

Chemical Fixation of Carbon Dioxide Catalyzed by Binaphthyldiamino Zn, Cu, and Co Salen-Type Complexes

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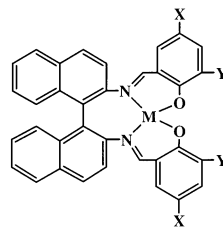
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Abstract: Binaphthyldiamino salen-type Zn, Cu, and Co complexes can efficiently catalyze reactions of epoxides with carbon dioxide in the presence of various catalytic amounts of organic bases. The simplest binaphthyldiamino salen-type Zn complex gave the five-membered cyclic carbonate **2** in excellent yield in the presence of triethylamine. A Lewis acid and Lewis base cocatalyzed mechanism is proposed.

Carbon dioxide is the earth's most abundant carbon resource and is used by green plants and anaerobic bacteria for chemical production on a massive scale. In contrast, man's industrial and laboratory utilization of carbon dioxide as a chemical feedstock is extremely small. During the last two decades of the twentieth century, the chemical fixation of carbon dioxide has received much attention from the viewpoint of carbon resources and environmental problems.¹ Especially the fixation of carbon dioxide by transition metal catalysts has seen significant progress.^{2–4} One of the major successes is the utilization of epoxides and carbon dioxide as starting materials to prepare the corresponding five-membered cyclic carbonate in the presence of a transition metal catalyst.^{5,6} De Pasquale disclosed a number of coordinatively unsaturated nickel(0) complexes such as Ni(PPh₃)₂ and Ni(PCy₃)₂, which are excellent catalysts.^{7a,b} Copper, tin, and tantalum systems also catalyze this reaction.^{7c,d} Kisch developed a catalyst system that can be applied at room temperature and under normal pressure.⁸ The vinyl ethylene carbonate can be formed from mono-



1a: M = Zn, X = Y = H; 1b: M = Cu, X = Y = H;
1c: M = Co, X = Y = H; 1d: M = Zn, X = Bu^t, Y = H;
1e: M = Cu, X = Bu^t, Y = H; 1f: M = Zn, X = Y = Cl.

FIGURE 1. Structures of binaphthyldiamino salen-type complexes.

epoxide of butadiene in 96% yield at room temperature, normal pressure, and with a reaction time of 15 min if Pd(PPh₃)₄ is used as the catalyst.⁹ While the advances have been significant, all suffer from either low catalyst stability/reactivity, air sensitivity, the need for a cosolvent, or the requirement of high pressure and/or high temperature or the catalyst required a special structure. Recently, Nguyen reported that an ethyldiamino or cyclohexyldiamino Cr(III) salen-type complex can efficiently catalyze the reaction of epoxide and carbon dioxide to give a five-membered cyclic carbonate in high TON and TOF.¹⁰ This result stimulated us to explore other salen-type metal complexes in this chemical fixation of carbon dioxide. Herein, we report unprecedented reactions of epoxides with carbon dioxide catalyzed by copper(II), zinc(II), and cobalt(II) salen-type complexes (Figure 1) derived from binaphthyldiamino Schiff bases.

To the best of our knowledge, copper(II), cobalt(II), and zinc(II) salen-type complexes have never been used in the chemical fixation of carbon dioxide.¹¹ During our investigations of catalytic asymmetric reactions using binaphthyldiamino Cu(II), Co(II), or Zn(II) salen-type metal complexes in supercritical CO₂ fluid, we examined the reaction of monosubstituted terminal epoxide with carbon dioxide in the presence of these catalysts at the same time. We delightfully found that the corresponding five-membered cyclic carbonate **2a** could be obtained in excellent yield in the presence of binaphthyldiamino Cu(II), Zn(II), or Co(II) salen-type metal complexes **1** (0.1 mol %) and organic bases (0.2 mol %) at 100 °C (Scheme 1). If only binaphthyldiamino salen-type metal complex **1** was used as a catalyst (0.1 mol %), no reaction occurred. The coexistence of organic bases such as DMAP, triethylamine (Et₃N), DBU, pyridine, or DABCO (0.2 mol %) is essential to promote this reaction. The scope and limitations of catalysts and reaction conditions have been carefully examined. The results were summarized in Table 1. In general, the unsubstituted binaphthyldiamino salen-type Zn(II), Cu(II), and Co(II) complexes **1a–c** (0.1 mol %) (Figure 1; M = Zn, Cu, or Co and X = Y = H) produce cyclic carbonate **2a** in higher yields in the

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(11) Kisch reported the reaction of epoxide with CO₂ in the presence of CoCl₂.⁸ Inoue reported the reaction of epoxide with CO₂ in the presence of a Zn catalyst.² These, however, do not involve salen-type complexes.

