

Article

Syntheses, Characterization, and Application of Tridentate Phenoxyimino-Phenoxy Aluminum Complexes for the Coupling of Terminal Epoxide with CO₂: From Binary System to Single Component Catalyst

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Abstract: A series of binuclear aluminum complexes **1–3** supported by tridentate phenoxyimino-phenoxy ligands was synthesized and used as catalysts for the coupling reaction of terminal epoxide with carbon dioxide. The aluminum complex **1**, which is catalytically inactive toward the coupling of epoxide with CO₂ by itself, shows moderate activity in the presence of excess nucleophiles or organic bases at high temperature. In sharp contrast to complex **1**, bifunctional complexes **2** and **3**, which incorporate tertiary amine groups as the built-in nucleophile, are able to efficiently transform terminal epoxide with CO₂ to corresponding cyclic carbonates as a sole product by themselves at 100 °C. The number of amine groups on the ligand skeleton and the reaction temperature exert a great influence on the catalytic activity. The bifunctional complexes **2** and **3** are also active at low carbon dioxide pressure such as 2 atm or atmospheric CO₂ pressure. Kinetic studies of the coupling reactions of chloropropylene oxide/CO₂ and styrene oxide/CO₂ using bifunctional catalysts under atmospheric pressure of CO₂ demonstrate that the coupling reaction has a first-order dependence on the concentration of the epoxide.

Keywords: aluminum complex; CO₂ fixation; bifunctional catalyst; cyclic carbonate



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1. Introduction

With the rapid development of the industry as well as the ever-growing human activity, a huge amount of CO₂ has been released to the air, which has caused severe environmental problems [1–4]. The utilization of CO₂ as feedstock to produce valuable chemicals is a promising way to solve this problem, but this conversion is limited due to the inertness of CO₂ [5]. The catalytic coupling reaction with epoxides represents one of the promising processes employing CO₂ to produce organic cyclic carbonate, which has found widespread applications in many respects [6–10]. Generally, the catalyst capable of achieving the transformation is comprised of nucleophile and Lewis acid. Thus, organic compounds and metal-based complexes have been employed as the Lewis acid for the coupling reaction, with the aid of nucleophiles to constitute the binary catalytic system. Usually, metal-based complexes display higher reactivity than organocatalysts for the coupling reaction. As a result of the diversity of the metal across the periodic table and the organic ligands of different structures, miscellaneous metal complexes based on aluminum [11–32], magnesium [33–36], chromium [37–42], cobalt [43–48], iron [49–53], and rare earth metals [54,55] have been innovated for the coupling reaction of CO₂ with epoxides. Of many metal complexes, aluminum complexes have been drawing attention due to their low price, easy availability, and the superior selectivity for the cyclic carbonate

over polymeric products [56]. It is well established that the electronic effects and steric hindrance around the aluminum center that can be finely tuned are crucial for the catalytic activity and the product selectivity. For example, optically active carbonate can be produced from the coupling of racemic epoxide with CO₂ when the chiral complexes are employed [44,45,57].

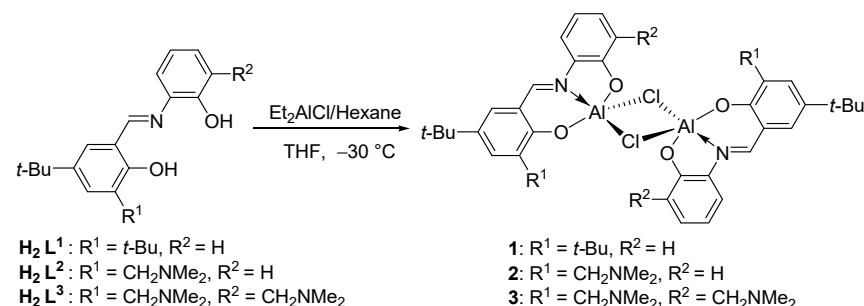
In addition to binary catalytic system, there is a tendency to employ a bifunctional catalyst in which nucleophile and Lewis metal complexes are constructed into one molecule as the one-component catalyst for the coupling of CO₂ with epoxides in the past decade [58–68]. Quaternary ammonium halide as a nucleophile is usually integrated into the metal complex to construct an ionic bifunctional catalyst. The pre-association of the nucleophilic halide to the metal complex via electrostatic attraction would effectively reduce the translational entropy penalty at the ring-opening step and the cyclization step as compared with the binary catalytic system [69]. Thus, the bifunctional catalyst loading for the coupling reaction is significantly reduced, and usually, a higher catalytic reactivity is achieved than that with the corresponding binary catalytic system. However, the incorporation of the quaternary onium salts into the metal complex impairs the solubility of the bifunctional catalyst. Another drawback is the thermostability of the ammonium halide-functionalized catalyst at elevated temperature [59], which undergoes ammonium salt decomposition pathways, including Zaitsev and Hoffman type eliminations [70–72] and retro-Menschutkin reactions [73–76]. Hence, it is important and necessary to develop bifunctional catalyst of high efficiency and stability at elevated temperature.

In this work, we present the syntheses of a series of aluminum complexes supported by novel tridentate phenoxyimino-phenoxy ligands and their catalytic behaviors for the coupling of terminal epoxides with CO₂. Compared with tetradentate salen-type ligand stabilized metal complexes, which are extensively employed for the coupling of epoxide with CO₂, aluminum complexes supported by tridentate ligands for this transformation are rare. As a result of the low coordination number of tridentate ligands, the resultant complexes are expected to have a more acidic metal center, which is supposed to benefit the activation of the epoxide ring and to facilitate the ring-opening. Moreover, an amine group was incorporated onto the ligand framework as the built-in nucleophile to construct neutral bifunctional complexes **2** and **3**, in order to avoid the decomposition of ammonium halide moiety under elevated temperature. Systematic investigation of the catalytic behaviors of the aluminum complexes **2** and **3** reveals that the neutral and ionic bifunctional complexes are highly active toward the coupling of epoxide to CO₂, whereas the unfunctionalized aluminum complex **1** is catalytically inactive by itself.

2. Results and Discussion

2.1. Syntheses and Characterization of Complexes 1–3

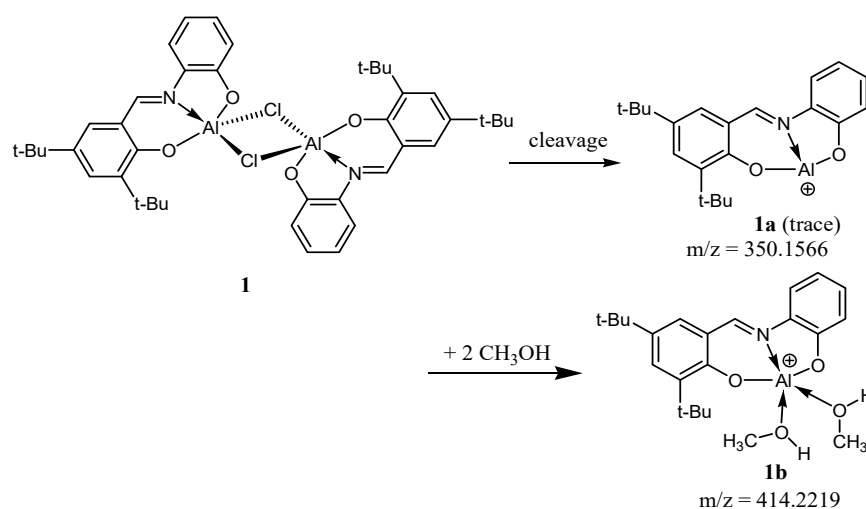
The tridentate ligand precursors H₂L¹–H₂L³ (see Scheme 1) were readily synthesized by reacting the substituted salicylaldehyde with substituted aminophenol in 1:1 molar ratio (see the experimental section in the supporting material). The three ligand precursors were identified by proton nuclear magnetic resonance (¹H NMR) and ¹³C-nuclear magnetic resonance (¹³C NMR) (Figures S1–S3 in the supporting material).



