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# Lithium organoaluminate complexes as catalysts for the conversion of CO<sub>2</sub> into cyclic carbonates

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Dedication ((optional))

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**Abstract:** Four lithium organoaluminate complexes containing bidentate pyrrolyl ligand were successfully synthesized, and their structural features were provided. These complexes were used as catalysts for chemical fixation of carbon dioxide with epoxides under mild conditions. Among them, complex  $\{[C_4H_3N(A|Et_3)(2-CH_2NH Li^Bu)]\}_2$  (4), in conjunction with tetrabutyl-ammonium iodide (TBAI) as cocatalyst, exhibits higher catalytic activities than other lithium organoaluminates. Epoxides reacted with CO<sub>2</sub> at 50 °C and 1 atm pressure to give the corresponding cyclic carbonates in yields of 62-99%.

#### Introduction

Because of carbon dioxide is a nontoxicity, abundance, availability, recyclability C1 resource, efficient utilization of CO<sub>2</sub> as a chemical feedstock is currently attracting much attention from both industry and academia filed.<sup>[1]</sup> In this regard, chemical fixation of carbon dioxide with epoxides to give the corresponding cyclic carbonates is an active field and extensively studied, even well commercialized.<sup>[2]</sup> This is because of the widespread use of cyclic carbonates as aprotic solvents, synthetic building blocks, electrolytes, monomers for polymerizations, industrial lubricants, and pharmaceutical intermediates so on.[3] Over the past two decades, great progress in the produce of cyclic carbonates from carbon dioxide and epoxides have been achieved. Many types of catalysts have been developed to effect chemical fixation of carbon dioxide with epoxides. For example, metal-based catalytic systems including zinc,[4] chromium,<sup>[5]</sup> iron,<sup>[6]</sup> cobalt,<sup>[7]</sup> magnesium,<sup>[8]</sup> vanadium,<sup>[9]</sup> tin<sup>[10]</sup> etc. have been used in such reactions. Among them, aluminium is considered an ideal choice for the ringopening of epoxides for abundant reserves, non-toxic, and high Lewis acidity. Though, salen, salophen and related ligand-based monometallic or bimetallic aluminium complexes have been proved to efficient catalysts.<sup>[11]</sup> Some efficient catalysts with aluminum metal centers capable of operating at ambient temperature and 1 atm CO<sub>2</sub> are also reported.<sup>[12]</sup> But for the moderate reactive styrene oxide, the Al-based catalysts still require higher catalyst loading and a long reaction time.<sup>[13]</sup> Thus, the development of novel, higher active Al-based catalytic systems under ambient conditions and pressure is desirable.

In view of lithium organoaluminates could exhibit greatly enhanced performances over traditional monometallic compound by switching on metal-metal synergistic effect, allowing to use milder reaction conditions, showing enhanced reactivities, and giving superior functional group tolerances.<sup>[14]</sup> Continuing our interest in the development of chemical fixation of  $CO_2$ .<sup>[15]</sup> herein, we report the synthesis of four lithium organoaluminate complexes chelated by substituted pyrrolyl ligand and their use as catalysts for chemical fixation of carbon dioxide with epoxides at mild temperature and 1 atm  $CO_2$ .

#### **Results and Discussion**

#### Synthesis and Characterization

The bidentate pyrrolyl ligand  $[C_4H_3NH(2-CH_2NH^tBu)]$  (L), obtained according to our previous reports,<sup>[16]</sup> was selected again for this study. The addition of a stoichiometric amount of AIR<sub>3</sub> and TMEDA at room temperature to a freshly prepared solution of LiL results in the generation of the lithium aluminate complexes (1 R = Me) and (3 R = Et) according to the reaction shown in Scheme 1. Complex (2) could be obtained in moderate yield from reacting AIMe<sub>3</sub> with one equiv of LiL in the presence of TMEDA in toluene at 70 °C for 3 h. And the complex (2) also could be achieved in quantitative yield by heating complex (1) in toluene at 70 °C via intramolecular methane elimination. Interesting, following the same procedure as for (1) in absence of TMEDA, unexpected complex (4) with 2:2:1 (L: lithium: AIEt<sub>3</sub>) molar ratio was isolated. All complexes were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, elemental analysis, and further confirmed by single-crystal X-ray diffraction.



