



## Intramolecularly two-centered cooperation catalysis for the synthesis of cyclic carbonates from CO<sub>2</sub> and epoxides

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### ABSTRACT

A catalyst system containing an electrophilic center and a sterically hindered nucleophilic center in one molecule was applied to the cycloaddition reaction of CO<sub>2</sub> and epoxides. This intramolecularly two-centered cooperation catalyst showed activity even at a high [epoxide]/[catalyst] ratio up to 50000 under mild conditions such as solvent-free, ambient temperature, and low CO<sub>2</sub> pressure. The reaction of CO<sub>2</sub> with (*S*)-propylene oxide at 80 °C in the presence of the bifunctional catalyst gives (*S*)-propylene carbonate in 96% ee with retention of stereochemistry.

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Catalytic transformation of CO<sub>2</sub> into useful organic compounds has received much attention because of its potential use as an abundant carbon source and its indirect role as an environmental pollutant.<sup>1</sup> The coupling of CO<sub>2</sub> with epoxides affording cyclic carbonates is one of the most extensively studied reactions with respect to the chemical fixation of CO<sub>2</sub>.<sup>2</sup> These carbonates can be used as aprotic polar solvents and as precursors for polymeric materials.<sup>3</sup> In recent decades, numerous catalyst systems including amines or in conjunction with phenols,<sup>4</sup> quaternary ammonium or phosphonium salts,<sup>5</sup> ionic liquids,<sup>6</sup> alkali metal or zinc salts,<sup>7</sup> organotin halides,<sup>8</sup> carbonyl metal complexes,<sup>9</sup> metal complexes of porphyrin, phthalocyanine and Salen<sup>10–12</sup> have been developed for this transformation. Prominent among these are binary catalyst systems, being the most efficient for the CO<sub>2</sub>/epoxides coupling reaction even at ambient temperature and low CO<sub>2</sub> pressure.<sup>13</sup> A general pattern in the reaction of CO<sub>2</sub> with epoxides has emerged, wherein catalysis involves activation of both epoxides and CO<sub>2</sub>. Our recent research found that the synergistic actions of an electrophile in conjunction with a nucleophile were more effective in catalyzing this reaction.<sup>12,13</sup> Since the reaction rate is dependent on the catalyst concentration, these binary systems usually show substantial loss in activity at a high [epoxide]/[catalyst] ratio. We believe that the nucleophilic attack of a nucleophile or an activated CO<sub>2</sub> at the activating epoxide, which could be activated by its coordination to an electrophile, is similar to a bimolecular process (Scheme 1). Therefore, the rate is directly proportional to the concentration of the nucleophile or the activated CO<sub>2</sub> in connection with the nucleophile and the activated epoxide with regard to the concentration of the electrophile. Recently, Lee and co-workers

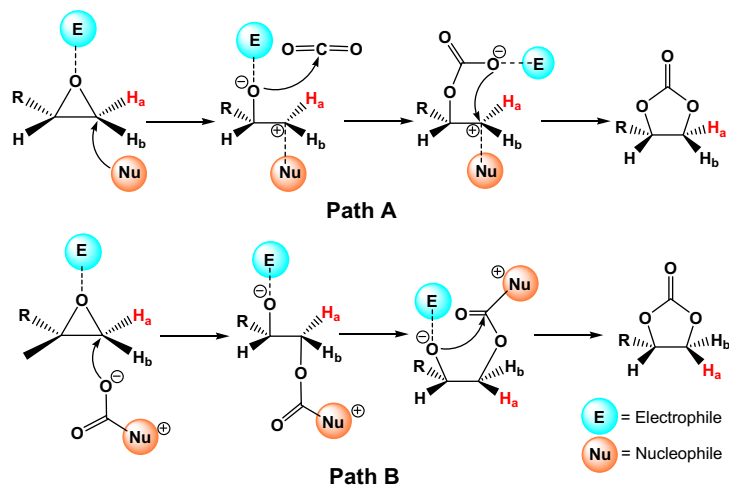
reported an elegant design of catalyst system containing a Lewis acidic metal center and a quaternary ammonium salt unit in a molecule, which showed high activity for polycarbonate synthesis even at high temperature and high [epoxide]/[catalyst] ratio.<sup>14</sup> Also, a similar bifunctional cobalt–Salen complex was designed and used as catalyst for cyclic carbonates synthesis.<sup>15</sup>

