



Cite this: *New J. Chem.*, 2021, 45, 13096

Received 19th May 2021,
Accepted 14th June 2021

DOI: 10.1039/d1nj02460d

rsc.li/njc

Cycloaddition of carbon dioxide and epoxides catalyzed by rare earth metal complexes bearing a Trost ligand†

Jun Cheng, Chengrong Lu* and Bei Zhao  *

A series of rare earth metal complexes (Sm (**1**), Eu (**2**), Y (**3**), Yb (**4**), and Lu (**5**)) based on Trost ligands were synthesized and well characterized, and catalyzed the cycloaddition of carbon dioxide and epoxides successfully. The combination of 1 mol% Sm-based complex **1** with 2 mol% tetrabutylammonium bromide (TBAB) was proved to be the optimal catalyst system for the formation of the monosubstituted cyclic carbonate at 70 °C under the atmospheric pressure. While for the more challenging disubstituted epoxides, the adduct cyclic carbonates were successfully obtained when the pressure of CO₂ was elevated to 0.7 MPa.

Introduction

In recent years, global warming has caused more and more serious environmental disasters, such as an abnormal climate, melting of glaciers and rising sea levels. The latest research shows that human activities have pushed today's CO₂ content in the atmosphere to the highest level during the past 23 million years, which has exceeded the absorption and conversion capacity of nature. Carbon capture, storage and utilization are the main strategies to achieve a carbon neutral status. The utilization of CO₂, a kind of abundant, non-toxic and renewable C1 resource, is of great significance in green and sustainable development. The chemical conversion of CO₂ has potential economic benefits, since many high value-added products are obtained from CO₂.^{1–3} The cycloaddition reaction of CO₂ with epoxides, a commonly used reaction for the chemical conversion of CO₂, has aroused great interest because of its 100% atom efficiency and the biocompatible and biodegradable products—carbonates.⁴ A number of catalysts have been developed for the cycloaddition reactions, including main-group metal complexes (e.g., Mg,⁵ Al,⁶ Ca,⁷ and Li⁸), transition-metal complexes (e.g. Cr,⁹ Co,¹⁰ Zn,¹¹ and Fe¹²) and organocatalysts.¹³ For example, Kim and coworkers employed dimeric aluminum

compounds to catalyze the cycloaddition of mono- and disubstituted epoxides and CO₂ at atmospheric CO₂ pressure, and room temperature to 75 °C.^{6f} Capacchione *et al.* used [OSSO]-type iron(III) complexes as catalysts, tetrabutylammonium bromide (TBAB) as a co-catalyst, and variously substituted epoxides were selectively converted into the corresponding cyclic carbonates at 35 °C under 0.1 MPa CO₂.^{12e} Dai *et al.* reported the conversion of CO₂ to cyclic carbonates under ambient conditions (room temperature, 0.1 MPa CO₂) with highly reactive one-component organocatalysts – a series of pincer-type compounds possessing an N-heterocyclic carbene precursor.^{13e} However, among the published studies, some harsh reaction conditions were required, such as a relatively high catalyst loading (>5 mol%),^{13a,c} a relatively higher temperature (>100 °C),^{5a,13g} and a high pressure (>1 MPa).^{5a,b,6a,b,d,12c,d,13b}

Rare earth metals have unique electronic structures, a strong oxygen affinity, and high Lewis acidity. Several rare earth metal complexes containing nitrogen or oxygen proligands were synthesized, which showed high reactivities in the cycloaddition reaction of CO₂ and epoxide.¹⁴ Yao and coworkers developed the first rare earth metal complex bearing a poly(phenolato) ligand to catalyze the cycloaddition reaction of monosubstituted epoxides under mild conditions (85 °C and 0.1 MPa CO₂) in the presence of tetrabutylammonium iodide (TBAI). Meanwhile, under 1 MPa CO₂, the same catalyst system is good for disubstituted epoxides.^{14a} Furthermore, the polyphenol proligands were modified by changing one of the substituents on the nitrogen from phenol to a smaller noncoordinating methyl group, and the desired rare earth metal complexes were synthesized to show excellent catalytic activity in the cycloaddition reaction of carbon dioxide with epoxides under ambient conditions, especially in the conversion of disubstituted epoxides

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China.
E-mail: zhaobei@suda.edu.cn

† Electronic supplementary information (ESI) available: Solid state structures, NMR spectra, and crystallographic data. CCDC 2075317 (complex **1**), 2075330 (complex **2**), 2074336 (complex **3**), 2075334 (complex **4**) and 2075318 (complex **5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1nj02460d

(room temperature, 0.1 MPa CO₂).^{14f} Around the same time, Otero's group developed a novel lanthanum heteroscorpionate catalyst, which showed exceptional catalytic activity for the synthesis of cyclic carbonates with a low catalyst loading (0.05–0.5 mol%).^{14c}

Different ligands lead to different chemical behaviors of the corresponding metal complexes, so one of the strategies for adjusting the effects of the metal-based catalysts is to change the ligands. In view of the excellent catalytic activity of rare earth metal complexes, a new type of rare earth metal dichloride supported by a Trost proligand – an easier to obtain [ONONO] proligand – was prepared and characterized, and further investigations of the catalytic reactivities in the cycloaddition reaction of CO₂ and epoxides were conducted.

Results and discussion

Synthesis of complexes 1–5

According to previous work, a Trost proligand with a semicrown structure was prepared using the commercially available prolinol.¹⁵ Metathesis reaction of the Trost proligand with rare earth metal precursors RE[N(SiMe₃)₂]Cl₂ proceeded readily in THF at room temperature and gave the corresponding rare earth metal dichlorides 1–5 in high yields of 65–90% (Scheme 1). The solid-state structures of complexes 1–5 were characterized by X-ray diffraction analysis, and were determined to be monomeric and isomorphic. Taking complex 1 as an example (Fig. 1), the central metal samarium is six-coordinated with two chlorine atoms and four oxygen atoms, which come from the Trost ligand and a coordinated THF molecule. The samarium atom is bonded in three ways, namely, a metal-aryloxy σ bond, a metal-alkoxy coordinate bond and a metal-chlorine σ bond. The average bond length of phenolato-Sm bonds is 2.232(12) Å, similar to the data reported in the complex [SmL₂]{[(THF)₃Li]₂(μ -Cl)} (H₂L = (S)-2,4-di-*tert*-butyl-6-[[2-(hydroxydiphenylmethyl)pyrrolidinyl]methyl]pheno) (2.239(5), 2.231(4) Å).^{16a} Considering the difference between the radius of the Sm(III) ion and the Yb(III) ion, the bond lengths of Sm-alkoxy coordinate bonds of 2.171(19) Å and 2.198(17) Å are comparable to the same kind of Yb–O bond length (2.067(5) Å) of the complex [LYb(LH)].^{16b} The average bond length of Sm–Cl bonds in complex 1 (2.738 Å) is longer than that of SmCl₃(THF)₄ (2.683 Å). On account of the observation of a peak at 3377 cm^{−1}, which is ascribed to the stretching vibration of the hydroxyl O–H bond (Fig. 2), and the acidity differences between the alcoholic hydroxyl and phenolic