Scheme 1. Synthetic Routes to Complexes (1-4).

Single crystals of (1) used to X-ray diffraction studies recrystallized from toluene at 5 °C and its molecular structure is shown in Fig. 1. The crystal contains a disordered toluene molecule remaining in the lattice which has been omitted in the molecular diagram. In the solid state, the bidentate pyrrolyl ligand acts as a bridge between the aluminium and lithium. atoms. The lithium atom is four coordinated by the Namino-atom of the pyrrolyl ligands, one ring C-atom and two nitrogen atoms of TMEDA to form a distorted tetrahedral geometry. The Li(1)-C(3) bond length is 2.486(6) Å which is much longer than earlier reported Li-C bond values (2.36-2.39 Å).[16c] The aluminium atom completes its tetracoordinated environment with the  $N_{pvrrole}$  atom and three methyl groups. The way in which the AIMe<sub>3</sub> fragment is bonded to the pyrrolyl nitrogen atom indicates that the formation of this species can be described as the aluminum precursor with the lithiated ligand to give a 1 : 1 Lewis adduct.

Block crystals of **(2)** were also obtained at room temperature from a saturated toluene. Its molecular structure is shown in Fig. 2. Each asymmetric unit of **(2)** has two molecules of  $\{C_4H_3N(AIMe_2)[2-CH_2N(^{t}Bu)Li(TMEDA)]\}$ . Here one molecule will be discussed for their structures are very similar. The lithium atom is three-coordinate and is bound by two nitrogen atoms of TMEDA and the N<sub>amino</sub>-atom of the pyrrolyl ligand. Three coordinate Li-N<sub>amino</sub> bond is 2.109(8) Å, which is much longer than that of the monomeric primary amido complex [Li(NHMes\*)(TMEDA)] (Li-N = 1.895(8) Å).<sup>[17]</sup> Two nitrogen atoms of pyrrolyl ligand and two methyl groups surround the aluminium atom, forming a distorted tetrahedral geometry.

Complex (3)'s structure is similar to that of complex (1). Its ORTEP drawing, selected bond lengths and angles are presented in Fig. 3. The only difference was that the lithium atom is five coordinated by the  $N_{amino}$ -atom of the pyrrolyl ligands,



Figure 1. ORTEP diagram of (1) (at 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.940(3), C(3)-Li(1) 2.486(6), N(2)-Li(1) 2.068(6), N(4)-Li(1) 2.084(6), N(3)-Li(1) 2.070(6), N(2)-C(5) 1.481(4); C(5)-N(2)-C(6) 115.5(3), C(5)-N(2)-Li(1) 100.3(2), N(2)-Li(1)-N(3) 115.1(3), N(2)-Li(1)-N(4) 138.4(3), N(3)-Li(1)-N(4) 89.0(2), N(2)-Li(1)-C(3) 90.7(2), N(3)-Li(1)-C(3) 119.5(3), N(4)-Li(1)-C(3) 106.9(3).



Figure 2. ORTEP diagram of (2) (at 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.869(4), Al(1)-N(2) 1.908(3), Li(1)-N(3) 2.045(8), Li(1)-N(2) 2.109(8), Li(1)-N(4) 2.183(7); N(1)-Al(1)-N(2) 87.87(17), N(3)-Li(1)-N(2) 126.4(4), N(3)-Li(1)-N(4) 86.6(3), N(2)-Li(1)-N(4) 140.0(4), C(5)-N(2)-C(6) 114.0(3), C(6)-N(2)-Al(1) 121.0(3), C(5)-N(2)-Li(1) 111.1(3), C(6)-N(2)-Li(1) 108.2(3), Al(1)-N(2)-Li(1) 89.5(3).

two ring C-atom and two nitrogen atoms of TMEDA in the solid state. The bonds length of Li(1)-C(3) and Li(1)-C(4) are 2.491(5) and 2.511(5) Å, respectively. Which are comparable with that of complex **(1)**.