In 2001, Nguyen group reported binary salenCr(III)Cl/ DMAP catalyst systems for epoxides/CO<sub>2</sub> coupling to cyclic carbonates, in which a cooperative mechanism involving two different metal species was proposed based on the requirement of both Lewis base-activation of CO<sub>2</sub> and Lewis acid-activation of the epoxide.<sup>12a</sup> Unfortunately, the binary systems did not efficiently operate at ambient temperature and low CO<sub>2</sub> pressure. In the present Letter, we report a catalytic system based on pyrrolidine SalenCr(III)X complexes containing an electrophilic center (Lewis acid metal ion) and a nucleophilic center (sterically hindered strong organic base) in one molecule (Fig. 1a–c). The selective anchoring of sterically hindered strong organic base such as 1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD) is based on the fact that CO<sub>2</sub> can be activated by bicyclic amidines through the formation of the zwitterionic compound, which can add to the epoxide via nucleophilic attack.<sup>4a,16</sup> Suppressed by steric repulsion, the organic base unit in this complex cannot coordinate to the central metal ion, so we can expect a high activity for the CO<sub>2</sub>/epoxides coupling by intramolecular cooperation catalysis of bifunctional electrophile–nucleophile units even at high [epoxide]/[catalyst] ratio and under low CO<sub>2</sub> pressure.

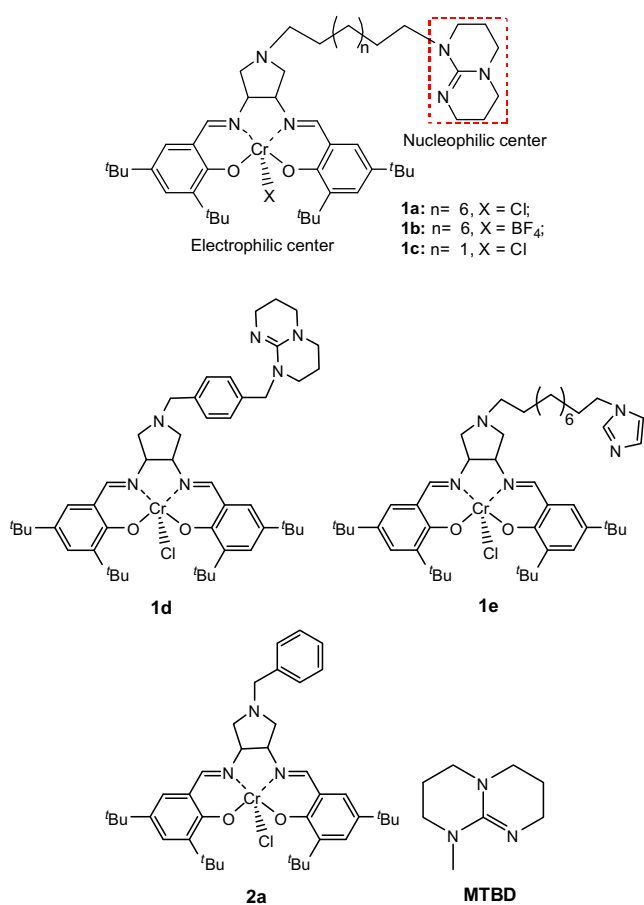
Since pyrrolidine SalenCr(III)X complexes **1a–e** and **2a** are easily dissolved in neat epoxides surveyed, the catalyzed coupling of CO<sub>2</sub> and epoxides does not require any organic co-solvent. Our initial studies showed that **1a**, a Salen chromium complex with an anchored sterically hindered TBD on its pyrrolidine ring, could effectively catalyze the cycloaddition of CO<sub>2</sub> to propylene oxide

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**Scheme 1.** The possible synergistic mechanisms of the cycloaddition of CO<sub>2</sub> to epoxides catalyzed by binary electrophile–nucleophile systems.



**Figure 1.** The structure of various pyrrolidine SalenCr(III)X complexes.

(PO) at a high [epoxide]/[catalyst] ratio of 5000 at ambient temperature (Table 1, entry 1), while **2a** or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) alone did not show any activity under the same conditions (entries 2 and 3). No by-product such as polycarbonates or polyester was observed.