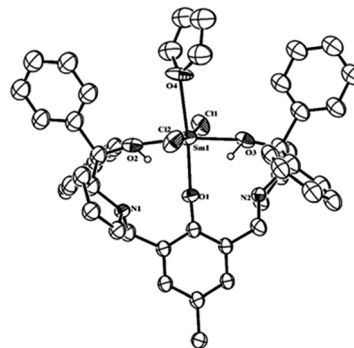


Fig. 1 Solid-state structure of complex 1 showing 30% probability thermal ellipsoids; for clarity, all other hydrogen atoms and solvent molecules are omitted except for alcoholic hydroxyl hydrogen. Selected bond lengths [Å] and bond angles [deg]: Sm1–O1 2.232(12), Sm1–O2 2.171(19), Sm1–O3 2.198(17), Sm1–O4 2.466(12), Sm1–Cl1 2.737(6), and Sm1–Cl2 2.739(7); O1–Sm1–O2 84.4(6), O1–Sm1–O3 86.0(6), O1–Sm1–O4 175.4(6), O2–Sm1–O3 170.4(5), O1–Sm1–Cl1 93.2(4), O1–Sm1–Cl2 94.7(4), O4–Sm1–Cl1 87.7(4), and O4–Sm1–Cl2 84.4(4).

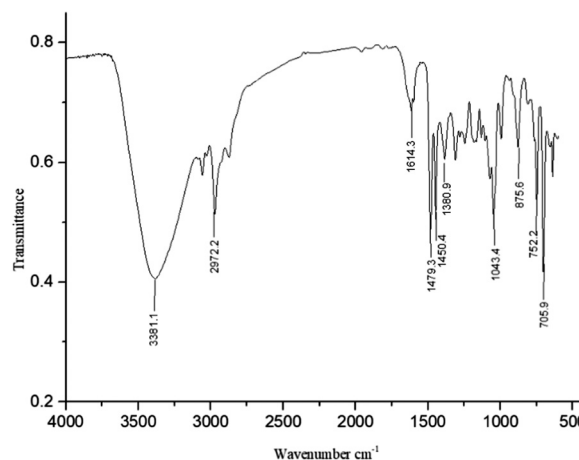


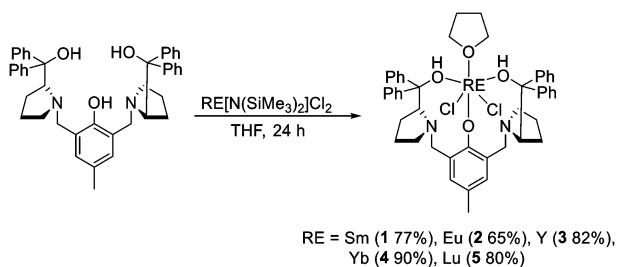
Fig. 2 IR spectrum of complex 1.

hydroxyl groups, the retaining of alcoholic hydroxyl hydrogen atoms in complex 1 was confirmed.

Catalytic reactivities

With the rare earth metal complexes 1–5 in hand, the cycloaddition of CO₂ and epoxides was investigated. Using epichlorohydrin **6a** as the template substrate, the addition reaction with CO₂ was conducted neat under atmospheric pressure in the presence of 1 mol% of the catalyst and 2 mol% of the co-catalyst. The results are listed in Table 1.

All the complexes catalyzed the cyclic addition of CO₂ to epichlorohydrin at room temperature, when tetrabutylammonium bromide (TBAB) acted as the co-catalyst. The decreasing order of reactivity of complexes 1–5 complied with the decreasing ionic radius (Sm(III) > Eu(III) > Y(III) > Yb(III) > Lu(III)), and complex 1 showed the highest reactivity (Table 1, entries 1–5). This is



Scheme 1 Synthesis of rare earth metal complexes 1–5.

Table 1 Screening of the catalytic conditions of the cycloaddition of CO₂ with epichlorohydrin **6a**^a

Entry	Cat.	Co-cat.	T/°C	Conv. ^{bc} /%
1	1	TBAB	25	65
2	2	TBAB	25	42
3	3	TBAB	25	36
4	4	TBAB	25	34
5	5	TBAB	25	30
6	—	TBAB	25	16
7	1	TBAI	25	60
8	1	TBAC	25	45
9	1	PPNCl	25	49
10	1	DMAP	25	60
11	1	TBAB	50	75
12	1	TBAB	60	92
13	1	TBAB	70	> 99
14 ^d	1	TBAB	70	95
15	—	TBAB	70	62

^a Reaction conditions: 1 mol% catalyst and 2 mol% co-catalyst, for 24 h.^b Determined by ¹H NMR spectroscopy. ^c Selectivities for the cyclic carbonate products are all > 99%. ^d 18 h.

consistent with the previously reported pattern, that is, rare earth metal complexes of larger ionic radii showed higher reactivities, attributed to the larger open coordination sphere suitable for substrate binding.^{8a,b,d} Different co-catalysts, tetrabutylammonium chloride (TBAC), bis(triphenylphosphine)iminium chloride (PPNCl), and 4-dimethylaminopyridine (DMAP) were also tested, and TBAB was proved to be the best performer (Table 1, entries 7–10). The decreasing reactivities, Br[−] > I[−] > Cl[−], were observed, presumably because of the balanced nucleophilicity and leaving ability of the bromide anion. The reaction time and temperature were screened subsequently (Table 1, entries 11–14). When the reaction temperature was raised to 70 °C, quantitative conversion of epichlorohydrin was achieved after 24 h (Table 1, entry 13). The yield of carbonate **7a** was slightly decreased to 95% if the reaction time was shortened to 18 h (Table 1, entry 14). Meanwhile, TBAB itself was found to have a catalytic effect on the reaction without complex **1**. The conversion of epichlorohydrin was 16% at room temperature and 62% at 70 °C (Table 1, entries 6 and 15). However, it is undeniable that the improvement was significant when the combination catalysis of complex **1** and TBAB was tested (Table 1, entries 1 vs. 6, and entries 13 vs. 15). Thus, the optimal conditions were confirmed as follows: 1 mol% catalyst **1**, 2 mol% co-catalyst TBAB, 70 °C, 24 h, and 0.1 MPa CO₂.

