

Efficient catalytic synthesis of optically active cyclic carbonates via coupling reaction of epoxides and carbon dioxide

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Abstract—Chiral Co(salen) complexes bearing the Lewis acid of group 13 can efficiently catalyze the reactions of carbon dioxide with epoxides in the presence of catalytic amounts of alkali metal salts, quaternary ammonium halide or ionic liquids. They exhibited excellent activity for producing enantiomerically enriched cyclic carbonates.

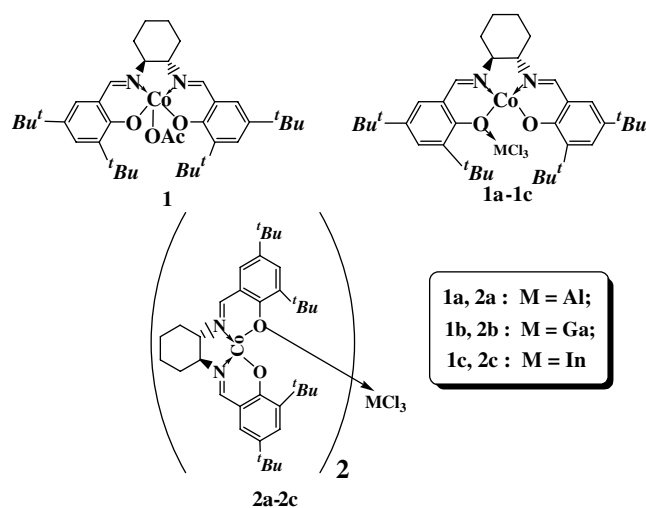
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The coupling reaction of carbon dioxide and epoxides to form cyclic carbonates and polycarbonates has received much attention in recent years.^{1–3} One of the most promising methodologies in this area is the chemical fixation of CO₂ onto epoxides to prepare the corresponding five-membered cyclic carbonates. These carbonates are valuable as organic synthetic intermediates, monomers, aprotic polar solvents, pharmaceutical/fine chemical intermediates, and are used in many biomedical applications.^{4–6} A number of well-defined and selective catalyst systems have been developed for this transformation.^{7–10} The formation of optically pure cyclic carbonates is based on the insertion of carbon dioxide into enantiomerically pure epoxides^{7–10} or the coupling reaction of carbon dioxide and racemic epoxides catalyzed by chiral Co(II)¹¹ or Co(III)^{1–3,12} salen-type complexes. Also, optically active cyclic carbonates could be obtained by enzyme-mediated enantioselective hydrolysis of racemic cyclic carbonates.^{13,14}

As a part of the ongoing development of the Co(salen) catalytic system, we reported recently chiral Co(salen) complexes bearing Lewis acids of group 13 elements which are very efficient and enantioselective for the ring opening of epoxides with a variety of nucleophiles.^{15a–c} We had much interest in the possibility of employing these complexes for direct synthesis of optically active cyclic carbonates from the racemic terminal epoxides. Herein, we describe a convenient synthetic route to opti-

cally active cyclic carbonates by a catalytic kinetic resolution process resulting from the coupling reaction of CO₂ with racemic epoxides using simple chiral Co(salen) complexes or Co^{II}(salen)/alkali hydroxides, Co^{II}(salen)/ionic liquid, and Co^{II}(salen)/quaternary ammonium halide catalyst systems.

A series of chiral Co(salen) complexes (**Scheme 1**) were screened in order to identify the most enantioselective and active catalyst for coupling reaction of CO₂ with propylene oxide. We delightfully found **1a–2c** to be much more active and selective than the analogous Co^{II}(salen) or Co^{III}(salen) complex.⁹ Complex **1**, complexes **2a** and



Scheme 1. Schematic diagram of chiral (salen)Co complexes.

Keywords: Chiral cobalt salen; Epoxides; Lewis acid; Resolution.

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2b treated with *p*-nitrobenzene sulfonic acid and Camphor sulfonic acid could also catalyze this reaction with 27.3%, 43.7%, and 54.0% ee's, respectively (Table 1, runs

Table 1. Enantioselective reaction of CO₂ and epoxides on the various chiral Co(salen) catalysts^a

Run	Epoxide	Cat	Mole ratio Epoxides/cat	Time (h)	PC ee/yield (%)	<i>K</i> _{rel} ^b
1	PO	1	1:0.005	3	27.3/4.9	1.8
2 ^c	PO	2a	1:0.005	3	43.7/15.7	2.8
3 ^d	PO	2b	1:0.005	5	54.0/15.9	3.7
4	PO	1a	1:0.005	4	70.3/19.6	6.8
5	PO	2a	1:0.005	3	67.8/19.3	6.1
6	PO	1b	1:0.005	3	66.1/17.5	5.6
7	PO	2b	1:0.005	3	66.4/18.8	5.7
8	PO	1c	1:0.005	3	64.8/17.8	5.4
9	PO	2c	1:0.005	3	66.5/18.3	5.7
10	PO	1a	1:0.01	5	67.3/28.4	6.6
11	PO	1a	1:0.005	4	70.3/19.6	6.8
12	PO	1a	1:0.001	5	81.0/11.3	10.5
13	PO	1a	1:0.0005	5	84.7/8.7	13.1
14	EB	1a	1:0.005	5	70.8/22.3	7.1
15	EB	1a	1:0.001	5	79.1/13.5	9.7
16	ECH	1a	1:0.005	5	47.7/23.5	3.3
17	ECH	1a	1:0.001	5	56.4/15.4	4.0

