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Heterobimetallic rare earth metal–zinc catalysts for reactions of epoxides and CO_2 under ambient conditions†

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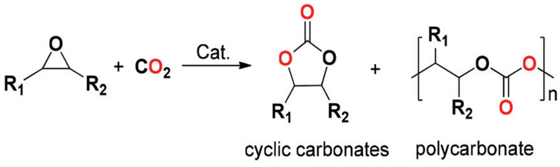
Four homodinuclear rare earth metal (RE) complexes **1–4** bearing a multidentate diglycolamine-bridged bis(phenolate) ligand were synthesized. In addition, seven heterobimetallic RE–Zn complexes **5–11** were prepared through a one-pot strategy. In these heterobimetallic complexes, two RE centers are bridged by either $Zn(OAc)_2$ or $Zn(OBn)_2$ moieties. All complexes were characterized by single crystal X-ray diffraction, elemental analysis, IR spectroscopy, and multinuclear NMR spectroscopy (in the case of diamagnetic complexes **1**, **4**, **7** and **11**). Moreover, the multi-nuclear structures of complexes **4** and **11** in solution were also studied by ^1H DOSY spectroscopy. These complexes were applied in catalyzing the coupling reaction of carbon dioxide (CO_2) with epoxides. $Zn(OAc)_2$- and $Zn(OBn)_2$-bridged heterobimetallic complexes showed comparable catalytic activities under ambient conditions and were more active than monometallic RE complexes. Significant synergistic effect in heterobimetallic complexes is observed. Mono-substituted epoxides were converted into cyclic carbonates under 1 atm CO_2 at 25 °C in 88–96% yields, whereas di-substituted epoxides reacted under 1 atm CO_2 at higher temperatures in 40–80% yields.

Introduction

Carbon dioxide (CO_2) is an abundant, renewable, and inexpensive natural resource that can be transformed into value-added compounds through chemical fixation.[1] Coupling of CO_2 with epoxides forms cyclic carbonates, which is a 100% atom economical reaction (Scheme 1). Cyclic carbonates find wide applications as non-protic solvents, lithium-ion battery electrolytes, fine chemical intermediates, *etc.*[2] Significant efforts have been made to address the general reactivity and selectivity issues associated with cyclic carbonate synthesis. A variety of catalysts including metal complexes[3] and organocatalysts[4] have been developed to catalyse this transformation. However, they in general require high temperature and/or high pressure of CO_2, and examples conducted under ambient conditions are very few.[5] Among these scarce catalytic systems, most of them focused on the reactions of monosubstituted epoxides, which include bimetallic Al(salen), Al(acen), Al(amidinate) and Al(ethanolateamine) complexes,[5a–e,l,t] Cr(salophen) complex,[5f] dinuclear macrocyclic iron complex,[5g] sulfur-bridged bis(phenolato) bismuth complex,[5h] μ-oxotetranuclear zinc and cobalt clusters,[5i] *N*,*N*-dialkylcarbamate iron complex,[5k] metal–porphyrin framework,[5p] metal–salen molecular cages,[5q] and organocatalysts,[5o,r,s] while reactions of more challenging disubstituted epoxides generally required elevated temperature/pressure. Notably, the calcium–crown ether catalyst reported by Werner and co-workers,[5m] and Zn and Cu complexes developed by Muralidharan and co-workers,[5n] catalysed the reactions of disubstituted terminal epoxides under ambient conditions.

Recently, Liu and co-workers reported heterometallic helicates featuring multiple zinc–rare earth metal (Zn–RE) units for the ambient chemical fixation of CO_2.[5j] The same group also



Scheme 1 Reaction of CO_2 and epoxides.

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† Electronic supplementary information (ESI) available: Solid state structures, NMR spectra, and crystallographic data. CCDC 1852420 for **3**, 1852421 for **1**, 1852422 for **4**, 1852637 for **2**, 1852727 for **7**, 1852728 for **8**, 1853071 for **11**, 1853073 for **10**, 1976682 for **5**, 1976683 for **6** and 1976684 for **9**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt03772a

