



Communication

# Self-Assembled Bimetallic Aluminum-Salen Catalyst for the Cyclic Carbonates Synthesis

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**Abstract:** Bimetallic bis-urea functionalized salen-aluminum catalysts have been developed for cyclic carbonate synthesis from epoxides and CO<sub>2</sub>. The urea moiety provides a bimetallic scaffold through hydrogen bonding, which expedites the cyclic carbonate formation reaction under mild reaction conditions. The turnover frequency (TOF) of the bis-urea salen Al catalyst is three times higher than that of a  $\mu$ -oxo-bridged catalyst, and 13 times higher than that of a monomeric salen aluminum catalyst. The bimetallic reaction pathway is suggested based on urea additive studies and kinetic studies. Additionally, the X-ray crystal structure of a bis-urea salen Ni complex supports the self-assembly of the bis-urea salen metal complex through hydrogen bonding.



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**Keywords:** aluminum; bimetallic catalyst; salen; urea; self-assembled; cyclic carbonate; epoxide; carbon dioxide

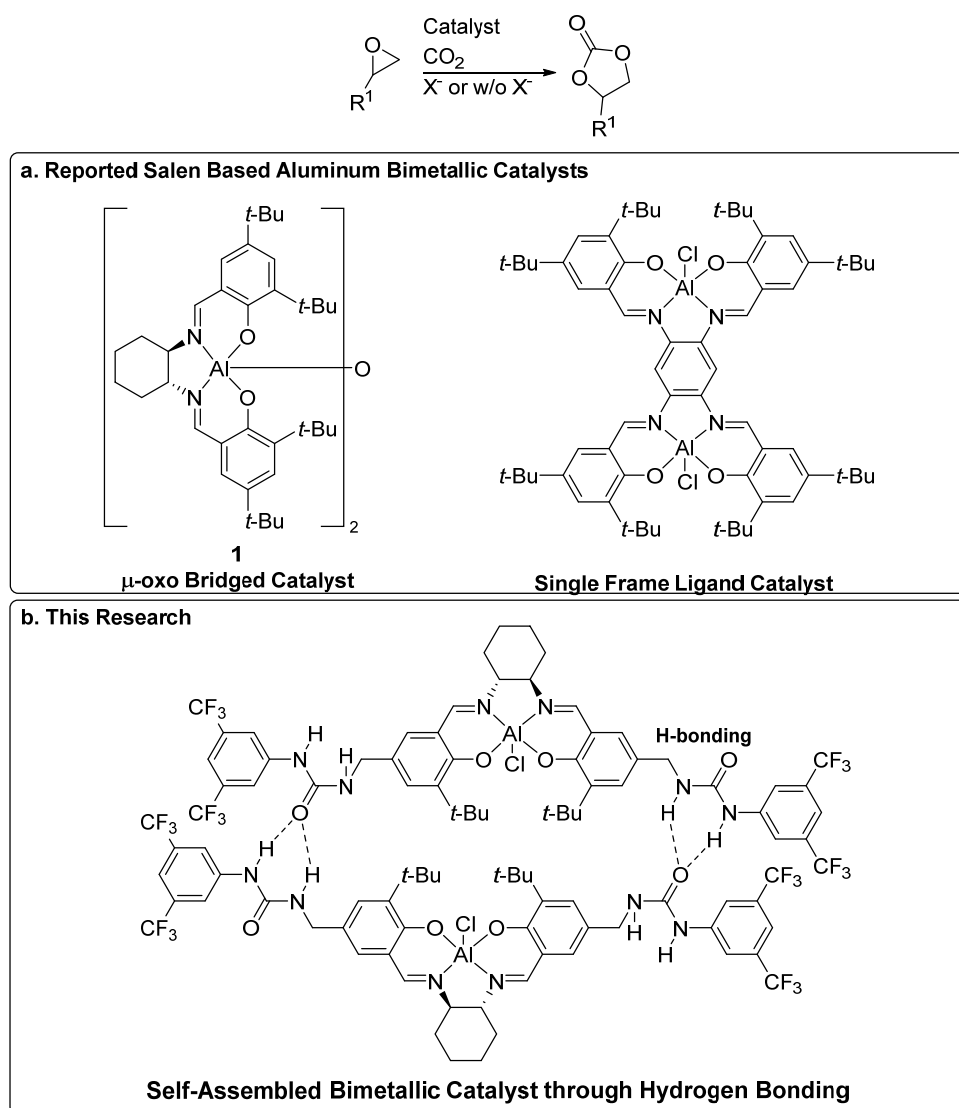
## 1. Introduction

The conversion of carbon dioxide (CO<sub>2</sub>) into value-added chemicals (carbon capture and utilization, CCU) is an area that has been increasingly studied over recent decades [1]. The conversion reaction of CO<sub>2</sub> and epoxides to cyclic organic carbonates has a 100% atom economy, and the cyclic carbonates are important intermediates for polymers [2,3], agrochemicals, pharmaceuticals [4], electrolytes in lithium-ion batteries [5], polar aprotic solvents [6,7], and temporal protecting groups for cis-diols [8]. Owing to the usefulness of cyclic carbonate compounds, various catalysts have been developed for the reaction between CO<sub>2</sub> and epoxides [9–15].