Scheme 1. The syntheses of complexes 1–3.

Subsequent syntheses of complexes **1–3** were conducted by the alkyl-elimination reaction of Et_2AlCl with the corresponding ligand precursors at low temperature, as illustrated in Scheme 1. In a typical procedure, a tetrahydrofuran (THF) solution of H_2L^1 was added dropwise to a stirred hexane solution of AlEt_2Cl at $-30\text{ }^\circ\text{C}$ to afford a yellow solution. The reaction was slowly warmed up to room temperature and stirred for another 4 h. After the removal of all the volatiles under reduced pressure, yellow solids were separated, which was followed by washing with cold hexane three times and drying to constant weight under vacuum. The structure of the isolated solids was characterized by the NMR technique with CDCl_3 as the solvent. The ^1H NMR spectrum shows no resonances of hydroxy groups or ethyl groups bound to aluminum. In the low field, the resonance of 8.06 ppm assignable to the imino moiety was observed, which slightly shifted to the low field when compared with that in free ligand precursor H_2L^1 (see Figure S4 in the supporting material). Two distinct resonances of 1.32 ppm and 0.84 ppm for the *t*Bu groups were found (1.49 and 1.35 ppm in the H_2L^1), indicating chelation of the tridentate ligand to aluminum. Moreover, the upfield shift of the imino group in the H_2L^1 from 8.72 to 8.06 ppm in the isolated complex suggested the coordination of nitrogen of the imino group to the aluminum center. Remarkably, no solvent molecules were detected in the ^1H NMR spectrum, suggesting that the isolated complex is THF-free.

In addition to the characterization by NMR, mass spectrometry (MS) was employed to characterize the isolated complex. A very weak peak at $m/z = 350.1566$ was detected, which corresponds to the cationic species **1a** having the formula of $\text{C}_{21}\text{H}_{25}\text{O}_2\text{NAl}$, as shown in Scheme 2. Interestingly, a strong signal was observed at $m/z = 414.2219$, which was assigned to the cationic species **1b** with the formula of $\text{C}_{23}\text{H}_{33}\text{O}_4\text{NAl}$. We supposed that the species **1b** was generated by the coordination of two methanol molecules to the cationic species **1a**. Thus, it is reasonable to interpret the weak signal of **1a** and the strong peak of **1b** on the mass spectrum. In the light of the strong signal of **1b** on the MS, no solvent detection on the ^1H NMR spectrum, and the coordination number of 5 usually adopted by aluminum complex, we expected that complex **1** should be a binuclear structure, with each aluminum center being surrounded by a phenoxyimino-phenoxy ligand and two chlorides, as presented in Scheme 2.



Scheme 2. Possible pathway for the formation of cationic species **1a** and **1b**.

Similarly, treatment of the ligand precursors H_2L^2 and H_2L^3 with AlEt_2Cl under low temperature resulted in the formation of bifunctional complexes **2** and **3**. The characterization of complex **2** by ^1H NMR showed the successful alkyl elimination between AlEt_2Cl and H_2L^2 . Moreover, there are no THF molecules detected on the ^1H NMR spectrum, suggesting that complex **2** is THF-free. The MS spectrum of complex **2** shows a m/z peak positioning at 397.1085. We tentatively ascribed this signal to the structure **2a**, which probably is an ethanol coordinated species, as illustrated in Figure 1. Meanwhile, a peak

at $m/z = 783.3226$ was detected, which is ascribed to the cationic species **2b**. Although a tertiary amine group is introduced into the molecule, the inner coordination of the amine group to the Al center is impossible because of the orientation of the tertiary amine group. Taking into account the coordination saturation of the aluminum, it is reasonable to assume the complex **2** adopts binuclear structure with dangling tertiary amine groups. Similar results were also observed for complex **3**, as indicated by the ^1H NMR and MS, which should also adopt a binuclear structure with dangling amine groups via chloride bridges.

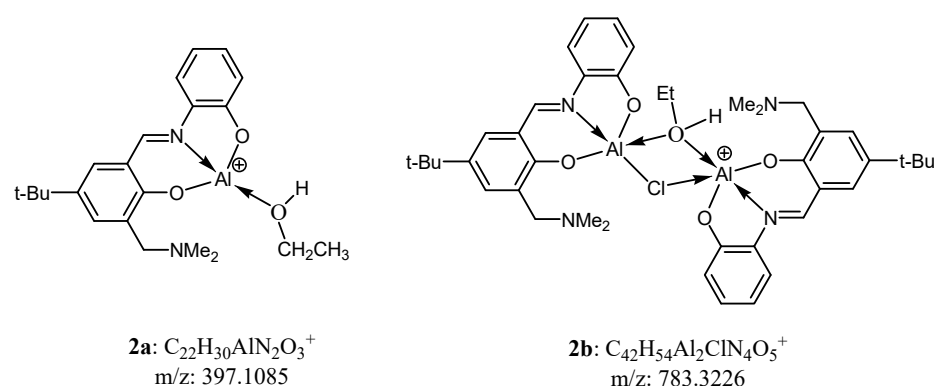
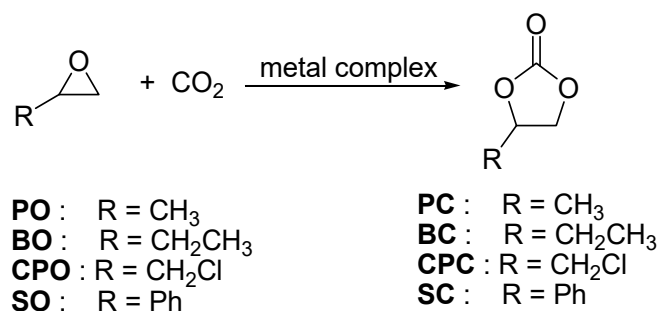


Figure 1. Possible structures of cationic species of **2a** and **2b** found in the MS of complex **2**.

2.2. Catalytic Performance of Complexes **1–3** in the Coupling Reactions of Terminal Epoxide with CO_2

To begin with, we examined the catalytic performance of complex **1** for the coupling of propylene oxide (PO) with CO_2 (see Scheme 3). Unfortunately, complex **1** was catalytically inactive by itself, which was in agreement with the previous literature reports [21,22]. When it was paired with a nucleophile or organic base, complex **1** showed moderate activity for the PO/ CO_2 coupling (see Tables S1–S4 in the supporting information). For instance, complex **1** in combination with tetrabutylammonium bromide (TBAB, 40 eq) catalyzed the PO/ CO_2 coupling to produce propylene carbonate (PC) as the sole product at 80°C under 20 atm CO_2 in 10 h with 91% PO conversion (see entry 8 in Table S1). There was no detection of any polymeric products as evidenced by the ^1H NMR spectrum of the reaction mixtures. It was also interesting to find that the complex **1**/TBAB (40 eq) system displayed a zeroth-order dependence on the PO throughout the coupling (see Table S2 and Figure S7, in the supporting material). This result is analogous to Han's report in which polymeric ionic liquid was employed as the catalyst for the PO/ CO_2 coupling reaction [77]. When other organobases such as 4-dimethylaminopyridine (DMAP) or 1-methylimidazole (1-MeIm) were employed as the cocatalysts, high cocatalyst loading was required for effective transformation (see Tables S3 and S4 in the supporting material). For instance, the binary system composed of complex **1**/DMAP (1/20) displayed lower catalytic activity than complex **1**/TBAB (1/20) at 60°C .



