

Communication

Zinc Iodide-Metal Chloride-Organic Base: An Efficient Catalytic System for Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides under Ambient Conditions

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Abstract: Development of an effective catalytic system for the cycloaddition of carbon dioxide to epoxides for the preparation of cyclic carbonates under mild conditions is of great importance. Herein, a mixture of zinc iodide, metal chlorides, and strong organic bases is demonstrated to be a useful catalytic system that works at room temperature under atmospheric pressure. The most efficient combination, zinc iodide-niobium chloride-7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (1.2-0.3-3.0 mol%), gave styrene carbonate (95%) from styrene oxide and CO₂ (balloon) at 25 °C for 24 h. Another combination, zinc iodide-zinc chloride-1,8-diazabicyclo[5.4.0]undec-7-ene (1.2-0.8-4.0 mol%), kept the catalytic activity for the preparation of propylene carbonate until the fourth run. Therefore, the reaction system was operationally simple, highly efficient, and proceeded under ambient conditions. The catalyst is composed of readily available reagents and is reusable. Thus, the method presented is a powerful tool for utilizing CO₂ as the starting material for the production of valuable chemicals.

Keywords: carbon dioxide; epoxides; cyclic carbonates



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1. Introduction

CO₂ is regarded as an ideal carbon source for organic synthesis because it is inexpensive, abundant, nontoxic, and renewable. Therefore, efficient transformation of CO₂ into valuable chemicals is important for creating greener and more sustainable industries. The cycloaddition of CO₂ and epoxides to afford five-membered cyclic carbonates is one of the most promising methods for utilizing CO₂, owing to the 100% atom economy of the reaction. Carbonates are widely used as polar aprotic solvents, electrolytes in lithium-ion batteries, and intermediates in the production of pharmaceuticals and fine chemicals. Accordingly, a wide range of methods involving metal-based catalysts and organocatalysts have been reported for the synthesis of cyclic carbonates using CO₂ [1–3]. For example, the catalytic components employed in this study—zinc halides [4–19], NbCl₅ [20–24], and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) [25]—have been previously used as catalysts for the cycloaddition of CO₂, often in combination with onium salts. In addition, zinc-based heterogeneous catalysts have been continuously reported [4–6,8,9,11–14,17–19,26–30]. Despite the extensive research in this area, pressurizing or/and heating are usually required to obtain cyclic carbonates from CO₂ and epoxides in satisfactory yields.

Owing to the growing environmental and energy concerns, the development of synthetic methodologies for the preparation of cyclic carbonates by harnessing CO₂ under mild conditions is gaining interest. Recently, metal complexes [31–42], metal-organic frameworks [43–45], and solid-supported reagents [46–52] have been reported for facile conversion of CO₂ and epoxides into cyclic carbonates, even under ambient conditions (around 25 °C under 0.1 MPa). However, these materials typically have complex chemical structures with relatively high molecular weights. Organocatalysts have been utilized under ambient conditions; however, they usually require loadings greater than 5 mol% [53–59].

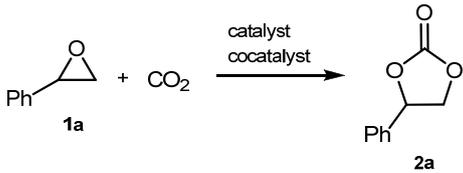
These limitations have spurred catalytic research toward the development of more effective and practical methods for the synthesis of cyclic carbonates under milder conditions.

We recently reported the selective guanidine-accelerated synthesis of carbonates from CO₂, glycerol, and alkyl halides [60]. In this study, we observed that a zinc complex formed between ZnI₂ and guanidine displayed catalytic activity for the cycloaddition of CO₂ and epoxides. Continuing our investigations in this area of research, we report the development of an efficient catalytic system for the conversion of CO₂ to cyclic carbonates using CO₂ at room temperature and atmospheric pressure. The catalyst was developed using simple metal halides and strong organic bases, and was catalytically active under ambient conditions.