Among the developed systems, bimetallic catalysis enhances catalytic performance in cyclic carbonate synthesis reactions. In pioneering studies, Lau and Tang independently reported single-framed hetero-bimetallic (Mn and Ru) [16] and homo-bimetallic (bi-Co) [17] catalysts for the coupling reaction between CO<sub>2</sub> and epoxides. North group also reported a  $\mu$ -oxo-bridged bimetallic salen aluminum catalyst [18,19]. Since then, various bimetallic catalysts have been developed, including single-framed bimetallic catalysts [16,17,20–22], bridged bimetallic catalysts [18,19,23–26], ligand-separated bimetallic catalysts [27,28], and covalent bond-tethered catalysts [29,30].

In some bimetallic catalytic reactions, two metal centers can cooperatively and simultaneously activate both reaction partners (i.e., epoxide and CO<sub>2</sub>), which leads to second-order reaction kinetics [31]. For example, North group reported bimetallic aluminum catalysts, where the  $\mu$ -oxo-bridged salen aluminum catalyst showed a 10-fold increase in turnover frequency (TOF) compared to a monometallic salen aluminum catalyst (Figure 1a  $\mu$ -oxo-bridged catalyst) [19]. In their proposed mechanistic scenarios,

one aluminum center was coordinated by ammonium-supported CO<sub>2</sub> and the other was coordinated by the epoxide [19,32]. North and co-workers also demonstrated that the  $\mu$ -oxo-bridged salen aluminum catalyst remained active in the absence of an ammonium halide cocatalyst [33]. Later, North group developed the single framed bimetallic salen aluminum catalyst (Figure 1a) [34].



**Figure 1.** Bimetallic catalysts for cyclic carbonates synthesis. (a) Reported bimetallic salen catalysts. (b) This research: self-assembled bimetallic catalysts through hydrogen bonding.

We previously reported self-assembling urea-functionalized salen cobalt catalysts for the hydrokinetic resolution of epoxides [35]. Those catalysts can self-assemble in solution through weak hydrogen bonding interactions [31,35]. Herein, we report that the self-assembling bimetallic strategy can also be applied to the salen-aluminum catalysts for the cyclic carbonate synthesis from CO<sub>2</sub> and epoxides [36–41].

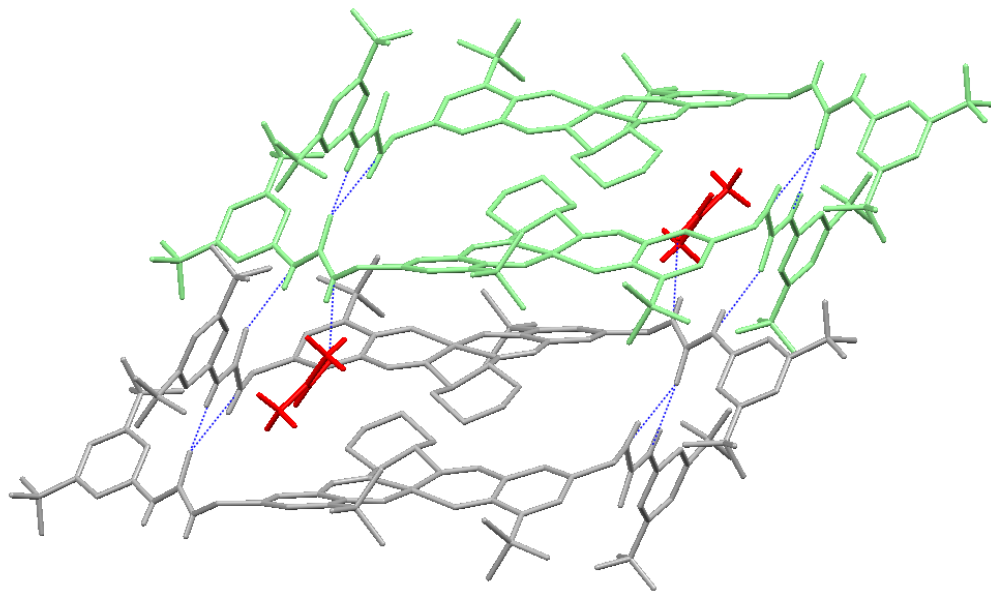
## 2. Results and Discussion

### 2.1. Catalyst Preparation

Bis-urea salen ligands were synthesized in five steps following a reported procedure. The ligands were prepared from commercially available 2-*tert*-butylphenol, and the overall yield was 44%. All intermediate compounds were checked by <sup>1</sup>H NMR [35]. Metalation with aluminum chloride was performed by a previously reported procedure that involved