Scheme 3. This is a figure. Schemes follow the same formatting.

It has been reported by North and Pasquale that quaternary ammonium halide would decompose at high temperature to generate tertiary amine and haloalkane [78]. The in situ generated tertiary amine, together with the remaining ammonium halide salts, assists the metal complex to convert propylene oxide and CO₂ to cyclic carbonate. Recently, Kim and his coworkers reported the coupling of epoxide with CO₂ catalyzed by a series of tertiary amines with moderate catalytic activity [79]. These results enlightened us to design amine-functionalized complex **2** as the single-component catalyst for the coupling of epoxide with CO₂. The catalytic results were compiled in Table 1. It was satisfying that the bifunctional complex **2** by itself succeeded in transforming the CO₂ and PO to PC. Analysis of the reaction mixture showed that PC was exclusively produced without the formation of any polymeric products as evidenced by ¹H NMR spectrum. Although complex **2** displayed very low activity at 80 °C (entries 1 and 2, in Table 1), however, the catalytic activity was considerably enhanced when the reaction was conducted at 100 °C. For instance, 68% of PO was converted to PC under 10 atm CO₂ in 10 h (entry 3, Table 1). In addition to the reaction temperature, increasing the CO₂ pressure accelerates the coupling reaction. Then, 94% of PO was transformed to PC at 20 atm CO₂ pressure within 10 h (entry 4, Table 1), suggesting that high CO₂ pressure, namely, the high CO₂ concentration facilitated the coupling reaction.

Table 1. The coupling reaction of terminal epoxide with CO₂ by the sole complex **2**¹.

Entry	Epoxide	P(CO ₂) (atm)	Temperature (°C)	Time (h)	Conversion ² (%)
1	PO	10	80	10	7
2	PO	20	80	10	8
3	PO	10	100	10	68
4	PO	20	100	10	94
5	BO	10	80	10	7
6	BO	20	100	10	49
7	CPO	10	80	10	12
8	CPO	20	80	10	26
9	CPO	10	100	5	36
10	CPO	10	100	10	52
11	CPO	10	100	24	90
12	CPO	20	100	5	40
13	CPO	20	100	10	62
14	SO	10	100	5	5
15	SO	10	100	10	11
16	SO	10	100	18	32
17	SO	10	100	24	75
18	SO	20	100	5	7
19	SO	20	100	10	15

¹ Conditions: Complex **2** (38.7 mg, 50 μmol), n₍₂₎/n_(epoxide) = 1/1000. ² Determined by ¹H NMR; No polymeric products were discovered as evidenced by ¹H NMR.

Subsequent examination of the catalytic performance of complex **2** in other terminal epoxides/CO₂ coupling reactions confirmed again the significance of the reaction temperature and CO₂ pressure. The 1,2-butylene oxide (BO) conversion of 7% at 80 °C under 10 atm CO₂ was improved to 49% when the reaction was performed at 100 °C under 20 atm of CO₂ pressure (entries 5 and 6, Table 1). Similar trends were also observed for the coupling of CO₂ with epichlorohydrin (or chloropropylene oxide, abbreviated as CPO) or styrene oxide (SO). The CPO conversion of 12% at 80 °C under 10 atm of CO₂ in 10 h was enhanced to 36%, 52%, and 90% within 5, 10, and 24 h, respectively, when the reaction temperature was simply increased to 100 °C (entries 7, 9–11, Table 1). As the CO₂ pressure was increased to 20 atm, the conversion of CPO rose to 40% in 5 h and 62% in 10 h under 20 atm CO₂ (entries 12 and 13, Table 1). As for the SO/CO₂ coupling, the reaction was quite sluggish

(entries 14–19, Table 1). High SO conversion can only be achieved after a long reaction time (entry 17, Table 1).

Complex **2** was capable of transforming CPO/CO₂ and SO/CO₂ to cyclic carbonate under atmospheric CO₂ pressure. The results were collected in Table 2, and the kinetic curves (conversion vs. reaction time) were depicted in Figure 2. As expected, the rate of the coupling of CO₂ with either CPO or SO under 1 atm CO₂ was extremely slow, which was partly due to the low CO₂ pressure. As can be seen from Figure 2, there is a surge in the CPO conversion after 36 h (the blue curve). This might be interpreted by the poor solubility of complex **2** in CPO. Therefore, the metal complex **2** was not well dispersed in the epoxide, leading to a heterogeneous system. Thus, the effective concentration of complex **2** was lower than the theoretical value at the beginning. With the proceeding of the coupling reaction, highly polar cyclic carbonate was generated, which in turn acted as solvent to dissolve complex **2**. Thus, the effective concentration of complex **2** was continuously increased in the course of the reaction until the full dissolution of complex **2**. This would accelerate the coupling, as is shown in Figure 2 (the blue curve). A similar situation took place in the case of SO/CO₂ coupling as well, where the reaction rate gradually increased with the reaction time, as indicated by the kinetic curve (the red curves in Figure 2).

Table 2. Complex **2** catalyzed chloropropylene oxide (CPO)/CO₂ and styrene oxide (SO)/CO₂ coupling under atmospheric CO₂ ¹.

Entry	Epoxide	Time (h)	Conversion (%)
1	CPO	5	6
2	CPO	10	11
3	CPO	24	28
4	CPO	36	35
5	CPO	48	68
6	SO	5	0.7
7	SO	10	2
8	SO	24	9
9	SO	36	17
10	SO	48	30
11	SO	60	42

¹ Conditions: Complex **2** (38.7 mg, 50 μ mol), $n_{(2)}/n_{(epoxide)} = 1/1000$, $P(\text{CO}_2) = 1$ atm, temperature is 100 °C. Other notes are the same as those in Table 1.

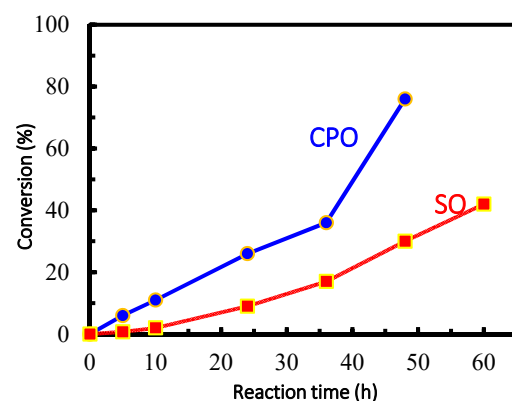


Figure 2. Kinetic curves (substrate conversion vs reaction time) of the coupling of CPO/CO₂ and SO/CO₂ by complex **2** under atmospheric CO₂ pressure at 100 °C.