2. Results

Synthesis of styrene carbonate, **2a**, from styrene oxide, **1a**, and CO₂ was investigated as a model reaction in the presence of metal halides and guanidine (Table 1). The combination of ZnI₂ and pentaalkylguanidine led to a 26% conversion to **2a** (entry 1). In contrast, the addition of ZnCl₂ as a cocatalyst substantially improved the conversion (entry 2). Catalytic activity almost completely disappeared in the absence of ZnI₂ and/or guanidine (entries 3 and 4). Thus, the combination of ZnI₂, ZnCl₂, and guanidine enhances the catalytic activity, indicating the presence of synergistic effects that contribute to the acceleration of the reaction.

Table 1. Cycloaddition of styrene oxide (**1a**) and CO₂ in the presence of zinc halides and guanidine ^a.



Entry	Catalyst	Cocatalyst	Conversion (%) ^b
1	ZnI ₂ / <i>t</i> BuN=C(NMe ₂) ₂	none	26
2	ZnI ₂ / <i>t</i> BuN=C(NMe ₂) ₂	ZnCl ₂	81
3	<i>t</i> BuN=C(NMe ₂) ₂	ZnCl ₂	1
4	none	ZnCl ₂	0

^a Reaction conditions: **1a** (10 mmol), CO₂ (0.1 MPa), ZnI₂/*t*BuN=C(NMe₂)₂ (1.0/2.2 mol%), ZnCl₂ (0.5 mol%), 25 °C, 18 h; ZnI₂/*t*BuN=C(NMe₂)₂ was prepared by mixing ZnI₂ and *t*BuN=C(NMe₂)₂ in ethanol followed by solvent removal. ^b Determined by ¹H-NMR area ratio.

The catalyst combination was further optimized by evaluating several metal chlorides, organic bases, and metal iodides to replace ZnCl₂, *N,N',N'',N'''*-*tert*-butyltetramethylguanidine, and ZnI₂, respectively (Table 2). The effect of the metal chlorides was first examined under the conditions described in entry 2 of Table 1 (combination A). Although all metal chlorides enhanced the catalytic reaction, their effects were significantly different. NbCl₅ afforded the best conversion (83%), which might be due to the suitable Lewis acidity of NbCl₅ for the cycloaddition in the presence of guanidines and ZnI₂. The effect of organic bases was then examined using NbCl₅ as a metal halide (combination B). The results indicated that a strong basicity was necessary to achieve good conversion, which was further evidenced by the low conversion observed for imidazole. Furthermore, the presence of sterically demanding substituents on the guanidines did not affect the cycloaddition conversion, and MTBD demonstrated the best conversion (86%). The effect of the metal iodide was further examined using NbCl₅ and MTBD (combination C). ZnI₂ was found to be the best iodide anion source despite its low number of iodine atoms per metal center. The catalytic activity of ZnI₂ was higher than that of ZnBr₂, which can be attributed to the facile generation of the iodide anion from ZnI₂ compared with the generation of the bromide anion from ZnBr₂. Additionally, although NbCl₅-Bu₄NBr (0.5–1 mol%) was reported to be an effective catalyst under mild conditions (45 °C) [20],

this catalytic system did not deliver good results (conversion: 11%) under the present conditions (NbCl₅-Bu₄NBr: 0.5–2 mol%, 25 °C). Our optimization results indicate that ZnI₂-NbCl₅-MTBD is the best combination, which probably leads to effective cooperative catalysis of acidic sites and iodide anions.

Table 2. Metal iodide/base and metal chlorides-catalyzed synthesis of styrene carbonate (**2a**) from styrene oxide (**1a**) and CO₂ ^a.

1a + CO ₂		metal iodide/base + metal chloride						2a
Combination A: ZnI ₂ / <i>t</i> BuN=C(NMe ₂) ₂ + metal chloride								
Metal chloride	NbCl ₅	ZnCl ₂	ZrCl ₄	BiCl ₃	FeCl ₃	MgCl ₂	CuCl ₂	
Conversion ^b (%)	83	81	75	75	73	71	41	
Combination B: ZnI ₂ /base + NbCl ₅								
Base ^c	MTBD	DBU	<i>t</i> BuG	<i>n</i> BuG	TBD	PhG	1,2-dimethylimidazole	
Conversion ^b (%)	86	84	83	83	80	65	22	
Combination C: Metal iodide (bromide)/MTBD + NbCl ₅								
Metal iodide (bromide)		ZnI ₂	SnI ₄	TiI ₄	BiI ₃	ZnBr ₂		
Conversion ^b (%)		86	80	55	50	44		