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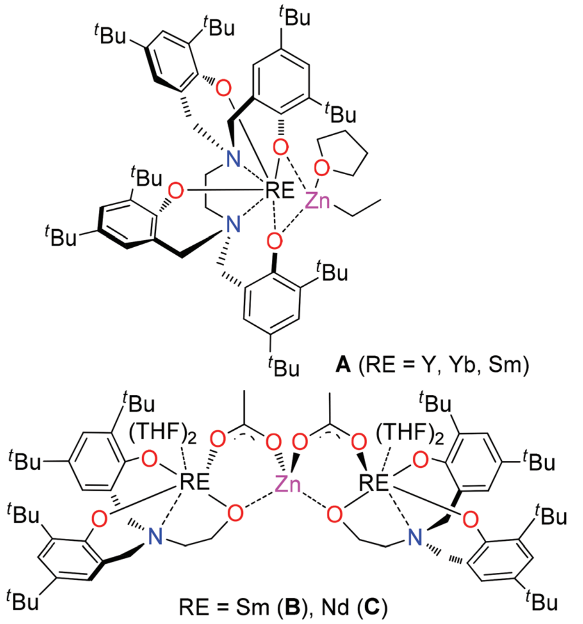


Fig. 1 Heterobimetallic RE–Zn complexes **A**, **B** and **C** (ref. 7 and 8).

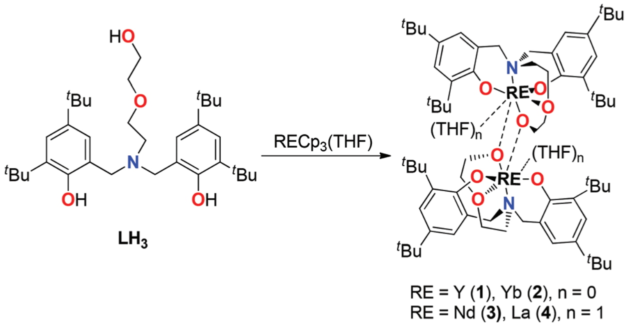
reported other heterometallic helicates or coordination polymers as efficient catalysts for the cycloaddition of epoxides and CO_2 under elevated temperature/pressure.[3h,6] Our group reported that RE–Zn complexes were stabilized by ethylenediamine-bridged tetra(phenolato) ligands (**A** in Fig. 1), which are active catalysts under ambient conditions.[7] We also reported heterometallic RE–Zn complexes **B** and **C** (Fig. 1) stabilized by the ethanolamine-bridged bis(phenolato) ligand, which, however, shows inferior activity as compared to that of homometallic RE metal complexes.[8] Although some above-discussed heterobimetallic complexes catalysed the cycloaddition of mono-substituted epoxides and CO_2 under ambient conditions, none of them showed any activity for reactions of di-substituted epoxides.

To develop more active catalysts, and to further investigate the structure–activity correlations, the ancillary ligands were then modified by introducing an extra oxygen donor to the previously reported ethanolamine-bridged bis(phenolato) ligand.[8] We herein report RE–Zn complexes stabilized by the diglycolamine-bridged bis(phenolate) ligand, which gave rise to significantly improved catalytic activity, and performed better through the cooperation of the two metal centers. A series of epoxides, including disubstituted terminal epoxides, were transformed into cyclic carbonates under ambient conditions.

Results and discussion

Complex synthesis

A multidentate bis(phenolate) ligand bearing a diglycolamine bridge was employed to stabilize multiple metal centers. The ligand precursor $\mathbf{LH_3}$ was readily prepared *via* the Mannich condensation of phenols and amino alcohol.[9] Homo-dinuclear complexes $RE_2L_2(THF)$ [RE = Y (**1**), Yb (**2**), Nd (**3**), La (**4**)] were synthesized in 82–90% yield by the reaction of $RECp_3(THF)$ with the ligand precursor $\mathbf{LH_3}$ (Scheme 2).



Scheme 2 Synthesis of rare earth metal complexes **1–4**.

Following the strategy developed for $Zn(OAc)_2$-bridged heterobimetallic complexes,[8] one-pot reactions of $\mathbf{LH_3}$ with $RECp_3(THF)$ followed by the addition of 0.5 equivalent of $Zn(OAc)_2$ gave rise to heterobimetallic complexes **5** (RE = Sm) and **6** (RE = Nd) in low yields of 20–25% (Scheme 3). Sm and Nd complexes were synthesized for comparison with RE–Zn analogous **B** and **C** stabilized by an ethanolamine-bridged ligand.