Complex (4) crystallized from diethyl ether solution. As illustrated in Figure 4, there is a dimeric framework consisting in complex (4), revealed by single crystal X-ray studies. The two ligand moieties are linked by Li1 and Li2 atoms, where the Li1 atom is six-coordinate and is bound by two ring C-atom,  $N_{amino-}$  atom of the pyrrolyl ligand and one ring C-atom, two N atoms of the other pyrrolyl ligand, and the Li2 atom is bonded to its

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central N-atom of pyrrole and one ring C-atoms of the other ligand. They are interlocked through n<sup>5</sup>-pyrrole rings to the Li2 atom, and the average bond length from lithium to the centroid of the pyrrole ring is about 2.368 Å. The results are similar to the reported Li-η<sup>5</sup>-pyrrole ring bond lengths, which are about 2.207-2.397 Å.<sup>[16a]</sup> In addition, the aluminum atom in complex (4) is also coordinated by the N<sub>pyrrole</sub> atom and three ethyl groups in a distorted tetrahedral manner.



Figure 3. ORTEP diagram of (3) (at 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.950(2), Li(1)-C(3) 2.491(5), Li(1)-C(4) 2.511(5), Li(1)-N(3) 2.075(5), Li(1)-N(2) 2.076(5), Li(1)-N(4) 2.100(5) N(2)-C(5) 1.484(3); C(5)-N(2)-C(6) 115.4(2), C(5)-N(2)-Li(1) 97.4(2), N(2)-Li(1)-N(3) 114.9(2), N(2)-Li(1)-N(4) 138.5(3), N(3)-Li(1)-N(4) 89.60(19), N(2)-Li(1)-C(3) 92.31(18), N(3)-Li(1)-C(3) 119.5(2), N(4)-Li(1)-C(3) 104.4(2).



Figure 4. ORTEP diagram of (4) (at 25% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.9704(13), Li(1)-C(3) 2.529(3), Li(1)-C(4) 2.511(5), Li(1)-C(13) 2.539(3), Li(1)- $N(4) \ 2.090(3), \ Li(1)-N(3) \ 2.085(3), \ Li(1)-N(2) \ 2.053(3), \ Li(2)-N(3) \ 2.032(3),$ Li(2)-C(2) 2.394(3), Li(2')-N(3) 2.380(3), Li(2')-C(10) 2.383(3), Li(2')-C(11) 2.379(3), Li(2')-C(12) 2.363(3), Li(2')-C(13) 2.336(3); Li(2)-N(3)-Li(1) 95.50(12), N(3)-Li(1)-N(4) 91.58(11), N(3)-Li(1)-C(3) 102.08(12), N(4)-Li(1)-C(3) 129.46(13), N(2)-Li(1)-N(3) 114.53(13), N(2)-Li(1)-N(4) 126.15(14), N(2)-Li(1)-C(3) 91.76(11), N(3)-Li(2)-C(2) 111.66(13).