^a Reaction conditions: **1a** (10 mmol), CO₂ (0.1 MPa), metal iodide/base (1.0/2.2 mol%), metal chloride (0.5 mol%), 25 °C, 18 h. ^b Determined by ¹H-NMR area ratio. ^c DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, G: N=C(NMe₂)₂, TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

ZnI₂ and MTBD complexes were prepared prior to NbCl₅ addition, and the catalytic system prepared by this process was used for the cycloaddition reaction. However, the simultaneous mixing of ZnI₂, MTBD, and NbCl₅ did not affect product conversion (Table 3). Therefore, NbCl₅ was found to be effective upon the direct addition of free guanidine. We further observed that the conversion depended significantly on the ZnI₂, MTBD, and NbCl₅ mole ratio. The use of a suitable ratio led to almost complete consumption of the starting material with a prolonged reaction time [ZnI₂:MTBD:NbCl₅ = 1.2:3.0:0.3, reaction time (24 h), conversion (99%), and isolated yield (95%)]. Overall, the optimized method is operationally simple, does not require the preformation of the catalyst, and allows the efficient cycloaddition of CO₂ and epoxides under ambient conditions.

Table 3. Comparison of conversions to styrene carbonate (**2a**) with and without the preformed ZnI₂/MTBD ^a.

1a + CO ₂		ZnI ₂ , MTBD, NbCl ₅	2a
		Catalyst ^b	Conversion ^c (%)
		ZnI ₂ /MTBD + NbCl ₅ ^d	86
		ZnI ₂ -MTBD-NbCl ₅ ^e	86

^a Reaction conditions: **1a** (10 mmol), CO₂ (0.1 MPa), 25 °C, 18 h. ^b ZnI₂ (1.0 mol%), MTBD (2.2 mol%), NbCl₅ (0.5 mol%). ^c Determined by ¹H-NMR area ratio. ^d After the preformation of ZnI₂/MTBD, NbCl₅ was added. ^e ZnI₂, MTBD, and NbCl₅ were added simultaneously.

The optimized conditions were used for the conversion of several epoxides in the presence of CO₂, and the corresponding five-membered cyclic carbonates were isolated in moderate to excellent yields (Table 4). Various terminal epoxides bearing aryl, alkyl, ether, chloro, long alkyl chains, and unsaturated groups reacted smoothly with CO₂ (atmospheric pressure) at room temperature to furnish the corresponding carbonates in high yields (entries 1–6). The bis-epoxide was also converted to the corresponding bis-cyclic carbonate in excellent yield (entry 7). However, the use of *N*-methylpyrrolidone (NMP) as a solvent was required to homogenize the reaction mixture in cases where the product precipitation

lowered the yield by hindering continuous stirring of the reaction mixture. Accordingly, the ZnI_2 - NbCl_5 -MTBD-catalyst system allowed the selective cycloaddition of CO_2 with terminal epoxides under solvent-free conditions and proceeded without by-product formation. However, internal epoxides did not afford the desired carbonates under ambient conditions. Nevertheless, the desired cycloaddition was achieved by increasing the reaction temperature and CO_2 pressure (entries 8 and 9). Remarkably, even a sterically hindered internal epoxide was converted to the corresponding carbonate product in moderate yield.

Table 4. Efficient synthesis of a cyclic carbonate (**2**) under mild conditions ^a.