The reaction temperature had a strong influence on the rate. An increase in the temperature from 25 to 80 °C resulted in a dramatic increase of TOF from 48 h<sup>-1</sup> to 1936 h<sup>-1</sup>. As expected, altering the

**Table 1**

The catalyzed coupling of CO<sub>2</sub> and propylene oxide (PO) at various conditions<sup>a</sup>

Entry	Catal.	PO/catal. (mol/mol)	T (°C)	P (MPa)	t (h)	TOF <sup>b</sup> (h <sup>-1</sup> )
1	<b>1a</b>	5000	25	0.5	24	48
2	<b>2a</b>	5000	25	0.5	24	<1
3	MTBD	5000	25	0.5	24	<1
4	<b>1a</b>	5000	80	2.0	1	1936
5	<b>1a</b>	20,000	25	0.5	24	46
6	<b>1a</b>	50,000	25	0.5	24	49
7	<b>1a</b>	20,000	80	2.0	1	1788
8 <sup>c</sup>	<b>2a</b> /MTBD	5000	25	0.5	24	<1
9 <sup>c</sup>	<b>2a</b> /MTBD	1000	25	0.5	24	6
10 <sup>c</sup>	<b>2a</b> /MTBD	500	25	0.5	24	10
11	<b>1b</b>	50,000	25	0.5	24	42
12	<b>1b</b>	5000	80	2.0	1	1819
13	<b>1c</b>	5000	25	0.5	24	42
14	<b>1c</b>	5000	80	2.0	1	2120
15	<b>1d</b>	5000	25	0.5	24	<1
16	<b>1d</b>	5000	80	2.0	1	27
17	<b>1e</b>	5000	25	0.5	24	<1
18 <sup>d</sup>	<b>1a</b>	5000	25	0.5	24	<1

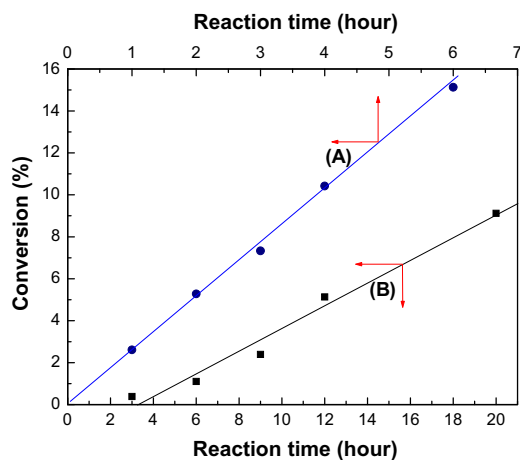
<sup>a</sup> The reaction was performed in neat propylene oxide.

<sup>b</sup> The rate is expressed in terms of turnover frequency (TOF, moles of cyclic carbonate product per mole of catalyst per hour).

<sup>c</sup> Compound **2a**/MTBD = 1:1 (molar ratio).

<sup>d</sup> In the presence of 2 equiv *N*-methylimidazole.

[epoxide]/[catalyst] ratio between 5000 and 50000 did not lead to an obvious change in activity (entries 1, 4–7). In contrast, with the use of binary catalyst system consisting of complex **2a** and MTBD, the reaction rate was significantly dependent on the catalyst concentration (entries 8–10), and a complete loss in catalyst activity was observed at 25 °C with [PO]/[catalyst] ratio of 5000. A long induction period of about 3 h was observed from the plot of conversion versus time at [PO]/[catalyst] ratio of 5000, at 40 °C and under 2.0 MPa pressure, while with complex **1a** as catalyst, no induction period was observed under the same conditions (Fig. 2). These results demonstrate that intramolecular two-centered cooperation catalysis of bifunctional units in complex **1a**, in which the central metal ion serves as an electrophilic center and the anchored TBD as a nucleophilic center, is the sole factor for maintaining activity of the catalyst at a high [epoxide]/[catalyst] ratio. Recently, Heldebrant et al. have reported that they were unable to spectroscopically observe adduct formation between 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, a sterically hindered strong organic base) and CO<sub>2</sub> under moderate CO<sub>2</sub> pressure and at ambient temperature, while single crystals of the bicarbonate salt of



**Figure 2.** Plots of conversion of the epoxide versus time, with the use of (A) **1a** alone, and (B) binary **2a**/MTBD as catalyst for the cycloaddition of CO<sub>2</sub> to PO at a condition of [PO]/[catalyst] ratio of 5000, 40 °C and 2.0 MPa pressure.

DBU were isolated in the presence of adventitious water.<sup>17</sup> Darenbourg and co-workers further concluded from some control experiments that bicarbonate generated by adventitious water was not likely the cocatalyst in the catalyst systems which consisted of SalenCr(III) and 4-(dimethylamino)pyridine.<sup>18</sup> Indeed, although every effort has been made to keep the coupling reaction anhydrous, we were concerned that trace quantities of water might be present, thereby leading to the formation of the bicarbonate salt of the anchored TBD under CO<sub>2</sub> atmosphere, which might be shown to have a deleterious effect on the reaction rate.