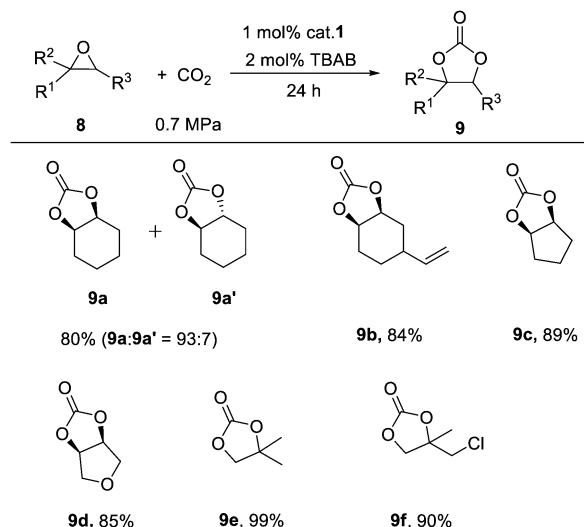
To study the scope of the cycloaddition, a series of mono-substituted terminal epoxides were examined, and the results are summarized in Table 2. In addition to the template substrate epichlorohydrin **6a**, simple monosubstituted epoxy compounds such as epibromohydrin, propylene oxide and 1,2-epoxyhexane (**6b–6e**) achieved quantitative conversion under the optimal conditions. When the alkyl group of the epoxide contains a double bond (**6f**), the cycloaddition reaction is also carried out smoothly, and the yield of cyclocarbonate **7f** is as high as 99%.

Table 2 Cycloaddition of monosubstituted terminal epoxides and CO₂ catalyzed by complex **1** and TBAB^{abc}

7a , 99%	7b , 99%	7c , 99%
7d , 99%	7e , 99%	7f , 99%
7g , 88%; 20% ^d	7h , 98%	7i , 95%
7j , 96%	7k , 99%	7l , 98%
7m , 82%	7n , 67%	7o , 89%
7p , 42%	7q , 65%; 93% ^e	7r , 75%; trace ^d

^a Reaction conditions: 0.02 mmol complex **1**, 0.04 mmol TBAB, 70 °C, 24 h, 0.1 MPa CO₂ pressure, neat. ^b Isolated yield. ^c Selectivities for the cyclic carbonate products are all > 99%. ^d Without complex **1**, determined by ¹H NMR spectroscopy. ^e 40 h.

For epoxides with different alkyloxy substituents, the corresponding cyclic carbonates **7h–7k** were produced in excellent yields, too, even including the ether subunit containing a double or triple bond (**7l** and **7m**). The epoxide containing the morpholine ring yielded 89% of the cycloaddition product **7o**; meanwhile, the morpholine ring is maintained. Unfortunately, for sterically hindered substrates, such as glycidyl 4-*tert*-butylbenzoate, the yield of the corresponding cyclic ester **7p** is only 42%. When a binary monosubstituted epoxy subunit in one molecule, such as 1,2,7,8-diepoxyoctane (**6q**), was tested, the cycloaddition occurred at both sides in 65% yield. Furthermore, when the reaction time was prolonged to 40 h, the yield was increased to 93%. It is of note that substrate **6r**, a compound with a monosubstituted epoxy group together with a 1,2-disubstituted epoxy group, undergoes cycloaddition with CO₂ only at the monosubstituted side under the current conditions. This indicates that the cycloaddition of the disubstituted epoxide is more challenging. In order to test again the necessity of complex **1**, the cycloaddition of CO₂ with **6g** or **6r** using TBAB as the catalyst was carried out, respectively.

Table 3 Cycloaddition of disubstituted epoxides with CO₂ catalyzed by complex **1** and TBAB^{ab}

^a Reaction conditions: 0.06 mmol complex **1**, 0.12 mmol TBAB, 70 °C, 24 h, 0.7 MPa CO₂, neat. ^b Isolated yield.

As expected, the outcomes were very poor, at 20% for **7g** and a trace amount for **7r**.

Subsequently, in order to realize the cycloaddition of disubstituted epoxides with CO₂, new catalytic conditions were investigated. To our delight, by only elevating the CO₂ pressure to 0.7 MPa, the template substrate cyclohexene oxide **8a** was converted to the corresponding cyclic carbonate **9a** in 80% yield. The substrate scope of the disubstituted epoxides was carried out and the results are listed in Table 3. The outcomes of both geminal and adjacent disubstituted epoxides are satisfactory. *ortho*-Disubstituted epoxides, such as 1,2-epoxy-4-vinyl cyclohexane epoxy cyclopentane and 3,4-tetrahydrofuran epoxides, produced the corresponding cyclic carbonates (**9b–9d**) in high yields (80–89%). For *gem*-disubstituted epoxides, the yields of cyclic carbonates (**9e** and **9f**) are even better than those of the *ortho*-disubstituted substrates under the same conditions. Compared with those of the reported rare earth metal complexes bearing the Trost ligand have not been significantly improved, and the conditions for the synthesis of cyclic carbonates are similar to those of the rare earth metal phenolates reported by Yao's group.^{14a,b}

Catalyst recycling

In the cycloaddition reaction of CO₂ and epoxide, the recyclability of the catalyst is one of the important parameters to evaluate the performance of the catalyst. To better understand the stability of the catalyst during the reaction, the recyclable reaction of epichlorohydrin **6a** and CO₂ catalyzed by complex **1** was investigated under atmospheric pressure using TBAB as the co-catalyst. The product was isolated by vacuum distillation after 24 h; subsequently, the catalyst was separated ready for

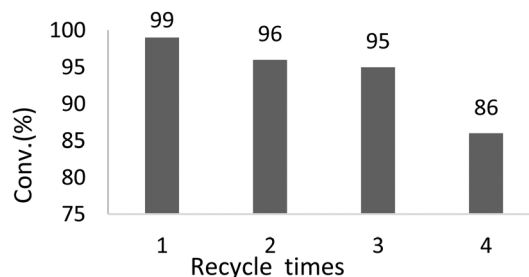


Fig. 3 Recycling of complex **1**. Reaction conditions: complex **1** (1 mol%), TBAB (2 mol%), CO₂ (0.1 MPa), 70 °C, and 24 h. Conversion of cyclic carbonate **7a** was determined by ¹H NMR spectroscopy.

the next catalytic cycle. As shown in Fig. 3, complex **1** was reused for three successive cycles with a negligible decline of the conversion of **6a**, from 99% to 95%, until the fourth cycle, which showed a significant decrease in conversion to 86%.

Kinetic study

We conducted a kinetic study to further understand the catalytic behavior of complex **1** for the cycloaddition reaction of epoxides and CO₂, using epichlorohydrin **6a** as a model substrate and ¹H NMR monitoring for 12 h (Fig. 4). The kinetic study showed that the reaction has a first-order relationship between substrate conversion and time, highlighting the catalyst stability under the reaction conditions tested.

