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Bifunctional Aluminum Catalyst for CO_2 Fixation: Regioselective Ring Opening of Three-Membered Heterocyclic Compounds

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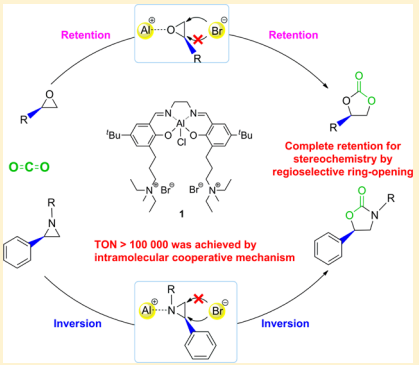
Supporting Information

ABSTRACT: Regioselective ring opening of three-membered heterocyclic compounds (epoxides or *N*-substituted aziridines) at various temperatures was observed in coupling reactions with CO_2 by the use of an aluminum−salen catalyst in conjunction with intramolecular quaternary ammonium salts as cocatalysts, affording the corresponding five-membered cyclic products with complete configuration retention at the methine carbon. Notably, this bifunctional aluminum-based catalyst exhibited nearly 100% regioselectivity for the ring opening at the methylene C−O bond for various terminal epoxides. This was true for those bearing an electron-withdrawing group, such as styrene oxide or epichlorohydrin, thereby affording the synthesis of various enantiopure cyclic carbonates that have previously been obtained only rarely by other methods. An intramolecular cooperative catalysis is suggested to contribute to the high activity and excellent stereochemistry control observed. Surprisingly, the highly selective ring opening at the methine carbon of *N*-substituted aziridines was found in the coupling with CO_2, predominantly giving 5-substituted oxazolininones with retention of configuration as a result of double inversion at the methine carbon.



INTRODUCTION

Efficient strategies for the fixation of carbon dioxide (CO_2) into economically competitive products are urgently sought in light of the growing concern over the greenhouse effect, which is mainly caused by emission-based CO_2, together with the necessity to find alternative feedstocks to fossil fuels.[1] One of the most promising reactions for the use of this abundant, inexpensive, nontoxic, and renewable resource is the coupling of CO_2 and epoxides to provide cyclic carbonates.[2] The driving force for this process is provided by the release of the ring-strain energy in the three-membered ring of the epoxide to afford the more stable five-membered cyclic product, even though CO_2 is such a thermodynamically stable molecule. The use of catalysts, especially aluminum-based binary or bifunctional electrophile−nucleophile systems, significantly facilitates this transformation under mild conditions.[3−6] The highest activity, with a turnover frequency (TOF) of up to 36 000 h^{-1}, was realized by an aluminum complex based on amino-triphenolate ligand.[6] Moreover, this catalyst system exhibited broad substrate scope and functional group tolerance in the formation of cyclic carbonates.

On the other hand, enantiopure cyclic carbonates are key intermediates in the synthesis of a variety of pharmaceutically important compounds and fine chemicals.[7] They can be prepared by the cyclization of chiral diols with poisonous triphosgene[8] or enzyme-mediated enantioselective hydrolysis of racemic cyclic carbonates with very low efficiency.[9] In 2004, we proposed a convenient route to optically active cyclic carbonates by a catalytic kinetic resolution process resulting from the coupling reaction of CO_2 and racemic epoxides.[10] Nonetheless, the relatively low activity and enantioselectivity as well as the rigorous reaction conditions, such as a low temperature of −25 °C,[11] significantly limited its application. Alternatively, the insertion of CO_2 into chiral epoxides is feasible for preparing enantiopure cyclic carbonates on a large scale, since enantioenriched substances are easily obtained by metal−salen-catalyzed hydrolytic kinetic resolution of terminal epoxides.[12] However, it proved to be very difficult to obtain highly enantiopure cyclic carbonates even using epoxides with greater than 99% enantiomeric excess (ee). The reason is that no effective catalyst is available to facilitate selective ring opening only at methylene C−O bond of terminal epoxides, while ring opening occurring at the methine C−O bond may cause a change in stereochemistry with inversion (Scheme 1).[13] As a consequence, the development of highly efficient catalyst systems for this regioselective transformation is highly desired.