SCHEME 1

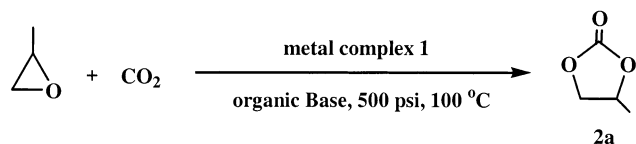


TABLE 1. Reactions of Propylene Oxide (PO) with CO₂ in the Presence of a Zn, Cu, or Co Complex and an Organic Base^a

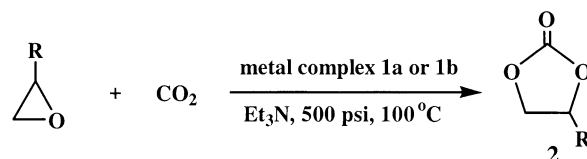
entry	catalyst	base ^b	yield (%) ^c	TON ^d
1	1a	DABCO	30	30
2	1a	Et ₃ N	86	856
3	1a	Et ₃ N ^e	90	901
4	1a	DBU	80	803
5	1a	DBU ^f	55	552
6	1a	DBU ^e	55	549
7	1a	DMAP	70	702
8	1a	DMAP ^e	20	204
9	1a	pyridine	83	833
10	1b	DMAP	40	397
11	1b	DMAP ^g	0	0
12	1b	DMAP ^h	12	121
13	1b	Et ₃ N	51	510
14	1c	DMAP	80	800
15	1c	Et ₃ N	91	913
16	1d	DMAP	5.3	52.7
17	1d	Et ₃ N	10	102
18	1e	DMAP	3	26
19	1e	DBU	14	141
20	1f	DMAP	13	132

^a Reaction conditions: PO (2.6 g, 4.5×10^{-2} mol), CH₂Cl₂ (5.0 mL), catalyst (4.5×10^{-5} mol). ^b Used 2.0 equiv of catalyst. ^c Isolated yields. ^d Moles of propylene carbonate produced per mole of catalyst. ^e Used 5 equiv of catalyst. ^f Used 3 equiv of catalyst. ^g Reaction was carried out at room-temperature catalyst. ^h Reaction was carried out at 100 °C for 2 h.

presence of an organic base (0.2–1.0 mol %) (Table 1, entries 1–7 and 9) and the substituted binaphthyl-diamino salen-type Zn(II) and Cu(II) complexes **1d,f** gave the cyclic carbonate in lower yields under the same conditions (Table 1, entries 16–20). Among the organic bases mentioned above, Et₃N and DBU are the best organic bases under the same conditions (Table 1, entries 1–8). In the presence of a large excess of Lewis bases such as DBU or DMAP, the effectiveness of this reaction was lowered (Table 1, entries 5, 6, and 8). But, organic base Et₃N did not impair this catalytic reaction (Table 1, entry 3). Using binaphthyl-diamino Cu(II) salen-type complex as a catalyst, the achieved yield is lower than those of the corresponding Zn(II) and Co(II) complexes under the same conditions (Table 1, entries 7, 10, and 14). The reaction temperature, reaction time, and pressure of carbon dioxide are important factors for effecting the yields of cyclic carbonate **2a**. When the reaction was carried out at room temperature or under a CO₂ atmosphere (1.0 kg/cm²), no reaction could take place (Table 1, entry 11). In the short reaction period of only 2 h at 100 °C, for example, cyclic carbonate **2a** is obtained in only 12% (Table 1, entry 12). The best reaction conditions involve the unsubstituted binaphthyl-diamino Zn(II) salen-type complex **1a** (0.1 mol %) and Et₃N (0.2 mol %) at 100 °C under a high pressure of CO₂ (500 psi, 36 kg/cm²) (Table 1, entries 2 and 3).

