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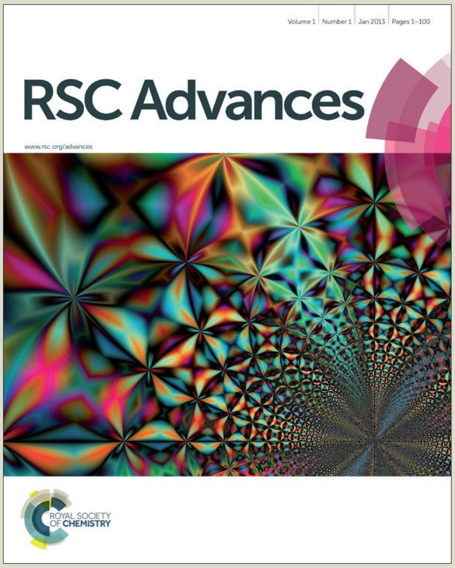

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Journal Name

ARTICLE

Lewis acid-base bifunctional aluminum-salen catalysts: synthesis of cyclic carbonates from carbon dioxide and epoxides†

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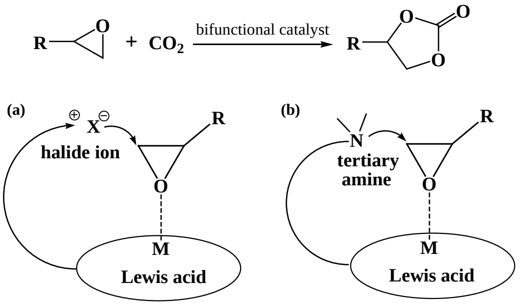
Two Lewis acid-base bifunctional monometallic aluminum-salen complexes were prepared based on a new type of salen ligands pending two N-methylhomopiperazine moieties at 3,3'-position. The Al(salen) complexes proved to be efficient and recyclable homogeneous catalysts towards the organic solvent-free synthesis of cyclic carbonates from epoxides and CO_2 in the absence of a co-catalyst, in which >90% yield of cyclic carbonate could be obtained under relatively mild conditions. The catalysts can be easily recovered and five times reused without significant loss of activity and selectivity. Furthermore, the Lewis acid-base cooperative activation mechanisms by the bifunctional Al(salen) complexes was proposed according to experimental data.

Introduction

Carbon dioxide (CO_2) is one of the greenhouse effect gases but it has been attracting much attention as a nontoxic, nonflammable, highly abundant and renewable C1 feedstock for organic synthesis in recent years.[1] One of the most promising reactions for the easy and economical chemical fixation of CO_2 is the synthesis of cyclic carbonates via the 100% atom-economical cycloaddition of epoxides with CO_2, since cyclic carbonates products are wildly used as electrolytes in lithium-ion batteries, fine chemical intermediates, and aprotic high-boiling polar solvents.[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 kinetically and thermodynamically stable molecule. The use of catalysts, expecially metallosalen-based binary or bifunctional electrophile-nucleophile systems,[3] significantly facilitates this transformation under relatively mild conditions. Among them, ionic bifunctionality (as shown in Scheme 1a, a Lewis acid (metal center) and a halide anion X- (nucleophile) are required) has proven to be highly useful in various cases to create more powerful catalyst mediators. On the other hand, for the first time, we recently reported a new type of bifunctional single-component M-salphen (salphen = N, N'-bis(salicyladehyde-o-phenylenediamine)) catalysts system (Scheme 1b) that involves tertiary amine moiety as Lewis base and metal center as Lewis acid within one structure.[4] The catalysis data support the synergistic effect of the Lewis acidic site and tertiary amine nucleophile resulting in markedly improved catalytic behaviour compared with a system that lacks a Lewis base. More importantly, this structural design increases the stability of catalysts compared with the ionic bifunctional systems, therefore enhances their recycling performance which are also decisive criteria for possible large-scale application. These results stimulate us to exploit the more efficient and easy-recycling bifunctional non-ionic salen catalysts towards the fixation of CO_2 for cyclic carbonates under mild conditions.



Scheme 1 Cooperative activation of epoxide with bifunctional catalysts.