Herein we report the bifunctional catalyst **1** consisting of an electrophilic metal ion and a nucleophilic quaternary ammonium salt in one molecule (Figure 1) for the coupling reaction of CO_2 with three-membered heterocyclic compounds (both epoxides and *N*-substituted aziridines). This catalyst exhibits excellent activity and unprecedented regioselectivity at various temperatures, affording the corresponding five-membered cyclic products with complete retention of configuration at the methine carbon. An intramolecularly cooperative catalysis is suggested to contribute to the high activity and excellent stereochemistry control.

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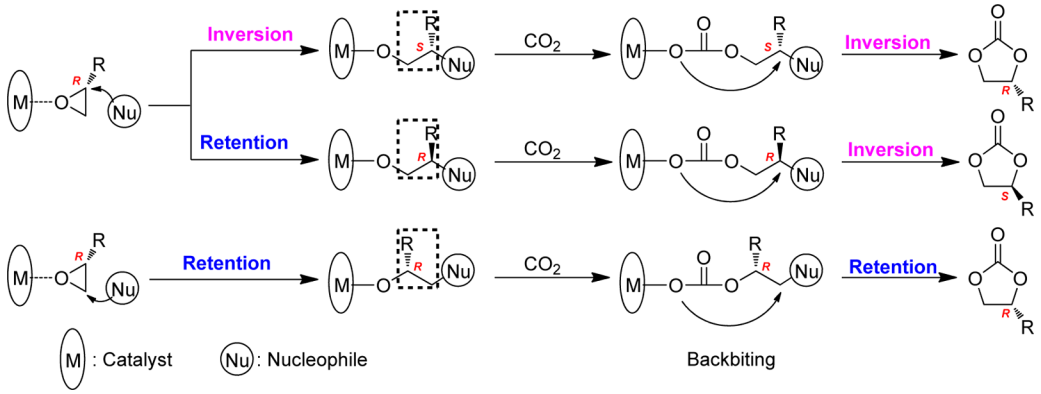
Scheme 1. Stereochemistry Involved in (*R*)-Epoxide Ring Opening at the Central Metal Ion of the Catalyst during the Coupling Reaction with CO_2



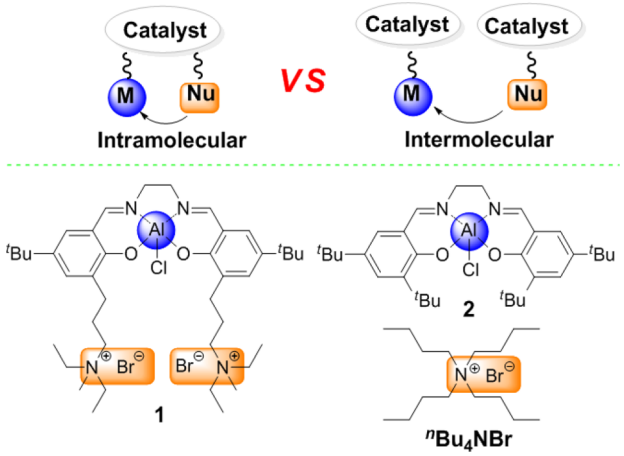
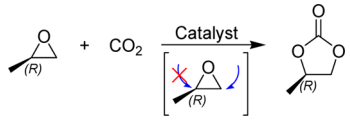


Figure 1. Bifunctional and binary catalyst systems used in this study.

RESULTS AND DISCUSSION

Initially, enantiopure propylene oxide (PO) was employed as model epoxide to test the activity and regioselectivity of bifunctional catalyst **1**. This catalyst exhibited good activity for the CO_2/(*R*)-PO coupling reaction at a [PO]/[catalyst] ratio of 10 000 under 80 °C. The resultant propylene carbonate had a high enantiopurity of more than 99% ee (Table 1, entry 1). The activity increased dramatically when the temperature was increased to 120 °C, and a TOF of up to 5240 h^{-1} was achieved (entry 3). More importantly, variation of the temperature did not lead to a decrease in enantioselectivity for propylene carbonate formation, which indicated that complex **1** exhibits regioselective ring opening of PO even at enhanced temperatures.[14] With a further increase in the molar ratio of epoxide to catalyst, no obvious changes in reaction rate and enantioselectivity were observed in this reaction (entries 3 and 4). Notably, when the reaction time was prolonged, quantitative conversion of the epoxide was achieved at a [PO]/[catalyst] ratio of 25 000 (entry 5). By contrast, the binary catalyst system composed of complex **2** in conjunction with ^{n}Bu$_4$NBr (2 equiv) showed a low activity, and only 8% of the epoxide was converted under the same conditions (entry 6). The significant difference in activity is shown by the plots of conversion versus reaction time (Figure 2). In addition, with complex **1** as the catalyst, no induction period was observed from the three-dimensional stack plots at 120 °C with a [PO]/[catalyst] ratio of 25 000, while an induction period of about 20 min appeared with the binary **2**/^{n}Bu$_4$NBr catalyst system under the same conditions (Figure 3).

