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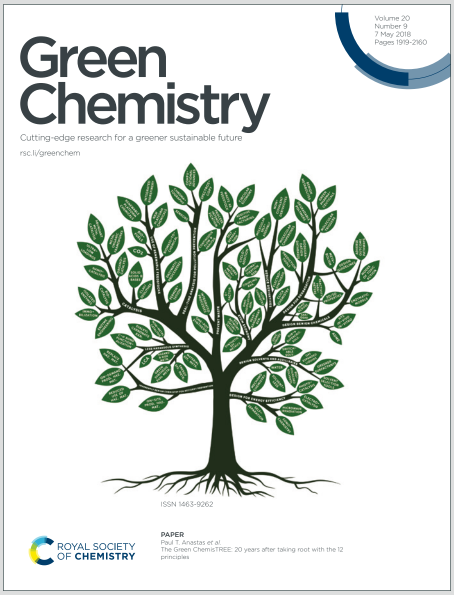

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Calcium carbide as a dehydrating agent for the synthesis of carbamates, glycerol carbonate, and cyclic carbonates from carbon dioxide

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Carbon dioxide (CO_2) is a nontoxic and inexpensive C1 building block, which can be used for the synthesis of valuable chemicals such as aromatic carbamates from anilines and methanol (MeOH), glycerol carbonate from glycerol, and cyclic carbonates from diols. However, these reactions generate water as byproduct and suffer from thermodynamic limits, which lead to low yields. Calcium carbide (CaC_2) is a renewable chemical, which can be recycled from calcium that is abundant in the Earth's crust. Furthermore, CaC_2 rapidly reacts with water. In this work, we used CaC_2 as dehydrating agent for the direct synthesis of carbamate (including polyurethane precursors) from amine, CO_2, and MeOH. All reagents were commercially available. In addition, CaC_2 was employed for the synthesis of glycerol carbonate from glycerol and CO_2 with a zinc catalyst and N-donor ligand. A similar protocol was applied to synthesize cyclic carbonates from diols and CO_2.

Introduction

Carbamates, which are precursors of polyurethanes, are important chemicals in medicinal and agricultural chemistry.[1-9] For example, in the polyurethane industry, isocyanates (R-NCO) generated by the thermal cracking of carbamate react with diols to produce polyurethanes.[4, 5, 10] Traditionally, carbamates are prepared from amines and phosgene ($COCl_2$) as a C1 synthon. Although this method is efficient, the determination of a nontoxic and green C1 building block is necessary to avoid the use of toxic phosgene lead.

CO_2 is a nontoxic and inexpensive gas. In addition, CO_2 is the main greenhouse gas, leading to an increase in the global temperature. The CO_2 can be considered as a renewable C1 building block in organic chemistry, which can be used to prepare valuable chemicals such as formic acid, MeOH, urea, salicylic acid, and polymers.[11-17] Carbamate can be directly synthesized from amine, CO_2, and alcohol.[1] One issue of this reaction is the thermodynamic limit, resulting in a low product yield.[18] A dehydrating agent can promote the shift of the reaction to the product side. Another issue is the synthesis of aromatic carbamate from aromatic amines (anilines) because aromatic amines have lower pK_a values than aliphatic amines, resulting in the low reactivities of aromatic amines.[19, 20] Although pioneer methods for the synthesis of carbamates from amines, CO_2, and organohalides (RX) were reported (Scheme 1A),[21-34] the use of alcohol as the coupling reagent is more sustainable compared with the use of organohalides (Scheme 1B). The synthesis of carbamates from amines, CO_2, and alcohols represents a new and sustainable method.[35-42] Dehydrating agents, such as acetals or ketals[43-45], nitriles[46-48], and Mitsunobu reagent,[49, 50] significantly improve the yields. Furthermore, metal alkoxides[51-53] and silicon alkoxides[54-56] (Scheme 1A) play bifunctional roles as dehydrating agents and alkoxy group donors.

CaC_2 is a stable solid, which can be produced from calcium, which is abundant in the Earth's crust.[57, 58] It has several applications in organic synthesis.[59] The CaC_2 rapidly reacts with water, and acetylene and energy are released (Scheme 1C). Han et al. reported the synthesis of dimethyl carbonate (DMC) from MeOH and CO_2 promoted by CaC_2.[60] We assume that water can be removed and energy can be released by the addition of CaC_2 to the system because the synthesis of carbamate from amine, CO_2, and alcohol is endothermic[18] and the byproduct is water, which leads to a shift of the carbamate synthesis reaction to the product side.