The Lewis acid of aluminum has already been successfully exploited to provide catalyst systems for the cycloaddition of CO_2 and epoxides.[3c-e, 5] Of these reports, the μ-oxo-bimetallic Al(salen) complexes have been developed by North and co-workers, which provided a highly-active system under room temperature and atmospheric pressure conditions. However, in this case the introduction of highly polar ionic groups to these complexes often leads to the decreased solubility of catalyst in epoxide substrate; in turn, relatively low catalytic activity was obtained compared to the binary catalyst system.[5f-i] More recently, Lu studied a bifunctional Al(salen) framework in conjunction with intramolecular quaternary ammonium salts as co-catalysts that can efficiently catalyze the regioselective ring opening of three-membered

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heterocyclic compounds (epoxides or N-substituted aziridines) at various temperatures in coupling reactions with CO_2, affording the corresponding five-membered cyclic products with complete configuration retention at the methane carbon.[3c], Ji recently also reported a series of monometallic Al (salen) complexes prepared by covalent linkage of the imidazolium-based ionic liquid moieties containing various polyether chains with the salen ligands, which presented excellent “CO_2 capture” capability in the context of organic carbonates formation.[3d] Furthermore, to date, the highest activity, with a turnover frequency of up to 36000 h^{-1}, was also realized by a binary ionic catalytic system consisting of an aluminum-aminotriphenolate complex and quaternary ammonium salt, and this catalyst system exhibited broad substrate scope and functional group tolerance in the formation of cyclic carbonates.[5c]

Based on above fact that aluminum represents the stronger Lewis acidity for the ring-opening of the epoxide[5] and our previous work towards the CO_2 fixation over bifunctional single-component M(salen) catalysts,[4] herein, we report two new bifunctional Al (salen) complexes (Scheme 2, achiral **1a** and chiral **1b**) consisting of tertiary amine moiety as Lewis base and metal center as Lewis acid within one molecule. The tertiary amine moieties in these two catalysts could not only increase the solubility of CO_2 in reaction liquid phase due to the large affinity of aliphatic amines towards CO_2, but also provide an inherent nucleophile in the reaction of CO_2 with epoxides under solvent-free and additive-free conditions. Notably, these catalysts are easily recycled and can be conveniently reused, which is an important aspect in the development of practical processes.

Experimental

Materials and methods

N-methylhomopiperazine, Propylene oxide (PO), 1,2-epoxybutane, epichlorohydrin, glycidol, allyl glycidyl ether, methyl glycidyl ether, syrene oxide and cyclohexene oxide were purchased from TCI. Diethyl aluminum chloride (Et_2AlCl, 1.0 M solution in toluene) were obtained by J&K Scientific Ltd. Other commercially available chemicals were laboratory grade reagents from local suppliers. All solvents were purified by standard procedures.[6] 5-bromo-2-hydroxy-3-(4-methyl-homopiperazine-1-ylmethyl)-benzaldehyde was synthesized according to our published procedures.[7] Mononuclear M(salphen) catalysts **2a** and **2b** were synthesized according to our recent work.[4] Mononuclear Al (salen) catalysts **3a** and **3b** were synthesized according to previous literature.[8]

Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. ^1H NMR and ^{13}C NMR were done on a Bruker Model AM-400 (400 MHz) spectrometer. ^{27}Al NMR spectra were recorded on a Bruker Avance III HD 600M spectrometer. Infrared (IR) spectra were measured from a KBr pellets on a Nicolet Model Nexus 470 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Mass spectra (MS) were measured on a Bruker HCT-plus mass spectrometer. Gas chromatography (GC) spectrometry was recorded on Agilent 7820A system that was equipped with a 0.25 mm × 30 m DB-WAX capillary column (or Supelco-β-DEX 225 chiral column) and the FID detector.

Synthetic procedures

Synthesis of salen Ligands H_2L^{S1} and H_2L^{S2}. The anhydrous ethanol solution (20 mL) of ethylenediamine (5 mmol, 0.3 g) was added dropwise into the solution of 5-bromo-2-hydroxy-3-(4-methyl-homopiperazine-1-ylmethyl)-benzaldehyde (10 mmol) in anhydrous ethanol (20 mL) in a 1:2 molar ratio at room temperature. The resulting mixture was refluxed for another 12 h; following this, the solvent was evaporated to dryness and the salen ligand H_2L^{S1} was obtained as an orange powder, used without further purification. Yield: 96%. ^1H NMR ($CDCl_3$), δ=8.34(2H), 7.50(2H), 7.34(2H), 3.94(4H), 3.70(4H), 2.79-2.81(8H), 2.69-2.72(8H), 2.40(6H), 1.86(4H). ^{13}C NMR($CDCl_3$), δ=164.4, 158.3, 135.1, 131.6, 128.9, 120.2, 110.2, 59.7, 58.2, 57.6, 56.9, 55.9, 54.5, 54.2, 46.9, 27.0, 18.5. MS ($MALDI^+$) for $C_{30}H_{42}Br_2N_6O_2$: m/z, calcd ($M + H^+$): 679.5, found: 679.2.