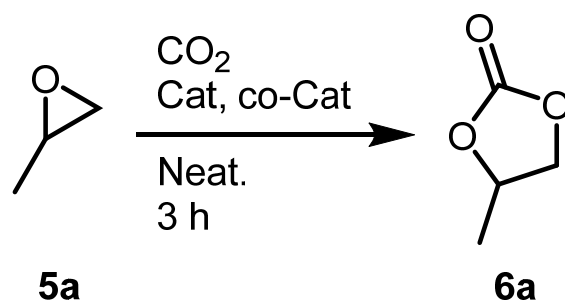
metal–metal distance between neighboring dimers is measured as 4.9 Å (Figure 4). The crystal structure of the bis-urea salen nickel complex supports the bimetallic scaffold of the bis-urea salen aluminum catalyst.



**Figure 4.** Hydrogen-bond packing structure of bis-urea salen nickel complex.

### 2.3. Optimization of Cyclic Carbonates Synthesis Reaction Conditions

The initial test reaction used for this study was the conversion of propylene oxide to propylene carbonate (Figure 5). The initial reaction was conducted in a closed system consisting of a Teflon sealed Schlenk flask at 1 bar of CO<sub>2</sub> and 45 °C. The bis-urea salen aluminum catalyst (**3b**) exhibited a TOF that was 13 times higher than a TOF of a standard salen-aluminum catalyst (**3a**) with tetrabutylammonium bromide ((*n*-Bu)<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>) (Table 1, Entries 1 and 2). Use of tetrabutylammonium iodide ((*n*-Bu)<sub>4</sub>N<sup>+</sup>I<sup>-</sup>) led to slightly higher TOF, compared to the use of TAB under the initial reaction conditions (1 bar of CO<sub>2</sub> and 45 °C) (Table 1, Entries 2 and 3). To increase the TOF, the reaction was conducted in a 10 mL stainless steel bomb reactor. At 10 bar of CO<sub>2</sub> and 90 °C, the bis-urea salen aluminum catalyst showed a higher TOF than previously reported monometallic salen aluminum catalyst (Table 1, Entries 4 and 5) and bridged salen bimetallic aluminum catalyst (Table 1, Entries 5 and 6). It is important to note that the urea moiety catalyst improves the TOF regardless of the conditions of the cyclic carbonate synthesis from CO<sub>2</sub> and epoxide reaction system.



**Figure 5.** Cyclic carbonate synthesis using salen-Al catalysts and tetrabutylammonium halides.

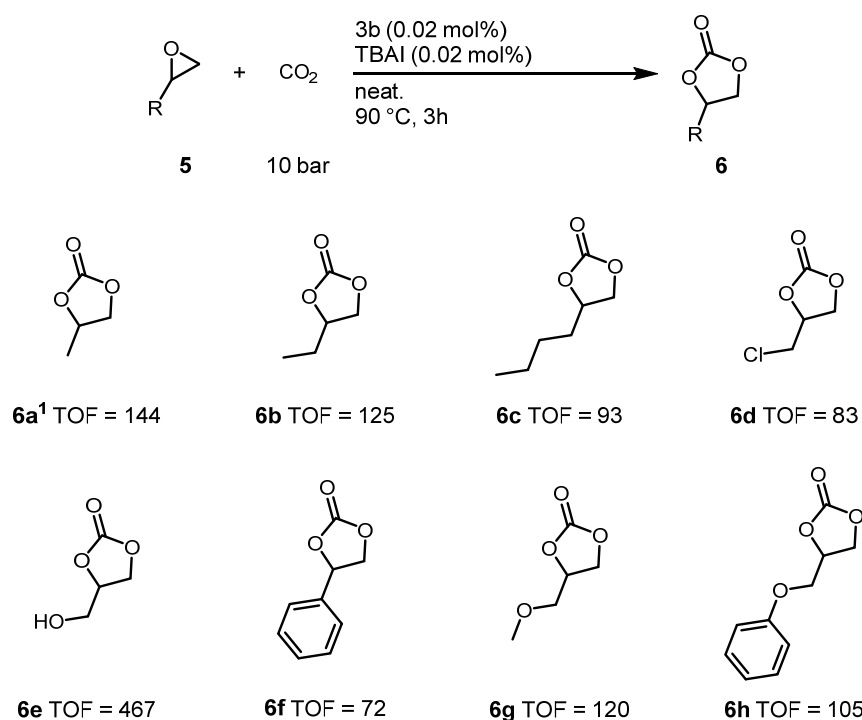
**Table 1.** Cyclic carbonate synthesis using salen-Al catalysts and tetrabutylammonium halides.