Table 1. (*R*)-Propylene Oxide/CO_2 Coupling Results[a]



entry	catalyst	[PO]/[Cat.]	temperature (°C)	time (h)	TOF (h^{-1})[b]	TON
1	**1**	10000	80	1	2210	2210
2	**1**	10000	100	1	4520	4520
3	**1**	10000	120	1	5240	5240
4	**1**	25000	120	2	5250	10500
5	**1**	25000	120	8	3100	24800
6[c]	**2**	25000	120	8	245	1960
7	**1**	100000	120	24	3380	81100
8	**1**	200000	120	48	2420	116230
9[d]	**1**	200000	120	48	2410	115880

[a]Typical reaction conditions: 100 mmol of PO, 2.5 MPa CO_2. The optical purities of all the resultant cyclic propylene carbonates were >99% ee based on chiral GC. [b]Turnover frequency (TOF) = moles of cyclic carbonate per mole of catalyst per hour. [c]In the presence of 2 equiv of ^{n}Bu$_4$NBr. [d]The catalyst was recycled.

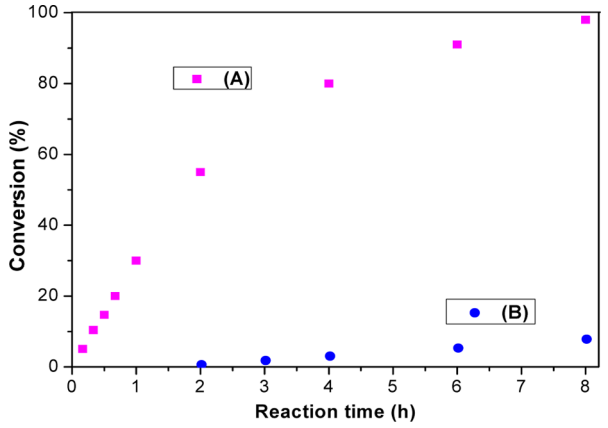


Figure 2. Plots of epoxide conversion vs time, with the use of (A) complex **1** alone or (B) the binary **2**/^{n}Bu$_4$NBr system (the molar ratio of **2** to ^{n}Bu$_4$NBr was 1/2) as the catalyst for the CO_2/PO coupling with a [PO]/[catalyst] ratio of 25 000 at 120 °C and a pressure of 2.5 MPa. The conversion was determinted by ^{1}H NMR spectroscopy.

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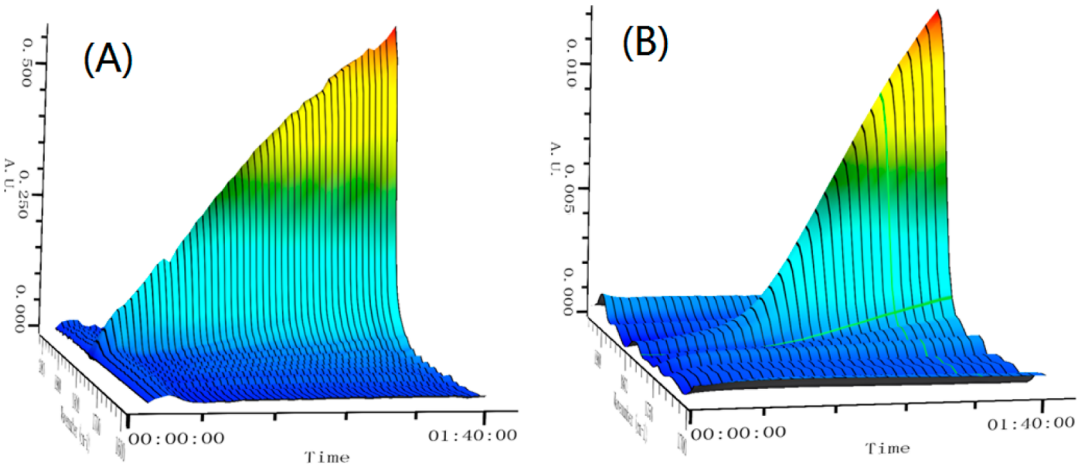
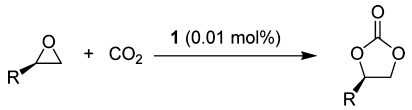