Under optimized reaction conditions, we next examined the chemical fixation reactions of the other monosubstituted

SCHEME 2



tuted terminal epoxides with carbon dioxide using either zinc(II) or copper(II) complexes **1a** and **1b**, respectively, in the presence of Et₃N (Scheme 2). The results are summarized in Table 2. From Table 2, it is very clear that, when the catalyst loading is up to 1.0 mol %, both **1a** and **1b** are very effective catalysts and almost all of the monosubstituted terminal epoxides can be completely transferred to the corresponding cyclic carbonate **2** in very high yields (Table 2).





















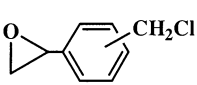
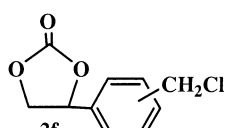
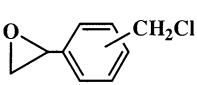
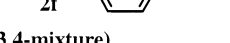
Compared to the results reported by Nguyen in which the cyclohexyldiamino Cr(III) salen-type metal complex was used as the catalyst, the reactivities are very similar between the two catalyst systems.¹⁰ They proposed a plausible mechanism according to Jacobsen's nucleophilic ring opening reaction of epoxides catalyzed by the Cr(III) salen-type metal complex.¹² The cyclohexyldiamino Cr(III) salen-type metal complex has a planar structure. The DMAP cocatalyst is necessary for the formation of the more electron-rich Cr(III) center in the salen–Cr(III)-DMAP complex, which is required to activate CO₂. This complex can then attack the activated epoxide by another salen–Cr(III) complex at the least sterically hindered carbon, leading to the formation of the dimeric intermediate, which eventually yields the cyclic carbonate product. However, in our binaphthyl-diamino Schiff base system, the metal catalysts are sterically more hindered. The crystal structure of a binaphthyl-diamino Co(II) salen-type complex (X = Y = H) has been disclosed by X-ray analysis (Figure 2, Supporting Information). The dissymmetric binaphthyl group has 70° dihedral angle. Thus, binaphthyl-diamino salen-type metal complexes have a sterically zigzagged structure (not a planar structure).¹³ It is impossible for two binaphthyl-diamino salen-type metal complexes to approach closely. However, our catalytic system still indicates very high catalytic activity. Considering the reaction mechanism, Kim showed that in the reaction of epoxide with CO₂ in the presence of ZnBr₂ and pyridine, the epoxy ring activated by Lewis acid ZnBr₂ was opened by the pyridine on the basis of the X-ray crystal structure.¹⁴ Then, the opened ring reacted further with CO₂ to give the corresponding cyclic carbonate. However, it is also well-known that an organic base can activate CO₂ as a Lewis base¹⁵ and the zwitterion [R₃N⁺C(O)O⁻] can open the aziridinyl and epoxy ring activated by a Lewis acid.¹⁶ To clarify the reaction mechanism, we synthesized *trans*-deuterioethene oxide as shown in Scheme 3 according to the literature (please see Experimental Section) and utilized it as the substrate in the reaction with CO₂ catalyzed by binaphthyl-diamino

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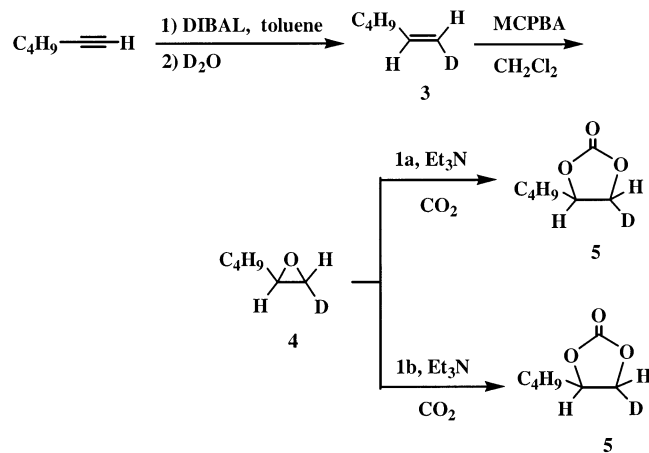
(13) For more crystal structures of binaphthyl-diamino metal complexes, please see: Cheng, M.-C.; Chan, M. C.-W.; Peng, S.-M.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1997**, 3479 and references therein.