The preparation of H_2L^{S2} was similar to that of H_2L^{S1} except that (R,R)-1,2-diaminocyclohexane was used in place of ethylenediamine. Yellow powder were obtained in 98%. ^1H NMR ($CDCl_3$), δ=8.20(2H), 7.47(2H), 7.21(2H), 3.67(4H), 3.31(2H), 2.70-2.82(16H), 2.41(6H), 1.72-1.88(8H), 1.46(2H), 1.26(2H). ^{13}C NMR($CDCl_3$), δ=163.1, 158.4, 135.0, 131.8, 129.0, 119.9, 110.0, 72.5, 57.6, 56.8, 55.6, 54.4, 54.2, 46.8, 32.9, 26.9, 24.1, 18.4. MS (ESI) for $C_{34}H_{48}Br_2N_6O_2$: m/z, calcd ($M + H^+$): 733.6, found: 733.2.

Synthesis of catalysts 1a and 1b. Under nitrogen protection and constant stirring at 40 °C, to a 100 mL round-bottom flask containing the above-obtained salen ligands H_2L^{S1} (or H_2L^{S2}) (4 mmol), anhydrous toluene (30 mL) was added via a hypodermic syringe to dissolve the ligand, and then a little excess of Et_2AlCl (1.0 M solution in toluene, 4.1 mL, 4.1 mmol) was added slowly. The reaction was highly exothermic and resulted in a yellow solution and a yellow solid. The resulting yellow mixture was refluxed for an additional 4 h. after removal of the solvent under vacuum, the mixture was washed with ether several times and then dried at 40 °C under vacuum to obtain light yellow powders of **1a** or **1d**. Yield: 90%. For **1a**: FT-IR (KBr): 3421, 2948, 1643, 1549, 1469, 1446, 1426, 1388, 1309, 1218, 1134, 1046, 877, 763, 690, 530. ^1H NMR (CD_3OD), δ= 8.50(2H), 7.69(2H), 7.54(2H), 3.90-4.08(8H), 3.30(4H), 3.20-3.36(8H), 3.00-3.15(4H), 2.77(6H), 2.11(4H). ^{13}C NMR(CD_3OD), δ=169.1, 163.9, 139.6, 137.0, 131.2, 129.9, 129.3, 126.3, 122.3, 107.9, 57.2, 56.9, 55.2, 54.7, 52.5, 45.7, 25.7. ^{27}Al NMR(CD_3OD), δ=70.0, 14.6, 7.8. MS ($MALDI^+$): 739.9 $[M+H]^+$. Anal. Calcd. for $C_{30}H_{40}AlBr_2ClN_6O_2$: C 48.76, H 5.46, N 11.37; found: C 49.18, H 5.48, N 11.22. For **1b**: FT-IR (KBr): 3501, 3001, 2934, 1630, 1598, 1478, 1464, 1427, 1389, 1361, 1302, 1269, 1233, 1201,

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1171, 1089, 1031, 974, 936, 866, 798, 769, 704, 558, 446. ^{1}H NMR (CD$_3$OD), δ= 8.43(2H), 7.69(2H), 7.20(2H), 3.99(4H), 3.48(2H), 3.25-3.38(8H), 2.80-2.95(8H), 2.31(6H), 1.98-2.17(8H), 1.50(4H). ^{13}C NMR(CD$_3$OD), δ=165.7, 163.6, 130.2, 129.3, 126.4, 122.2, 108.1, 65.3, 58.0, 57.0, 56.7, 55.2, 52.2, 45.6, 28.4, 25.1, 21.6. ^{27}Al NMR(CD$_3$OD), δ= 70.0, 13.7, 8.8. MS (MALDI$^+$): 794.3[M+H]$^+$. Anal. Calcd. for $C_{34}H_{48}Br_2N_6O_2$: C 51.36, H 6.08, N 10.57; found: C 50.75, H 5.69, N 10.82.