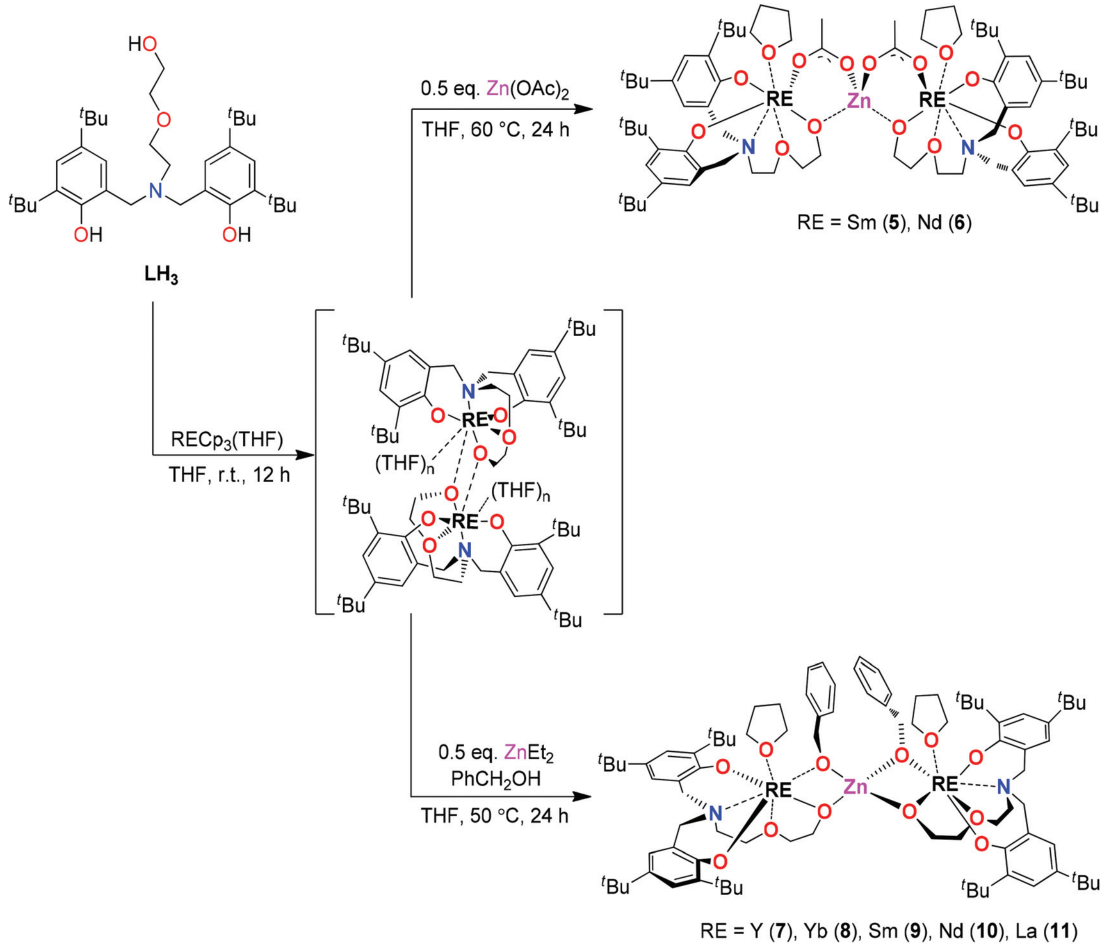
The construction of heterobimetallic $Zn(OBn)_2$-bridged complexes was achieved through one-pot reactions of $\mathbf{LH_3}$ with $RECp_3(THF)$, $ZnEt_2$ and $PhCH_2OH$, which worked more straightforwardly, and generated complexes **7–11** in good yields of 77–87% (Scheme 3).

All complexes were characterized by single crystal X-ray diffraction, elemental analysis, and IR spectroscopy. Diamagnetic complexes **1**, **4**, **7** and **11** were also characterized by multinuclear NMR spectroscopy.