Figure 3. Three-dimensional stack plots of IR spectra recorded every 30 secondes during the coupling reaction of PO with CO_2 utilizing (A) complex **1** or (B) the binary **2**/^{n}Bu$_4$NBr system (the molar ratio of **2** to ^{n}Bu$_4$NBr was 1/2) as the catalyst at a [PO]/[catalyst] ratio of 25000, 120 °C, and a pressure of 2.5 MPa.

A catalyst's power is estimated not only by its activity (TOF) but also by its durability, as indicated by the turnover number (TON). The latter may be more important for industrial applications. To achieve a high TON, we investigated the coupling reaction at a much higher molar ratio of PO to complex **1** (Table 1, entries 7 and 8). The results show that a high TON of 116 230 was realized at a [PO]/[catalyst] ratio of 200 000.[15] The unreacted PO and formed propylene carbonate could be separated easily by simple fractional distillation. The residual aluminum complex could be recycled without further treatment, and no obvious loss in activity and regioselectivity was observed (entry 9).

Moreover, the bifunctional catalyst **1** was also applied a variety of enantiopure epoxides to prepare the corresponding chiral cyclic carbonates by coupling with CO_2. The results are summarized in Table 2. It was found that this catalyst was very efficient for terminal epoxides with an electron-donating group, such as 1,2-butene oxide or 1,2-hexene oxide, at 120 °C (entries 1 and 2). (*S*)-Phenyl glycidyl ether was found to be a highly reactive epoxide (entry 3), and the diol derived from the hydrolysis of the resulting (*R*)-cyclic carbonate was shown to have an enantioselectivity of >99% ee with the *S* configuration in excess, demonstrating that the reaction proceeded with complete retention of stereochemistry at the methine carbon.

Table 2. Various Enantiopure Epoxide/CO_2 Coupling Results[a]



entry	R	temperature (°C)	time (h)	TOF (h^{-1})[b]	ee (%)[c]
1	Et (*R*)	120	3	3300	>99 (*R*)
2	^{n}Bu (*R*)	120	12	830	>99 (*R*)
3	CH_2OPh (*S*)	120	7	1210	>99 (*R*)
4	CH_2Cl (*S*)	120	8	1240	67 (*S*)
5	Ph (*R*)	120	12	750	83 (*R*)
6	CH_2Cl (*S*)	60	24	410	99 (*S*)
7	Ph (*R*)	80	24	400	99 (*R*)
8[d]	Ph (*R*)	80	24	75	99 (*R*)

[a]Typical reaction conditions: 100 mmol of enantiopure epoxide, 0.01 mmol of complex **1**, 2.5 MPa CO_2, except for entry 8. [b]Turnover frequency (TOF) = moles of cyclic carbonate per mole of catalyst per hour. [c]Enantiomeric excess of the resulting cyclic carbonate, as determined by chiral GC or HPLC. [d]The reaction was carried out at 0.1 MPa CO_2.

Although much-studied metal- or organocatalysts can mediate the coupling reaction of CO_2 with epichlorohydin or styrene oxide, rare success was reported for the synthesis of enantiopure cyclic carbonates from these epoxides with an electron-withdrawing group.[16] In the present study, we were interested in the coupling reaction of CO_2 with (*S*)-epichlorohydrin or (*R*)-styrene oxide to prepare the corresponding highly enantiopure cyclic carbonates. At a high temperature of 120 °C, complex **1** showed lower regioselectivity for the coupling reaction (Table 2, entries 4 and 5). Fortunately, a decrease in the reaction temperature from 120 to 60 °C led to dramatic increases in enantiopurity of the formed chloromethyl(ethylene carbonate) from 67% to 99% ee (entry 6) and phenyl(ethylene carbonate) from 83 to 99% ee (entry 7),[17] respectively. Notably, the bifunctional catalyst proved to be very efficient for the (*R*)-styrene oxide/CO_2 coupling reaction even under a CO_2 pressure of 0.1 MPa at 80 °C (entry 8).[18] It is worthwhile to note here parenthetically that in a previous study regarding CO_2/styrene oxide coupling mediated by a multichiral cobalt(III) complex in conjunction with an ammonium salt, a highest enantioselectivity of 93.1% ee was observed in the resulting cyclic styrene carbonate obtained from the enantiopure epoxide with 99% ee at ambient temperature,[11d] indicating the difficulty in controlling the regioselective ring opening for this kind of epoxide.