The success of complex **2** as a single-component catalyst motivated us to examine the catalytic performance of complex **3**, which has more tertiary amine groups on the ligand skeleton for the coupling of epoxides toward CO₂. The catalytic results were collected in Table 3. As anticipated, complex **3** displayed higher activity than complex **2** did under the

same conditions, which was tentatively attributed to the incorporation of one more amine group. Similar to complex 2, complex 3 exhibited low activity at 80 °C. For example, 14% of PO was transformed to PC under 20 atm CO₂ in 10 h (entry 1, Table 3). However, the catalytic activity was dramatically improved by increasing the temperature to 100 °C, with the 64% conversion of PO in 5 h, and 99% in 10 h (entries 2 and 3, Table 3). The significance of reaction temperature was also observed in the BO/CO₂ coupling. The BO conversion of 5% at 80 °C was dramatically increased to 76% when the reaction temperature was increased to 100 °C at 10 atm CO₂ pressure (entries 4 and 5, Table 3). Similarly, enhancing the CO₂ pressure to 20 atm gave rise to 95% of BO conversion in 10 h (entry 6, Table 3), which was much higher than that of the coupling reaction catalyzed by complex 2 (entry 6, Table 1).

Table 3. The coupling reaction of terminal epoxide with CO₂ by the sole complex 3¹.

Entry	Epoxide	P(CO ₂) (atm)	Temperature (°C)	Time (h)	Conversion (%)
1	PO	20	80	10	14
2	PO	20	100	5	64
3	PO	20	100	10	99
4	BO	10	80	10	5
5	BO	10	100	10	76
6	BO	20	100	10	95
7	CPO	20	100	5	92
8	CPO	20	100	10	98
9	SO	20	100	10	50
10	SO	20	100	24	99

¹ Conditions: Complex 3 (44.4 mg, 50 μmol), $n_{(3)}/n_{(\text{epoxide})} = 1/1000$. Other notes are the same as those in Table 1.

Complex 3 displayed high catalytic activity for the CPO/CO₂ and SO/CO₂ coupling. Taking the CPO/CO₂ coupling as an example, complex 3 converted 92% of CPO in 5 h at 100 °C under 20 atm of CO₂ to produce the corresponding carbonate (entry 7, Table 3), and a higher conversion rate of 98% was achieved in 10 h (entry 8, Table 3). When SO was used as the substrate, 50% of the SO was converted to the corresponding cyclic carbonate in 10 h at 100 °C under 20 atm of CO₂ (entry 9, Table 3). Nearly complete conversion of SO was achieved by extension of the reaction time to 24 h (entry 10, Table 3).

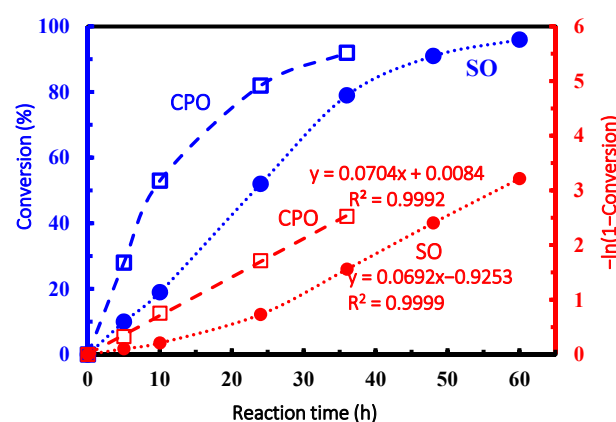
Complex 3 also displayed high activity toward CPO/CO₂ coupling under low CO₂ pressure. For example, 85% of CPO was converted to cyclic carbonate at 100 °C within 5 h under constant 2 atm CO₂ pressure (entry 1, Table 4). Prolonging the reaction time to 10 h gave rise to the nearly complete conversion of CPO (entry 2, Table 4). Complex 3 was still active under atmospheric CO₂ pressure, but the activity dropped sharply. For example, the conversion of CPO was only 28% in 5 h and 55% in 10 h (entries 1 and 2, Table 4), owing to the low concentration of CO₂ dissolved in CPO. By further extending the reaction time, high conversion of CPO was achieved (entries 3–6, Table 4). However, for SO/CO₂ coupling, complex 3 displayed very low activity. The conversion of SO was only 26% in 10 h when the reaction was performed at 100 °C, maintaining the CO₂ pressure at constant 2 atm (entry 7, Table 4). Lower SO conversion was expected, as the reaction was carried out at atmospheric CO₂ pressure. Analogous to CPO/CO₂ coupling, a high conversion of SO can be achieved by extending the reaction time (entries 8–14, Table 4).

Table 4. The coupling of epoxide/CO₂ under low CO₂ pressure by complex **3**¹.

Entry	Epoxide	P(CO ₂) (atm)	Time (h)	Conversion (%)
1	CPO	2	5	85
2	CPO	2	10	98
3	CPO	1	5	28
4	CPO	1	10	55
5	CPO	1	24	83
6	CPO	1	36	91
7	SO	2	10	26
8	SO	1	5	10
9	SO	1	10	19
10	SO	1	24	50
11	SO	1	36	82
12	SO	1	48	92
13	SO	1	60	96

¹ Conditions: Complex **3** (44.4 mg, 50 μ mol), $n_{(3)}/n_{(\text{epoxide})} = 1/1000$, the temperature is 100 °C. Other notes are the same as those in Table 1.

Kinetic studies of the coupling reactions of CPO/CO₂ and SO/CO₂ at atmospheric CO₂ pressure by complex **3** are plotted in Figure 3. It is clear that the CPO/CO₂ coupling is faster than the SO/CO₂ coupling under the same conditions (the blue curves in Figure 3). It is worth noting that the coupling of CPO/CO₂ has a first-order dependence on CPO concentration throughout the coupling reaction, as illustrated in Figure 3 (the red dash line, $-\ln(1-\text{Conversion})$ vs. time). This may indicate a better solubility of complex **3** in CPO than that of complex **2**, which was tentatively ascribed to the incorporation of more amine groups on the ligand framework. Differing from CPO/CO₂ coupling, the kinetic curve ($-\ln(1-\text{Conversion})$ vs. time) of SO/CO₂ coupling shows an increase in the slope during the early stage of the reaction (the red dot curve in Figure 3), reflecting the heterogeneous nature of the system owing to the poor solubility of complex **3** in SO. As the reaction proceeded, more SC was produced, which in turn helped to dissolve complex **3**, increasing the catalyst concentration and speeding up the coupling reaction. After some time, complex **3** was totally dissolved, forming a homogeneous system and maintaining constant concentration. Thus, a linear relationship was observed at the late stage of the coupling reaction, demonstrating a first-order dependence on SO concentration. The linear relation at the late stage also suggested the high stability of complex **3** under elevated temperature such as 100 °C.

**Figure 3.** Kinetic curves of CPO/CO₂ and SO/CO₂ coupling catalyzed by complex **3** at 100 °C at atmospheric CO₂ pressure.

3. Materials and Methods

2-aminophenol (99%), 4-tertbutylphenol, aqueous dimethylamine solution (40 wt%), 3,5-ditertbutylsalicylaldehyde (98%), and diethyl aluminum chloride (1 mol/L, in hexane) were purchased from Energy Chemical (Anqing, China) and used as received. Propylene oxide, 1,2-butylene oxide, epichlorohydrin, and styrene oxide obtained from Energy Chemical (Anqing, China) were distilled over CaH_2 before use. THF and hexane were pre-dried over 4 Å molecular sieves before distillation over sodium with benzophenone as the indicator under an argon atmosphere and stored over freshly cut sodium in a glovebox. CO_2 (99.999% purity) was purchased from Shenyang Hongsheng Gas Limited Corporation, Suzhou, China. Ethanol and formic acid were used as received without further handling.