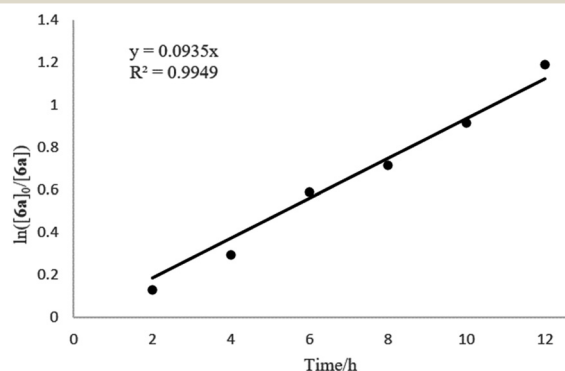
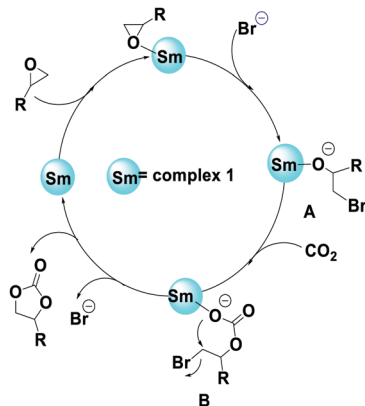


Fig. 4 Plot of $([6a]_0/[6a])$ against time. Reactions were carried out at 70 °C neat in the presence of 0.1 MPa CO₂ with 0.04 mmol TBAB and 0.02 mmol complex **1**. $[6a]_0$, initial concentration of epichlorohydrin **6a**; $[6a]$, the concentration of **6a**.

Mechanism

Based on previous reports on the formation mechanism of cyclic carbonates¹⁷ and the present results, a possible mechanism for the current system is proposed (Scheme 2). The epoxide is activated by the samarium center of catalyst **1**, and the bromide anion in TBAB subsequently attacks the less hindered side of the epoxide to generate the terminal alkoxide (A). Carbon dioxide then inserts into the Sm–O bond, forming carbonate intermediate (B). Finally, the cyclic carbonate is formed by



Scheme 2 Proposed mechanism cycle for carbonate synthesis catalyzed by complex 1.

intramolecular nucleophilic attack, and complex 1 is released for the next catalytic cycle.

Conclusions

In summary, a series of rare earth metal complexes (Sm (1), Eu (2), Y (3), Yb (4), and Lu (5)) based on the Trost proligand were prepared and well characterized. The investigation of the catalytic reactivities in the cycloaddition reaction of carbon dioxide with epoxides was carried out. Under mild conditions (70 °C, 0.1 MPa CO₂), Sm-based complex 1 showed excellent reactivities in catalyzing the cycloaddition of CO₂ and mono-substituted terminal epoxides bearing different functional groups in the presence of TBAB. Furthermore, disubstituted epoxides were successfully transformed to the corresponding cyclic carbonates at 70 °C, while elevation of pressure to 0.7 MPa CO₂ is required. Recyclability tests of the catalytic system and a kinetic study were conducted as well.

Experimental

Materials and instrumentation

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, except for ligand precursor synthesis. Crystal data were collected on Gemini Atlas and Japan Rigaku Saturn 724+ X-ray diffractometers. Structures were solved and refined using the OLEX2 program. NMR (¹H, ¹³C) spectra were recorded using a Bruker Ascend 400 spectrometer. All the epoxy compounds were purchased and dried with CaH₂ and distilled before use. Solvents, such as THF, DCM, and hexane, were degassed and distilled over sodium benzophenone ketyl before use. The Trost proligand was prepared according to optimization of the literature methods.¹⁵

Experimental procedure

Synthesis of complexes 1–5. To a THF solution of the Trost proligand (1 mmol), a solution of RE[N(SiMe₃)₂]Cl₂ (1 mmol) in THF was added slowly. The mixture was stirred overnight at room temperature. After THF had been removed under

vacuum, the solid residue was washed with hexane to remove HN(SiMe₃)₂. Crystals were obtained at room temperature from a solution in a mixed solvent of DCM and THF.

Characteristic data of complexes 1–5

H₂LSmCl₂·THF (1). Colorless crystals, 0.71 g, yield 77%; IR (KBr, cm⁻¹) ν 3381, 2960, 1477, 1448, 1382, 1066, 883, 748, 703; anal. calcd for C₄₇H₅₃Cl₂N₂O₄Sm·THF: C, 60.62; H, 5.74; N, 3.01. Found: C, 60.54; H, 5.69; N, 2.90.

H₂LEuCl₂·2THF (2). Colorless crystals, 0.60 g, yield 65%; IR (KBr, cm⁻¹) ν 3381, 2972, 1479, 1450, 1380, 1043, 875, 752, 705; anal. calcd for C₄₇H₅₃Cl₂N₂O₄Eu·2THF: C, 60.96; H, 6.12; N, 2.79. Found: C, 61.32; H, 6.13; N, 2.86.

H₂LYCl₂·THF (3). Colorless crystals, 0.71 g, yield 82%; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.96 (d, *J* = 7.8 Hz, 1H, ArH), 7.69 (d, *J* = 7.4 Hz, 4H, ArH), 7.58 (d, *J* = 7.8 Hz, 3H, ArH), 7.22 (m, 8H, ArH), 7.03 (m, 4H, ArH), 6.65–6.32 (m, 2H, ArH), 5.48 (s, 1H, OH), 4.07–3.68 (m, 2H, NCH₂Ar), 3.41 (m, 1H, NCH), 3.20 (m, 2H, CH₂, NCH₂Ar), 2.82 (m, 1H, NCH), 2.65 (m, 2H, NCH₂), 2.25 (m, 2H, NCH₂), 2.04 (m, 3H, CH₃), 1.98–1.77 (m, 2H, CH₂), 1.63 (m, 2H, CH₂), 1.51–1.35 (m, 4H, CH₂). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.0, 154.6, 153.1, 148.8, 148.0, 147.9, 128.5, 128.1, 127.2, 126.6, 126.4, 126.2, 125.8, 125.1, 124.8, 124.2, 120.3, 81.0, 78.9, 77.9, 76.2, 70.7, 57.1, 54.6, 30.0, 29.4, 24.1, 23.8, 20.8, 20.5, 20.1. IR (KBr, cm⁻¹) ν 3356, 2970, 1485, 1450, 1380, 1049, 881, 748, 707. Anal. calcd for C₄₇H₅₃Cl₂N₂O₄Y·THF: C, 64.91; H, 6.14; N, 3.22. Found: C, 64.99; H, 6.22; N, 3.23.

H₂LYbCl₂·THF (4). Colorless crystals, 0.85g, yield 90%; IR (KBr, cm⁻¹) ν 3404, 2970, 1487, 1444, 1382, 1064, 879, 748, 705; anal. calcd for C₄₇H₅₃Cl₂N₂O₄Yb·THF: C, 59.18; H, 5.60; N, 2.94. Found: C, 58.82; H, 5.99; N, 2.55.