Glycerol is a coproduct of the production of biodiesel, which is the alcoholysis product of fatty acid. Glycerol has wide applications such as in the polymer production, pharmaceuticals, as food additive, and convert to other valuable chemicals.[61-65] One application is the conversion of glycerol to glycerol carbonate, which can be used for solvents, electrolyte liquids, cement and concrete, and cosmetics.[66-69] The synthesis of glycerol carbonate from glycerol requires a C1 synthon such as DMC, urea, or CO_2. When using CO_2, the transformation of glycerol to glycerol carbonate is difficult due

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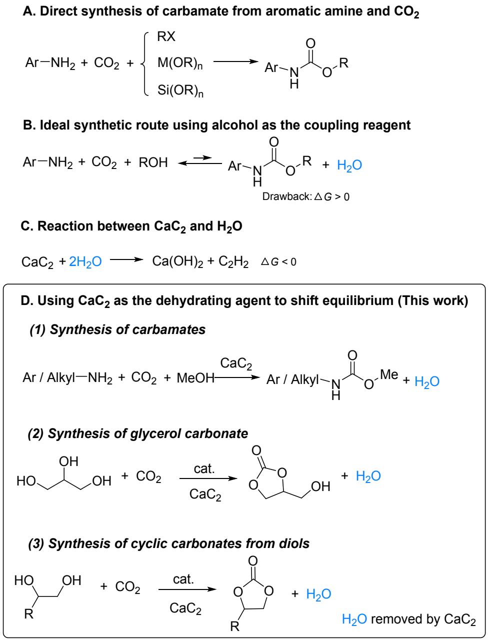
to the thermodynamic limit (ΔG = +23.92 kJ mol^{-1}) and low equilibrium constant ($K = 6.4 \times 10^{-5}$).[70] Procedures with various catalysts were documented.[71-85] Recently, it has been reported that the use of nitriles as dehydrating agents promotes the synthesis of glycerol carbonate from glycerol and CO_2.[86-89] Epoxides are also efficient additives[90] because cyclic carbonates are generated as C1 synthons to react with glycerol.



Scheme 1 Synthesis of carbamates from amines and CO_2.

In this paper, we describe the application of CaC_2 as a dehydrating agent for the direct synthesis of carbamates from amines, CO_2, and MeOH. Both aromatic and aliphatic carbamates were synthesized, with a yield reaching 98%. In addition, dicarbamates, that is, polyurethane precursors, with industrial applications were synthesized. Furthermore, based on the use of CaC_2, glycerol carbonate was successfully and directly synthesized from glycerol and CO_2 catalyzed using a zinc catalyst and N-donor ligand, with a 92% yield. The same protocol was also used for the synthesis of cyclic carbonates from diols and CO_2, with a yield reaching up to 98%. The above-mentioned three processes are summarized in Scheme 1D. The CaC_2 itself is a sustainable chemical and promotes the transformation of CO_2 into valuable products.

Results and Discussion

Initial research was carried out to synthesize methyl *N*-phenylcarbamate (**1**) from aniline, CO_2, and MeOH. The model reaction conditions were set to a 24-hour reaction at 180°C. Without CaC_2, no product was obtained (Table 1, entry 1) based on high-performance liquid chromatography (HPLC). Even if a CaC_2 equivalent of five was added, a reaction did not occur (Table 1, entry 2). The results show that the addition of a base (K_2CO_3) increases the yield of **1** to 28% (Table 1, entry 3). To increase the yield, we used a polar solvent instead of MeOH. Acetonitrile (MeCN, 3 mL) was used as solvent and the MeOH concentration (reagent) was reduced to 7.5 mmol (Table 1 entry 4). Based on this reaction, a yield of 72% was obtained. These results suggest that the base could be used to abstract a proton from aniline, which has a lower pK_a value than aliphatic amines. The yield could be increased by adding a polar solvent. The MeOH was used as the reagent in this reaction (Table 1, entry 4). Based on the use of 15 mmol MeOH (Table 1, entry 5), the yield of **1** was 98%. In addition to MeCN, other polar solvents, such as *N*,*N*-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) are also suitable for the reaction (see Supporting Information). However, based on the use of a higher concentration of MeOH (30 mmol, Table 1, entry 6), the yield decreased to 61% due to the cleavage of **1** to aniline through alcoholysis. The addition of more K_2CO_3 (2 mmol, entry 7) did not promote the reaction because a base promotes the alcoholysis of **1**. To sum up, entry 5 in Table 1 represents the best reaction conditions for further research.