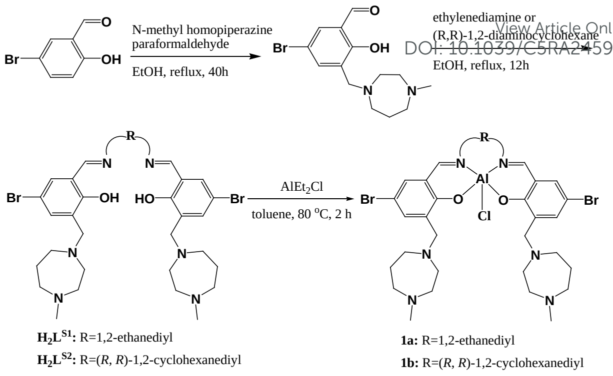
Representative procedure for the reaction of CO$_2$ with epoxides. A 10-mL stainless steel reactor was added with catalyst (0.1 mmol) and a magnetic stirring bar. Then the epoxide (10.0 mmol) was added and the steel reactor was charged under a constant pressure of CO$_2$ (2 MPa) for 1 min and heated to the desired temperature. After reaction completion, the reactor was cooled down to 0 °C and the excess CO$_2$ was released carefully. The reaction mixture was collected by adding 5 mL of ether and a sample was taken for GC analysis (using 1,3,5-trimethylbenzene as an internal standard) to determine yield and selectivity.

For recycling studies of catalyst **1a** (or **1b**), propylene carbonate was separated from the catalyst by adding ether. The catalyst precipitates was recovered by centrifugation. Afterwards, the catalyst was dried at 50 °C for 6 h in vacuum. By adding the same amount of epoxide (10.0 mmol), the next catalytic run was started.

Results and discussion

Preparation of catalysts

The synthetic route for the Al(salen) catalysts **1a** and **1b** is illustrated in Scheme 2. The first key step in the preparation was accomplished by an aromatic Mannich reaction, introducing a tertiary amine group (N-methylhomopiperazine) into 3-position of 5-bromosalicyladehyde, which allowed the subsequent aldehydic-amide (2:1) condensation with ethylenediamine or (R,R)-1,2-diaminocyclohexane to form salen ligands. Treatment of the salen ligand with diethyl aluminum chloride (1.0 M solution in toluene) under nitrogen gave light yellow solid powders of **1a** or **1d**. All attempts to obtain a single crystal of **1a** (or **1d**) suitable for X-ray crystallography were unsuccessful, partly due to the coordination between Al^{3+} and salen ligands is rapid and the inert coordination bonds between Al^{3+} cation and ligand anion make ligand-exchange reactions slow, which is unfavorable for crystal growth.[9] These two catalysts are miscible in some organic solvents, for example, methanol, ethanol and DMF, but can be precipitated with other organic solvents, for example, n-hexane, ether and chloroform. It is suggested that **1a** or **1d** should be an easily recoverable catalyst for the cycloaddition reaction by simple phase separation techniques *via* changing the solvents.



Scheme 2 Synthesis route of catalysts **1a** and **1b**.

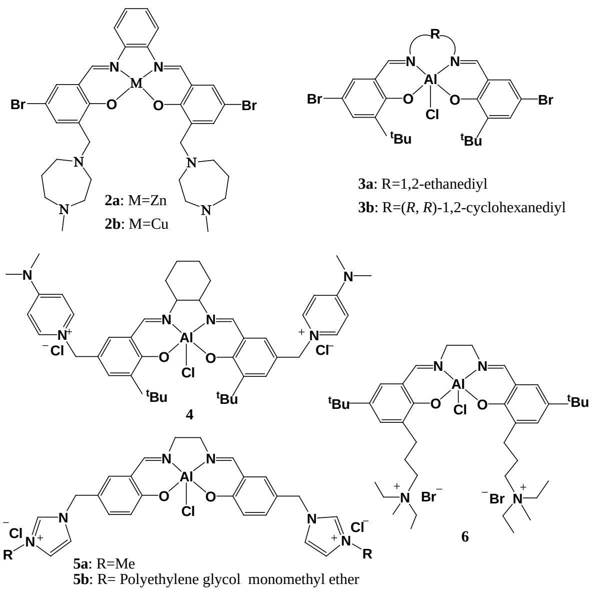


Chart 1 The structures of other M(salen) catalysts.