H₂LLuCl₂·2THF (5). Colorless crystals, 0.76 g, yield 80%; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.96 (d, *J* = 7.7 Hz, 1H, ArH), 7.69 (d, *J* = 7.5 Hz, 4H, ArH), 7.58 (d, *J* = 7.8 Hz, 3H, ArH), 7.27 (d, *J* = 7.5 Hz, 8H, ArH), 7.14–6.92 (m, 4H, ArH), 6.70–6.32 (m, 2H, ArH), 5.47 (s, 1H, OH), 4.08–3.68 (m, 2H, NCH₂Ar), 3.44 (m, 1H, NCH), 3.20 (s, 2H, NCH₂Ar), 2.86 (m, 1H, NCH), 2.70 (m, 2H, NCH₂), 2.33–2.08 (m, 2H, NCH₂), 2.05 (m, 3H, CH₃), 1.98–1.79 (m, 2H, CH₂), 1.61 (m, 2H, CH₂), 1.47 (m, 4H, CH₂); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.4, 154.7, 153.1, 148.9, 147.9, 128.1, 127.3, 126.4, 124.2, 120.3, 70.9, 70.7, 57.1, 29.4, 24.1, 20.2; IR (KBr, cm⁻¹) ν 3384, 2970, 1487, 1448, 1382, 1074, 877, 750, 705; anal. calcd for C₄₇H₅₃Cl₂N₂O₄Lu·2THF: C, 59.59; H, 5.98; N, 2.73. Found: C, 59.38; H, 5.83; N, 3.01.

General procedure for cyclic carbonate synthesis under 0.1 MPa CO₂

In a typical experiment, complex 1 (18.6 mg, 0.02 mmol), TBAB (12.8 mg, 0.04 mmol), and epichlorohydrin (156 μL, 2 mmol) were added to a 5 mL flask equipped with a magnetic stirring bar under argon. The round bottomed flask was then degassed and filled with CO₂. The mixture was heated at 70 °C for 24 h. After the reaction, a drop of the resulting mixture was analyzed by ¹H NMR spectroscopy to determine the yield and selectivity. Conversion was determined through comparing the integration of the product and the yield. The analytically pure product was

isolated by column chromatography (petroleum ether: ethyl acetate = 1 : 10) and confirmed by comparison with the literature data.^{4,6c,13h,14d-f}

General procedure for the cycloaddition of CO₂ to epoxides under 0.7 MPa CO₂

Reactions were carried out in a 100 mL stainless steel Parr reactor with a stirring bar inside and a needle valve for injection. Complex **1** (93 mg, 0.1 mmol) and TBAB (64 mg, 0.2 mmol) were dissolved in the epoxides. The reactor was pressurized to 0.7 MPa with CO₂, and heated at 70 °C for 24 h. The analytically pure product was isolated by column chromatography (petroleum ether and ethyl acetate) and confirmed by comparison of ¹H NMR spectra with the literature data.^{6c,14f}

Catalyst recycling study

In a typical run, epichlorohydrin (185.0 mg, 2 mmol), complex **1** (18.6 mg, 0.02 mmol), and TBAB (12.8 mg, 0.04 mmol) were placed in a Schlenk tube, to which a balloon charged with CO₂ was connected. The reaction was heated at 70 °C for 24 h. The resulting sample was analyzed using ¹H NMR spectroscopy. The product and reactant were separated from the catalytic system by vacuum distillation under 110 °C. Fresh substrate was added to the residue for the new run.

Characterization data of cyclic carbonates

4-Chloromethyl-1,3-dioxolan-2-one (7a)^{6c}. Light yellow liquid, 270.3 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 5.00 (m, 1H, OCH), 4.60 (t, *J* = 8.6 Hz, 1H, OCH₂), 4.41 (m, 1H, OCH₂), 3.78 (m, 2H, ClCH₂).

4-Bromomethyl-1,3-dioxolan-2-one (7b)^{13h}. Light yellow liquid, 358.3 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.97 (m, 1H, OCH), 4.57 (m, 1H, OCH₂), 4.32 (m, 1H, OCH₂), 3.60 (m, 2H, Br CH₂).

4-Methyl-1,3-dioxolan-2-one (7c)^{14d}. Light yellow liquid, 202.1 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.92–4.82 (m, 1H, CHO), 4.62–4.52 (t, *J* = 8.0 Hz, 1H, OCH₂), 4.04 (t, *J* = 7.8 Hz, 1H, OCH₂), 1.50 (m, 3H).

5-Ethyl-1,3-dioxolan-2-one (7d)^{13h}. Light yellow liquid, 285.4 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.71 (m, 1H, CHO), 4.54 (t, *J* = 8.0 Hz, 1H, OCH₂), 4.08 (t, *J* = 7.8 Hz, 1H, OCH₂), 1.77 (m, 2H, CH₂), 1.39 (m, 4H, CH₂), 0.93 (t, *J* = 7.0 Hz, 3H, CH₃).

4-Decylalkyl-1,3-dioxolan-2-one (7e)^{14e}. Light yellow liquid, 452.0 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.71 (m, 1H, OCH), 4.52 (t, *J* = 8.0 Hz, 1H, OCH₂), 4.06 (t, *J* = 7.8 Hz, 1H, OCH₂), 1.89–1.75 (m, 1H), 1.74–1.64 (m, 1H), 1.50–1.42 (m, 1H), 1.29 (m, 15H), 0.87 (t, *J* = 7.0 Hz, 3H).

4-(3-Butenyl)-1,3-dioxolan-2-one (7f)⁴. Light yellow liquid, 281.4 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 5.81 (m, 1H, CH=CH₂), 5.16–5.02 (t, *J* = 13.8 Hz, 2H, CH=CH₂), 4.75 (m, 1H, OCH), 4.55 (t, *J* = 8.2 Hz, 1H, OCH₂), 4.15–4.05 (t, *J* = 7.8 Hz, 1H, OCH₂), 2.23 (m, 2H, CH₂CH₂), 2.04–1.75 (m, 2H, CH₂CH₂).

4-Phenyl-1,3-dioxolan-2-one (7g)^{14d}. White solid, 288.9 mg, yield 88%; ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.36 (m, 5H, ArH),

5.70 (t, *J* = 8.0 Hz, 1H, OCH), 4.83 (t, *J* = 8.4 Hz, 1H, OCH₂), 4.37 (t, *J* = 8.2 Hz, 1H, OCH₂).

4-(Phenoxymethyl)-1,3-dioxolan-2-one (7h)^{6c}. White solid, 380.3 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 2H, ArH), 7.02 (m, 1H, ArH), 6.91 (m, 2H, ArH), 5.03 (m, 1H, OCH), 4.66–4.50 (m, 2H, OCH₂), 4.28–4.11 (m, 2H, OCH₂).

4-((Benzyloxy)methyl)-1,3-dioxolan-2-one (7i)^{14e}. Light yellow liquid, 426.6 mg, yield 95%; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (m, 5H, ArH), 4.87–4.79 (m, 1H, OCH), 4.62 (m, 2H, OCH₂), 4.54–4.36 (m, 2H, OCH₂), 3.69 (m, 2H, OCH₂).