The reaction temperature is also an important factor affecting the synthesis of **1** from aniline, CO_2, and MeOH due to its thermodynamically unfavorable properties. Based on our results[51, 53-56] and those of other groups,[47, 48] high-temperature reactions are often required. Figure 1 provides information about the yields as a function of the temperature and time. The yields strongly depend on the temperature between 150°C and 180°C. At 150°C, the yield of **1** is only 36% after a 24 h reaction. However, at 180°C, the yield of **1** reaches 93% after an 8 h reaction and slightly increases to 98% after 24 h. We did not observe the decomposition of **1** at 180°C, which contrasts our previous results.[54]

Based on the optimized conditions, we expanded the substrates and included aromatic amines, aliphatic amines, and diamines (Scheme 2). Products **1** to **11** represent carbamates synthesized from aromatic amines. The isolated yields reach up to 98%. Our protocol tolerates functional group such as halides (products **6**, **7**, and **8**), unsaturated bonds (products **9** and **10**), and cyanide (product **11**). Substrates with electron withdrawing groups are not preferable (product **11**). Moderate yields were obtained by using aliphatic amines products (**12**, **13**, and **14**). We successfully synthesized polyurethane precursors (products **15**, **16**, and **17**) from 2,4-diaminotoluene (TDA), 4,4'-diaminodiphenylmethane (MDA), and hexamethylenediamine (HMDA). Products **15**, **16**, and **17** have industrial applications in the preparation of toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), and hexamethylene diisocyanate (HDI), respectively, by thermal cracking.

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Table 1 Reaction optimization for the synthesis of **1** from aniline, CO_2, and MeOH dehydrated by CaC_2. [a]

Entry	amount of MeOH	amount of K_2CO_3	solvent	yield of **1**[b]
1[c]	3 mL	0	MeOH itself	trace
2	3 mL	0	MeOH itself	trace
3	3 mL	1 mmol	MeOH itself	28%
4	7.5 mmol	1 mmol	MeCN	72%
5	**15 mmol**	**1 mmol**	**MeCN**	**98%**
6	30 mmol	1 mmol	MeCN	61%
7	15 mmol	2 mmol	MeCN	60%

[a] Reaction conditions: aniline (0.5 mmol), CaC_2 (2.5 mmol), K_2CO_3, solvent (3 mL), CO_2 (5 MPa in a 10 mL autoclave), 24 h, 180°C. [b] Yields were determined by HPLC using toluene as the internal standard. [c] Without CaC_2.