General procedures: All reactions sensitive to air and moisture were carried out in a glovebox filled with dry argon. Proligands H_2L^1 – H_2L^3 were synthesized according to the literature methods and structurally identified by ^1H NMR and ^{13}C NMR [24]. The aluminum complexes **1**–**3** were prepared by equimolar reaction of the proligands with AlEt_2Cl in a glovebox filled with argon. The structures of complexes **1**–**3** were characterized by ^1H NMR, ^{13}C NMR, and MS. The coupling of epoxide with CO_2 was carried in a stainless-steel autoclave equipped with a magnetic stirring bar. The reaction mixture was analyzed by the ^1H NMR spectra with CDCl_3 as a solvent. The ^1H and ^{13}C NMR spectra were recorded using Bruker AVANCE III 500 MHz spectrometer (Billerica, MA, USA). Mass spectra of complexes **1**–**3** were obtained in the electrospray positive mode (ESI+) on Thermo LTQ Orbitrap XL spectrometer (Waltham, MA, USA), samples were diluted in methanol or ethanol, at DUT Chemistry Analysis & Research Centre, Dalian University of Technology (Dalian, China).

3.1. Coupling Reaction of Epoxide with CO_2 by Aluminum Complex **1**

The typical procedure for the coupling of PO with CO_2 by complex **1** under elevated pressure is as follows. Complex **1** and cocatalyst were dissolved in PO in a Schlenk tube. Then, the solution was transferred via syringe into the pre-dried autoclave under CO_2 atmosphere. Then, the autoclave was pressurized with CO_2 and heated. After the designated time, the autoclave was cooled in an ice bath. The excess of the CO_2 was vented out. The conversion of PO was determined by GC analysis and ^1H NMR of the reaction mixture, and the yield was calculated based on isolated propylene carbonate. The results showed that the GC result was consistent with that by weight analysis of the PC.

3.2. Coupling Reaction of Epoxide with CO_2 by Bifunctional Aluminum Complexes

The typical procedure for the coupling of PO with CO_2 by complex **2** or **3** under elevated pressure is as follows. Complex **2** (38.7 mg, 50 μmol) was first placed in the pre-dried autoclave. After the internal atmosphere of the autoclave was displaced by CO_2 three times, PO was injected, which was followed by charging CO_2 to 20 atm. Then, the autoclave was heated for the designated time. The analysis was the same as the above method.

The typical procedure for the coupling of CO_2 with CPO by complex **2** or **3** at atmospheric CO_2 pressure is as follows. Complex **2** (38.7 mg, 50 μmol) was placed in a 10 mL round-bottom flask in a glovebox. The flask was taken out, which was equipped with a balloon. The flask was vacuumed and recharged with CO_2 . After the injection of a prescribed amount of CPO, the flask was heated and maintained at 100 °C. The samples were taken out periodically and analyzed by Agilent GC to determine the conversion of CPO.

4. Conclusions

We have demonstrated the synthesis of a series of aluminum complexes **1**–**3**. Structural characterization by NMR and MS suggested the formation of binuclear structures via the chloride. Although complex **1** can be activated by either a nucleophile or an organic base to enable the coupling of terminal epoxide with CO_2 , the excess use of cocatalyst unambiguously hampers its practical application. In contrast, the bifunctional complexes **2**

and **3** containing tertiary amine as the built-in nucleophile are highly active catalysts by their own for the coupling of CO₂ with terminal epoxides. For bifunctional complexes **2** and **3**, high temperature facilitates the rapid transformation. It is found that the incorporation of more amine groups in the metal complex greatly enhances the catalytic activity. The bifunctional complexes are even active under low CO₂ pressure at the expense of catalytic activity to some extent. This work may shed light on the design of metal-based catalyst of high activity for the coupling of terminal epoxide with CO₂.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/2/145/s1>, Figure S1: ¹H NMR spectrum of proligand H₂L¹ in CDCl₃, Figure S1: ¹H NMR spectrum of proligand H₂L² in DMSO-d₆, Figure S3: ¹H NMR spectrum of proligand H₂L³ in DMSO-d₆, Figure S4: ¹H NMR spectrum of the complex **1** in CDCl₃, Figure S5: ¹H NMR spectrum of the complex **2** in DMSO-d₆, Figure S6: ¹H NMR spectrum of the complex **3** in DMSO-d₆, Figure S7: Kinetic study of coupling of PO/CO₂ mediated by **1**/TBAB (1:40 molar ratio), PO conversion vs. reaction time, Table S1: Cycloaddition of CO₂ to PO mediated by complex **1** and TBAB, Table S2: Effect of reaction time on the PO conversion, Table S3: Coupling of CO₂/PO catalyzed by **1**/DMAP, Table S4: Coupling of CO₂/PO catalyzed by **1**/1-MeIm.

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References

1. Dibenedetto, A.; Angelini, A.; Stufano, P. Use of carbon dioxide as feedstock for chemicals and fuels: Homogeneous and heterogeneous catalysis. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 334–353. [CrossRef]
2. Yu, B.; Diao, Z.-F.; Guo, C.-X.; He, L.-N. Carboxylation of olefins/alkynes with CO₂ to industrially relevant acrylic acid derivatives. *J. CO₂ Util.* **2013**, *1*, 60–68. [CrossRef]
3. Drees, M.; Cokoja, M.; Kühn, F.E. Recycling CO₂? Computational Considerations of the Activation of CO₂ with Homogeneous Transition Metal Catalysts. *ChemCatChem* **2012**, *4*, 1703–1712. [CrossRef]
4. Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W.A.; Kuehn, F.E. Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge? *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537. [CrossRef] [PubMed]
5. Omae, I. Aspects of carbon dioxide utilization. *Catal. Today* **2006**, *115*, 33–52. [CrossRef]
6. Cokoja, M.; Wilhelm, M.E.; Anthofer, M.H.; Herrmann, W.A.; Kuehn, F.E. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts. *ChemSusChem* **2015**, *8*, 2436–2454. [CrossRef] [PubMed]
7. Maeda, C.; Miyazaki, Y.; Ema, T. Recent progress in catalytic conversions of carbon dioxide. *Catal. Sci. Technol.* **2014**, *4*, 1482–1497. [CrossRef]
8. Xu, K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem. Rev.* **2004**, *104*, 4303–4417. [CrossRef]
9. Schaeffner, B.; Schaeffner, F.; Verevkin, S.P.; Boerner, A. Organic Carbonates as Solvents in Synthesis and Catalysis. *Chem. Rev.* **2010**, *110*, 4554–4581. [CrossRef]
10. Shaikh, A.A.G.; Sivaram, S. Organic carbonates. *Chem. Rev.* **1996**, *96*, 951–976. [CrossRef]
11. Lu, X.B.; Feng, X.J.; He, R. Catalytic formation of ethylene carbonate from supercritical carbon dioxide/ethylene oxide mixture with tetradentate Schiff-base complexes as catalyst. *Appl. Catal. Gen.* **2002**, *234*, 25–33. [CrossRef]
12. Fuchs, M.A.; Altesleben, C.; Zevaco, T.A.; Dinjus, E. An Efficient Homogeneous Chloro-Aluminum- N₂O₂ Catalyst for the Coupling of Epoxides with Carbon Dioxide. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4541–4545. [CrossRef]