4-(Propoxymethyl)-1,3-dioxolan-2-one (7j)^{14e}. Light yellow liquid, 334.2 mg, yield 96%; ¹H NMR (400 MHz, CDCl₃) δ 4.80 (m, 1H, OCH), 4.49 (t, *J* = 8.4 Hz, 1H, OCH₂), 4.42–4.36 (t, *J* = 7.2 Hz, 1H, OCH₂), 3.67 (m, 1H, CH₂O), 3.61 (m, 1H, CH₂O), 3.51 (t, *J* = 6.6 Hz, 2H, OCH₂), 1.56 (m, 2H, CH₂–CH₂), 1.36 (m, 2H, CH₂–CH₂), 0.92 (t, *J* = 7.4 Hz, 3H, CH₃).

4-(Methoxymethyl)-1,3-dioxolan-2-one (7k)^{6c}. Light yellow liquid, 261.6 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.87–4.79 (m, 1H, OCH), 4.50 (t, *J* = 8.4 Hz, 1H, OCH₂), 4.41–4.35 (t, *J* = 7.2 Hz, 1H, OCH₂), 3.65 (m, 1H, OCH₂O), 3.57 (m, 1H, OCH₂O), 3.43 (s, 3H, OCH₃).

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (7l)^{14d}. Light yellow liquid, 309.9 mg, yield 98%; ¹H NMR (400 MHz, CDCl₃) δ 5.86 (m, 1H, CH=CH₂), 5.32–5.18 (m, 2H, CH=CH₂), 4.82 (m, 1H, OCH), 4.54 (t, *J* = 8.4 Hz, 1H, OCH₂), 4.42–4.36 (t, *J* = 7.2 Hz, 1H, OCH₂), 4.05 (m, 2H, OCH₂), 3.65 (m, 2H, OCH₂).

4-((Prop-2-yn-1-yloxy)methyl)-1,3-dioxolan-2-one (7m)^{14e}. Light yellow liquid, 256.0 mg, yield 82%; ¹H NMR (400 MHz, CDCl₃) δ 4.91–4.83 (m, 1H, OCH), 4.52 (t, *J* = 8.4 Hz, 1H, OCH₂), 4.40 (t, *J* = 7.2 Hz, 1H, OCH₂), 4.32–4.18 (m, 2H, CH₂O), 3.85–3.71 (m, 2H, CH₂C), 2.50 (s, 1H, CCH).

4-Hydroxymethyl-1,3-dioxolan-2-one (7n)^{6c}. Light yellow liquid, 158.2 mg, yield 67%; ¹H NMR (400 MHz, CDCl₃) δ 4.88–4.77 (m, 1H, OCH), 4.58–4.37 (m, 2H, OCH₂), 3.99 (m, 1H, CH₂OH), 3.74 (m, 1H, CH₂OH).

4-(Morpholinomethyl)-1,3-dioxolan-2-one (7o)^{6c}. Light yellow liquid, 333.2 mg, yield 89%; ¹H NMR (400 MHz, CDCl₃) δ 4.84 (s, 1H, OCH), 4.52 (t, *J* = 8.3 Hz, 1H, OCH₂), 4.27–4.19 (m, 1H, OCH₂), 3.67 (d, *J* = 9.2 Hz, 4H, OCH₂CH₂N), 2.67 (d, *J* = 5.6 Hz, 2H, CH₂), 2.55 (d, *J* = 9.4 Hz, 4H, OCH₂CH₂N).

(2-Oxo-1,3-dioxolan-4-yl)-methyl 4-(tert-butyl)benzoate (7p)^{6c}. Light yellow liquid, 233.7 mg, yield 42%; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H, ArH), 7.48 (d, *J* = 8.5 Hz, 2H, ArH), 5.05 (s, 1H, OCH), 4.65–4.55 (m, 2H, OCH₂), 4.53 (s, 1H, OCH₂), 4.41 (d, *J* = 8.7 Hz, 1H, OCH₂), 1.34 (s, 9H, O(CH₃)₃).

4,4-(Butane-1,4-diyl)-bis-1,3-dioxolan-2-one (7q)^{6c}. Light yellow liquid, 299.2 mg, yield 65%; ¹H NMR (400 MHz, CDCl₃) δ 4.73 (s, 2H, OCH₂), 4.55 (s, 2H, OCH₂), 4.08 (s, 2H, OCH₂), 1.78 (d, *J* = 23.5 Hz, 4H, CH₂CH₂), 1.53 (d, *J* = 44.5 Hz, 4H, CH₂CH₂).

4-(7-Oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one (7r)^{14f}. Light yellow liquid, 276.2 mg, yield 75%; ¹H NMR (400 MHz, CDCl₃) δ 4.55–4.29 (m, 2H, OCH₂), 4.15–4.02 (m, 1H, OCH), 3.10 (m, 2H, OCH₂), 2.17–0.95 (m, 7H, CH₂).

1,2-Cyclohexane carbonate (cis-9a)^{6c}. Light yellow liquid, 227.4 mg, yield 80%; ¹H NMR (400 MHz, CDCl₃) δ 4.68

(m, 2H, OCHCH₂), 1.98–1.86 (m, 4H, OCHCH₂), 1.67–1.59 (m, 2H, CH₂), 1.42 (m, 2H, CH₂).

5-Vinylhexahydrobenzo[d][1,3]dioxol-2-one (cis-9b)^{14f}. Light yellow liquid, 282.5 mg, yield 84%; ¹H NMR (400 MHz, CDCl₃) δ 5.88–5.65 (m, 1H, CH=CH), 5.18–4.96 (m, 2H, CH), 4.934.58 (m, 2H, CH=CH₂), 2.49–2.13 (m, 2H, CH₂), 1.94 (m, 2H, CH₂), 1.75–1.48 (m, 2H, CH₂), 1.45–1.16 (m, 1H, CH).

Tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one (cis-9c)^{6c}. Light yellow liquid, 228.0 mg, yield 89%; ¹H NMR (400 MHz, CDCl₃) δ 5.11 (m, 2H, OCHCH₂), 2.15 (m, 2H, CH₂), 1.86–1.64 (m, 4H, CH₂).

Tetrahydrofuro-4H-cyclopenta[d][1,3]dioxol-2-one (cis-9d)^{6c}. Pale yellow liquid, 217.8 mg, yield 85%; ¹H NMR (400 MHz, CDCl₃) δ 5.11 (s, 2H, OCH₂), 4.23–4.20 (m, 2H, CH₂), 3.54–3.51 (m, 2H, CH₂).

4,4-Dimethyl-1,3-dioxolan-2-one (9e)^{6c}. Light yellow liquid, 229.9 mg, yield 99%; ¹H NMR (400 MHz, CDCl₃) δ 4.17 (s, 2H, OCH₂), 1.54 (s, 6H, CH₃).

4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one (9f)^{14f}. Light yellow liquid, 271.0 mg, yield 90%; ¹H NMR (400 MHz, CDCl₃) δ 4.52 (d, *J* = 8.8 Hz, 1H, OCH₂), 4.17 (d, *J* = 8.8 Hz, 1H, OCH₂), 3.74 (d, *J* = 11.9 Hz, 1H, CH₂Cl), 3.61 (d, *J* = 11.9 Hz, 1H, CH₂Cl), 1.64 (s, 3H, CH₃).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge financial support from the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 19KJA320007), the project of scientific and technologic infrastructure of Suzhou (SZS201708), and PAPD.