#### Synthesis of cyclic carbonates

Ĵ	<b>CO₂</b> + ∠	CH <sub>3</sub>	ОСН	3
Entry	Cat. (mol %)	Cocat. (mol %)	Solvent	Yield (%) <sup>[b]</sup>
1	1 (3)	Bu₄NI (2.5)	THF	37
2	<b>2</b> (3)	Bu₄NI (2.5)	THF	29
3	<b>3</b> (3)	Bu₄NI (2.5)	THF	44
4	4 (3)	Bu₄NI (2.5)	THF	63
5		Bu₄NI (2.5)	THF	trace
6	4 (3)	-	THF	10

1	1 (3)	Bu₄NI (2.5)	THF	37
2	<b>2</b> (3)	Bu₄NI (2.5)	THF	29
3	<b>3</b> (3)	Bu₄NI (2.5)	THF	44
4	<b>4</b> (3)	Bu₄NI (2.5)	THF	63
5		Bu₄NI (2.5)	THF	trace
6	4 (3)	-	THF	10
7	Ligand	Bu₄NI (2.5)	THF	trace
8	TMEDA	Bu₄NI (2.5)	THF	trace
9	4 (5)	Bu₄NI (2.5)	THF	98
10	4 (5)	Bu₄NI (1.0)	THF	42
11	<b>4</b> (10)	Bu₄NI (2.5)	THF	95
12	<b>4</b> (5)	Bu₄NBr (2.5)	THF	51
13	4 (5)	Bu₄NCI (2.5)	THF	38
14	4 (5)	Bu₄NI (2.5)	None	6
15	<b>4</b> (5)	Bu₄NI (2.5)	Toluene	59
16	<b>4</b> (5)	Bu₄NI (2.5)	Hexane	trace
17	<b>4</b> (5)	Bu₄NI (2.5)	Et <sub>2</sub> O	34
18	<b>4</b> (5)	Bu₄NI (2.5)	$CH_2CI_2$	7
19 <sup>[c]</sup>	<b>4</b> (5)	Bu₄NI (2.5)	THF	67
20 <sup>[d]</sup>	<b>4</b> (5)	Bu₄NI (2.5)	THF	42

[a] Reaction conditions: epoxypropane (2 mmol), CO<sub>2</sub> (1 atm), THF (1 mL), 50 °C, 24 h. [b] Yield determined by <sup>1</sup>H NMR spectroscopy using trichloroethylene as an internal standard. [c] 12 h, [d] 30 °C.

After the successful synthesis of lithium organoaluminates, complex (1-4) were screened for the conversion of epoxy propane into propylene carbonate at 50 °C and one atm CO<sub>2</sub> pressure for 24 h using 3 mol% of complex (1-4) and 2.5 mol% of TBAI (Table 1, For the complex 4 is a tetranuclear dimmer structure in the solid state, the loading amount is calculated in terms of monomers). As can be seen from entries 1-4, complex (4) had the most activity, probably due to it's the higher nucleophilicity and lower alkalinity than other complexes. Control experiments indicated neither TBAI nor complex (4) alone displayed obvious catalytic activity in the absence of the other catalyst component under the current reaction conditions (Table 1, entries 5-6). The reactions were carried out using the aminopyrrole ligand itself and TMEDA in a combination of TBAI as catalysts. Trace amounts of cyclic carbonates were observed, respectively (Table 1, entries 7-8). It is worth noting that when 5

mol% complex (4) and 2.5 mol% TBAI loading was used at 50 °C, the reaction afforded the desired carbonate in nearly quantitative yield within 24 h (Table 1, entries 9-11). In consideration of complex (4) was one of the most active catalysts, further investigations and the effect of the cocatalyst were carried out. The experimental results showed that the catalytic activity of I, Br, and CI was I>Br>CI (Table 1, entries 7 and 12-13) for tetrabutylammonium salts at 50 °C and one atm carbon dioxide pressure. These agreed with previous research.<sup>[17]</sup> Next, different solvents, including toluene, hexane, diethyl ether, dichloromethane was screened, as was the solvent-free reaction (Table 1, entries 14-18). However, lower yields were obtained in all cases, which indicated that the solvent also plays an important role on the reactivity of this reaction. In addition, more experiments were carried out on the reaction time and temperature. The result proved when the reaction time shorted from 24 h to 12 h, the yield of propylene carbonate declined to 67% (entry 19), when the temperature dropped from 50°C to 30°C, the yield declined to 42% (entry 20). The best temperature for obtaining a satisfactory yield was 50 °C. In addition, the control reactions were carried out using 2aminopyrrolyl lithium complex {[2-(CH<sub>2</sub>NHCMe<sub>3</sub>)C<sub>4</sub>H<sub>3</sub>N]Li(THF)}<sub>2</sub>, [15] 2-aminopyrrolyl dilithium compounds {μ-η<sup>5</sup>:η<sup>1</sup>-2- $(Me_3CNCH_2)C_4H_3N]Li_2(TMEDA)$ <sup>[16]</sup> with the same supporting ligand as catalysts (see supporting information). The NMR results show that mono-, di-lithioaminopyrroyl complexes did not exhibit higher reactivity compared with the lithium organoaluminate complex. It indicates that an alkali-metal combine with a more electronegative metal Al, could exhibit enhanced performance than their monometallic areatly components.