Entry	R ¹	R ²	2	Yield (%) ^b
1	Ph	H	2a	95
2	Me	H	2b	90
3 ^c	CH ₂ OPh	H	2c	92
4	CH ₂ Cl	H	2d	85
5 ^c	C ₈ H ₁₅	H	2e	89
6	CH ₂ OCH ₂ CH=CH ₂	H	2f	89
7 ^d		H	2g	95
8 ^e	(CH ₂) ₄	Ph	2h	38 ^f
9 ^e	Ph (<i>trans</i>)	Ph	2i	53 ^g

^a Reaction conditions: epoxides (10 mmol), CO_2 (0.1 MPa), ZnI_2 (1.2 mol%), NbCl_5 (0.3 mol%), MTBD (3.0 mol%), 25 °C, 24 h. ^b Isolated yields. ^c NMP (1 mL) was added. ^d ZnI_2 (2.4 mol%), NbCl_5 (0.6 mol%), MTBD (6.0 mol%). ^e CO_2 (1.0 MPa), ZnI_2 (4.0 mol%), NbCl_5 (1.0 mol%), MTBD (10.0 mol%), 120 °C. ^f Mixture of *cis/trans* (84/16). ^g Only *trans*.

After studying the scope of the catalytic reaction, we evaluated the reusability of the catalyst system. The reusability of ZnI_2 - NbCl_5 -MTBD was assessed using the reaction of propylene oxide (**1b**) with CO_2 (Table 5). After the first experiment, the product was isolated by the distillation of the crude mixture because of the homogeneous system, and the residual catalyst in the reaction vessel was used for two subsequent runs under the same reaction conditions without any pretreatment. Unfortunately, a slight decrease in yield was observed in the second run, which was maintained in the third run (catalyst A). The reduction in catalytic efficiency can be attributed to the partial decomposition of NbCl_5 and MTBD during distillation. Therefore, we further examined the cycloaddition using a metal chloride and an organic base, which are less moisture- and heat-sensitive under similar conditions. The use of ZnCl_2 and DBU instead of NbCl_5 and MTBD led to similar conversions during the recycling experiments, although larger quantities of the reagents were required (catalyst B). Thus, the ZnI_2 - ZnCl_2 -DBU system is a highly stable cycloaddition catalyst that does not display any significant decrease in catalytic activity until the fourth run.

Table 5. Reuse of catalyst in the synthesis of propylene carbonate (**2b**) from propylene oxide (**1b**) and CO₂ ^a.

1b + CO ₂ $\xrightarrow{\text{catalyst A or B}}$ 2b				
Catalyst A: ZnI ₂ -NbCl ₅ -MTBD ^b				
Cycle	1	2	3	
Yield (%)	84	67	68	
Catalyst B: ZnI ₂ -ZnCl ₂ -DBU ^c				
Cycle	1	2	3	4
Yield (%)	78	81	85	83

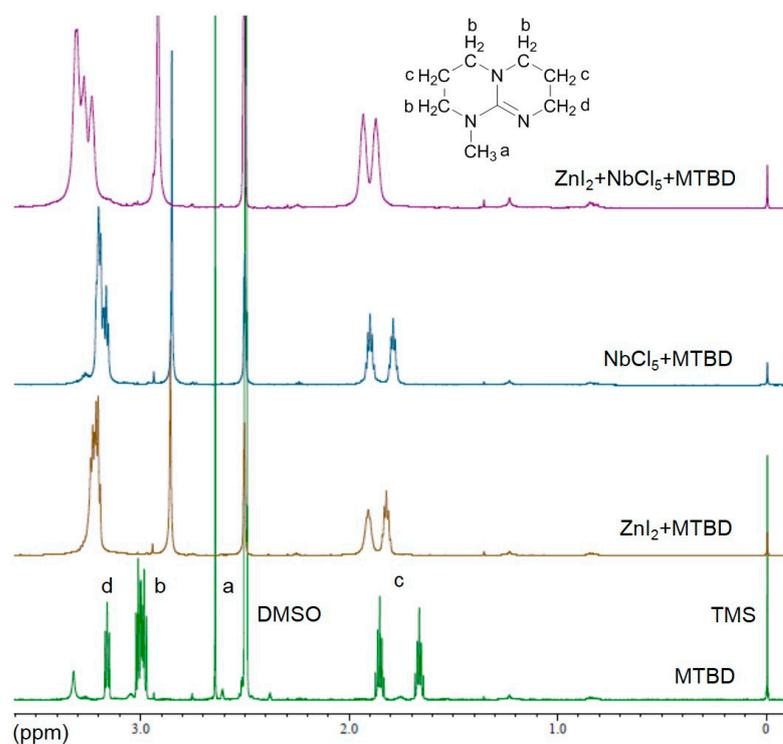
^a Reaction conditions: **1b** (10 mmol), CO₂ (0.1 MPa), 25 °C, 24 h. ^b ZnI₂ (1.2 mol%), NbCl₅ (0.3 mol%), MTBD (3.0 mol%). ^c ZnI₂ (1.2 mol%), ZnCl₂ (0.8 mol%), DBU (4.0 mol%).