Notes and references

- 1 M. D. Burkart, N. Hazari, C. L. Tway and E. L. Zeitler, Opportunities and challenges for catalysis in carbon dioxide utilization, *ACS Catal.*, 2019, **9**, 7937.
- 2 A. Dibenedetto and F. Nocito, The future of carbon dioxide chemistry, *ChemSusChem*, 2020, **13**, 6219.
- 3 Z. E. Zhang, S. Y. Pan, H. Li, J. C. Cai, A. G. Olabi, E. J. Anthony and V. Manovic, Recent advances in carbon dioxide utilization, *Renewable Sustainable Energy Rev.*, 2020, **125**, 109799.
- 4 L. Y. Hua, B. X. Li, C. P. Han, P. F. Gao, Y. R. Wang, D. Yuan and Y. M. Yao, Synthesis of homo- and heteronuclear rare earth metal complexes stabilized by ethanolamine-bridged bis(phenolato) ligands and their application in catalyzing reactions of CO₂ and epoxides, *Inorg. Chem.*, 2019, **58**, 8775.
- 5 (a) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Y. Hasegawa, 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; (b) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, A bifunctional catalyst for carbon dioxide fixation: cooperative double activation of epoxides for the synthesis of cyclic carbonates, *Chem. Commun.*, 2012, **48**, 4489.
- 6 (a) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martín and A. W. Kleij, A powerful aluminum catalyst for the synthesis of highly functional organic carbonates, *J. Am. Chem. Soc.*, 2013, **135**, 1228; (b) W. M. Ren, Y. Liu and X. B. Lu, Bifunctional aluminum catalyst for CO₂ fixation: regioselective ring opening of three-membered heterocyclic compounds, *J. Org. Chem.*, 2014, **79**, 9771; (c) P. F. Gao, Z. W. Zhao, L. J. Chen, D. Yuan and Y. M. Yao, Dinuclear aluminum poly(phenolate) complexes as efficient catalysts for cyclic carbonate synthesis, *Organometallics*, 2016, **35**, 1707; (d) J. Rintjema, R. Epping, G. Fiorani, E. Martín, E. C. Escudero-Adán and A. W. Kleij, Substrate-controlled product divergence: conversion of CO₂ into heterocyclic products, *Angew. Chem., Int. Ed.*, 2016, **55**, 3972; (e) M. Cozzolino, K. Press, M. Mazzeo and M. Lamberti, Carbon dioxide/epoxide reactions catalyzed by bimetallic salalen aluminum complexes, *ChemCatChem*, 2016, **8**, 455; (f) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. Castro-Osma, M. North and R. S. Rojas, Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates, *ChemCatChem*, 2018, **10**, 2271; (g) Y. Kim, K. Hyun, D. Ahn, R. Kim, M. H. Park and Y. Kim, *ChemSusChem*, 2019, **12**, 4211.
- 7 (a) X. Liu, S. Zhang, Q. W. Song, X. F. Liu, R. Ma and L. N. He, Cooperative calcium-based catalysis with 1,8 diazabicyclo[5.4.0]undec-7-ene for the cycloaddition of epoxides with CO₂ at atmospheric pressure, *Green Chem.*, 2016, **18**, 2871; (b) L. Longwitz, J. Steinbauer, A. Spannenberg and T. Werner, Calcium-based catalytic system for the synthesis of bio-derived cyclic carbonates under mild conditions, *ACS Catal.*, 2018, **8**, 665.
- 8 Z. Q. Guo, Y. Xu, J. B. Chao and X. H. Wei, Lithium organoaluminate complexes as catalysts for the conversion of CO₂ into cyclic carbonates, *Eur. J. Inorg. Chem.*, 2020, 2835.
- 9 (a) R. L. Paddock and S. T. Nguyen, Chemical CO₂ fixation: Cr(III) salen complexes as highly efficient catalysts for the coupling of CO₂ and epoxides, *J. Am. Chem. Soc.*, 2001, **123**, 11498; (b) X. B. Lu, B. Liang, Y. J. Zhang, Y. Z. Tian, Y. M. Wang, C. X. Bai, H. Wang and R. Zhang, Asymmetric catalysis with CO₂: Direct synthesis of optically active propylene carbonate from racemic epoxides, *J. Am. Chem. Soc.*, 2004, **126**, 3732; (c) J. Castro-Osma, K. J. Lamb and M. North, Cr(salophen) complex catalyzed cyclic carbonate synthesis at ambient temperature and pressure, *ACS Catal.*, 2016, **6**, 5012.
- 10 (a) R. L. Paddock and S. T. Nguyen, Chiral (salen)Co^{III} catalyst for the synthesis of cyclic carbonates, *Chem. Commun.*, 2004, 1622; (b) C. X. Miao, J. Q. Wang, Y. Wu, Y. Du and L. N. He, Bifunctional metal-salen complexes as efficient catalysts for the fixation of CO₂ with epoxides under solvent-free, *ChemSusChem*, 2008, **1**, 236.