Entry	Catalyst (mol%)	Cocatalyst (mol%)	CO <sub>2</sub> (Bar)	T (°C)	TOF (h <sup>-1</sup> ) <sup>1</sup>
1 <sup>2</sup>	<b>3a</b> (1)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> Br <sup>-</sup> (1)	1	45	1
2	<b>3b</b> (0.02)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> Br <sup>-</sup> (0.02)	1	45	13
3	<b>3b</b> (0.02)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> I <sup>-</sup> (0.02)	1	45	17
4	<b>3a</b> (0.02)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> I <sup>-</sup> (0.02)	10	90	65
5	<b>3b</b> (0.02)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> I <sup>-</sup> (0.02)	10	90	144
6	<b>1</b> (0.02)	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> I <sup>-</sup> (0.02)	10	90	47 <sup>3</sup>

<sup>1</sup> Determined by <sup>1</sup>H NMR using mesitylene internal standard <sup>2</sup> 12 h reaction <sup>3</sup> TOF = TON/h·[Al].

#### 2.4. Cyclic Carbonate Synthesis Reactions for Various Epoxides

The epoxide substrate scope was studied for the conversion reactions of various terminal epoxides (**5a–5h**) to cyclic organic carbonates (**6a–6h**). The bis-urea salen aluminum catalyst was most active when alkyl- or hydroxyalkyl-substituted terminal epoxides were used (**5a–5c**, **5e**, and **5g**). The TOF was affected by the steric demands of the epoxides (**5a–5c**). Chloroalkyl-substituted epoxides (**5d**) and styrene oxide (**5f**) showed low TOFs. However, alkoxy-substituted epoxides (**5e**, **5g**, **5h**) showed higher activity than other terminal epoxides, as previously reported [27]. Use of low amounts of catalyst **3b** (0.02 mol%) and cocatalyst ((*n*-Bu)<sub>4</sub>N<sup>+</sup>I<sup>-</sup>, 0.02 mol%) were allowed under comparatively mild conditions (90 °C, pCO<sub>2</sub> = 10 bar) for various epoxide substrates (Figure 6).



**Figure 6.** Scopes of epoxides. Reaction conditions: Epoxide (47 mmol), CO<sub>2</sub> (10 bar), Catalyst (10 mg, 0.0094 mmol), (*n*-Bu)<sub>4</sub>N<sup>+</sup>I<sup>-</sup> (3.5 mg, 0.0094 mmol), reaction was carried out in a 10 mL sealed stainless steel pressure bomb reactor. All TOFs are determined by <sup>1</sup>H NMR using mesitylene internal standard (1.0 mmol, 0.1 mL). <sup>1</sup> 3.5 h reaction.

#### 2.5. Origin of Beneficial Urea Effects

In the monomeric salen aluminum catalyst system, 0.08 mol% (4 equivalent with respect to the catalyst) of urea additive was added and tested under the optimized conditions; notably, the TOF did not increase. The free urea in the reaction system did not appear to affect the reaction (Figure 7) (Table 2, Entries 1 and 2).

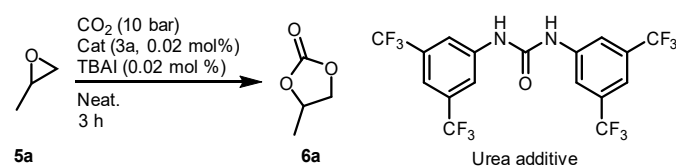


Figure 7. Urea additive study.

Table 2. Urea additive study.

Entry	Urea Additive (mol%)	TOF ( $\text{h}^{-1}$ )
1	-	64
2	0.08 mol%	65

We speculated that the TOF enhancement could occur owing to the bimetallic character enabled by the hydrogen bonding between urea groups of the ligand. Thus, we plotted a reaction rate vs. the changes in the amount of catalyst **3b**. The graph showed a clear second-order functional graph ( $R^2 = 0.9977$ ), suggesting a bimetallic reaction pathway (Figure 8) [35].