3. Discussion

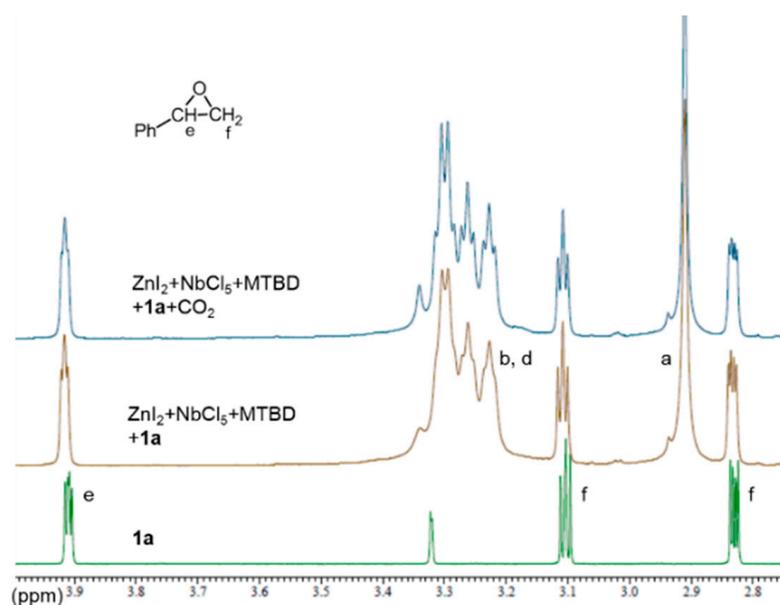
The catalytic system was examined by ¹H-NMR in DMSO-d₆ using tetramethylsilane as an internal standard. The addition of ZnI₂ or NbCl₅ to the MTBD led to a downfield shift in the peaks corresponding to the MTBD (Figure 1A). In addition, the addition of NbCl₅ to the MTBD and ZnI₂ resulted in a further downfield shift in the MTBD peaks. These changes are indicative of MTBD coordination to ZnI₂ and NbCl₅. Moreover, the addition of styrene oxide (**1a**) to the complexes led to a slight downfield shift of the **1a** signals, which suggests coordination of the formed complexes with **1a** (Figure 1B). However, because bubbling CO₂ into the mixture did not cause changes in the chemical shifts, the MTBD complex coordinated with ZnI₂ and NbCl₅ might be less able to interact with CO₂. Furthermore, the coordination of ZnI₂ and NbCl₅ to MTBD was also confirmed by the changes in the IR spectra (Figure S1). Accordingly, considering the key contribution of iodide to the catalyst activity (almost no reaction occurred in the absence of ZnI₂, Table 1, entries 2 vs. 3), the main catalytic effect should operate via the synergistic activation of epoxides by the acidity of the niobium and zinc complexes, followed by the nucleophilic attack of the iodide anion. The proposed catalytic cycle for the synthesis of cyclic carbonates is shown in Scheme 1 [61–63]. The epoxide ring was activated by coordination with the Nb and Zn acidic sites. The iodide anion generated from the reaction between ZnI₂ and guanidines simultaneously attacks the epoxide ring to form an intermediate [I] (path A). The other path B, including the attack of MTBD followed by exchanging the MTBD moiety by the iodide, can also be proposed. Nucleophilic addition of the alkoxide to CO₂ forms a hemicarbonatate intermediate [II]. Because the iodide anion is a good leaving group, the ring closure of the metal carbonatate occurs smoothly, affording the desired cyclic carbonate.