Catalytic performances

Firstly, the activity of various homogeneous monometallic catalysts were tested at 100 °C and 2 MPa of CO$_2$ pressure using the cycloaddition reaction of propylene oxide (PO) with CO$_2$ with 1 mol% catalyst loading, because our recently reported bifunctional single-component Zn(salphen) complex (Chart 1, **2a**) presented good yield for this reaction under above conditions (Table 1, entry 1).[4] The yield and selectivity were determined by using GC and ^{1}H NMR, and in all examined cases, the selectivity for five-membered cyclic propylene carbonate (PC) was higher than 99%. We delightfully found that PC could be obtained in excellent yield in the presence of Al(salen) catalysts **1a** and **1b** (Table 1, entries 2 and 3), as expected that aluminum has stronger Lewis acidity for the ring-opening of the epoxide. However, so far we have not achieved *ee* value based on chiral GC analysis (Supelco-β-DEX 225 chiral column) when chiral catalyst **1b** was used for the synthesis of optically active cyclic carbonates. This is in accordance with that the high enantioselectivity is very hard to achieve at high temperatures in asymmetric catalysis.

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Table 1 Results of the cycloaddition reaction of PO with CO_2 in the presence of various catalysts.[a]

Entry	Catalyst	Co-catalyst	Yield[b]/%
1	**2a**	none	90
2	**1a**	none	96
3	**1b**	none	95
4	**3a**	none	<5
5	**3b**	none	<5
6	none	N-methylhomopiperazine	<5
7	**3a**	N-methylhomopiperazine	85
8	**3b**	N-methylhomopiperazine	85
9	**3a**	Et_3N	86
10	**3a**	NBu_4Br	85

[a]General reaction conditions: 10 mL stainless-steel autoclave, PO (10 mmol), catalyst (0.1 mmol), CO_2 pressure (2 MPa). [b]The yields were determined by GC.

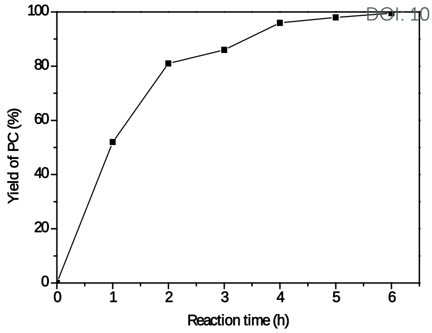


Fig. 1 The influence of the reaction time on the PC yield. Reaction conditions: 10 mmol of PO with 1 mol% **1a**, 2 MPa of CO_2, 100 °C.

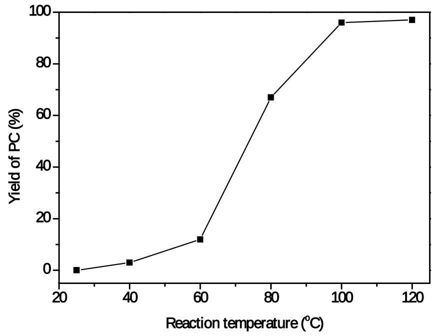


Fig. 2 Effect of the reaction temperature on the PC yield. Reaction conditions: 10 mmol of PO with 1 mol% **1a**, 2 MPa of CO_2, 4 h.

For a better understanding of the role of the tertiary amine moieties in N-methylhomopiperazine, the control complexes **3a** and **3b** without N-methylhomopiperazine were prepared for comparison (Chart 1). If only **3a**, **3b** or N-methylhomopiperazine was used as catalyst alone, no reaction occurred (Table 1, entries 4-6), illustrating that the coexistence of organic base and Al(salen) is essential to promote this reaction. On the contrary, the binary catalyst system of **3a** (or **3b**) and N-methylhomopiperazine in a molar ratio of 1/2 gave PC in 85% yields under the same conditions (Table 1, entries 7 and 8), obviously lower than that of **1a** (or **1b**). These phenomena were also observed in M(salphen) (Chart 1, **2a** and **2b**) catalytic systems[4] and reported by Liu and Darensbourg in an aluminum-salen complex bearing appended quaternary ammonium salt substituent (Chart 1, **4**).[3e] In addition, in the presence of 2 mol% of other usual nucleophiles such as Et_3N and NBu_4Br, the activity of the formed binary catalytic systems for this reaction still remained (Table 1, entries 9 and 10), but was less than those of **1a** and **1b**. These results unambiguously account for that the Lewis base and Lewis acid sites in **1a** (or **1b**) work together to enhance the catalytic activity.