13. Clegg, W.; Harrington, R.W.; North, M.; Pasquale, R. Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium-Salen Complexes. *Chem. Eur. J.* **2010**, *16*, 6828–6843. [[CrossRef](#)] [[PubMed](#)]
14. Kasuga, K.; Nagao, S.; Fukumoto, T.; Handa, M. Cycloaddition of carbon dioxide to propylene oxide catalysed by tetra-*t*-butylphthalocyaninatoaluminium(III) chloride. *Polyhedron* **1996**, *15*, 69–72. [[CrossRef](#)]
15. Woo, W.H.; Hyun, K.; Kim, Y.; Ryu, J.Y.; Lee, J.; Kim, M.; Park, M.H.; Kim, Y. Highly Active Salen-Based Aluminum Catalyst for the Coupling of Carbon Dioxide with Epoxides at Ambient Temperature. *Eur. J. Inorg. Chem.* **2017**, 5372–5378. [[CrossRef](#)]
16. Wu, X.; North, M. A Bimetallic Aluminium(Salphen) Complex for the Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide. *ChemSusChem* **2017**, *10*, 74–78. [[CrossRef](#)] [[PubMed](#)]
17. Li, C.-Y.; Liu, D.-C.; Ko, B.-T. Synthesis, characterization and reactivity of single-site aluminium amides bearing benzotriazole phenoxide ligands: Catalysis for ring-opening polymerization of lactide and carbon dioxide/propylene oxide coupling. *Dalton Trans.* **2013**, 42, 11488–11496. [[CrossRef](#)]
18. Melendez, J.; North, M.; Pasquale, R. Synthesis of cyclic carbonates from atmospheric pressure carbon dioxide using exceptionally active aluminium(salen) complexes as catalysts. *Eur. J. Inorg. Chem.* **2007**, 3323–3326. [[CrossRef](#)]
19. Qin, Y.; Guo, H.; Sheng, X.; Wang, X.; Wang, F. An aluminum porphyrin complex with high activity and selectivity for cyclic carbonate synthesis. *Green Chem.* **2015**, *17*, 2853–2858. [[CrossRef](#)]
20. Aida, T.; Inoue, S. Activation of carbon dioxide with aluminum porphyrin and reaction with epoxide. Studies on (tetraphenylporphinato)aluminum alkoxide having a long oxyalkylene chain as the alkoxide group. *J. Am. Chem. Soc.* **1983**, *105*, 1304–1309. [[CrossRef](#)]
21. Lu, X.B.; Zhang, Y.J.; Jin, K.; Luo, L.M.; Wang, H. Highly active electrophile-nucleophile catalyst system for the cycloaddition of CO₂ to epoxides at ambient temperature. *J. Catal.* **2004**, *227*, 537–541. [[CrossRef](#)]
22. Lu, X.B.; Zhang, Y.J.; Liang, B.; Li, X.; Wang, H. Chemical fixation of carbon dioxide to cyclic carbonates under extremely mild conditions with highly active bifunctional catalysts. *J. Mol. Catal. Chem.* **2004**, *210*, 31–34. [[CrossRef](#)]
23. Rintjema, J.; Kleij, A.W. Aluminum-Mediated Formation of Cyclic Carbonates: Benchmarking Catalytic Performance Metrics. *ChemSusChem* **2017**, *10*, 1274–1282. [[CrossRef](#)] [[PubMed](#)]
24. Gao, P.; Zhao, Z.; Chen, L.; Yuan, D.; Yao, Y. Dinuclear Aluminum Poly(phenolate) Complexes as Efficient Catalysts for Cyclic Carbonate Synthesis. *Organometallics* **2016**, *35*, 1707–1712. [[CrossRef](#)]
25. Cozzolino, M.; Press, K.; Mazzeo, M.; Lamberti, M. Carbon Dioxide/Epoxide Reactions Catalyzed by Bimetallic Salalen Aluminum Complexes. *ChemCatChem* **2016**, *8*, 455–460. [[CrossRef](#)]
26. Castro-Osma, J.A.; Lara-Sanchez, A.; North, M.; Otero, A.; Villuendas, P. Synthesis of cyclic carbonates using monometallic, and helical bimetallic, aluminium complexes. *Catal. Sci. Technol.* **2012**, *2*, 1021–1026. [[CrossRef](#)]
27. Rios Yepes, Y.; Quintero, C.; Osorio Melendez, D.; Daniliuc, C.G.; Martinez, J.; Rojas, R.S. Cyclic Carbonates from CO₂ and Epoxides Catalyzed by Tetra- and Pentacoordinate Amidinate Aluminum Complexes. *Organometallics* **2019**, *38*, 469–478. [[CrossRef](#)]
28. Whiteoak, C.J.; Kielland, N.; Laserna, V.; Castro-Gomez, F.; Martin, E.; Escudero-Adan, E.C.; Bo, C.; Kleij, A.W. Highly Active Aluminium Catalysts for the Formation of Organic Carbonates from CO₂ and Oxiranes. *Chem. Eur. J.* **2014**, *20*, 2264–2275. [[CrossRef](#)]
29. Castro-Osma, J.A.; North, M.; Wu, X. Development of a Halide-Free Aluminium-Based Catalyst for the Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide. *Chem. Eur. J.* **2014**, *20*, 15005–15008. [[CrossRef](#)]
30. Supasitmongkol, S.; Styring, P. A single centre aluminium(III) catalyst and TBAB as an ionic organo-catalyst for the homogeneous catalytic synthesis of styrene carbonate. *Catal. Sci. Technol.* **2014**, *4*, 1622–1630. [[CrossRef](#)]
31. Kim, S.H.; Han, S.Y.; Kim, J.H.; Kang, Y.Y.; Lee, J.; Kim, Y. Monomeric or Dimeric Aluminum Complexes as Catalysts for Cycloaddition between CO₂ and Epoxides. *Eur. J. Inorg. Chem.* **2015**, 2015, 2323–2329. [[CrossRef](#)]
32. Whiteoak, C.J.; Kielland, N.; Laserna, V.; Escudero-Adan, E.C.; Martin, E.; Kleij, A.W. A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates. *J. Am. Chem. Soc.* **2013**, *135*, 1228–1231. [[CrossRef](#)] [[PubMed](#)]
33. Ema, T.; Miyazaki, Y.; Koyama, S.; Yano, Y.; Sakai, T. A bifunctional catalyst for carbon dioxide fixation: Cooperative double activation of epoxides for the synthesis of cyclic carbonates. *Chem. Commun.* **2012**, 48, 4489–4491. [[CrossRef](#)] [[PubMed](#)]
34. Bai, D.; Duan, S.; Hai, L.; Jing, H. Carbon Dioxide Fixation by Cycloaddition with Epoxides, Catalyzed by Biomimetic Metalloporphyrins. *ChemCatChem* **2012**, *4*, 1752–1758. [[CrossRef](#)]
35. Raghavendra, B.; Shashank, P.V.S.; Pandey, M.K.; Reddy, N.D. CO₂/Epoxide Coupling and the ROP of epsilon-Caprolactone: Mg and Al Complexes of gamma-Phosphino-ketiminates as Dual-Purpose Catalysts. *Organometallics* **2018**, *37*, 1656–1664. [[CrossRef](#)]
36. Ema, T.; Miyazaki, Y.; Shimonishi, J.; Maeda, C.; Hasegawa, J.-Y. Bifunctional Porphyrin Catalysts for the Synthesis of Cyclic Carbonates from Epoxides and CO₂: Structural Optimization and Mechanistic Study. *J. Am. Chem. Soc.* **2014**, *136*, 15270–15279. [[CrossRef](#)]
37. Darensbourg, D.J.; Fang, C.C.; Rodgers, J.L. Catalytic coupling of carbon dioxide and 2,3-epoxy-1,2,3,4-tetrahydronaphthalene in the presence of a (Salen)(CrCl)-Cl-III derivative. *Organometallics* **2004**, *23*, 924–927. [[CrossRef](#)]
38. Castro-Osma, J.A.; North, M.; Wu, X. Synthesis of Cyclic Carbonates Catalysed by Chromium and Aluminium Salphen Complexes. *Chem. Eur. J.* **2016**, *22*, 2100–2107. [[CrossRef](#)]