^a Reaction conditions: propylene oxide (PO), 1,2-epoxybutane (EB), epichlorohydrin (ECH), CO₂ (5 atm), temperature 25 °C.

^b $K_{rel} = \ln[1 - c(1 + ee)] / \ln[1 - c(1 - ee)]$.

^c Catalyst treated by *p*-nitrobenzene sulfonic acid.

^d Catalyst treated by camphor sulfonic acid.

1–3).¹⁷ Analogous results were obtained by using the monomeric and dimeric catalysts (Table 1, runs 4–9); Furthermore, monomeric catalyst **1a** was identified as the most effective among the catalytic series and it was selected for further study. It is evident from runs (Table 1, runs 10–17) that lower catalyst loading amount was more beneficial for improving optical purity of the products, but had an effect on the rate of the reaction. Also, 1,2-epoxybutane (EB) could be transformed to the corresponding cyclic carbonates with improved enantiomeric purity, using **1a** as the catalyst in the presence of [BMIm]OH (Table 2, run 20). But epichlorohydrin (ECH) displayed lower enantiomeric purity in the presence of [BMIm]OH. In the case of ECH, the participation of chloro group affected the enantiomeric purity and selectivity of the corresponding cyclic carbonate (Table 2, run 21).

Organic solvents were found to have no crucial effect on the enantioselectivity, the use of solvents like *tert*-butyl methyl ether, ethyl acetate, dichloromethane led to 70.6%, 71.4%, and 69.5% ee for produced propylene carbonate, respectively.

A remarkable variety of active catalysts including simple alkali metal salts, quaternary ammonium salts, and ionic liquids have been successfully employed for the CO₂/epoxides coupling processes.^{7–10,18–22}

The enantiomeric purity of the product was increased by decreasing the loading amount of catalyst or by the addition of inorganic base as an additive (Table 1, runs 10–13; Table 2, runs 1–8, 13–14). Several alkali metal salts were tested as co-catalyst, with an increase in basi-

Table 2. CO₂ coupling reaction with racemic propylene oxide, epoxy butane and epichlorohydrine^a

Run	Co-catalyst	Mole ratio PO/cat/co-cat	PC ee/yield (%)	TOF ^b (h ⁻¹)	<i>K</i> _{rel}
1	K ₂ CO ₃	1:0.02:0.1	59.5/49.4	5	6.9
2	K ₂ CO ₃	1:0.01:0.1	72.4/30.8	6	8.5
3	K ₂ CO ₃	1:0.005:0.1	78.5/25.0	10	10.7
4	K ₂ CO ₃	1:0.001:0.1	79.6/17.7	35	13.3
5	K ₂ CO ₃	1:0.001:0.01	81.8/13.7	27	11.3
6	K ₂ CO ₃	1:0.001:0.05	81.6/21.6	43	12.3
7	KHCO ₃	1:0.001:0.05	80.9/16.8	34	11.1
8	KOH	1:0.001:0.05	83.7/23.6	47	14.5
9 ^c	[EMIm]Br	1:0.001:0.0001	50.0/32.4	65	3.8
10	[EMIm]OH	1:0.001:0.01	55.5/55.6	185	7.0
11	[EMIm]OH	1:0.001:0.001	64.8/48.0	160	8.5
12	[EMIm]OH	1:0.001:0.0005	65.7/46.4	155	8.4
13	[EMIm]OH	1:0.001:0.0001	74.8/43.2	144	12.2
14	[EMIm]OH	1:0.0005:0.0005	78.8/39.8	265	8.0
15 ^d	[BMIm]OH	1:0.001:0.0001	83.2/45.1	148	15.7
16	<i>n</i> -Bu ₄ NI	1:0.0005:0.0005	27.5/48.3	322	2.2
17	<i>n</i> -Bu ₄ NBr	1:0.0005:0.0005	40.8/46.4	309	3.3
18	<i>n</i> -Bu ₄ NCl	1:0.0005:0.0005	68.1/47.8	319	9.8
19	<i>n</i> -Bu ₄ NOH	1:0.0005:0.0005	75.0/45.5	303	10.6
20 ^e	[BMIm]OH	1:0.001:0.0001	80.8/25.7	103	10.0
21 ^f	[BMIm]OH	1:0.001:0.0001	50.4/12.7	105	3.2

^a Reaction conditions: reaction time: runs (1–8) 5 h; runs (9–21) 3 h; CO₂ (5 atm), temperature 25 °C.