The influence of reaction time on the PC yield is shown in Fig. 1. The reaction was conducted at 100 °C and 2 MPa of CO_2 pressure. The yield of PC increased with increasing time at the beginning and approached about 100% after a reaction time of 6 h. Fig. 2 shows the effect of the temperature on the cycloaddition reaction catalyzed by **1a** at 2 MPa of CO_2 pressure in the temperature range of 25-120 °C, with a reaction time of 4 h. At a temperature higher than 100 °C, nearly all of the PO could be converted into PC. The yield of PC decreased obviously with decreasing the temperature below 100 °C. The figure illustrates that the yield was only 67% at 80 °C with a reaction time of 4 h, indicating that temperature has great influence on this reaction, especially under 100 °C, although aluminium ion exhibits stronger Lewis acidity. Under lower temperature, using chiral **1b** as the catalyst, we also investigated the asymmetric catalytic performance of the reaction of racemic PO with CO_2. Unfortunately, only about 5% *ee* of PC at 60 °C (1-2% *ee* at 80 °C) was achieved. We believe that it is very difficult to achieve high enantioselectivity in this reaction because it requires a higher reaction temperature (>80 °C). Furthermore, the effect of CO_2 pressure on the PC yield was also investigated. When the CO_2 pressure decreased from 2 to 1 MPa, the yield of PC drastically decreased, and even increasing this reaction time to 12 h, only about 40% of PC was obtained. The reaction could basically not occur under room temperature and atmospheric pressure even for 72 h. It is known that lower CO_2 pressure could reduce the solubilization effect of CO_2 in the solution of PO; in turn, the yield was decreased.[10]

Table 2 summarizes the catalytic performances of recent reported one-component Al(salen) catalysts on cycloaddition reaction of CO_2 to PO. In general, since different reaction conditions such as catalysts loading, CO_2 pressure, reaction temperature and time were used, it is hard to critically evaluate and compare the efficacy of these mononuclear Al(salen) complexes. Nevertheless, the aluminum-salen catalysts reported upon herein are competitive with most catalysts currently available, including transition and main group metals as well as organo-catalysts. The extensive summary of catalysts and their activities for this process were reported in recent reviews.[2a,11]

Table 2 Comparison with other one-component Al(salen) catalysts on cycloaddition reaction of CO_2 with PO.[a]

Cat.	[PO]/[Cat.]	CO_2 Pres./MPa	Temp./°C	Time/h	Yield/%	Ref.
1a	100	2.0	100	4	96.0	This work
4	2000	3.0	120	5	74.3	3e
5a	200	1	100	2.5	49.0	3d
5b	200	1	100	2.5	98.0	3d
6	25000	2.5	120	4	80.0	3c

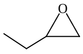
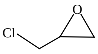
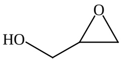
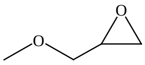
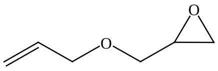
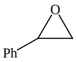
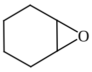
[a] The structures of catalysts **4**, **5a**,**5b** and **6** are depicted in Chart 1.

Having established that **1a** and **1b** are highly active catalysts for PC formation, various epoxides, such as 1,2-epoxybutane, epichlorohydrin, glycidol, allyl glycidyl ether, methyl glycidyl ether, syrene oxide and cyclohexene oxide were used as the substrate for the reaction system. As shown in Table 3, the two Al(salen) catalysts can tolerate functionalities such as alkene, alkyl halide, alcohol, ether, and substituted aryl groups. Both electron-withdrawing and electron-donating terminal epoxides can be converted to the corresponding cyclic carbonates with high conversion and excellent selectivity. The very good conversions (for only 1h) of epichlorohydrin and glycidol (Table 3, entries 3-6) can be explained by the electron-withdrawing substituents.[12] These substituents result in facilitated nucleophilic attack of the N-methylhomopiperazine during the ring opening of the epoxide. Unfortunately, the internal epoxide, cyclohexene oxide, which is known to undergo cycloaddition with CO_2 poorly, is converted to the corresponding cyclic carbonate with a yield of 45 and 42 % by **1a** and **1b** (Table 3, entries 11 and 12) even after prolonging the reaction time to 12 h, respectively, presumably due to the high steric hindrance.[12a]

Recycling capability

Besides the catalyst activity, the recycling capability is also decisive criteria for possible large-scale application. Based on the concept of "one-phase catalysis and two-phase separation"[13] and the special solubility of **1a** and **1b**, the catalyst could be precipitated from the reaction solution by the addition of ether. The upper organic phase was obtained by simple centrifugation and the lower catalyst solid can be reused by adding fresh reaction substrates. Experiments were conducted to examine the recyclability of catalyst **1a** (or **1b**) using PO as the substrate under the optimal reaction conditions. The results indicate that **1a** could be reused for five successive runs without any significant loss in catalytic activity, and the selectivity still remained at 98% (see Fig. 3, Fig. S15 for **1b**, Supporting Information). In addition, these catalysts exhibited stability to moisture. For example, when **1a** was immersed in distilled water overnight at ambient temperature, following drying, it maintained catalytic activity with a yield of 95% for the production of PC under the optimal reaction conditions. In this regard, it should also be noted that no special precautions were taken to purify either PO or CO_2. These considerations are of utmost importance when utilizing impure sources of CO_2 as that obtained from power plant flue gases or other CO_2 producers.