39. Ramidi, P.; Sullivan, S.Z.; Gartia, Y.; Munshi, P.; Griffin, W.O.; Darsey, J.A.; Biswas, A.; Shaikh, A.U.; Ghosh, A. Catalytic Cyclic Carbonate Synthesis Using Epoxide and Carbon Dioxide: Combined Catalytic Effect of Both Cation and Anion of an Ionic Cr-v(O) Amido Macrocyclic Complex. *Ind. Eng. Chem. Res.* **2011**, *50*, 7800–7807. [\[CrossRef\]](#)
40. Cuesta-Aluja, L.; Djoufak, M.; Aghmiz, A.; Rivas, R.; Christ, L.; Masdeu-Bulto, A.M. Novel chromium (III) complexes with N-4-donor ligands as catalysts for the coupling of CO₂ and epoxides in supercritical CO₂. *J. Mol. Catal. Chem.* **2014**, *381*, 161–170. [\[CrossRef\]](#)
41. Adolph, M.; Zevaco, T.A.; Altesleben, C.; Walter, O.; Dinjus, E. New cobalt, iron and chromium catalysts based on easy-to-handle N-4-chelating ligands for the coupling reaction of epoxides with CO₂. *Dalton Trans.* **2014**, *43*, 3285–3296. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Iksi, S.; Aghmiz, A.; Rivas, R.; Dolores Gonzalez, M.; Cuesta-Aluja, L.; Castilla, J.; Orejon, A.; El Guemmout, F.; Masdeu-Bulto, A.M. Chromium complexes with tridentate NN'O Schiff base ligands as catalysts for the coupling of CO₂ and epoxides. *J. Mol. Catal. Chem.* **2014**, *383*, 143–152. [\[CrossRef\]](#)
43. Ambrose, K.; Robertson, K.N.; Kozak, C.M. Cobalt amino-bis(phenolate) complexes for coupling and copolymerization of epoxides with carbon dioxide. *Dalton Trans.* **2019**, *48*, 6248–6260. [\[CrossRef\]](#)
44. Lu, X.B.; Liang, B.; Zhang, Y.J.; Tian, Y.Z.; Wang, Y.M.; Bai, C.X.; Wang, H.; Zhang, R. Asymmetric catalysis with CO₂: Direct synthesis of optically active propylene carbonate from racemic epoxides. *J. Am. Chem. Soc.* **2004**, *126*, 3732–3733. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Chang, T.; Jin, L.; Jing, H. Bifunctional Chiral Catalyst for the Synthesis of Chiral Cyclic Carbonates from Carbon Dioxide and Epoxides. *ChemCatChem* **2009**, *1*, 379–383. [\[CrossRef\]](#)
46. Reiter, M.; Altenbuchner, P.T.; Kissling, S.; Herdtweck, E.; Rieger, B. Amine-bis(phenolato)cobalt(III) Catalysts for the Formation of Organic Carbonates from Carbon Dioxide and Epoxides. *Eur. J. Inorg. Chem.* **2015**, *2015*, 1766–1774. [\[CrossRef\]](#)
47. Yu, C.-Y.; Chuang, H.-J.; Ko, B.-T. Bimetallic bis(benzotriazole iminophenolate) cobalt, nickel and zinc complexes as versatile catalysts for coupling of carbon dioxide with epoxides and copolymerization of phthalic anhydride with cyclohexene oxide. *Catal. Sci. Technol.* **2016**, *6*, 1779–1791. [\[CrossRef\]](#)
48. Adolph, M.; Zevaco, T.A.; Altesleben, C.; Staudt, S.; Walter, O.; Dinjus, E. New ionic cobalt(III) complexes based on the N, N-bis(2-pyrazinecarboxamide)-1,2-benzene ligand: Application to the formation of organic carbonates from epoxides and CO₂. *New J. Chem.* **2015**, *39*, 9858–9865. [\[CrossRef\]](#)
49. Buonerba, A.; De Nisi, A.; Grassi, A.; Milione, S.; Capacchione, C.; Vagin, S.; Rieger, B. Novel iron(III) catalyst for the efficient and selective coupling of carbon dioxide and epoxides to form cyclic carbonates. *Catal. Sci. Technol.* **2015**, *5*, 118–123. [\[CrossRef\]](#)
50. Buchard, A.; Kember, M.R.; Sandeman, K.G.; Williams, C.K. A bimetallic iron(III) catalyst for CO₂/epoxide coupling. *Chem. Commun.* **2011**, *47*, 212–214. [\[CrossRef\]](#)
51. Whiteoak, C.J.; Martin, E.; Martinez Belmonte, M.; Benet-Buchholz, J.; Kleij, A.W. An Efficient Iron Catalyst for the Synthesis of Five- and Six-Membered Organic Carbonates under Mild Conditions. *Adv. Synth. Catal.* **2012**, *354*, 469–476. [\[CrossRef\]](#)
52. Della Monica, F.; Buonerba, A.; Capacchione, C. Homogeneous Iron Catalysts in the Reaction of Epoxides with Carbon Dioxide. *Adv. Synth. Catal.* **2019**, *361*, 265–282. [\[CrossRef\]](#)
53. Della Monica, F.; Vummaleti, S.V.C.; Buonerba, A.; De Nisi, A.; Monari, M.; Milione, S.; Grassi, A.; Cavallo, L.; Capacchione, C. Coupling of Carbon Dioxide with Epoxides Efficiently Catalyzed by Thioether-Triphenolate Bimetallic Iron(III) Complexes: Catalyst Structure-Reactivity Relationship and Mechanistic DFT Study. *Adv. Synth. Catal.* **2016**, *358*, 3231–3243. [\[CrossRef\]](#)
54. Zhao, Z.; Qin, J.; Zhang, C.; Wang, Y.; Yuan, D.; Yao, Y. Recyclable Single-Component Rare-Earth Metal Catalysts for Cycloaddition of CO₂ and Epoxides at Atmospheric Pressure. *Inorg. Chem.* **2017**, *56*, 4568–4575. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Wang, C.; Liu, X.; Dai, Z.; Sun, Y.; Tang, N.; Wu, J. Yttrium complex supported by a sterically encumbering N-anchored tris-arylphenoxide ligand: Heteroselective ROP of rac-lactide and CO₂/epoxide coupling. *Inorg. Chem. Commun.* **2015**, *56*, 69–72. [\[CrossRef\]](#)
56. Luinstra, G.A.; Haas, G.R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. On the formation of aliphatic polycarbonates from epoxides with chromium(III) and aluminum(III) metal-salen complexes. *Chem. Eur. J.* **2005**, *11*, 6298–6314. [\[CrossRef\]](#)
57. North, M.; Quek, S.C.Z.; Pridmore, N.E.; Whitwood, A.C.; Wu, X. Aluminum(salen) Complexes as Catalysts for of Terminal Epoxides via CO₂ Coupling. *ACS Catal.* **2015**, *5*, 3398–3402. [\[CrossRef\]](#)
58. North, M.; Young, C. Bimetallic aluminium(acen) complexes as catalysts for the synthesis of cyclic carbonates from carbon dioxide and epoxides. *Catal. Sci. Technol.* **2011**, *1*, 93–99. [\[CrossRef\]](#)
59. Rulev, Y.A.; Gugkaeva, Z.; Maleev, V.I.; North, M.; Belokon, Y.N. Robust bifunctional aluminium-salen catalysts for the preparation of cyclic carbonates from carbon dioxide and epoxides. *Beilstein. J. Org. Chem.* **2015**, *11*, 1614–1623. [\[CrossRef\]](#)
60. Martinez, J.; Castro-Osma, J.A.; Alonso-Moreno, C.; Rodriguez-Dieguez, A.; North, M.; Otero, A.; Lara-Sanchez, A. One-Component Aluminum(heteroscorpionate) Catalysts for the Formation of Cyclic Carbonates from Epoxides and Carbon Dioxide. *ChemSusChem* **2017**, *10*, 1175–1185. [\[CrossRef\]](#)
61. de la Cruz-Martinez, F.; Martinez, J.; Gaona, M.A.; Fernandez-Baeza, J.; Sanchez-Barba, L.F.; Rodriguez, A.M.; Castro-Osma, J.A.; Otero, A.; Lara-Sanchez, A. Bifunctional Aluminum Catalysts for the Chemical Fixation of Carbon Dioxide into Cyclic Carbonates. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5322–5332. [\[CrossRef\]](#)
62. Melendez, J.; North, M.; Villuendas, P. One-component catalysts for cyclic carbonate synthesis. *Chem. Commun.* **2009**, 2577–2579. [\[CrossRef\]](#) [\[PubMed\]](#)