^b The rate is expressed in terms of turnover frequency [TOF = (mol of cyclic carbonates) (mol of catalyst · h)⁻¹].

^c [EMIm]Br = 1-ethyl-3-methylimidazolium bromide.

^d [BMIm]OH = 1-butyl-3-methylimidazolium hydroxide.

^e EB is used as a reactant.

^f ECH used as a reactant.

city resulting in a corresponding increase in activity and selectivity. Especially, addition of KOH, K_2CO_3 or $KHCO_3$ was effective to improve the % ee's of resultant propylene carbonate (Table 2, runs 6–8). KOH adsorbs CO_2 easily to form $KHCO_3$, showing the similar effect in enantioselectivity as $KHCO_3$ (runs 7 and 8). To the best of our knowledge, our catalytic system showed the highest enantioselectivity for the cycloaddition of CO_2 to epoxides under mild conditions among the reported catalysts.^{12,16} Only a moderate improvement in catalytic reactivity (yield) was obtained when alkali metal salts were introduced as co-catalysts; however, the activity was greatly enhanced with addition of catalytic amount of quaternary ammonium halides or ionic liquids.

It is interesting that both the anion and cation of co-catalysts in the binary catalyst systems gave a significant impact on the enantiomeric purity and reaction rate. The existence of co-catalysts such as $[EMIm]OH$ is very essential to promote this reaction (Table 2, run 15) whereas the use of complex **1a** alone shows only 11.3% conversion (Table 1, run 12). Better catalytic performance was achieved with the co-catalysts consisting of $EMIm^+$ or $BMIm^+$ cations and OH^- anion (Table 2, runs 13–15). Added $n-Bu_4N^+$ cation also accelerate the reaction rates in the formation of propylene carbonate, albeit with a decrease in enantioselectivity. However, $n-Bu_4NOH$ was effective as a co-catalyst, showing the increase in yield with relatively high enantioselectivity at low loading amount of salen catalyst (Table 2, run 19).

The result stimulated us to design catalyst systems based on chiral (salen)Co complex in conjunction with these co-catalysts. We proposed the plausible mechanism for this chemical fixation reaction of CO_2 (Scheme 2), previous reports also suggest that the synergistic actions of an electrophile for epoxide activation with a nucleophile for CO_2 activation were more effective in catalyzing this reaction.^{1–3,12,16} However, OH^- anions also can make HCO_3^- ions by adsorbing CO_2 in the reaction system. The addition of the OH^- anion containing salt accelerated the reaction rate with high % ee's.

In conclusion, we explored efficient chiral Co(salen) complexes systems for the cycloaddition of CO_2 to epox-

ides in the presence of alkali metal salts, quaternary ammonium halides or ionic liquids. The anion, cation and loading amount of co-catalysts can play a significant role in determining the system's selectivity in addition to the activity. Efforts are underway to elucidate the mechanistic details and explore other applications of the catalytic systems.

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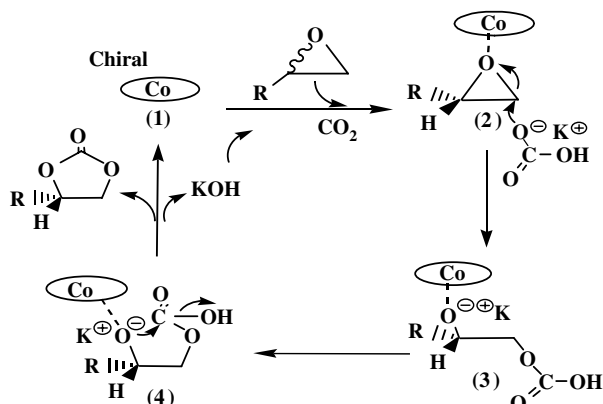
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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.014.

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Scheme 2. Representative mechanism for CO_2 /epoxide coupling in the presence of inorganic base additives.

- reported that in the absent of co-catalyst yielded only a trace amount of the product. See Refs. 1–3.
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 21. Propylene carbonate: ^1H NMR (CDCl_3 , 400 MHz): δ 1.49 (d, 3H, CH_3), 4.02 (t, 1H, CH_2O), 4.55 (t, 1H, CH_2O), 4.85 (q, 1H, CHO); ^{13}C NMR (CDCl_3): δ 151.7, 70.2, 70.5, 21.5. Choropropylene carbonate: ^1H NMR (CDCl_3 , 400 MHz): δ 3.73–3.83 (m, 2H), 4.42 (q, 1H), 4.61 (t, 1H), 5.10 (m, 1H). 1,2-Butene carbonate: ^1H NMR (CDCl_3 , 400 MHz): δ 1.03 (t, 3H), 1.80 (d, 1H), 4.17 (t, 1H), 4.55 (t, 1H), 4.70 (d, 1H).
 22. See [Supplementary data](#) for ESIMS and UV analysis.