Table 3 Reactions of other epoxides with CO_2 catalyzed by **1a** and **1b**.[a]

Entry	Epoxide	Catalyst	Time/h	Yield[b]/%
1		**1a**	4	95
2		**1b**	4	94
3		**1a**	1	99
4		**1b**	1	99
5		**1a**	1	99
6		**1b**	1	98
7		**1a**	4	92
8		**1b**	4	95
9		**1a**	4	94
10		**1b**	4	95
11		**1a**	4	90
12		**1b**	4	92
13		**1a**	12	45
14		**1b**	12	42

[a]Reaction conditions: epoxide (10 mmol), catalyst (0.1 mmol), 2 MPa of CO_2, 100 °C. [b]The yields were determined by GC.

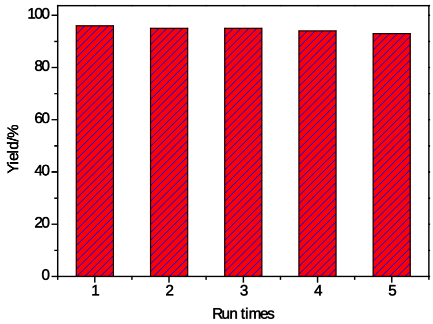


Fig. 3 Recyclability of **1a** for the reaction of PO with CO_2. Reaction conditions: epoxide (10 mmol), catalyst (0.1 mmol), 2 MPa of CO_2, 100 °C, 4 h.

The comparative FT-IR analysis of the fresh catalyst **1a** with the recovered **1a** after the 5th reuse in the cycloaddition reaction was performed, and the results are shown in Fig. 4 (Fig. S16 for **1b**, Supporting Information). All the FT-IR spectra show characteristic vibration bands at around 1640 cm^{-1} and 1550 cm^{-1}, which are associated with the stretching vibration modes of C=N and C–O, respectively.[3d, 14] The stretching vibration of tertiary amine groups at 1050 cm^{-1} suggests the intact methylhomopiperazine-based moieties on the ligands.[7] Moreover, ^{27}Al NMR spectra of **1a** and the recovered **1a** have all been found to display broad strong resonances around 70 ppm (see Fig. 5, Fig. S14 for **1b**, Supporting Information), which are attributed to the five-coordinate aluminum species. These results indicate that the recovered catalysts structure did not change after catalytic reaction.

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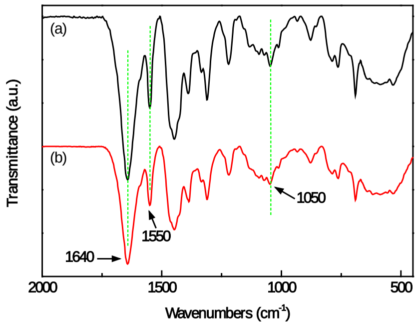


Fig. 4 FT-IR spectra of **1a** (a) and the recovered **1a** (b) after the 5th reuse in the reaction of PO with CO_2.

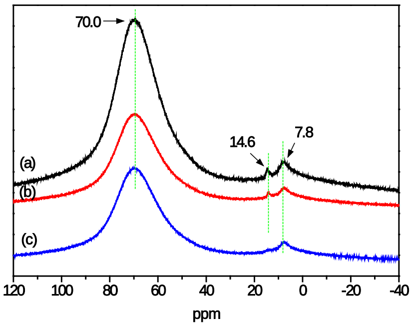
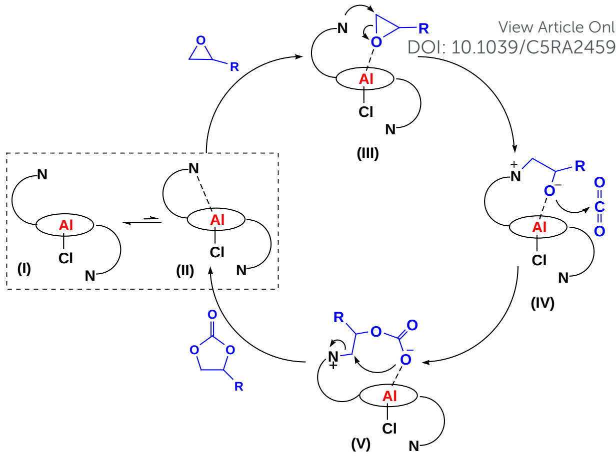


Fig. 5 ^{27}Al NMR spectra of **1a** (a), the recovered **1a** (b) and **3a** (c).