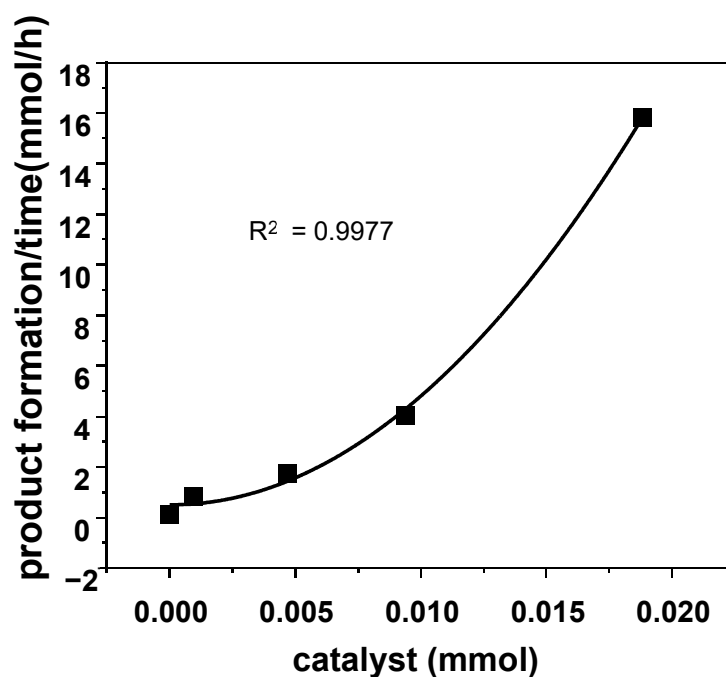
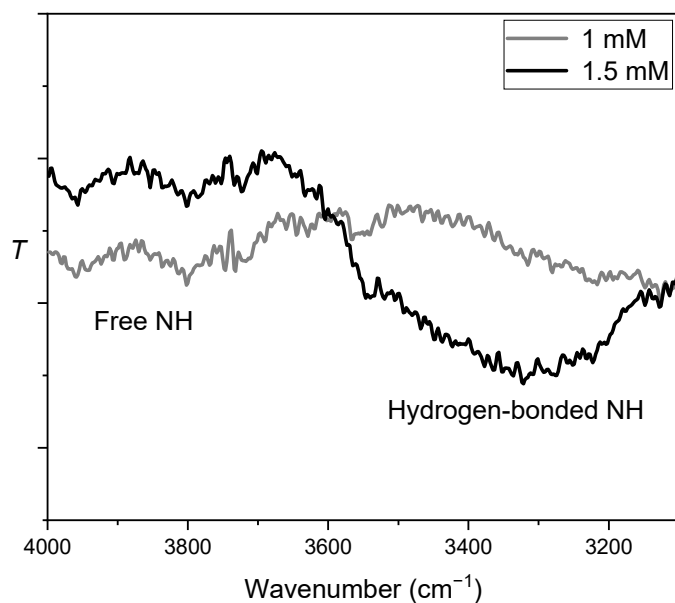


Figure 8. Kinetic analysis of the reaction order (Second order,  $R^2 = 0.9977$ ). Reaction conditions: Epoxide (47 mmol),  $\text{CO}_2$  (10 bar),  $(n\text{-Bu})_4\text{N}^+\text{I}^-$  (3.5 mg, 0.0094 mmol),  $90^\circ\text{C}$ , 3 h, reaction was carried out in a 10 mL sealed stainless steel pressure bomb reactor. All TOFs are determined by  $^1\text{H}$  NMR using mesitylene internal standard (1.0 mmol, 0.1 mL).

FTIR spectroscopy study was conducted to obtain more direct experimental evidence for self-association through urea-urea hydrogen bonding in solution. Bis-urea salen Al catalyst (**3b**) in THF was measured by FTIR at  $25^\circ\text{C}$ . The FTIR experiments revealed the intensity of hydrogen bonded NH stretching vibration ( $\tilde{\nu} = 3444\text{ cm}^{-1}$ ) increased with increasing concentration, and the intensity of free NH stretching vibration ( $\tilde{\nu} = 3966\text{ cm}^{-1}$  and  $3808\text{ cm}^{-1}$ ) decreased with increasing concentration. The results of FTIR experiments suggest intermolecular hydrogen bonding between bis-urea salen Al complexes in THF solution (Figure 9 See Supplementary Materials for more details) [35].



**Figure 9.** The NH stretching region of the FTIR spectra of **3b** in THF at two different concentration (1 mM (grey), 1.5 mM (black)) at 25 °C.