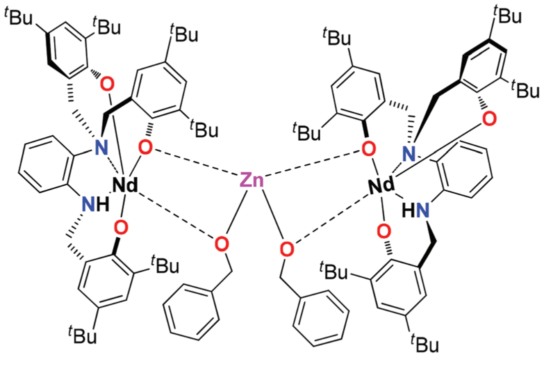
Solid-state structures of complexes **1–11** are depicted in Fig. 3, 4, and S1–9.† In complex **4**, each La center is bound with five oxygen atoms and one nitrogen atom from the two ligands and one THF molecule, adopting a pentagonal bipyramidal geometry. The solid-state structure of complex **11** reveals a trinuclear architecture, involving one Zn and two La centers. The two $[LaO_2Zn]$ coordination planes have a dihedral angle of 70°. The lengths of the La–O bonds of complexes **4** and **11** are almost identical (*i.e.*, La–OPh 2.30 Å, $La–OCH_2$ 2.42 Å, $La–O(CH_2)_2$ 2.64 Å), while the Zn–O bonds in complex **11** are *ca.* 1.94 Å. The distances of the Zn–O bonds in complex **6** fall in the range of 1.931–1.988 Å, which are in a similar range as those of the previously reported $Zn(OAc)_2$-bridged Nd–Zn complex **C**.[8] The Zn–O bonds in complex **10** are shorter than those of the $Zn(OBn)_2$-bridged Nd–Zn complex **D** (Fig. 2; 1.932, 1.956 *vs.* 1.947, 1.979 Å).[10]

The RE–Zn distances of different heterobimetallic complexes are listed and compared (Table 1).[8] The $Zn(OBn)_2$-bridged complexes have RE–Zn distances of *ca.* 3.4 Å, whereas the $Zn(OAc)_2$-bridged ones have RE–Zn distances of *ca.* 3.8 Å.

The ^1H NMR spectrum of **4** displays one set of signals for the ligand, suggesting a symmetrical structure in solution. In the ^1H NMR spectrum of complex **11**, additional signals corresponding to benzyloxy groups are observed. The methyl-



Scheme 3 Synthesis of heterobimetallic rare earth metal–zinc complexes **5–11**.



D

Fig. 2 Heterobimetallic RE–Zn complex **D** (ref. 11).

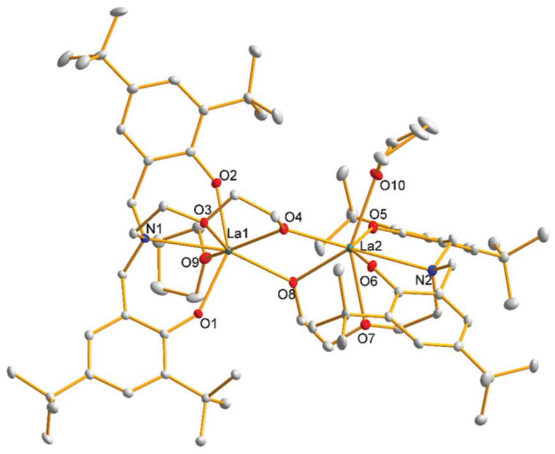


Fig. 3 The molecular structure of complex **4**·2tol with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

ene group of benzyloxy groups resonates at 5.33 ppm, which shifts downfield compared to that of free $PhCH_2OH$, corroborating its coordination.

The diffusion coefficients (*D*) of complexes **4** and **11** are determined to be 4.02×10^{-10} and 3.61×10^{-10} m^2 s^{-1}, respectively. The fact that the latter is 10% lower than the former suggests a larger aggregate of complex **11** than of **4** in solution. Moreover, for solutions of $LaCp_3(THF)$, H_3L, complexes **4** and **11** which are of the same concentration, the correlation

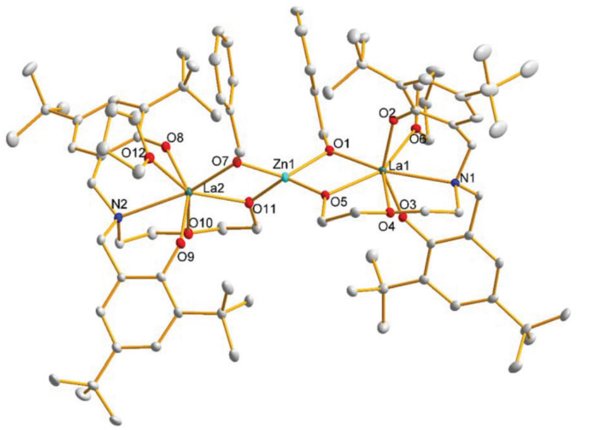


Fig. 4 The molecular structure of complex **11**·4THF with thermal ellipsoids drawn at the 20% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