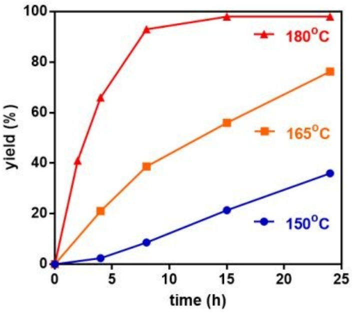
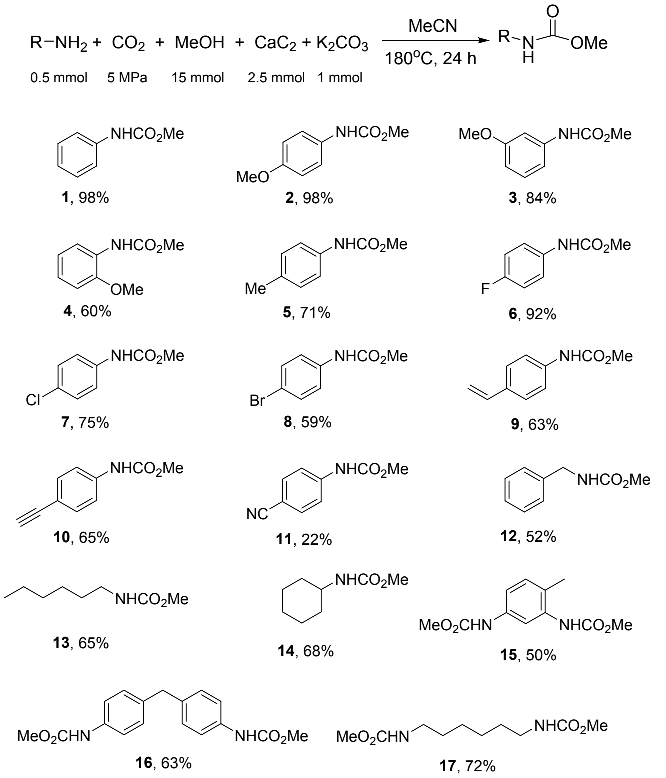
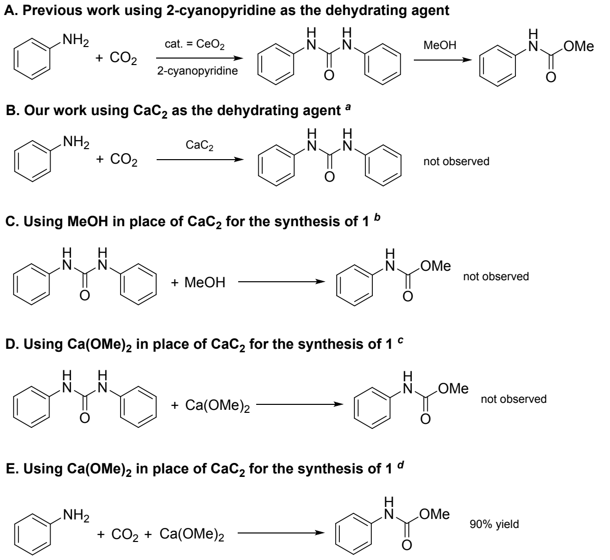


Figure 1 Temperature dependent catalytic synthesis of **1**. Reaction conditions: aniline (0.5 mmol), CaC_2 (2.5 mmol), MeOH (15 mmol) K_2CO_3 (1 mmol), MeCN (3 mL), CO_2 (5 MPa in a 10 mL autoclave). The yield of **1** was determined by HPLC analysis.



Scheme 2 The synthesis of various carbamates. Yields were isolated yields.

Tomishige et al. previously claimed that 1,3-diphenyl urea is an important intermediate for the synthesis of **1** from aniline, CO_2, and MeOH catalyzed by CeO_2 and dehydrated by 2-cyanopyridine (Scheme 3A).[47] In our work, we did not observe the formation of 1,3-diphenyl urea during the preparation of **1**. In addition, we used a similar method to prepare 1,3-diphenyl urea from aniline, CO_2, and CaC_2. However, we did not detect 1,3-diphenylurea (Scheme 3B), which suggests that it is not intermediate based on our protocol. Furthermore, using 1,3-diphenylurea to react with MeOH or $Ca(OMe)_2$ could not obtain 1 (Scheme 3C and Scheme 3D). Han et al. reported $Ca(OMe)_2$ to be an intermediate for the synthesis of DMC using MeOH and CO_2 dehydrated by CaC_2.[60] We used $Ca(OMe)_2$ as the reagent for the synthesis of **1** instead of MeOH and CaC_2. We obtained a yield of 90% for **1** (Scheme 3E). This is in agreement with Han's result and illustrates that $Ca(OMe)_2$ generated from CaC_2 and MeOH is an intermediate based on our method. Furthermore, we observed the reaction of CaC_2 and MeOH at 60 °C, which was terminated within six hours (Figure 2).



Scheme 3 Control experiments to determine the reaction intermediate. [a] Reaction condition: aniline (0.5 mmol), CaC_2 (2.5 mmol), K_2CO_3 (1.0 mmol), MeCN (3 mL), CO_2 (5 MPa in a 10 mL autoclave), 24 h, 180°C. [b] Reaction condition: 1,3-diphenylurea (0.5 mmol), MeOH (7.5 mmol), K_2CO_3 (1 mmol), 24 h, 180°C. [c] Reaction condition: 1,3-diphenylurea (0.5 mmol), $Ca(OMe)_2$ (0.5 mmol), K_2CO_3 (1 mmol), 24 h, 180°C.[d] Reaction

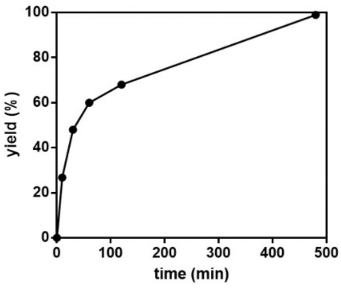


Figure 2 Reaction between CaC_2 (1 mmol) and MeOH (75 mmol) to yield $Ca(OMe)_2$ at 60 °C.