Scheme 2. Substrate scope in the coupling of  $CO_2$  with various epoxides catalyzed by (4) /  $\textit{n-Bu}_4\text{NI.}^{[a]}$ 



[a] T Reaction conditions: epoxides (2 mmol), CO<sub>2</sub> (1 atm), THF (1.0 mL), 50 °C, 24 h. Yield determined by <sup>1</sup>H NMR using trichloroethylene as an internal standard; isolated yields were given in parentheses.

Under the optimized reaction conditions, ten terminal epoxides with carbon dioxide were chosen to investigate using 5 mol% of complex (4) and 2.5 mol% of TBAI at 50 °C and 1 atm carbon dioxide pressure. The reaction was been analyzed by <sup>1</sup>H NMR spectroscopy to give the NMR yield after 24 h, and the cyclic carbonate was isolated and purified to give the chemical isolated yield. The corresponding results are listed in Scheme 2. In general, good-to-excellent yields (62-99%) were obtained when non-functionalized and functionalized aliphatic epoxides were used, indicating that the catalyst possessed a broad substrate scope. However, lower conversions were obtained when using alvoidol due to complex (4) is sensitive to hydroxyl group which could affect the catalytic conversion. In addition, the yield of cyclic carbonates decreases with longer alkyl groups of epoxides, indicating that the chain length and steric hindrance from the substituents on the epoxides did affect the catalytic activity. These results agree with the generally proposed mechanism of cyclic carbonate synthesis catalyzed by a Lewis acid and nucleophile combination.<sup>[12]</sup> Anyway, comparing to other aluminum complexes.<sup>[12a-12b, 12g-12h, 13]</sup> this lithium organoaluminate exhibits moderate catalytic activity when using the moderate reactive styrene oxide as a substrate (TON = 19.8, TOF =  $0.83 \text{ h}^{-1}$ ). Unfortunately, this catalyst system did not show high catalytic activity with internal epoxides. In addition, isotopic labeling of <sup>13</sup>CO<sub>2</sub> was also used in the reaction and the corresponding product was obtained (see Figure S6 in the supporting information).

#### Conclusion

In conclusion, a series of lithium organoaluminate complexes containing bidentate pyrrolyl ligands were synthesized and characterized by C, H and N microanalysis, NMR spectroscopy, and single crystal X-ray structural analysis. They proved to be an effective class of catalysts for the generation of cyclic carbonates by the coupling of CO<sub>2</sub> and epoxides under mild temperature and CO<sub>2</sub> pressure. In this catalytic system, various epoxides with CO<sub>2</sub> can be turn into the desired cyclic carbonates in good-to-excellent yields.