Table 1 RE–Zn distances of heterobimetallic complexes

Complex	$Zn(OBn)_2$-bridged complexes	$Zn(OAc)_2$-bridged complexes
Distance of RE–Zn (Å)	Sm–Zn 3.38 (**9**) Nd–Zn 3.41 (**10**) La–Zn 3.44 (**11**) Nd–Zn 3.39 (**D**)	Sm–Zn 3.82 (**B**) Nd–Zn 3.84 (**C**) Sm–Zn 3.78 (**5**) Nd–Zn 3.82 (**6**)

between lg D and their molecular weights ($\lg(M_W)$) shows good linearity (Fig. 5, Table S1†). The VT NMR experiments of **11** in d_8-toluene were conducted in the range of 25–100 °C, which revealed no obvious change (Fig. S20†). These findings prove that the trinuclear structure of **11** is maintained in solution.[11]

In addition, the hydrodynamic radius r_h of complex **11** was determined to be 12.9 ± 0.5 Å, which was essentially the same as the average crystalline radius of 12.0 ± 0.5 Å (Table S2, Fig. S23†).[12,13] The hydrodynamic radius (11.6 ± 0.5 Å) and crystalline radius (10.6 ± 0.5 Å) of complex **4** were also determined to be roughly consistent, further proving that solid-state and solution structures are consistent.

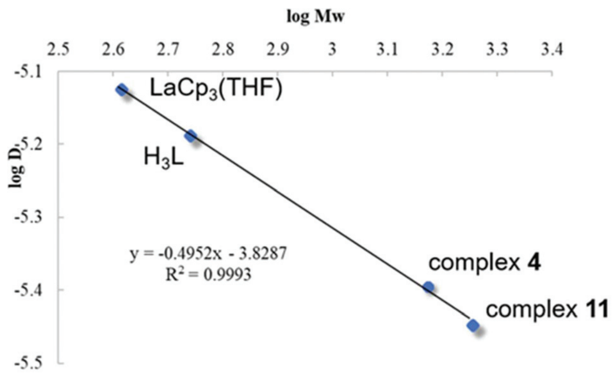


Fig. 5 Log–log-relationship between the diffusion coefficients in the ^1H DOSY NMR spectra and Mw of compounds. Conditions for DOSY experiment: samples in THF-d_8 with a concentration of 0.056 M, 25 °C, 400 MHz.

Catalytic study

With these complexes in hand, the catalytic potential of rare earth metal complexes **1–4** was first evaluated under atmospheric pressure using 1,2-epoxyhexane as a template substrate and tetrabutylammonium halide as the co-catalyst.

Under identical conditions (0.2 mol% catalyst, 100 °C), lanthanum complex **4** gave the highest yield of 90% (Table 2, entry 4).[8,14] The large atomic radius which results in a larger space for substrate binding may together be the reasons for the higher activity. Different co-catalysts were studied of which tetrabutylammonium bromide (TBAB) gave the best yield of 92% at 80 °C under 1 atm CO_2 pressure (Table 2, entries 5–10). The decreasing activity sequence of $Br^- > I^- > Cl^-$ was observed, possibly because Br^- has balanced nucleophilic and leaving abilities. PPNCl performed better than TBAC (Table 2, entries 8 and 9), mainly due to the weaker ion pairing of Cl^- with the PPN cation.[15] The yield gradually decreased as the temperature decreased, and only 15% yield was obtained at 25 °C (Table 2, entries 10–13).

To conduct reactions under ideal atmospheric conditions (*i.e.*, 25 °C, 1 atm CO_2 pressure), the loadings of catalyst and co-catalyst were increased to 0.5 mol% and 1 mol%, respectively. Indeed, in the presence of RE–Zn complexes, >60% yields were achieved under atmospheric conditions (Table 3, entries 2–8). $Zn(OAc)_2$- and $Zn(OBn)_2$-bridged complexes showed comparable activities under these conditions (Table 3, entries 2, 3 *vs.* 6, 7). For complexes **7–11**, a similar trend of larger ionic radii giving higher activity was observed (*vide supra*) (Table 3, entries 4–8).

A comparison between heterobimetallic RE–Zn complexes and monometallic RE complexes showed that the former are significantly more active (Table 3, entries 1 and 8).