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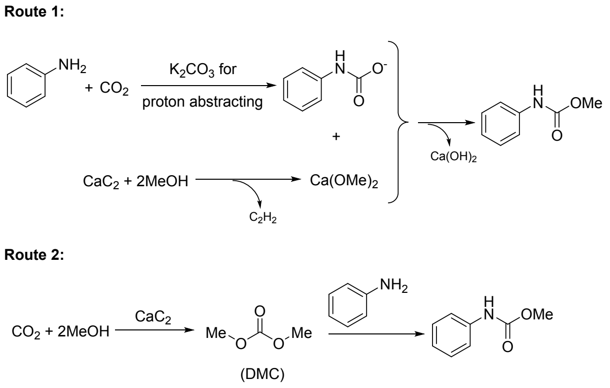
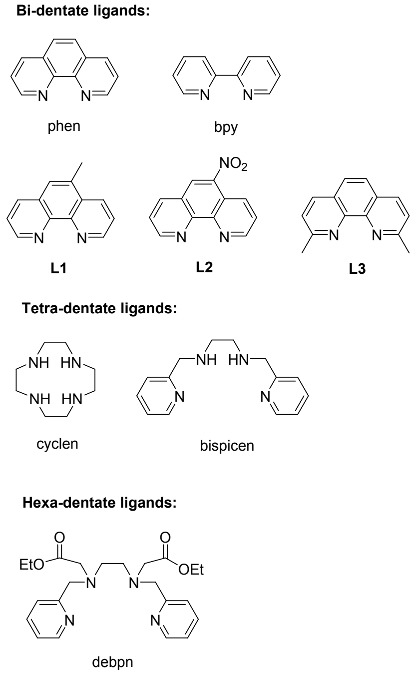
condition: aniline (0.5 mmol), $Ca(OMe)_2$ (2.5 mmol), K_2CO_3 (1.0 mmol), MeCN (3 mL), MeOH (15 mmol), CO_2 (5 MPa in a 10 mL autoclave), 24 h, 180°C.

Based on our results, we propose a mechanism for the synthesis of **1** from aniline, CO_2, and MeOH dehydrated by CaC_2 (Scheme 4, route 1). On one hand, one proton in aniline was abstracted by the base after the addition of CO_2. On the other hand, the reaction of CaC_2 and MeOH yielded $Ca(OMe)_2$ and released C_2H_2. The carbamic anion reacted with $Ca(OMe)_2$ to yield **1**. The byproduct was $Ca(OH)_2$, which was a non-harmful chemical. Another possible route (Scheme 4, route 2) started from CO_2 and MeOH to yield a small amount of DMC dehydrated by CaC_2. Then DMC reacted with aniline to yield **1**. The excess MeOH pushed the equilibrium to the product side.



Scheme 4 Proposed mechanism.



Scheme 5 N-donor ligands used in this work

The CaC_2 is an efficient dehydrating agent for the synthesis of carbamate from amine, CO_2, and MeOH. Based on our results, we think that CaC_2 is a good candidate for the preparation of glycerol carbonate (**18**) from glycerol and CO_2 because the byproduct of this reaction is water (Scheme 1D). The initial synthesis of glycerol carbonate was carried out using 0.5 mmol glycerol, 2.5 mmol CaC_2, 5 MPa CO_2 in 3 mL NMP as starting materials. The reaction was carried out for 24 h at 180°C. Without any catalyst, the yield was 16% (Table 2, entry 1). Subsequently, we screened a zinc-based catalyst with 1,10-phenanthroline (phen) as the ligand (Table 2, entries 2−7). $Zn(OAc)_2$/phen was an efficient catalyst in our previous study. However, the yield of glycerol carbonate was only 42% (Table 2, entry 2). Based on the use of $ZnSO_4$, $ZnCl_2$, $ZnBr_2$, and ZnI_2, the yield reached up to 67% (Table 2, entries 3−6). Heyn, North, and their co-workers reported the use of $Zn(OTf)_2$ as a catalyst for the synthesis of cyclic carbonates from diols and CO_2.[91, 92] In our study, $Zn(OTf)_2$/phen was also an efficient catalyst, yielding 92% glycerol carbonate (Table 2, entry 7) due to the strong Lewis acidity of $Zn(OTf)_2$. Without the ligand, the yield decreased to 37% (Table 2, entry 8). The solvent effect was also investigated (Table 2, entries 9−14). The results show that a polar solvent is preferable for this process. The time- and temperature-dependence of the synthesis of glycerol carbonate was investigated from 150°C to 180°C (Figure 3).