A change in the axial X group of pyrrolidine SalenCr(III)X from Cl<sup>-</sup> to BF<sub>4</sub><sup>-</sup> (a non-nucleophilic anion, **1b**) does not cause an obvious decrease in activity (entries 11 and 12). It is worth noting that the properties of the spacer linked through the nitrogen atoms in the backbone of the pyrrolidine Salen ligand and nucleophilic TBD play an important role in maintaining intramolecularly two-centered cooperation catalysis of the bifunctional chromium complexes. A flexible spacer is usually a prerequisite for obtaining excellent catalytic activity at high [epoxide]/[catalyst] ratio. The complex **1d** with the *p*-xylylene spacer hardly showed any activity at a [epoxide]/[catalyst] ratio of 5000 (entries 15 and 16). These results further indicate that the enhanced activity in the cycloaddition of CO<sub>2</sub> to PO be completely ascribed to the synergistic actions between the electrophilic metal ion and the nucleophilic TBD in the complexes **1a–c**.

Surprisingly, substituted imidazole (a coordination base, **1e**) for sterically hindered TBD anchored on the pyrrolidine ring of SalenCr(III)X resulted in nearly complete loss in activity at ambient temperature (entry 17). Interestingly, in the presence of 2 equiv *N*-methylimidazole, the complex **1a** also did not show any activity for this reaction under the same conditions (entry 18). It could be ascribed to the coordination of *N*-methylimidazole to the central metal ion, thereby retarding the activation of the epoxide. These results indicate that the steric repulsion originating from TBD effectively inhibits its coordination to Lewis acidic metal ion, thereby remains as intramolecular cooperative catalysis of nucleophilic–electrophilic centers during the reaction.

The complex **1a** containing nucleophilic and electrophilic centers was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in high rate and 100% selectivity (Table 2). Among the epoxides surveyed, ethylene oxide was found to be the most reactive, one and a TOF up to 3338 h<sup>-1</sup> was observed in the coupling reaction of CO<sub>2</sub> at 80 °C. A prolonged time of 8 h nearly resulted in the quantitative conver-

**Table 2**

The coupling reaction of CO<sub>2</sub> with various epoxides catalyzed by the complex **1a**<sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield (%)	TOF (h <sup>-1</sup> )
1			1	66.7	3338
2			1	38.7	1936
3			8	97.4	609
4			1	23.0	1150
5			1	30.0	1500
6			1	30.0	1498

<sup>a</sup> The reaction was performed in neat epoxide at 80 °C and 2.0 CO<sub>2</sub> MPa, epoxide/**1a** = 5000 (molar ratio).

sion (Table 2, entry 3). Notably, the reaction of CO<sub>2</sub> with (*S*)-propylene oxide gave (*S*)-propylene carbonate in 96% ee with retention of stereochemistry at 80 °C. However, complex **1a** was inactive for the coupling reaction of CO<sub>2</sub> and cyclohexene oxide, perhaps due to the steric hindrance of the epoxide, significantly affecting the nucleophilic ring-opening of the coordinated cyclohexene oxide attacked by sterically hindered nucleophilic center. An attempt for direct synthesis of optically active cyclic carbonates from the racemic epoxides by a catalytic kinetic resolution process<sup>13</sup> was also performed in the cycloaddition of CO<sub>2</sub> and PO in the presence of chiral (*R,R*)-**1a** as catalyst, but the enantioselectivity of the resulted propylene carbonate was less than 40% ee and the corresponding *K*<sub>rel</sub> was in the range of 1.5–2.5.

In summary, a catalyst containing both an electrophilic center and a sterically hindered nucleophilic center in one molecule was synthesized and applied to the coupling of CO<sub>2</sub> and epoxides. The bifunctional catalyst system is active even at a high [epoxide]/[catalyst] ratio up to 50000, while the conventional binary electrophile–nucleophile catalyst system completely loses its activity under the same conditions. The reaction was carried out with perfect atom economy under solvent-free and very mild conditions such as ambient temperature and low CO<sub>2</sub> pressure. The design of two-centered catalyst in the present study is in connection with a green chemistry approach to catalysis: solvent-free and very low catalyst loading.<sup>19</sup> Further exploration of intramolecularly cooperative catalysis for other applications is now underway in our laboratory.

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## Supplementary data

Synthetic details and characterization of various pyrrolidine Salen ligands and their corresponding chromium complexes **1a–e**, as well as representative procedure for the cycloaddition reaction of CO<sub>2</sub> with epoxide. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.035.

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