#### **Experimental Section**

#### General Information

All syntheses and manipulations of air-sensitive materials were performed under inert atmosphere using standard Schlenk techniques. Et<sub>2</sub>O and THF were distilled from sodium benzophenone, and toluene and hexane were dried by sodium potassium alloy and distilled under inert atmosphere before using. The chemicals were purchased from commercial sources (purity > 97%) and used as received unless otherwise indicated. Carbon dioxide (99.999%) was used as received without further purification. <sup>1</sup>H NMR (600 MHz), <sup>13</sup>C NMR (150.9 MHz) spectra of the compounds were recorded on a BRUKER AVANCE III 600MHz instrument at 298 K. Single X-ray diffraction data of the compounds were collected on a Bruker Smart Apex CCD diffractometer

using monochromated Mo Ka radiation,  $\lambda$  = 0.71073 Å. A total of N reflections was collected by using  $\omega$  scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS). Elemental analyses were performed on a Vario EL-III instrument. High-resolution mass spectrometry (HRMS) were recorded with electrospray ionization (ESI) in positive ion mode on an Thermo Scientific Q Exactive instrument.

#### Synthesis of {C<sub>4</sub>H<sub>3</sub>N(AIMe<sub>3</sub>)[2-CH<sub>2</sub>NH(<sup>t</sup>Bu)Li(TMEDA)]}·C<sub>7</sub>H<sub>8</sub> (1)

A n-BuLi hexane solution (3.0 mmol, 2.2 M in hexane) was added dropwise to a toluene (15 mL) solution of [C<sub>4</sub>H<sub>3</sub>NH(2-CH<sub>2</sub>NH<sup>t</sup>Bu)] (0.457 g, 3.0 mmol) at 0 °C under nitrogen. After the reaction mixture was stirred at room temperature for 3 h, immediately followed by addition of a solution of Al(Me)<sub>3</sub> (3.0 mmol, 2.0 M in toluene). And the mixture was then stirred for another 6 h, and the TMEDA (0.45 mL, 3 mmol) was introduced via syringe, the solution was filtered and concentrated. After two days, the suitable crystals for X-ray diffraction analysis were obtained. Yield: 0.723g, 55%. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>+C<sub>5</sub>D<sub>5</sub>N) δ 7.41 (s, 1H,  $C_4H_3N$  ), 6.32 (s, 1H,  $C_4H_3N$  ), 6.18 (s, 1H,  $C_4H_3N$ ), 4.09 (d, J = 8.1 Hz, 2H, CH<sub>2</sub>NBu<sup>t</sup>), 1.92 (s, 4H, TMEDA), 1.86 (s, 12H, TMEDA), 1.06 (s, 9H,  $CH_2NBu^4$ ), -0.19 (s, 9H, Al( $CH_3$ )<sub>3</sub>); <sup>13</sup>C NMR (151 MHz,  $C_6D_6$ )  $\delta$  136.73 (C<sub>4</sub>H<sub>3</sub>N), 113.45 (C<sub>4</sub>H<sub>3</sub>N), 107.35 (C<sub>4</sub>H<sub>3</sub>N), 104.89(C<sub>4</sub>H<sub>3</sub>N), 57.18 (TMEDA), 50.84 (C(CH<sub>3</sub>)<sub>3</sub>), 45.93 (TMEDA), 41.86 (CH<sub>2</sub>NBu<sup>t</sup>), 29.24 (C(CH<sub>3</sub>)<sub>3</sub>), -4.89 (Al(CH<sub>3</sub>)<sub>3</sub>). Anal. Calcd for C<sub>25</sub>H<sub>48</sub>AlLiN<sub>4</sub>: C, 68.46; H, 11.03; N, 12.77. Found: C, 68.21; H, 10.99; N, 12.72.