In contrast to terminal epoxides with electron-donating groups, the nucleophilic ring opening of epoxides with electron-withdrawing groups, such as styrene oxide, preferentially occurs at the methine C−O bond rather than the methylene C−O bond.[19] As previously mentioned, attack at the methine carbon may cause a change in stereochemistry with inversion. In addition, it is well-accepted that ring closure by attack of the carboxylate species at the methine carbon predominantly causes a change in stereochemistry with inversion (Scheme 1). Therefore, there are two different approaches for obtaining the highly enantiopure cyclic carbonate derived from chiral styrene oxide or epichlorohydrin: (1) complete retention of stereochemistry at the methine carbon through selective ring

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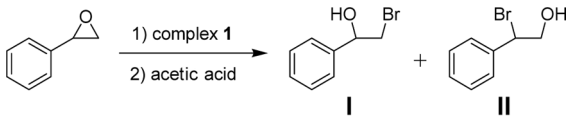
opening of terminal epoxides at the methylene C−O bond or (2) two consecutive S_N2 processes at the methine carbon occurring in both the ring-opening and ring-closure steps. Recently, Chisholm and co-workers performed an elegant study to investigate the stereochemical consequences of the ring-opening event in the chromium tetraphenylporphyrin-mediated coupling reaction of CO_2 and styrene oxide.[20] In order to ascertain which route was responsible for the high stereochemistry control in this coupling reaction, the stoichiometric reaction between complex **1** and styrene oxide was performed at various temperatures to gain insight into the regioselectivity by examining the resultant bromoalcohols, **I** and **II** shown in Scheme 2, respectively. The formation of compound **I** would

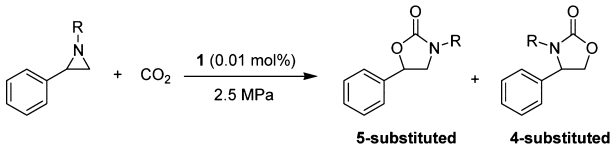
Scheme 2. Regioselective Ring Opening of Styrene Oxide by Complex 1



imply nucleophilic attack of Br^- at the methylene carbon, while the formation of **II** would mean attack at the methine carbon. It was found that compound **I** was produced predominantly at room temperature or even up to 80 °C (see the Supporting Information). These results indicated that complex **1** exhibited high regioselectivity for ring opening of (*R*)-styrene oxide at the methylene C−O bond at 80 °C. Further increasing the reaction temperature to 120 °C led to an obvious loss in regioselectivity, and both **I** and **II** were detected in a molar ratio of 8:2. On the basis of these results, we can conclude that attack at the methine carbon affords a 3:2 ratio of inversion to retention in the coupling reaction of CO_2 and styrene oxide catalyzed by complex **1** at 120 °C, consistent with 83% ee for the resultant phenyl(ethylene carbonate).