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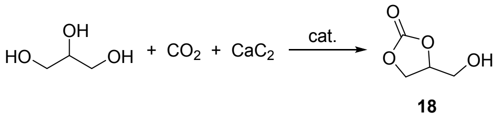
Table 2 Reaction optimization for the catalytic synthesis of glycerol carbonate from glycerol and CO_2 dehydrated by CaC_2.[a]



Entry	catalyst	ligand	solvent	yield of glycerol carbonate[b]
1	none	none	NMP	16%
2	$Zn(OAc)_2$	phen	NMP	42%
3	$ZnSO_4$	phen	NMP	25%
4	$ZnCl_2$	phen	NMP	36%
5	$ZnBr_2$	phen	NMP	49%
6	ZnI_2	phen	NMP	67%
7	**$Zn(OTf)_2$**	**phen**	**NMP**	**92% (88%[c])**
8	$Zn(OTf)_2$	none	NMP	37%
9	$Zn(OTf)_2$	phen	DMAc	58%
10	$Zn(OTf)_2$	phen	DMF	49%
11	$Zn(OTf)_2$	phen	MeCN	42%
12	$Zn(OTf)_2$	phen	MEK	23%
13	$Zn(OTf)_2$	phen	THF	18%
14	$Zn(OTf)_2$	phen	toluene	6%
15	$Zn(OTf)_2$	phen[d]	NMP	67%
16	$Zn(OTf)_2$	phen[e]	NMP	49%
17	$Zn(OTf)_2$	bpy	NMP	56%
18	$Zn(OTf)_2$	cyclen[f]	NMP	80%
19	$Zn(OTf)_2$	bispicen[f]	NMP	58%
20	$Zn(OTf)_2$	debpn[g]	NMP	25%

[a] Reaction conditions: glycerol (0.5 mmol), CaC_2 (2.5 mmol), Zn salt (0.025 mmol), phen (0.075 mmol), solvent (3 mL), CO_2 (5 MPa in a 10 mL autoclave), 24 h, 180°C. [b] Yields were determined by ^1H NMR using mesitylene as the internal standard. [c] Isolated yield. [d] 0.050 mmol phen. [e] 0.025 mmol phen. [f] 0.0375 mmol for tetra-*N*-donor ligands. [g] 0.025 mmol for hexa-donor ligands. Abbreviations: DMF: *N*,*N*-dimethylformamide; MEK: methyl ethyl ketone; THF: tetrahydrofuran; bpy: 2,2'-bipyridine; cyclen: 1,4,7,10-tetrazacyclododecane; bispicen: *N*,*N*'-bis(2-pyridylmethyl)-1,2-ethanediamine; debpn: *N,N*'-bis(2-pyridylmethyl)-bis(ethylacetate)-1,2-ethanediamine.

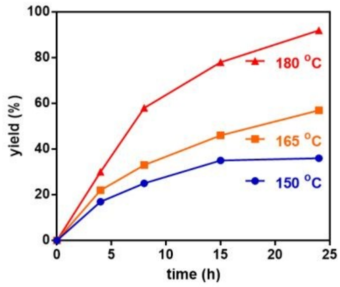
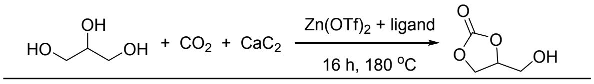


Figure 3 Temperature dependent catalytic synthesis of glycerol carbonate. Reaction conditions: glycerol (0.5 mmol), CaC_2 (2.5 mmol), NMP (3 mL), CO_2 (5 MPa in a 10 mL autoclave). The yield of glycerol carbonate was determined by ^1H NMR.