#### Synthesis of $\{C_4H_3N(AIMe_2)[2-CH_2N(^tBu)Li(TMEDA)]\}$ (2)

A n-BuLi hexane solution (3.0 mmol, 2.2 M in hexane) was added dropwise to a toluene (15 mL) solution of [C<sub>4</sub>H<sub>3</sub>NH(2-CH<sub>2</sub>NH<sup>t</sup>Bu)] (0.457 g, 3.0 mmol) at 0 °C under nitrogen. After the reaction mixture was stirred at room temperature for 3 h, immediately followed by addition of a solution of Al(Me)<sub>3</sub> (3.0 mmol, 2.0 M in toluene). And the mixture was then stirred for another 3 h at 70 °C, and the TMEDA (0.45 mL, 3 mmol) was introduced via syringe, the solution was filtered and concentrated. After two days, the suitable crystals (2) for X-ray diffraction analysis were obtained. Yield: 0.624g, 63%.  $^{1}$ H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>+C<sub>5</sub>D<sub>5</sub>N)  $\delta$  7.07 (s, 1H,  $C_4H_3N$  ), 6.49 (s, 1H,  $C_4H_3N$ ), 6.15 (s, 1H,  $C_4H_3N$ ), 4.44 (s, 2H, CH<sub>2</sub>NBu<sup>t</sup>), 2.03 (d, J = 19.1 Hz, 4H, TMEDA), 1.90 (d, J = 12 Hz, 12H, TMEDA), 1.54 (s, 9H, CH<sub>2</sub>NB $u^{1}$ ), -0.23 (d, J = 3.8 Hz, 6H, Al(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (151 MHz,  $C_6D_6$ )  $\delta$  142.79 ( $C_4H_3N$ ), 119.64 ( $C_4H_3N$ ), 109.17 (C<sub>4</sub>H<sub>3</sub>N), 99.92 (C<sub>4</sub>H<sub>3</sub>N), 57.56 (TMEDA), 51.67 (C(CH<sub>3</sub>)<sub>3</sub>), 46.14 (TMEDA), 45.81 (CH<sub>2</sub>NBu<sup>t</sup>), 31.14 (C(CH<sub>3</sub>)<sub>3</sub>), -4.90 (Al(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>17</sub>H<sub>36</sub>AlLiN<sub>4</sub>: C, 61.80; H, 10.98; N, 16.96. Found: C, 61.64; H, 10.93; N, 16.88.

#### Synthesis of {C<sub>4</sub>H<sub>3</sub>N(AIEt<sub>3</sub>)[2-CH<sub>2</sub>NH(<sup>t</sup>Bu)Li(TMEDA)]} (3)

Following the same procedure as for (1) but with Al(Et)<sub>3</sub> (3.0 mmol, 2.0 M in toluene), compound (3) was recrystallized as colorless crystals from a saturated diethyl ether and toluene mixed solution. Yield: 0.664g, 57%. <sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-THF): 6.54 (s, 1H, C<sub>4</sub>H<sub>3</sub>N), 5.88(s, 1H, C<sub>4</sub>H<sub>3</sub>N), 5.81 (s, 1H, C<sub>4</sub>H<sub>3</sub>N), 3.67(s, 2H, CH<sub>2</sub>NBu<sup>t</sup>), 2.30 (s, 4H, TMEDA), 2.15 (s, 12H, TMEDA), 1.10 (s, 9H, CH<sub>2</sub>NBu<sup>t</sup>), 0.85 (br, 9H, -CH<sub>2</sub>CH<sub>3</sub>), 0.11 (br, 6H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, d<sub>8</sub>-THF): 129.81 (C<sub>4</sub>H<sub>3</sub>N), 116.01(C<sub>4</sub>H<sub>3</sub>N), 106.78 (C<sub>4</sub>H<sub>3</sub>N), 104.55 (C<sub>4</sub>H<sub>3</sub>N), 57.96 (TMEDA), 51.44 (C(CH<sub>3</sub>)<sub>3</sub>), 45.23 (TMEDA), 39.89 (CH<sub>2</sub>NBu<sup>t</sup>), 28.33 (C(CH<sub>3</sub>)<sub>3</sub>), 18.63(-CH<sub>2</sub>CH<sub>3</sub>), 6.33 (-CH<sub>2</sub>CH<sub>3</sub>); Anal. Calcd for C<sub>21</sub>H<sub>46</sub>AlLiN<sub>4</sub>: C, 64.92; H, 11.93; N, 14.42. Found: C, 64.67; H, 11.87; N, 14.39.