Previous reports on styrene carbonate synthesis revealed that the preceding combination of metal halides and organic bases afforded good yields under severe conditions. For example, SnCl₄ [64] or ZnI₂ [5,13,15] were employed in combination with bases under 0.3 MPa-75 °C or 1–3 MPa-60–150 °C, respectively. Additionally, ZnI₂ [6–8] or NbCl₅ [24] in combination with base-HX also were used under heating and pressurized CO₂ conditions (30–130 °C, 1–2 MPa). Therefore, the higher efficiency reported herein supports the occurrence of cooperative catalysis by ZnI₂, NbCl₅, and MTBD. In this catalytic system, the coordination of ZnI₂ and NbCl₅ to MTBD may hold I[−] derived from ZnI₂ closer to the Lewis acids and increase the solubility of their metal halides in the reaction mixture, thus enhancing the activity of this reaction. Furthermore, although several effective catalysts for the preparation of styrene carbonate, even under ambient conditions, have already been reported [31–42,44–46,48–55,58,59], they usually require a long time for multistep preparation (overnight to 30 days, 1–3 steps), simultaneous use of a relatively high-loading tetrabutylammonium halide (1–50 mol%), and/or the use of significant quantities despite low catalytic loadings (73–1737 mg for 10 mmol of styrene oxide). However, our reaction allows convenient coupling with a relatively low-loading catalyst composed of readily available reagents (ZnI₂-NbCl₅-MTBD: 92 mg for 10 mmol). In addition, while TON (mol of product/mol of metal) and TOF [TON/time (h)] of previous catalysts cited here are 16–2760

and 0.7–58 for the production of styrene carbonate, respectively, those of our one are 63 and 2.6, respectively. Thus, our catalytic system shows near average values among them except the highest TON and TOF [46] attained in the presence of tetrabutylammonium bromide (7.2 mol%) as a cocatalyst.

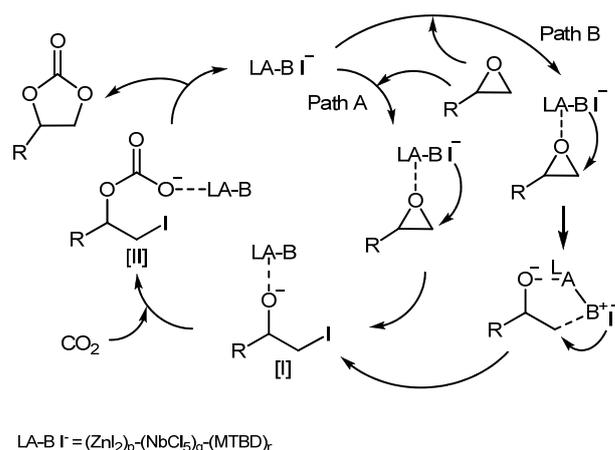


(A)



(B)

Figure 1. $^1\text{H-NMR}$ of a mixture of catalysts, styrene oxide (**1a**), and CO_2 ; (A) ZnI_2 (0.04 mmol), NbCl_5 (0.01 mmol), and MTBD (0.1 mmol); (B) ZnI_2 - NbCl_5 -MTBD, **1a** (0.1 mmol), and CO_2 .



Scheme 1. Plausible mechanism for the cycloaddition of styrene oxide and CO₂.

4. Materials and Methods

4.1. Materials

ZnI₂, ZnCl₂, NbCl₅, DBU, MTBD, epoxides, deuterated solvents, and CO₂ (99.5%) were used without further purification. NMP (super dehydrated) and EtOH (super dehydrated), purchased from Wako Pure Chemical Industries Ltd., were used without further treatment.

4.2. Methods

A general procedure for ZnI₂/organic base + metal chloride-catalyzed synthesis of styrene carbonate (**2a**) from styrene oxide (**1a**) and CO₂

ZnI₂ (0.1 mmol), organic bases (0.22 mmol), EtOH (0.4 mL), and a magnetic stirring bar were placed in a glass vessel connected to an injection port with a 3-way cock. The mixture was stirred at 60 °C for 3 h and was evaporated around 25 °C under reduced pressure to afford the ZnI₂/organic base complex. To the complex, metal chlorides (0.05 mmol) and **1a** (10 mmol) were added, and the vessel was charged with CO₂ from a balloon. The reaction mixture was stirred at 25 °C for 24 h under a 0.1 MPa pressure of CO₂. The conversions to the desired carbonates were determined based on the ¹H NMR area ratios (**2a**/**1a**+**2a**).