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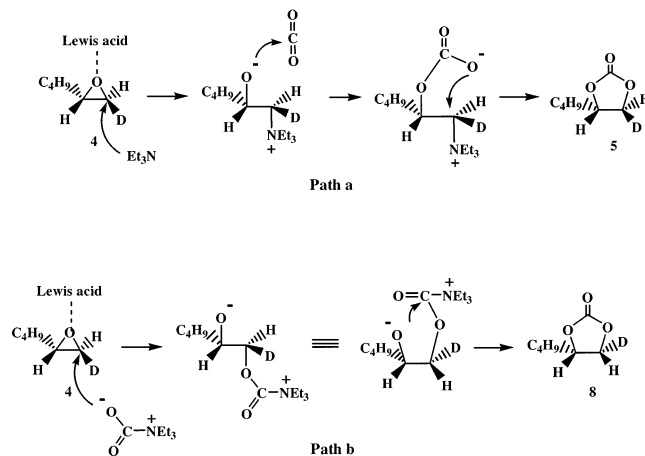
TABLE 2. Reactions of Various Epoxides with CO₂ in the Presence of Zn and Cu Complexes and Et₃N^a

Entry	epoxide	Cat.	product	yield (%) ^b
1		1a		100
2		1b		99
3		1a		96
4		1b		94
5		1a		96
6		1b		94
7		1a		100
8		1b		100
9		1a		90
10		1b		89
11		1a		95
12		1b		89

^a Reaction conditions: epoxide (4.5×10^{-3} mol), CH₂Cl₂ (5.0 mL), catalyst (4.5×10^{-5} mol), Et₃N (9.0×10^{-5} mol). ^b Isolated yield.

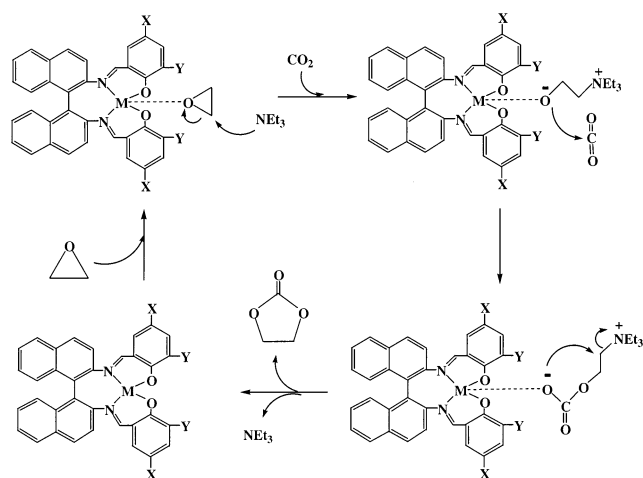
SCHEME 3

salen-type metal complexes **1a** and **1b** (Scheme 3). The deuterated ethene carbonate formed was analyzed with the authentic samples prepared as shown in Scheme 4 (Supporting Information) according to the literature (please see Experimental Section). We found that deuterated ethene carbonate **5** was formed exclusively. This

SCHEME 5

result suggests that the formation of cyclic carbonate in our reaction system proceeded via path a as shown in Scheme 5, namely, the epoxy ring activated by Lewis acid **1a** or **1b** is first opened by amine and then reacts with CO₂ to give the corresponding deuterated ethene carbon-

SCHEME 6



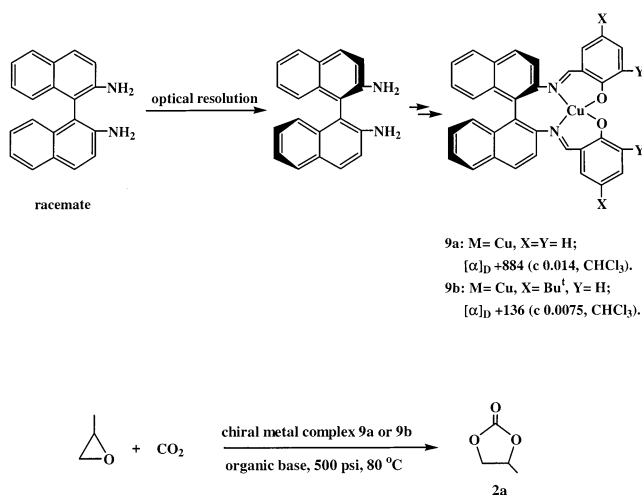
ate **5**, because if the reaction proceeded via path b, another deuterated ethene carbonate **8** having the opposite configuration of the deuterium atom in **5** would be formed exclusively (Scheme 5).