### 3. Conclusions

In conclusion, the self-assembly strategy was successfully applied to the functionalized salen-aluminum catalysts for cyclic carbonate synthesis reaction from CO<sub>2</sub> and epoxide. The bis-urea functionalized salen ligands were designed to self-assemble through urea-urea hydrogen bonding. The bimetallic urea salen aluminum complex showed an improved reaction rate (up to 13 times at 1 bar of CO<sub>2</sub>, 45 °C and up to 2.2 times at 10 bar of CO<sub>2</sub>, 90 °C) in the cyclic carbonate formation from epoxides with CO<sub>2</sub>. Free urea additive studies and kinetic studies were performed to confirm bimetallic reaction pathway. FTIR spectroscopy study provided an experimental evidence for urea-urea hydrogen bonding in solution. This work demonstrates that hydrogen bonding can be applied to the catalysts for cyclic carbonate synthesis reaction. It is important to note that the urea moiety improves the TOF regardless of the reaction conditions. Modifications of the ligand structures to further improve the catalyst are currently in progress.

**Supplementary Materials:** The following are available online: 1. Materials and instrumentation; 2. Catalyst preparation; 3. Cyclic carbonates synthesis; 4. X-ray experiment; 5. Crystal structure of bis-urea salen Ni complex (**4**, Park4); Table S1. Crystal data and structure refinement for park4; Table S2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for park4.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor; Table S3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for park4; Table S4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for park4. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$ ; Table S5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for park4; Table S6. Hydrogen bonds for park4 [ $\text{\AA}$  and  $^\circ$ ]; 6. Mass spectrum of a bis-urea salen aluminum catalyst (**3b**); 7. FTIR spectrum of bis-urea salen aluminum catalyst (**3b**).