Table 2 Catalytic production of cyclic carbonate from CO_2 with 1,2-epoxyhexane mediated by dinuclear catalysts **1–4**[a]

Entry	Catalyst	Co-catalyst	T [°C]	Conversion[b,c] [%]
1	**1**	TBAI	100	65
2	**2**	TBAI	100	60
3	**3**	TBAI	100	80
4	**4**	TBAI	100	90
5	**4**	TBAI	80	75
6	**4**	BTAB[d]	80	83
7	**4**	TOAB[e]	80	85
8	**4**	TBAC	80	43
9	**4**	PPNCl	80	81
10	**4**	TBAB	80	92
11	**4**	TBAB	60	71
12	**4**	TBAB	40	40
13	**4**	TBAB	25	15

[a] Reaction conditions: 0.2 mol% catalyst, 0.2 mol% co-catalyst, 1 atm CO_2 pressure, 18 h, solvent free. [b] Determined by ^1H NMR spectroscopy. [c] Selectivity for the cyclic carbonate product were all >99%. [d] (2-Bromoethyl)trimethylammonium bromide. [e] Tetra-*n*-octylammonium bromide.

Table 3 Catalytic production of cyclic carbonate from CO_2 with 1,2-epoxyhexane mediated by complexes **4–11**[a]

Entry	Catalyst	Co-catalyst	Conversion[b,c] [%]
1	**4**	TBAB	46
2	**5**	TBAB	67
3	**6**	TBAB	73
4	**7**	TBAB	79
5	**8**	TBAB	75
6	**9**	TBAB	60
7	**10**	TBAB	80
8	**11**	TBAB	88
9	**11**	—	6
10	$ZnEt_2$ + $2PhCH_2OH$	TBAB	10
11[d]	**11**	TBAB	94

[a] Reaction conditions: 0.5 mol% catalyst, 1 mol% co-catalyst, 25 °C, 24 h, 1 atm CO_2 pressure. [b] Determined by ^1H NMR spectroscopy. [c] Selectivity for the cyclic carbonate product were all >99%. [d] Reaction conditions: 0.5 mol% catalyst, 2 mol% co-catalyst, 25 °C, 24 h, 1 atm CO_2 pressure.

Heterometallic complexes showed almost one-fold higher activity than homo-analogues, as evidenced by their kinetic constants (Fig. 6). It is also noteworthy that the mixture of $ZnEt_2$ and $PhCH_2OH$ gave a low yield of 10% (Table 3, entry 10). These findings strongly suggest that cooperation between the RE and Zn centers exists, which accounts for the enhanced activity of the heterobimetallic complexes. The absence of the co-catalyst TBAB led to almost complete deactivation (Table 3, entry 9).

The adjustment of the catalyst to co-catalyst ratios gave a good yield of 94% (Table 3, entry 11) in the presence of 1 atm CO_2 at 25 °C, which in general required shorter reaction times compared to the RE–Zn helicate catalyst system.[5j]

To explore the scope of the heterobimetallic catalyst, a variety of epoxides were examined under the aforementioned optimized conditions, and the results are summarized in Table 4. All the monosubstituted epoxides with different types of functional groups, *e.g.*, aryl, ether and ester groups, were converted into their corresponding cyclic carbonates **12b–12i** in good yields (88–96%) at 25 °C and 1 atm CO_2.

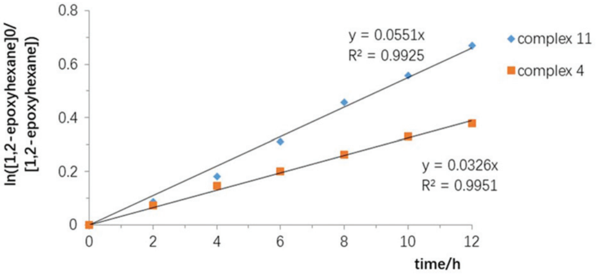
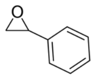
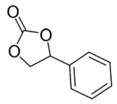
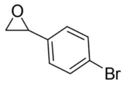
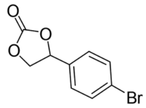
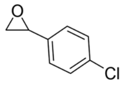
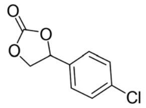
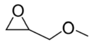
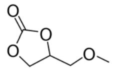
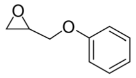
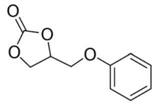
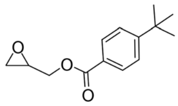
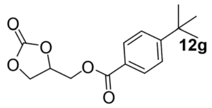
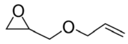
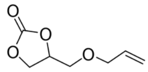
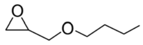
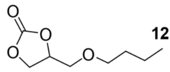


Fig. 6 Reaction monitoring with ^1H NMR spectroscopy (condition: Table 3, entries 1 and 8). Rate constants are determined to be 0.0551 h^{-1} (blue cycle) and 0.0326 h^{-1} (red square), respectively.