Oxazolidinones, as important compounds in synthetic and medicinal chemistry,[21] could be produced by the carboxylation of CO_2 with aziridines, another class three-membered cyclic compounds with high ring-strain energy.[22] In contrast with the sole product resulting from the cycloaddition of epoxides and CO_2, the coupling reaction of aziridines with CO_2 is proven to give two oxazolidinones (5-substituted and 4-substituted ones). Indeed, the complex **1**-mediated coupling reaction of *N*-methyl-2-phenylaziridine with CO_2 at 120 °C concurrently formed 5-substituted and 4-substituted oxazolidinones in a 4:1 ratio (Table 3, entry 1). A decrease in reaction temperature from 120 to 80 °C resulted in nearly exclusive generation of the 5-substituted oxazolidinone (entry 3). These results are different from those for the same coupling reaction mediated by our previously reported *N*-heterocyclic carbene−CO_2 adduct, in which the variation of temperature had no influence on the regioselectivity of ring opening for *N*-substituted aziridines.[23] Investigations of the substituent group found that the coupling reaction of ethyl- or benzyl-substituted aziridines with CO_2 afforded the 5-substituted products exclusively (entries 4 and 5). These results demonstrated that complex **1** shows high regioselectivity for the ring opening of *N*-substituted aziridines occurring at methine C−N bond, which is distinctly different from the coupling reaction of CO_2 and styrene oxide. Furthermore, the coupling reactions of CO_2 with (*R*)-1-benzyl-2-phenylaziridine and (*R*)-1-butyl-2-phenylaziridine afforded (*R*)-5-substituted oxazolidinones with high enantiopurity of up to 99% ee (entries 6 and 7).[24] A possible formation pathway involving two consecutive S_N2 processes at the same carbon is suggested in Scheme 3.[25] The nucleophilic ring opening of *N*-substituted aziridine at the methine C−N bond leads to complete inversion of configuration at the methine carbon. This is followed by backbiting with regard to the attack of the carbamate species at the methine carbon after the insertion of CO_2. This process also results in complete inversion of the stereochemistry at the methine carbon. As a result, the configuration of the methine carbon of the 5-substituted oxazolininone is the same as that of the employed *N*-substituted aziridine because of the double inversion. North and co-workers recently reported the synthesis of oxazolidinones from epoxides and aromatic or aliphatic isocyanates mediated by a bimetallic aluminum−salen complex.[26] More-

Table 3. *N*-Substituted Aziridine/CO_2 Coupling Reaction Results[a]



entry	R	temperature (°C)	time (h)	TOF (h^{-1})[b]	regioselectivity (%)[c]	ee (%)[d]
1	Me	120	6	1633	80:20	–
2	Me	100	6	1383	91:9	–
3	Me	80	12	716	>99:<1	–
4	Et	80	16	624	100:0	–
5	Bn	80	24	410	100:0	–
6[e]	Bn (*R*)	80	24	405	100:0	99 (*R*)
7[f]	^{n}Bu (*R*)	80	24	415	100:0	99 (*R*)

[a]Typical reaction conditions: 50 mmol of *N*-substituted aziridine, 0.005 mmol of **1**, 5.0 mL of $CHCl_3$, 2.5 MPa CO_2. The conversions of *N*-substituted aziridines to the corresponding oxazolidinones were determined by ^{1}H NMR spectroscopy. [b]Turnover frequency (TOF) = total moles of 5-substituted and 4-substituted oxazolidinones per mole of catalyst per hour. [c]Molar ratio of 5-substituted oxazolininone to 4-substituted oxazolidinone, as determined by ^{1}H NMR spectroscopy. [d]Enantiomeric excess of the resulting 5-substituted oxazolidinones as determined by chiral HPLC. [e](*R*)-1-Benzyl-2-phenylaziridine was used, and the (*R*)-5-substituted oxazolidinone was obtained. [f](*R*)-1-Butyl-2-phenylaziridine was used, and the (*R*)-5-substituted oxazolidinone was obtained.

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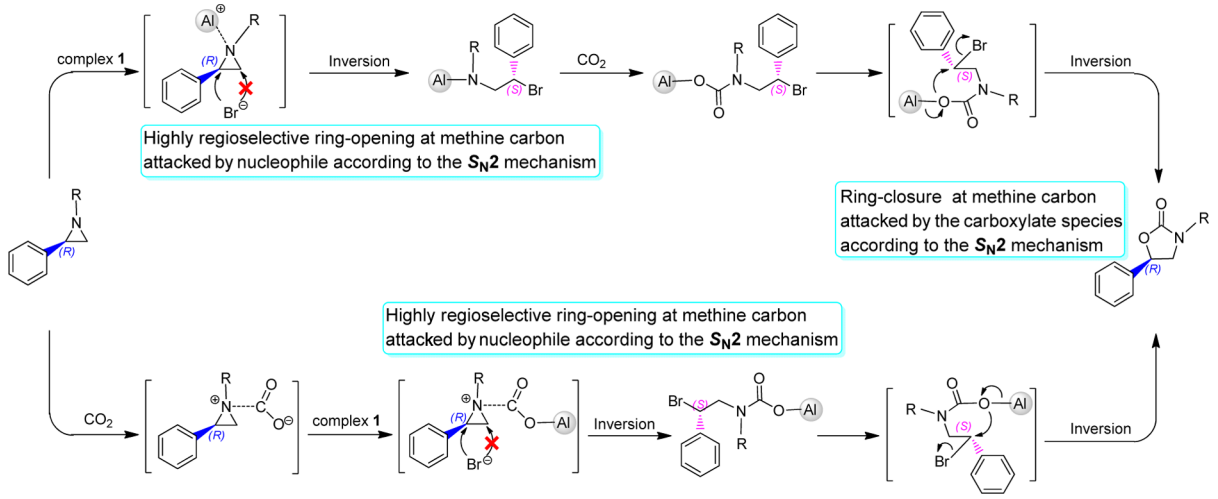
Scheme 3. Possible Mechanism of the Coupling Reaction of CO_2 with (*R*)-1-Alkyl-2-phenylaziridine Mediated by Complex 1 To Give the Corresponding (*R*)-5-Substituted Oxazolidinone with Complete Retention of Stereochemistry[25]