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## References

1. Baena-Moreno, F.M.; Rodríguez-Galán, M.; Vega, F.; Alonso-Fariñas, B.; Arenas, L.F.V.; Navarrete, B. Carbon capture and utilization technologies: A literature review and recent advances. *Energy Sources Part A Recovery Util. Environ. Eff.* **2019**, *41*, 1403–1433. [[CrossRef](#)]
2. Clements, J.H. Reactive Applications of Cyclic Alkylene Carbonates. *Ind. Eng. Chem. Res.* **2003**, *42*, 663–674. [[CrossRef](#)]
3. Paul, S.; Romain, C.; Shaw, J.; Williams, C.K. Sequence Selective Polymerization Catalysis: A New Route to ABA Block Copoly(ester-b-carbonate-b-ester). *Macromolecules* **2015**, *48*, 6047–6056. [[CrossRef](#)]
4. Zhang, H.; Liu, H.-B.; Yue, J.-M. Organic Carbonates from Natural Sources. *Chem. Rev.* **2014**, *114*, 883–898. [[CrossRef](#)] [[PubMed](#)]
5. Yun, J.; Zhang, L.; Qu, Q.; Liu, H.; Zhang, X.; Shen, M.; Zheng, H. A Binary Cyclic Carbonates-Based Electrolyte Containing Propylene Carbonate and Trifluoropropylene Carbonate for 5V Lithium-Ion batteries. *Electrochim. Acta* **2015**, *167*, 151–159. [[CrossRef](#)]
6. Lopes, E.J.C.; Ribeiro, A.P.C.; Martins, L.M.D.R.S. New Trends in the Conversion of CO<sub>2</sub> to Cyclic Carbonates. *Catalyst* **2020**, *10*, 479. [[CrossRef](#)]
7. Beattie, C.; North, M.; Villuendas, P. Proline-Catalysed Amination Reactions in Cyclic Carbonate Solvents. *Molecules* **2011**, *16*, 3420–3432. [[CrossRef](#)]
8. Laserna, V.; Fiorani, G.; Whiteoak, C.J.; Martin, E.; Escudero-Adán, E.; Kleij, A.W. Carbon dioxide as a Protecting Group: Highly Efficient and Selective Catalytic Access to Cyclic *cis*-Diol Scaffolds. *Angew. Chem. Int. Ed.* **2014**, *53*, 10416–10419. [[CrossRef](#)]
9. Rehman, A.; Saleem, F.; Javed, F.; Ikhlaq, A.; Ahmad, S.W.; Harvey, A. Recent advances in the synthesis of cyclic carbonates via CO<sub>2</sub> cycloaddition to epoxides. *J. Environ. Chem. Eng.* **2021**, *9*, 105113–105130. [[CrossRef](#)]
10. North, M.; Pasquale, R.; Young, C. Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. *Green Chem.* **2010**, *12*, 1514–1539. [[CrossRef](#)]
11. Decortes, A.; Castilla, A.M.; Kleij, A.W. Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO<sub>2</sub> to Epoxides. *Angew. Chem. Int. Ed.* **2010**, *49*, 9822–9837. [[CrossRef](#)] [[PubMed](#)]
12. Rintjema, J.; Epping, R.; Fiorani, G.; Martin, E.; Escudero-Adán, E.; Kleij, A.W. Substrate-Controlled Product Divergence: Conversion of CO<sub>2</sub> into Heterocyclic Products. *Angew. Chem. Int. Ed.* **2016**, *55*, 3972–3976. [[CrossRef](#)] [[PubMed](#)]
13. Kim, Y.; Hyun, K.; Ahn, D.; Kim, R.; Park, M.; Kim, Y. Efficient Aluminum Catalysts for the Chemical Conversion of CO<sub>2</sub> into Cyclic Carbonates at Room Temperature and Atmospheric CO<sub>2</sub> Pressure. *ChemSusChem* **2019**, *12*, 4211–4220. [[CrossRef](#)]
14. Noh, J.; Kim, Y.; Park, H.; Lee, J.; Yoon, M.; Park, M.; Kim, Y.; Kim, M. Functional group effects on a metal-organic framework catalyst for CO<sub>2</sub> cycloaddition. *J. Ind. Eng. Chem.* **2018**, *64*, 478–483. [[CrossRef](#)]
15. Hong, M.; Kim, Y.; Kim, H.; Cho, H.; Baik, M.; Kim, Y. Scorpionate Catalysts for Coupling CO<sub>2</sub> and Epoxides to Cyclic Carbonates: A Rational Design Approach for Organocatalysts. *J. Org. Chem.* **2018**, *83*, 9370–9380. [[CrossRef](#)] [[PubMed](#)]
16. Man, M.L.; Lam, K.C.; Sit, W.N.; Ng, S.M.; Zhou, Z.; Lin, Z.; Lau, C.P. Synthesis of Heterobimetallic Ru-Mn Complexes and the Coupling Reactions of Epoxides with Carbon Dioxide Catalyzed by these Complexes. *Chem. Eur. J.* **2006**, *12*, 1004–1015. [[CrossRef](#)]
17. Wang, J.; Wu, J.; Tang, N. Synthesis, characterization of a new bicobalt complex [Co<sub>2</sub>L<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)<sub>2</sub>Cl<sub>2</sub>] and application in cyclic carbonate synthesis. *Inorg. Chem. Commun.* **2007**, *10*, 1493–1495. [[CrossRef](#)]
18. Meléndez, 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. Clegg, W.; Harrington, R.W.; Pasquale, R.; North, M. Cyclic carbonate synthesis catalysed by bimetallic aluminium-salen complexes. *Chem. Eur. J.* **2010**, *16*, 6828–6843. [[CrossRef](#)]
20. 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](#)]
21. Cozzolino, M.; Press, K.; Mazzeo, M.; Lamberti, M. Carbon dioxide/epoxide reaction catalyzed by bimetallic salalen aluminum complexes. *ChemCatChem* **2016**, *8*, 455–460. [[CrossRef](#)]
22. Cozzolino, M.; Melchionno, F.; Santulli, F.; Mazzeo, M.; Lamberti, M. Aldimine-thioether-phenolate based mono- and bimetallic zinc complexes as catalysts for the reaction of CO<sub>2</sub> with cyclohexene oxide. *Eur. J. Inorg. Chem.* **2020**, *2020*, 1645–1653. [[CrossRef](#)]
23. Whiteoak, C.J.; Martin, E.; Escudero-Adán, E.; Kleij, A.W. Stereochemical Divergence in the Formation of Organic Carbonates Derived from Internal Epoxides. *Adv. Synth. Catal.* **2013**, *355*, 2233–2239. [[CrossRef](#)]
24. Buonerba, A.; Nisi, A.D.; Grassi, A.; Milione, S.; Vagin, S.; Rieger, B.; Capacchione, C. 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](#)]
25. 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](#)]