Reaction mechanism

At first, N-methylhomopiperazine moieties in **1a** (or **1b**) adopt a ship-shape conformation locating above and below the salen plane, similar to our previous reported crystal structure of Cu(salphen) (chart 1, **2b**),[4] which can also be proved by the ^{27}Al NMR spectrum of **1a**. Because ^{27}Al NMR is sensitive to the symmetry, chemical environment, and coordination number around the metal center, this spectroscopic probe should be useful in assessing differences in coordination types of aluminum complexes.[15] As shown in Fig. 4, ^{27}Al NMR spectra of **1a** was found to display broad strong resonances at 70.0 ppm and two weak signal around 14.6 and 7.8 ppm, which are assigned to the five-coordinate aluminum species and two different six-coordinate species (one perhaps is N-methylhomopiperazine coordinated species, and another is solvent-coordinated species), respectively, since an upfield chemical shift is attributed to an increase in aluminum's coordination number.[16] While in the spectrum of neat complex **3a** that lacks the pending N-methylhomopiperazine, only one weak signal is in the range 0- 15 ppm, which is assigned to the solvent-coordinated aluminum species. In recent studies, Liu and Ji also observed six-coordinate Al(salen) complexes tethered onium salt groups in one structure by ^{27}Al NMR spectra.[3d, 3e] These species existed in equilibrium with the five-coordinate complexes and exhibited enhanced catalytic activity for the reaction of epoxides and CO_2.



Scheme 3 A plausible mechanism for the reaction of epoxide with CO_2 catalyzed by **1a** or **1b**.

Scheme 3 outlines the proposed reaction pathway. Firstly, the tertiary amine N atom of the pending N-methylhomopiperazine coordinates to the metal in the remaining *trans* axial position, thus generating a six-coordinated intermediate (**II**). Secondly, the reaction is initiated through the subtitution coordination by the oxygen atom of the epoxide and meanwhile, favoring the tertiary amine nucleophilic attack of the less-hinder carbon atom of epoxide (**III**) activated by the metal center. Next, the formed alkoxide species (**IV**) acts in turn as a nucleophile that attacks CO_2 to form a metal carbonate species (**V**). The subsequent ring-closure forms cyclic carbonate, and in the meantime, the catalyst is regenerated. In one word, the Lewis base and Lewis acid work together to open the epoxy ring and then react with CO_2 to give the corresponding cyclic carbonates *via* a ring-opening and recycling process in one-component catalyst. Previous reports also suggested the similar requirement of both Lewis base activation of CO_2 and Lewis acid activation of epoxide in the binary catalyst systems.[3n] It should be also noted that the "CO_2 sorption" capability originating from tertiary amine moieties in our catalysts could not be ignored, because the larger affinity of aliphatic amines towards CO_2 has been confirmed in reported literatures.[17]

Conclusions

In summary, two Lewis acid-based bifunctional catalysts pending N-methylhomopiperazine moieties have been prepared and examined as one-component catalysts for the cycloaddition of epoxides and CO_2 to provide cyclic carbonates. These two catalysts were significantly more efficient than their binary analogues under relatively mild conditions. Furthermore, the catalysts are thermally and moisture stable, and can be facilely separated and recycled five times without significant loss in catalytic activity. Combined with other advantages of Al(salen) complexes (low cost, environmental benign and ease of synthesis), these catalysts thus show high potential in the field of CO_2 fixation.

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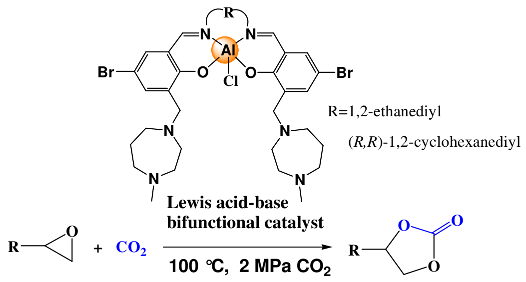

Two Lewis acid-base bifunctional Al(salen) complexes proved to be efficient and recyclable one-component catalysts for CO_2 fixation.