over, the exclusive formation of *cis*-oxazolidinones in the coupling reaction of *meso*-epoxides with isocyanates gave a mechanism involving a double inversion of configuration at different carbons of the epoxide. By contrast, our study showed that the configuration of the methine carbon of 5-substituted oxazolininones is the same as that of the employed *N*-substituted aziridines as a result of double inversion at the same carbon.

CONCLUSION

We have presented a bifunctional catalyst consisting of an electrophilic aluminum center and a nucleophilic quaternary ammonium salt in one molecule that shows high activity for the coupling reaction of CO_2 with three-membered heterocyclic compounds (epoxides or *N*-substituted aziridines) by intramolecular two-center cooperative catalysis. Regioselective ring opening of these heterocyclic compounds at various temperatures was achieved in the coupling reactions with CO_2, affording the corresponding five-membered cyclic products with complete retention of configuration at the methine carbon. Notably, this catalyst exhibited nearly 100% regioselectivity for the ring opening at the methylene C−O bond for various terminal epoxides, even ones bearing an electron-withdrawing group, such as styrene oxide and epichlorohydrin, thus allowing the synthesis of various enantiopure cyclic carbonates that were rarely obtained previously. Contrarily, highly selective ring opening at the methine carbon occurred in the coupling of *N*-substituted aziridines with CO_2 even at a high temperature of 80 °C, which predominantly gave 5-substituted oxazolininones with retention of configuration as a result of double inversion at the methine carbon.

EXPERIMENTAL SECTION

Synthesis of the Ligand of Complex 1. To a mixture of 5-(*tert*-butyl)-3-(3-(diethylamino)propyl)-2-hydroxybenzaldehyde (1.50 g, 5.15 mmol) in acetonitrile (10 mL) in a 25 mL flask wrapped in aluminum foil was added iodomethane (0.48 mL, 7.73 mmol). This mixture was stirred at 25 °C for 24 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10/1) as the mobile phase to give the quaternary ammonium salt (2.05 g, 92%) as a white solid. A mixture of 1,2-diaminoethane (0.060 g, 1.0 mmol) and the obtained quaternary ammonium salt (0.87 g, 2.0 mmol) in methanol (30 mL) was stirred for 8 h at ambient temperature, and then the solvent was evaporated. The residue was dissolved in dichloromethane (10 mL), and then diethyl ether (100 mL) was added slowly. The precipitate was collected by suction filtration and dried in vacuo to yield a bright-yellow solid. The resultant solid was dissolved in dichloromethane (40 mL) in a 100 mL flask wrapped in aluminum foil, and $AgBF_4$ (0.40 g, 2.0 mmol) was added. The mixture was stirred for 12 h and then filtered to remove the Ag byproduct. To the filtrate was added LiBr (0.86 g, 10.0 mmol), and the solution was stirred for another 2 h and then filtered to remove the inorganic salt. The solvent was removed in vacuo to afford the ligand as a bright-yellow solid (0.80 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.13 (s, 2H), 7.01 (s, 2H), 3.82 (m, 4H), 3.28−3.32 (m, 8H), 3.18−3.22 (m, 4H), 2.94 (s, 6H), 2.62 (t, J = 6.8 Hz, 4H), 1.89−1.95 (m, 4H), 1.12−1.18 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 156.5, 141.6, 130.4, 126.9, 126.3, 117.8, 60.1, 59.8, 57.1, 48.0, 34.0, 31.4, 27.0, 22.2, 8.1; HRMS (m/z) calcd for $[C_{40}H_{68}N_4O_2]^{2+}$ 318.2667, found 318.2656.