26. Montoya, C.A.; Gómez, C.F.; Paninho, A.B.; Najdanovic-Visak, V.; Martins, L.M.D.R.S.; da Silva, M.F.C.G.; Pombeiro, A.J.L.; Ponte, M.N.; Nunes, A.V.M.; Mahmudov, K.T. Cyclic carbonate synthesis from CO<sub>2</sub> and epoxides using zinc(II) complexes of arylhydrazones of β-diketones. *J. Catal.* **2016**, *335*, 135–140. [[CrossRef](#)]
27. Whiteoak, C.J.; Martin, E.; Belmonte, M.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](#)]
28. Arunachalam, R.; Chinnaraja, E.; Subramanian, S.; Suresh, E.; Subramanian, P.S. Catalytic Conversion of Carbon Dioxide Using Binuclear Double-Stranded Helicates: Cyclic Carbonate from Epoxides and Diol. *ACS Omega* **2020**, *5*, 14890–14899. [[CrossRef](#)]
29. Maeda, C.; Taniguchi, T.; Ogawa, K.; Ema, T. Bifunctional Catalysts Based on *m*-Phenylene-Bridged Porphyrin Dimer and Trimer Platforms: Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides. *Angew. Chem. Int. Ed.* **2015**, *54*, 134–138. [[CrossRef](#)]
30. He, S.; Wang, F.; Tong, W.-L.; Yiu, S.-M.; Chan, M.C.W. Topologically diverse shape-persistent bis-(Zn-salphen) catalysts: Efficient cyclic carbonate formation under mild conditions. *Chem. Commun.* **2016**, *52*, 1017–1020. [[CrossRef](#)]
31. Park, J.; Hong, S. Cooperative bimetallic catalysis in asymmetric transformations. *Chem. Soc. Rev.* **2012**, *41*, 6931–6943. [[CrossRef](#)]
32. Beattie, C.; Villuendas, P.; Young, C.; North, M. Influence of Temperature and Pressure on Cyclic Carbonate Synthesis Catalyzed by Bimetallic Aluminum Complexes and Application to Overall *syn*-Bis-hydroxylation of Alkenes. *J. Org. Chem.* **2013**, *78*, 419–426. [[CrossRef](#)]
33. Castro-Osma, J.A.; Leitner, W.; Muller, T.E.; North, M.; Offermans, W.K. Unprecedented Carbonato Intermediates in Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium(Salen) Complexes. *ChemSusChem* **2016**, *9*, 791–794. [[CrossRef](#)]
34. 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](#)]
35. Park, J.; Lang, K.; Abboud, K.A.; Hong, S. Self-Assembly Approach toward Chiral Bimetallic Catalysts: Bis-Urea-Functionalized (Salen)Cobalt Complexes for the Hydrolytic Kinetic Resolution of Epoxides. *Chem. Eur. J.* **2011**, *17*, 2236–2245. [[CrossRef](#)] [[PubMed](#)]
36. Broghammer, F.; Brodbeck, D.; Junge, T.; Peters, R. Cooperative Lewis acid–onium salt catalysis as tool for the desymmetrization of *meso*-epoxides. *Chem. Commun.* **2017**, *53*, 1156–1159. [[CrossRef](#)] [[PubMed](#)]
37. Deacy, A.C.; Moreby, E.; Phanopoulos, A.; Williams, C.K. Co(III)/Alkali-Metal(I) Heterodinuclear Catalysts for the Ring-Opening Copolymerization of CO<sub>2</sub> and Propylene Oxide. *J. Am. Chem. Soc.* **2020**, *142*, 19150–19160. [[CrossRef](#)] [[PubMed](#)]
38. Deacy, A.C.; Durr, C.B.; Kerr, R.W.F.; Williams, C.K. Heterodinuclear catalysts Zn(II)/M and Mg(II)/M, where M = Na(I), Ca(II) or Cd(II), for phthalic anhydride/cyclohexene oxide ring opening copolymerisation. *Catal. Sci. Technol.* **2021**, *11*, 3109–3118. [[CrossRef](#)]
39. Noh, E.; Na, S.; Sujith, S.; Kim, S.-W.; Lee, B. Two Components in a Molecule: Highly Efficient and Thermally Robust Catalytic System for CO<sub>2</sub>/Epoxide Copolymerization. *J. Am. Chem. Soc.* **2007**, *129*, 8082–8083. [[CrossRef](#)]
40. Lidston, C.A.L.; Abel, B.A.; Coates, G.W. Bifunctional Catalysis Prevents Inhibition in Reversible-Deactivation Ring-Opening Copolymerizations of Epoxides and Cyclic Anhydrides. *J. Am. Chem. Soc.* **2020**, *142*, 20161–20169. [[CrossRef](#)]
41. Hubbell, A.K.; Coates, G.W. Nucleophilic Transformations of Lewis Acid-Activated Disubstituted Epoxides with Catalyst-Controlled Regioselectivity. *J. Org. Chem.* **2020**, *85*, 13391–13414. [[CrossRef](#)] [[PubMed](#)]
42. Quek, S.C.Z.; Pridmore, N.E.; Whitwood, A.C.; Wu, X.; North, M. Aluminum(salen) Complexes as Catalysts for the Kinetic Resolution of Terminal Epoxides via CO<sub>2</sub> Coupling. *ACS Catal.* **2015**, *5*, 3398–3402.