### Synthesis of ${[C_4H_3N(AIEt_3)(2-CH_2NHLi^Bu)][C_4H_3NLi(2-CH_2NH^Bu)]}_2$ (4)

A n-BuLi hexane solution (3.0 mmol, 2.2 M in hexane) was added dropwise to a toluene (15 mL) solution of  $[C_4H_3NH(2-CH_2NH^{1}Bu)]$  (0.457 g, 3.0 mmol) at 0 °C under nitrogen. After the reaction mixture was stirred at room temperature for 3 h, immediately followed by addition of a solution of Al(Et)<sub>3</sub> (1.5 mmol, 2.0 M in hexane). And the mixture was then stirred for another 6 h at room temperature, the white solid was isolated by filtration and recrystallized from a saturated diethyl ether solution as colorless crystals of (**4**). Yield: 0.658g, 51%. <sup>1</sup>H NMR (600 MHz,

 $\begin{array}{l} C_6 D_6 + C_5 D_5 N) : \ 7.44 \ (s, \ 4H, \ C_4 H_3 N), \ 6.85 \ (s, \ 4H, \ C_4 H_3 N), \ 6.69 \ (s, \ 4H, \\ C_4 H_3 N), \ 4.90 \ (d, \ 8H, \ CH_2 N Bu^t), \ 1.22 \ (br, \ 18H, \ -CH_2 CH_3), \ 0.88 \ (s, \ 36H, \\ CH_2 N Bu^t), \ 0.27 \ (s, \ 12H, \ -CH_2 CH_3); \ ^{13} C \ NMR \ (150 \ MHz, \ C_6 D_6) : \ 139.61 \\ (C_4 H_3 N), \ 128.35 \ (C_4 H_3 N), \ 107.35 \ (C_4 H_3 N), \ 106.62 \ (C_4 H_3 N), \ 50.59 \\ (C(CH_3)_3), \ 43.73 \ (CH_2 N Bu^t), \ 30.62 \ (-CH_2 CH_3), \ 28.97 \ (C(CH_3)_3), \ 1.39 \ (-CH_2 CH_3); \ Anal. \ Calcd \ for \ C_{48} H_{90} Al_2 Li_4 N_8 : \ C, \ 66.96; \ H, \ 10.54; \ N, \ 13.01. \\ Found: \ C, \ 66.81; \ H, \ 10.48; \ N, \ 12.95. \end{array}$ 

### General procedure for the synthesis of cyclic carbonates under ambient conditions

A 50 mL sealed tube with a magnetic stirring bar was evacuated and backfilled will  $CO_2$  for three times, lithium organoaluminate (4) (0.0430 g, 0.1 mmol), (*n*–Bu)<sub>4</sub>NI (0.0184 g, 0.05 mmol), epoxide (0.14 mL, 2.0 mmol), and 1.0 mL THF were successively added. The mixture was stirred at 50 °C (heating mantle temperature) for 24 h. It was then cooled down to room temperature. And the reaction was quenched with H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The yields were determined by <sup>1</sup>H NMR spectroscopy with trichloroethylene (90 µL, 1 mmol) as an internal standard. Then, the reaction mixture was purified on silica gel column chromatography (petroleum ether/EtOAc: 2/1-3/1). The product was characterized by NMR spectroscopy.

CCDC 1942510 (for 1), 1942511 (for 2), 1942512 (for 3) and 1942513 (for 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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## Entry for the Table of Contents

**FULL PAPER** 

Key Topic: Lithium organoaluminates



Four new lithium organoaluminate complexes were synthesized and their structural features were provided. In conjunction with tetrabutylammonium iodide, these complexes were proved to be a series of efficient catalysts for chemical fixation of carbon dioxide with epoxides at 50 °C and 1 atm pressure, giving the corresponding cyclic carbonates in yields of 62-99%.

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