A general procedure for ZnI₂-NbCl₅-MTBD-catalyzed synthesis of cyclic carbonates **2** from epoxides **1** and CO₂

ZnI₂ (0.12 mmol), MTBD (0.3 mmol), NbCl₅ (0.03 mmol), and **1** (10 mmol) were placed with a magnetic stirring bar in a glass vessel connected to an injection port with a 3-way cock. NMP was added as the solvent in the experiments for glycidyl phenyl ether (**1c**) and 1,2-epoxydecane (**1e**). The vessel was charged with CO₂ from a balloon, and the reaction mixture was stirred at 25 °C for 24 h under a 0.1 MPa pressure of CO₂. The obtained crude product was purified by silica gel column chromatography (silica gel 60) to isolate **2**. The products **2b** and 4-chloromethyl-1,3-dioxolan-2-one (**2d**) were purified by distillation instead of purification on silica gel column chromatography.

A procedure for reuse of ZnI₂-NbCl₅-MTBD and ZnI₂-ZnCl₂-DBU in the synthesis of propylene carbonate (**2b**) from propylene oxide (**1b**) and CO₂

The carbonate **2b** was synthesized from **1b** and CO₂ according to the procedure described above, using ZnI₂-NbCl₅-MTBD or ZnI₂-ZnCl₂-DBU. The crude **2b** was purified by distillation under reduced pressure to obtain pure **2b**. To the residual catalyst in the reaction vessel, fresh **1b** (10 mmol) was added, CO₂ was charged from a balloon, and the reaction mixture was stirred at 25 °C for 24 h in next recycle experiment. The resulting liquid was purified by distillation to afford **2b**, and the residual catalyst was further used for the third run.

A procedure for ¹H NMR measurement to examine the reaction mechanism.

ZnI₂ (0.04 mmol), MTBD (0.1 mmol), NbCl₅ (0.01 mmol), and DMSO-d₆ + 0.03% TMS (0.75 mL) were placed in an NMR tube, for studying the coordination of metal halides to

MTBD. The ^1H NMR spectrum was acquired. After that, **1a** (0.1 mmol) was added to the complex, and ^1H NMR was acquired again. CO_2 was bubbled into the mixture, and the ^1H NMR was acquired again.

5. Conclusions

The ZnI_2 - NbCl_5 -MTBD-catalyzed synthesis of carbonates is a powerful tool for utilizing CO_2 under extremely mild conditions. The catalytic system allowed the conversion of various terminal epoxides into the corresponding cyclic carbonates in high yields (85–95%) with a relatively low-loading catalyst (92 mg for 10 mmol of epoxides) under ambient conditions. The catalyst was also prepared in situ by simply mixing readily available reagents and could be used under solvent-free conditions; thus, it is a practical and environmentally benign reagent. To the best of our knowledge, no catalysts composed of two different metal halides or organic bases have been reported for the synthesis of carbonates. As has already been observed for some metal-organic framework catalysts [65,66], the use of a dual Lewis acid catalytic system in combination with nucleophiles is believed to be a promising strategy for the development of synergistic catalysts for the cycloaddition of CO_2 .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13081214/s1>, Characterization of Compounds **2a–i** [34,67–69], Figure S1: IR spectra of MTBD, ZnI_2 +MTBD, NbCl_5 +MTBD, and ZnI_2 + NbCl_5 +MTBD.

Author Contributions: Conceptualization, M.M. and T.M.; methodology, T.N., S.N. and M.M.; formal analysis, T.N., S.N. and M.M.; investigation, M.M.; data curation, M.M.; writing—original draft preparation, M.M.; writing—review and editing, M.M.; supervision, T.M.; project administration, M.M.; funding acquisition, M.M., T.N. and T.M. All authors have read and agreed to the published version of the manuscript.

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