Table 4 Cycloaddition of CO_2 with epoxides catalyzed by complex **11** and NBu_4Br[a]

Entry	Substrate	Product	Yield[b,c]
1		 **12b**	93%
2		 **12c**	95%
3		 **12d**	96%
4		 **12e**	95%
5		 **12f**	95%
6		 **12g**	96%[d]
7		 **12h**	88%
8		 **12i**	96%

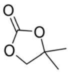
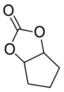
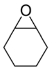
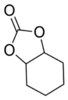
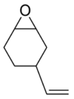
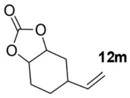
[a] Reaction conditions: 0.5 mol% complex **11**, 2 mol% TBAB, 25 °C, 1 atm CO_2, 24 h. [b] Isolated yield. [c] Selectivity for the cyclic carbonate product were all >99% unless otherwise stated. [d] 40 h.

Disubstituted epoxides are challenging substrates due to their increased steric hindrance, which in general require elevated temperature/pressure to ensure good conversions.[5] Achieving the transformation of disubstituted epoxides under ambient conditions remains a challenging task. It is noteworthy that the reaction of a disubstituted terminal epoxide at 25 °C gave the cyclic carbonate **12j** in 87% yield after prolonging the reaction time to 40 h (Table 5, entry 1). Compared to literature reports, the heterobimetallic complex gave a similar yield with less catalyst loading.[5m,n]

In addition, the reactions of disubstituted internal epoxides, *i.e.*, cyclopentene oxide and cyclohexene oxide, were converted into cyclic carbonates in the presence of 1 atm CO_2 at an elevated temperature of 80–100 °C in 40–80% yield (Table 5, entries 2–4). This is one of the few catalysts capable of converting internal epoxides under 1 atm pressure.[5m,n] At an elevated pressure of 30 atm, a higher conversion of cyclohexene oxide and less poly(carbonate) was detected, resulting in better selectivity (Table 5, entry 3).

The catalytic activities of homodinuclear complex **4** and heterobimetallic complex **11** were compared in catalyzing the reactions of disubstituted epoxides and CO_2 under identical conditions. The latter showed higher activity compared to complex **4** in catalyzing the reactions of 1,1- and 1,2-disubstituted epoxides (Table 5). The reactions of cyclohexene oxide and 1,2-epoxy-4-vinylcyclohexane gave rise to mixtures of cyclic carbonates, poly(ether) and poly(carbonate), and the

Table 5 Cycloaddition of CO_2 with epoxides catalyzed by complex **4** or **11** and NBu_4Br^a

Entry	Substrate	T (°C)	t (h)	Product	Yield[b] (complex **11**)	Yield[b] (complex **4**)
1		25	40	 **12j**	87%	70%
2		80	24	 **12k**	80%[c]	74%[d]
3		00	24	 **12l**	51%[e]86%[f]	45%[g]
4		100	40	 **12m**	40%[h]	51%[i]

[a] Reaction conditions: 0.5 mol% catalyst, 2 mol% TBAB, 1 atm CO_2. [b] Isolated yield. [c] 13% poly(ether) was detected. [d] 4% poly(ether) was detected. [e] 48% *cis* and 3% *trans* isomers, 38% poly(carbonate) and 9% poly(ether) were detected. [f] 25 °C, 30 atm CO_2; 73% *cis* and 13% *trans* isomers, 8% poly(carbonate) and 5% poly(ether) were detected. [g] 35% *cis* and 10% *trans* isomers, 2% poly(carbonate) and 6% poly(ether) were detected. [h] 50% poly(ether) was detected. [i] 10% poly(ether) was detected.

reactions catalyzed by heterobimetallic complex **11** resulted in higher conversions than those of homodinuclear complex **4**.

Based on the above-discussed results, a synergism between metal centers is proposed to explain the enhanced activity of the heterobimetallic system (Fig. S24†). The catalytic cycle starts with the coordination of epoxide with one of the rare earth metal centers, followed by the attack of the co-catalyst (NBu_4Br) to cause the ring-opening process.[16] CO_2 may be activated by the zinc center, which is attacked by the alkoxide group resulting from the ring-opening. In addition, the Zn center contributes to stabilizing the resulting carbonate, as has been proved computationally. Finally, an intramolecular nucleophilic substitution leads to cyclization along with the release of the bromide anion.