- 11 (a) R. M. Haak, A. Decortes, E. C. Escudero-Adán, M. M. Belmonte, E. Martin, J. Benet-Buchholz and A. W. Kleij, Shape-persistent octanuclear zinc salen clusters: synthesis, characterization, and catalysis, *Inorg. Chem.*, 2011, **50**, 7934; (b) A. Decortes, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, Efficient carbonate synthesis under mild conditions through cycloaddition of carbon dioxide to oxiranes using a Zn(salphen) catalyst, *Chem. Commun.*, 2010, **46**, 4580; (c) W. Desens, C. Kohrt, A. Spannenberg and T. Werner, A novel zinc based binary catalytic system for CO₂ utilization under mild conditions, *Org. Chem. Front.*, 2016, **3**, 156; (d) R. Ma, L. N. He and Y. B. Zhou, An efficient and recyclable tetraoxo-coordinated zinc catalyst for the cycloaddition of epoxides with carbon dioxide at atmospheric pressure, *Green Chem.*, 2016, **18**, 226.
- 12 (a) C. J. Whiteoak, E. Martin, E. Escudero-Adán and A. W. Kleij, Stereochemical divergence in the formation of organic carbonates derived from internal epoxides, *Adv. Synth. Catal.*, 2013, **355**, 2233; (b) F. D. Monica, B. Maity, T. Pehl, A. Buonerba, A. D. Nisi, M. Monari, A. Grassi, B. Rieger, L. Cavallo and C. Capacchione, [OSSO]-type iron(III) complexes for the low-pressure reaction of carbon dioxide with epoxides: catalytic activity, reaction kinetics, and computational study, *ACS Catal.*, 2018, **8**, 6882; (c) K. A. Andrea, T. R. Brown, J. N. Murphy, D. Jagota, D. McKearney, C. M. Kozak and F. M. Kerton, *Inorg. Chem.*, 2018, **57**, 13494; (d) E. Fazekas, G. S. Nichol, M. P. Shaver and J. A. Garden, Stable Fe(III) phenoxyimines as selective and robust CO₂/epoxide coupling catalysts, *Dalton Trans.*, 2018, **47**, 13106; (e) F. D. Monica, A. Buonerba, V. Paradiso, S. Milione, A. Grassi and C. Capacchione, [OSSO]-type Fe(III) metallate as single-component catalyst for the CO₂ cycloaddition to epoxides, *Adv. Synth. Catal.*, 2019, **361**, 283; (f) E. Y. Seong, J. H. Kim, N. H. Kim, K. H. Ahn and E. J. Kang, Multifunctional and sustainable Fe-iminopyridine complexes for the synthesis of cyclic carbonates, *ChemSusChem*, 2019, **12**, 409.
- 13 (a) C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, Merging sustainability with organocatalysis in the formation of organic carbonates by using CO₂ as a feedstock, *ChemSusChem*, 2012, **5**, 2032; (b) Y. B. Wang, D. S. Sun, H. Zhou, W. Z. Zhang and X. B. Lu, CO₂, COS and CS₂ adducts of N-heterocyclic olefins and their application as organocatalysts for carbon dioxide fixation, *Green Chem.*, 2015, **17**, 4009; (c) L. Wang, G. Y. Zhang, K. Kodama and T. Hirose, An efficient metal- and solvent-free organocatalytic system for chemical fixation of CO₂ into cyclic carbonates under mild conditions, *Green Chem.*, 2016, **18**, 1229; (d) S. Sopen, E. Martin, E. C. Escudero-Adán and A. W. Kleij, Pushing the limits with squaramide-based organocatalysts in cyclic carbonate synthesis, *ACS Catal.*, 2017, **7**, 3532; (e) N. Liu, Y. F. Xie, C. Wang, S. J. Li, D. H. Wei, M. Li and B. Dai, Cooperative multifunctional organocatalysts for ambient conversion of carbon dioxide into cyclic carbonates, *ACS Catal.*, 2018, **8**, 9945; (f) J. Y. Hu, J. Ma, H. Z. Liu, Q. L. Qian, C. Xie and B. X. Han, Dual-ionic liquid system: an efficient catalyst for chemical fixation of CO₂ to cyclic carbonates under mild conditions, *Green Chem.*, 2018, **20**, 2990; (g) X. Wu, C. T. Chen, Z. Y. Guo, M. North and A. C. Whitwood, *ACS Catal.*, 2019, **9**, 1895; (h) Y. H. Hao, D. Yuan and Y. M. Yao, Metal-free cycloaddition of epoxides and carbon dioxide catalyzed by triazole-bridged bisphenol, *ChemCatChem*, 2020, **12**, 4346.
- 14 (a) J. Qin, P. Wang, Q. Y. Li, Y. Zhang, D. Yuan and Y. M. Yao, Catalytic production of cyclic carbonates mediated by lanthanide phenolates under mild conditions, *Chem. Commun.*, 2014, **50**, 10952; (b) B. Xu, P. Wang, M. Lv, D. Yuan and Y. M. Yao, Transformation of Carbon Dioxide into Oxazolidinones and Cyclic Carbonates Catalyzed by Rare-Earth-Metal Phenolates, *ChemCatChem*, 2016, **8**, 2466; (c) J. Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, J. A. Castro-Osma, A. Lara-Sánchez and A. Otero, An efficient and versatile lanthanum heteroscorpionate catalyst for carbon dioxide fixation into cyclic carbonates, *ChemSusChem*, 2017, **10**, 2886; (d) Z. W. Zhao, J. Qin, C. Zhang, Y. R. Wang, D. Yuan and Y. M. Yao, Recyclable single-component rare-earth metal catalysts for cycloaddition of CO₂ and epoxides at atmospheric pressure, *Inorg. Chem.*, 2017, **56**, 4568; (e) L. Y. Qu, I. D. Rosalb, Q. Y. Li, Y. R. Wang, D. Yuan, Y. M. Yao and L. Maron, Efficient CO₂ transformation under ambient condition by heterobimetallic rare earth complexes: experimental and computational evidences of a synergistic effect, *J. CO₂ Util.*, 2019, **33**, 413; (f) X. Xin, H. W. Shan, T. Tian, Y. R. Wang, D. Yuan, H. P. You and Y. M. Yao, Conversion of CO₂ into cyclic carbonates under ambient conditions catalyzed by rare-earth metal complexes bearing poly(phenolato) ligand, *ACS Sustainable Chem. Eng.*, 2020, **8**, 13185; (g) K. Yin, L. Y. Hua, L. Y. Qu, Q. Y. Yao, Y. R. Wang, D. Yuan, H. P. You and Y. M. Yao, Heterobimetallic rare earth metal-zinc catalysts for reactions of epoxides and CO₂ under ambient conditions, *Dalton Trans.*, 2021, **50**, 1453.
- 15 (a) D. P. Zhao, L. J. Mao, L. Q. Wang, D. X. Yang and R. Wang, Catalytic asymmetric construction of tetrasubstituted carbon stereocenters by conjugate addition of dialkyl phosphine oxides to β,β -disubstituted α,β -unsaturated carbonyl compounds, *Chem. Commun.*, 2012, **48**, 889; (b) B. M. Trost, C.-I. Hung and G. Mata, Dinuclear metal-prophenol catalysts: development and synthetic applications, *Angew. Chem., Int. Ed.*, 2020, **59**, 4240; (c) Y. L. Sun, C. R. Lu, B. Zhao and M. Q. Xue, Enantioselective hydroboration of ketones catalyzed by rare-earth metal complexes containing Trost ligands, *J. Org. Chem.*, 2020, **85**, 10504.
- 16 (a) Q. Q. Qian, Y. F. Tan, B. Zhao, T. Feng, Q. Shen and Y. M. Yao, Asymmetric epoxidation of unsaturated ketones catalyzed by heterobimetallic rare earth-lithium complexes bearing phenoxy functionalized chiral diphenylprolinolate ligands, *Org. Lett.*, 2014, **16**, 4516; (b) C. Zeng, D. Yuan, B. Zhao and Y. M. Yao, Highly Enantioselective epoxidation of α,β -Unsaturated ketones catalyzed by rare-earth amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{RE}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with phenoxy-functionalized chiral prolinols, *Org. Lett.*, 2015, **17**, 2242.
- 17 (a) M. North and R. Pasquale, Mechanism of cyclic carbonate synthesis from epoxides and CO₂, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946; (b) C. Martín, G. Fiorani and A. W. Kleij, Recent advances in the catalytic preparation of cyclic organic carbonates, *ACS Catal.*, 2015, **5**, 1353.