Synthesis of Complex 1. In a glovebox, the ligand (0.37 g, 0.45 mmol), Et_2AlCl (0.9 M, 0.5 mL, 0.45 mmol), and 10 mL of dichloromethane were added to a flask. The mixture was stirred for 12 h at 25 °C, and then the solvent was removed under reduced pressure. The resulting solid was washed with hexane and dried in vacuo to give complex **1** (0.34 g, 85%) as a yellow solid. The aluminum complex is sensitive to air and moisture and should be stored in a glovebox. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.23 (s, 2H), 7.015 (s, 2H), 3.92 (m, 4H), 3.27−3.35 (m, 12H), 2.96 (s, 6H), 2.74 (t, J = 6.8 Hz, 4H), 2.11−2.14 (m, 4H), 1.14−1.19 (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 160.9, 139.0, 133.5, 130.3, 128.9, 118.0, 60.9, 56.6, 53.4, 47.8, 33.7, 31.2, 27.1, 22.6, 8.0; HRMS (m/z) calcd for $[C_{40}H_{66}N_4O_2AlCl]^{2+}$ 348.2345, found 348.2311.

Representative Procedure for the Coupling Reaction of CO_2 with Epoxides. The reactions of CO_2 and epoxides were carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical procedure, complex **1** (0.01 mmol) was added to a Schlenk flask (50 mL) equipped with a three-way stopcock, and then propylene oxide (100 mmol) was added by means of a hypodermic syringe in a nitrogen atmosphere. The mixture was charged into the autoclave via a syringe in a CO_2 atmosphere. The autoclave was put into a bath and heated to the desired temperature. Then CO_2 was charged into the autoclave, and the pressure was kept constant during the reaction. After the expiration of the desired time, the excess gases were vented. The remaining mixture was degassed and fractionally distilled under reduced pressure or purified by column chromatography on silica gel to obtain the cyclic carbonate.

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■ ASSOCIATED CONTENT

Supporting Information

General experimental procedures, characterizations of the catalyst, and determination of enantiomeric excess for cyclic products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Very recently, He and Sakakura reported a phosphonium chloride covalently bound to a fluorous polymer that was proved to be an efficient catalyst for the coupling reaction of epoxides and CO_2 under supercritical CO_2 conditions. The authors also found that this catalyst could mediate the coupling reaction of (*R*)-styrene oxide to yield the enantiopure cyclic carbonate with 99% ee and retention of stereochemistry at 150 °C and a CO_2 pressure of 8.0 MPa, although the authors did not provide a detailed chiral analysis of the resultant product. See: Song, Q.-W.; He, L.-N.; Wang, J.-Q.; Yasuda, H.; Sakakura, T. *Green Chem.* **2013**, *15*, 110−115. For comparison, we performed this reaction under the same conditions but using ^{n}Bu$_4$NBr as the catalyst. Surprisingly, the results showed that enantiomeric excess of the formed (*R*)-styrene carbonate was less than 10%, which indicated that the ring opening of (*R*)-styrene oxide preferentially occurs at the methine C−O bond rather than the methylene C−O bond.

(17) At 25 °C, enantiopure styrene carbonate was obtained from the coupling reaction of CO_2 and (*R*)-styrene oxide (>98% ee) by the use of a bimetallic aluminum−salen complex in the presence of tetrabutylammonium bromide as a cocatalyst (see ref 5c). However, the enantiomeric excess of the resultant styrene carbonate was difficult to access from the figures provided in the Supporting Information.

(18) Azaphosphatranes, as highly active and robust organocatalysts, are efficient for the coupling reaction of CO_2 with styrene oxide to selectively afford the corresponding cyclic product at a CO_2 pressure of 0.1 MPa. See: Chatelet, B.; Joucla, L.; Dutasta, J. P.; Martinez, A.; Szeto, K.; Dufaud, V. *J. Am. Chem. Soc.* **2013**, *135*, 5348−5351.

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