63. Luo, R.; Zhou, X.; Chen, S.; Li, Y.; Zhou, L.; Ji, H. Highly efficient synthesis of cyclic carbonates from epoxides catalyzed by salen aluminum complexes with built-in “CO₂ capture” capability under mild conditions. *Green Chem.* **2014**, *16*, 1496–1506. [\[CrossRef\]](#)
64. Martinez, J.; de la Cruz-Martinez, F.; Gaona, M.A.; Pinilla-Penalver, E.; Fernandez-Baeza, J.; Rodriguez, A.M.; Castro-Osma, J.A.; Otero, A.; Lara-Sanchez, A. Influence of the Counterion on the Synthesis of Cyclic Carbonates Catalyzed by Bifunctional Aluminum Complexes. *Inorg. Chem.* **2019**, *58*, 3396–3408. [\[CrossRef\]](#)
65. Ren, W.-M.; Liu, Y.; Lu, X.-B. Bifunctional Aluminum Catalyst for CO₂ Fixation: Regioselective Ring Opening of Three-Membered Heterocyclic Compounds. *J. Org. Chem.* **2014**, *79*, 9771–9777. [\[CrossRef\]](#)
66. Tian, D.; Liu, B.; Zhang, L.; Wang, X.; Zhang, W.; Han, L.; Park, D.-W. Coupling reaction of carbon dioxide and epoxides efficiently catalyzed by one-component aluminum-salen complex under solvent-free conditions. *J. Ind. Eng. Chem.* **2012**, *18*, 1332–1338. [\[CrossRef\]](#)
67. Tian, D.; Liu, B.; Gan, Q.; Li, H.; Darensbourg, D.J. Formation of Cyclic Carbonates from Carbon Dioxide and Epoxides Coupling Reactions Efficiently Catalyzed by Robust, Recyclable One-Component Aluminum-Salen Complexes. *ACS Catal.* **2012**, *2*, 2029–2035. [\[CrossRef\]](#)
68. Ren, Y.; Jiang, O.; Zeng, H.; Mao, Q.; Jiang, H. Lewis acid-base bifunctional aluminum-salen catalysts: Synthesis of cyclic carbonates from carbon dioxide and epoxides. *RSC Adv.* **2016**, *6*, 3243–3249. [\[CrossRef\]](#)
69. Hong, M.; Kim, Y.; Kim, H.; Cho, H.J.; Baik, M.-H.; Kim, Y. Scorpionate Catalysts for Coupling CO₂ and Epoxides to Cyclic Carbonates: A Rational Design Approach for Organocatalysts. *J. Org. Chem.* **2018**, *83*, 9370–9380. [\[CrossRef\]](#)
70. Hanhart, W.; Ingold, C.K. CXXXIX.—The nature of the alternating effect in carbon chains. Part XVIII. Mechanism of exhaustive methylation and its relation to anomalous hydrolysis. *J. Chem. Soc.* **1927**, 997–1020. [\[CrossRef\]](#)
71. Hughes, E.D.; Ingold, C.K.; Patel, C.S. 135. Influence of poles and polar linkings on the course pursued by elimination reactions. Part XVI. Mechanism of the thermal decomposition of quaternary ammonium compounds. *J. Chem. Soc.* **1933**, 526–530. [\[CrossRef\]](#)
72. De la Zerda, J.; Neumann, R.; Sasson, Y. Hofmann decomposition of quaternary ammonium salts under phase-transfer catalytic conditions. *J. Chem. Soc. Perkin Trans. 2* **1986**, 823–826. [\[CrossRef\]](#)
73. Hofman, A.W., IX. Contributions towards the history of the monamines.—No. III. Compound ammonias by inverse substitution. *Proc. R. Soc. Lond.* **1859**, *10*, 594–596.
74. Collie, N.; Schryver, S.B. LIII. The action of heat on the chlorides and hydroxides of mixed quaternary ammonium compounds. *J. Chem. Soc. Trans.* **1890**, *57*, 767–782. [\[CrossRef\]](#)
75. Zaki, A.; Fahim, H. Some quaternary ammonium salts and their decomposition products. *J. Chem. Soc.* **1942**, 270–272. [\[CrossRef\]](#)
76. Gordon, J.E. Fused Organic Salts. III.1a Chemical Stability of Molten Tetra-*n*-alkylammonium Salts. Medium Effects on Thermal R₄N⁺X[−] Decomposition. RBr + I[−] = RI + Br[−] Equilibrium Constant in Fused Salt Medium. *J. Org. Chem.* **1965**, *30*, 2760–2763. [\[CrossRef\]](#)
77. Xie, Y.; Zhang, Z.; Jiang, T.; He, J.; Han, B.; Wu, T.; Ding, K. CO₂ cycloaddition reactions catalyzed by an ionic liquid grafted onto a highly cross-linked polymer matrix. *Angew. Chem. Int. Ed.* **2007**, *46*, 7255–7258. [\[CrossRef\]](#)
78. North, M.; Pasquale, R. Mechanism of Cyclic Carbonate Synthesis from Epoxides and CO₂. *Angew. Chem. Int. Ed.* **2009**, *48*, 2946–2948. [\[CrossRef\]](#)
79. Cho, W.; Shin, M.S.; Hwang, S.; Kim, H.; Kim, M.; Kim, J.G.; Kim, Y. Tertiary amines: A new class of highly efficient organocatalysts for CO₂ fixations. *J. Ind. Eng. Chem.* **2016**, *44*, 210–215. [\[CrossRef\]](#)