entry 18).

To demonstrate the practical applicability of the new developed protocol, two representative substrates (**2c**, **2f**) were selected to prepare the corresponding diol and triol products *via* column chromatography, respectively. After successive hydroboration and hydrolysis, the corresponding desired 1,2-butanediol and glycerol were obtained in high total isolated yields (**Scheme 1**).

Scheme 1. Catalytic synthesis of boronate esters and alcohols

 $\begin{array}{c} & \begin{array}{c} & & \\ & &$

The high catalytic activity of the low-valent magnesium(I) **1** in the formation of methyl boronate ester from various carbonates prompted us to explore its ability to reduce CO_2 directly under similar conditions. To our delight, low-valent magnesium(I) **1** is able to catalyze carbon dioxide to afford the desired methoxy boronate in high yield using 5 mol% of **1** at 100 °C for 15 h (**Scheme 2**). **Scheme 2**. Hydroboration of CO_2 catalyzed by **1**

 $\frac{\text{CO}_2 + \text{HBpin}}{\text{(1 atm)}} \xrightarrow{5 \text{ mol}\% \text{ Mg(1) 1}} \frac{5 \text{ mol}\% \text{ Mg(1) 1}}{100 \text{ }^\circ\text{C}, 15\text{h}} \xrightarrow{\text{CH}_3\text{OBpin}} + \text{O(Bpin)}_2$

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$R_1 0^{1}$	rt, 1	$\begin{array}{c} & & \\ h & & \\ \end{array} $	- K ₂	OBpin
Entry	Substrate	Products		Yield (%)ª
1		OBpin	3a	99
2		OBpin	3b	99
3	Br _{(CH₂)5} 0 0	Br (CH ₂)5 OBpin + OBpin	3c	96
4		OBpin + OBpin	3d	95
5	Ph O Ph	Ph OBpin	3e	96
6	⟨ _s ⟩ ↓ 0 ↓ 0 ∩ ∩	S + OBpin + OBpin	3f	99
7		BpinO OBpin	3g	95
8		OBpin OBpin	3h	99
9	C ₆ H ₁₃ 0	C ₆ H ₁₃ OBpin OBpin	3i	96

^a The reaction was monitored by ¹H NMR spectroscopy.

Encouraged by the above organic carbonates hydroboration results, we then examined the similar esters hydroboration that can provide the corresponding alcohols and diols. We started our investigation with the reduction of ethyl acetate as a model substrate with 2 equiv. of HBpin under various reaction conditions. In the absence of any catalyst, the hydroboration between ethyl acetate and 2 equiv. of HBpin did not gave any alkoxyl boronate product in C₆D₆ after 1 h. Even increasing temperature to 70 °C, no any conversion could be observed after 15 h (Table S1, entries 1,2). This is similar to that the catalyst free hydroboration of benzyl benzoate exhibited a very negligible conversion.²⁰ However, when 5 mol% catalyst of 1 was added into the above mixture, the reaction completed in less than 10 min at room temperature. Lowering the catalyst loading of 1 to 1 mol%, a slightly longer reaction time (40 min) was required (Table S1, entries 3,4). When in solvent-free condition, the hydroboration of ethyl acetate also completed in 1 h (Table S1, entry 5). Decreasing the catalyst loading of 1 to 0.1 mol%, the reaction proceed smoothly with 99% yield in 5 h (Table S1, entries 6,7).

Success in the hydroboration of ethyl acetate promoted us to explore the substrate scope of a variety of esters. Hydroboration of various esters containing a wide range of functional groups including aliphatic, alkyl halides, conjugated double bonds, aromatic and thiophene all provided high yields in short time. Result of these catalytic esters hydroboration is summarized in **Table 3**. The corresponding alkoxyl boronate ester products were obtained in very high yield under 1 mol% of 1 in 1 h at room temperature for all esters tested. It should be noted that this catalytic system shows selectivity for the ester group over olefin group (Table 3, entry 4). The hydroboration of cyclic esters including lactide catalyzed by 1 also

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produced the corresponding dialkoxyl boronates in quantitative yield that could be further hydrolyzed to diols (Table 3, entries 7-9).

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In order to gain further insight into the reaction mechanism of carbonate hydroboration catalyzed by magnesium(I) complexes, some stoichiometric reactions between magnesium(I) 1 and HBpin or carbonate were attempted. The stoichiometric reaction between 1 and ethylene carbonate in 1:1 or 1:2 molar ratio has been performed, however, no new intermediate was observed via ¹H and ¹³C NMR spectra. The dimeric magnesium boryloxide complex $[(^{XyI}Nacnac)Mg(\mu-OBpin)]_2$ was obtained from the stoichiometric reaction between 1 and HBpin (1:2 or excess molar ratio etc). This is same to the report by Jones et al. that reactions of three magnesium(I) dimers with different equivalents of HBpin (1:2, 1:5 or 1:20) lead to complex mixtures of many products including a plethora of magnesium(II) complexes with oxygen-based fragments.²⁵ Based on the complex reactivity of magnesium(I) 1 towards HBpin it is difficult to propose a mechanism. We also conducted the reaction of ethyl formate (the plausible intermediate) with HBpin, the corresponding hydroboration products were found only in the presence of 1 (Scheme S1).

In conclusion, we have demonstrated the excellent catalytic performance of magnesium(I) 1 for the hydroboration of a wide range of CO2-derived cyclic five- and six-membered carbonates, linear carbonates, polycarbonates, and even carbon dioxide under mild condition. The new main group low-valent magnesium(I) catalytic system provides an indirect route for the conversion of CO₂ into methanol, value-added diol and even triol in high yield. The Mg(I)-catalyzed protocol is efficient than the corresponding transition metal manganese and divalent magnesium(II) catalyzed hydroboration of organic carbonates. In addition, it could act as an efficient precatalyst in the catalytic hydroboration of various esters under mild conditions as well. Further studies of the reaction mechanism and other potential catalytic applications of magnesium(I) complexes are in progress in our group.

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There are no conflicts to declare.

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The magnesium(I) complex was employed as a highly efficient precatalyst for the hydroboration of carbonates and esters under mild conditions.