On the basis of the above results, in Scheme 6, we proposed the plausible mechanism for this chemical fixation reaction of CO₂. We believe that, in fact, this system is cocatalyzed by a Lewis base amine and Lewis acid **1a** or **1b**. The Lewis base and Lewis acid work together to open the epoxy ring and then react with CO₂ to give the corresponding cyclic carbonate via a ring-opening and recyclization process. Previous reports also suggest the parallel requirement of both Lewis base activation of the CO₂ and Lewis acid activation of the epoxide.^{4,16}

Using chiral binaphthyldiamino salen-Cu complexes **9a** and **9b** prepared from chiral (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine as the catalyst, we also investigated the catalytic asymmetric version of the catalytic reaction of epoxide with CO₂ (Scheme 7). However, so far we have only achieved 5% ee of the carbonate at 80 °C (1~2% ee at 100 °C) based on chiral GC analysis (Scheme 7) [GC column, HP chiral (20% permethylated β-cyclodextrin) 30 × 0.25 × 0.25 mm; injection temp = 250 °C; detection temp = 250 °C]. We believe that it is very difficult to achieve high enantioselectivity in this reaction because it requires a higher reaction temperature (>80 °C). At lower temperatures (<80 °C), the yield of carbonate will be significantly decreased. In general, the high enantioselectivity is very hard to achieve at high temperatures in catalytic asymmetric chemistry.

In conclusion, we explored efficient binaphthyldiamino salen-type copper(II), cobalt(II), and zinc(II) complex systems for the production of cyclic carbonate **2** from the reactions of epoxides with carbon dioxide in the presence

SCHEME 7



9a: M= Cu, X=Y= H;
[α]_D +884 (c 0.014, CHCl₃),
9b: M= Cu, X= Bu', Y= H;
[α]_D +136 (c 0.0075, CHCl₃).

chiral complex 9a: 23% yield, 3% ee.
chiral complex 9b: 31% yield, 5% ee.

of a catalytic amount of organic base. The reaction mechanism has been disclosed by isotope-labeling experiments. Cyclic carbonate **2** is the sole product in this reaction. More importantly, the catalysts used in this catalytic system are extremely stable and can be recycled at least 10 times, and their activity is still unchanged. Efforts are underway to elucidate the mechanistic details of the reaction and explore other applications of the catalyst system.

Experimental Section

General Methods. Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz, respectively. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel-coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

Representative Procedure for the Reaction of Epoxide with Carbon Dioxide. A 100 mL stainless pressure reactor was charged with complex **1a** (25 mg, 4.5 × 10⁻⁵ mol), propylene oxide (2.6 g, 4.5 × 10⁻² mol), Et₃N (9.0 mg, 9 × 10⁻⁵ mol), and CH₂Cl₂ (5.0 mL). The reaction vessel was placed under a constant pressure of carbon dioxide for 5 min to allow the system to equilibrate and then heated to 100 °C for 16 h. The vessel was then cooled to ambient temperature; the pressure was released, and the contents were transferred to a 50 mL round-bottom flask. Unreacted substrate and solvent were removed in vacuo, and the residue was purified by silica gel column chromatography (eluent: 1/4 petroleum ether/EtOAc) to give cyclic carbonate **2a** as a colorless liquid.

Acknowledgment. We thank the State Key Project of Basic Research (Project 973) (No. G2000048007) and the National Natural Science Foundation of China for financial support (20025206 and 20272069).

Supporting Information Available: ORTEP diagrams of **1c**, Figure 2, Scheme 4, experimental procedures and data for compounds mentioned herein, ¹³C NMR charts of **2a–f**, and ¹H NMR charts of **5–8** and reaction products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) For the interaction of organic bases with CO₂, it is well-known that organic bases (R₂NH) can coordinate to CO₂ to give a R₂NCO₂⁻ complex. Please see: (a) Inoue, S.; Yamazaki, Y. *Organic and Bioorganic Chemistry of Carbon Dioxide*; Kodansha, Ltd.: Tokyo, 1982; p 31. (b) Abila, M.; Choi, J.-C.; Sakakura, T. *Chem. Commun.* **2001**, 2238. (c) George, M.; Weiss, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 10393. Very recently, a molecular complex of DBU and CO₂ was isolated from the reaction of DBU with CO₂. Perez, E. R.; Silva, M. O.; Costa, V. C.; Rodrigues-Filho, U. P.; Franco, D. W. *Tetrahedron Lett.* **2002**, *43*, 4091.

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