Table 3 Ligand effects of substituted 1,10-phenanthrolines for the catalytic synthesis of glycerol carbonate from glycerol and CO_2 dehydrated by CaC_2.[a]



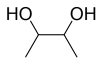
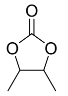
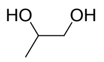
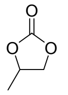
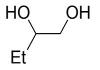
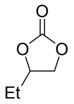
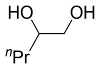
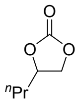
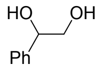
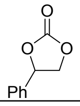
Entry	ligand	effect compared with phen	yield of glycerol carbonate[b]
1	phen	---	72%
2	**L1**	electron donating	87%
3	**L2**	electron withdrawing	43%
4	**L3**	steric effect	62%

[a] Reaction conditions: glycerol (0.5 mmol), CaC_2 (2.5 mmol), $Zn(OTf)_2$ (0.025 mmol), ligand (0.075 mmol), NMP (3 mL), CO_2 (5 MPa in a 10 mL autoclave), 16 h, 180°C. [b] Yields were determined by ^1H NMR using mesitylene as the internal standard.

The substitution of 5-methyl, 5-nitro, and 2,9-dimethyl groups with 1,10-phenantholines, L1, L2, and L3 was investigated and $Zn(OTf)_2$ was used as the catalyst for the synthesis of glycerol carbonate from glycerol and CO_2. The reactions were carried out for 16 h at 180°C. The results show that the ligand with the electron donating group (Me in L1) is the best (Table 3, entry 2). In contrast, L2 contains an electron withdrawing group (NO_2), which hinders the reaction (Table 3, entry 3). Ligand L3 contains two methyl groups; however, the steric effect hinders the reactivities. Thus, L3 performs worse than phen. Indeed, a similar trend was obtained for the $Zn(OAc)_2$/ligand-catalyzed hydrosilylation of CO_2 to silyl formate in our previous study.[93]

After the successful synthesis of glycerol carbonate from glycerol and CO_2, we focused on diols to synthesize cyclic carbonates from diols and CO_2 dehydrated by CaC_2. In many studies, the synthesis of cyclic carbonates from epoxides and CO_2 was reported.[94-100] However, epoxides are toxic and highly reactive due to their strained triangle structures and some epoxides have low boiling points and are explosive (e.g., ethylene oxide, boiling point = 10.4°C; propylene oxide, boiling point = 35°C). Diols and polyols are derived from biomass. Thus, the use of diols as substrates is considered to be a sustainable method to produce cyclic carbonates.[101, 102] This process was carried out under dehydrating agent-free conditions.[92, 103-109] Nevertheless, a dehydrating agent or an additive, including ketals,[110, 111] nitriles,[91, 112-115] organic halides,[116-119] epoxides,[120] and propargylic alcohols,[121-125] could promote the cyclic carbonate yield. In this study, we report the use of diols and CO_2 for the synthesis of cyclic carbonates with CaC_2 catalyzed by $Zn(OTf)_2$/phen. The reaction conditions are the same as that used for the synthesis of glycerol carbonate in this study. Five diols were successfully converted to the corresponding cyclic carbonates, as summarized in Table 4. The NMR yields were 83%–98% based on our method for products **19**–**23**.

Table 4 Synthesis of cyclic carbonates from diols and CO_2 dehydrated by CaC_2 catalyzed by $Zn(OTf)_2$ / phen. [a]

substrate	product	yield[b] (isolated yield)
	 **19**	84% (80%)
	 **20**	98% (92%)
	 **21**	89% (82%)
	 **22**	95% (87%)
	 **23**	83% (77%)

[a] Reaction conditions: diol (0.5 mmol), CaC_2 (2.5 mmol), $Zn(OTf)_2$ (0.025 mmol), phen (0.075 mmol), NMP (3 mL), CO_2 (5 MPa in a 10 mL autoclave), 24 h, 180°C. [b] Yields were determined by ^1H NMR using mesitylene as the internal standard.

Conclusions

We used CaC_2, a sustainable chemical that can be recycled from calcium, which is abundant in the Earth's crust, as dehydrating agent to promote CO_2 transformation reactions. Three reactions were investigated, that is, the (1) synthesis of carbamates from amines, (2) synthesis of glycerol carbonate from glycerol, and (3) synthesis of cyclic carbonates from diols. The combination of $Zn(OTf)_2$ and phen represents an efficient catalyst for the synthesis of glycerol carbonate and cyclic carbonates. Products **15**, **16**, and **17** are valuable precursors for the polyurethane industry. Several polyols are derivatives from biomass, which provides sustainable synthesis pathways. The utilization of CO_2 for the production of valuable chemicals is ongoing in our laboratory.

Experimental Section

Materials

CO_2 was purchased from Showa Tansan. All of the other chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Wako Chemicals in the best grade, stored under N_2, and used without further purification. CaC_2 was purchased from Sigma-Aldrich (technical grade, 80%), and was grinded to powder by mortar and pestle. Ligands bispicen and debpn were synthesized using the reported works.[126-128]

Caution: High pressure CO_2 gas cylinders should be handled with care and located in an open area with fresh air, although we did not encounter any accident.

Instruments

The catalytic reactions were carried out in a 10 mL stainless-steel autoclave with a gas-pressure monitor (max. 25 MPa). All of the oxygen-free operations were done in a glovebox. Reaction mixtures were heated in Sibata Chemi-300 Synthesizer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a 400 MHz Bruker NMR Spectrometer at room temperature. Product mixtures were analyzed with a Shimadzu HPLC with $MeOH/H_2O$ (v:v=7:3) as the mobile phase at 40 °C. Carbamates were isolated with a Yamazen AI-580 Single Channel Automated Flash Chromatography System by using *n*-hexane and dichloromethane as eluents. Molecular weights were determined with a Shimadzu GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer (GC–MS) with electron ionization mode.

General procedure for the synthesis of carbamates

For the synthesis of **1**: To a 10 mL steel autoclave, CaC_2 (200 mg, 2.5 mmol), K_2CO_3 (138 mg, 1 mmol), MeCN (3 mL), MeOH (480 mg, 15 mmol), and aniline (46.5 mg, 0.5 mmol) were added in a glove box. The autoclave was sealed tightly and filled with CO_2 to 3 MPa at room temperature. The autoclave was then heated to 180 °C and the pressure was gently adjusted to 5 MPa. After 24 h reaction, the autoclave was cooled down to room temperature, and CO_2 was released slowly. The solvent was removed *in vacuo*, and re-dissolved in 30 mL dichloromethane washed with water (30 mL, 3 times). Isolated product was purified with automated flash chromatography with *n*-hexane and dichloromethane as the eluents. A white powder (148 mg, 98%) was obtained after dried *in vacuo*. The product was characterized with ^1H NMR, $^{13}C\{^1H\}$ NMR, and GC–MS, consistent with authentic chemical. Other carbamates were synthesized in the same way, and consistent with either authentic materials or literatures. For the synthesis of dicarbamates (products **15**, **16**, and **17**), 0.25 mmol substrate was used.

General procedure for the synthesis of glycerol carbonate and cyclic carbonates

For the synthesis of glycerol carbonate from glycerol: to a 10 mL steel autoclave, CaC_2 (200 mg, 2.5 mmol), $Zn(OTf)_2$ (9.1 mg, 0.025 mmol), 1,10-phenanthroline (13.5 mg, 0.075 mmol), NMP (3 mL), and glycerol (46 mg, 0.5 mmol) were added in a glove box. The autoclave was sealed tightly and filled with CO_2 to 3 MPa at room temperature. The autoclave was then heated to 180 °C and the pressure was gently adjusted to 5 MPa. After 24 h reaction, the autoclave was cooled down to room temperature, and CO_2 was released slowly. The solution was dissolved in 20 mL water, and the organic product was extracted by ethyl acetate. Isolated product was purified with automated flash chromatography with *n*-hexane and ethyl acetate as the eluents. The product was characterized with ^1H NMR, $^{13}C\{^1H\}$ NMR, and GC–MS, consistent with authentic chemical. For the synthesis of cyclic carbonates from diols: the procedure was similar to the synthesis of glycerol carbonate except diol was added in place of glycerol.

Conflicts of interest

There are no conflicts to declare.

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Calcium carbide was used as a sustainable dehydrating agent for synthesis carbamates, glycerol carbonate, and cyclic carbonates directly from CO_2.