The catalytic activities of a series of heterobimetallic complexes were compared under identical conditions (Table 6). Upon comparing complexes **5** and **6** bearing the diglycolamine-bridged bis(phenolate) ligand with complexes **B** and **C** bearing the ethanolamine-bridged ligand, the former gave *ca.* 20% higher yields (Table 6, entries 1–4), demonstrating that the extra donor well stabilized the metal centers during the catalytic process. The $Zn(OAc)_2$-bridged complexes **5** and **6** are comparably active as $Zn(OBn)_2$-bridged complexes **9** and **10** (Table 6, entries 1, 2 and 5, 6). Another two hetero-bimetallic complexes **D** and **A** showed inferior activity than complexes **6**, **7**, and **10** (Table 6, entries 7 and 8).

These findings prove that the diglycolamine-bridged bis(phenolate) ligand is a privileged scaffold for highly active heterobimetallic complex construction. Ligands of higher electron densities (Table 6, entries 1, 2 *vs.* 3, 4) resulted in higher yields of cyclic carbonates. Complex **D** is least active in cyclic carbonate synthesis (Table 6, entry 7), while it is highly active in poly(carbonate) synthesis,[10] which may be correlated with the least electron-donating ligand. It is thus tentatively concluded that more electron-donating ligands may be beneficial for cyclic carbonate formation, while less electron-donating ligands may be beneficial for poly(carbonate) formation. The unambiguous correlation between the electronic properties of the ligands and the catalytic performance of the complexes requires further investigation.

Heterobimetallic complexes **5** and **6** have been applied in the copolymerization of cyclohexene oxide and CO_2, which gave moderate yields of 62% and 37%, respectively (Table 7,

Table 6 Comparison of RE–Zn complexes in catalysing the cycloaddition of CO_2 with 1,2-epoxyhexane[a]

Entry	Catalyst	Conversion[b,c] (%)
1	**5 (Sm–Zn)**	67
2	**6 (Nd–Zn)**	73
3	**B (Sm–Zn)**	50
4	**C (Nd–Zn)**	53
5	**9 (Sm–Zn)**	60
6	**10 (Nd–Zn)**	80
7	**D (Nd–Zn)**	50
8	**A (Y–Zn)**	58
9	**7 (Y–Zn)**	79

[a] Reaction conditions: 0.5 mol% catalyst, 1 mol% co-catalyst TBAB, 25 °C, 24 h, 1 atm CO_2 pressure. [b] Determined by ^1H NMR spectroscopy. [c] Selectivity for the cyclic carbonate product were all >99%.

Table 7 Comparison of RE–Zn complexes towards the copolymerization of CO_2 and cyclohexene oxide[a]

Entry	Initiator	Yield[b] (%)	Polycarbonate[c] (%)	M_n ($\times 10^4$)	$Đ^d$
1	**5**	62	99	12.9	2.73
2	**6**	37	99	14.5	8.95
3[e]	**B**	58	59	4.1	8.42
4[e]	**C**	42	59	2.5	8.72

[a] Reaction conditions: $V_{Tol}/V_{CHO} = 1/1$, [initiator]/[CHO] = 1/125, 70 °C, 24 h, 30 bar CO_2 pressure. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. [d] Determined by GPC *versus* polystyrene standards. [e] Data from ref. 8.

entries 1 and 2). Upon comparison with complexes **B** and **C**, complexes **5** and **6** showed better activity for cyclic carbonate synthesis than for copolymerization, which is consistent with the electron properties of ligands (*vide supra*).

Conclusion

In conclusion, a series of homometallic RE metal complexes and heterobimetallic RE–Zn complexes stabilized by multidentate ancillary ligands have been prepared and characterized. In the presence of RE–Zn complexes, the conversion of CO_2 into cyclic carbonates was achieved at room temperature and 1 atm CO_2 pressure in 40–96% yields. Moreover, challenging disubstituted epoxides were also transformed into cyclic carbonates under 1 atm CO_2 pressure at elevated temperatures. The obvious synergistic effect was proved by the enhanced catalytic activity of heterometallic RE–Zn complexes. Further studies on the construction of heterometallic complexes and their catalytic applications are in progress in our laboratory.

Experimental

Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out in a glovebox or using standard Schlenk techniques under argon. The solvents were dried by refluxing with sodium (tetrahydrofuran, toluene, and hexane) or CaH_2 (1,2-dimethoxyethane). The epoxides were dried over CaH_2. All solid starting materials were dried at 50 °C for more than one day under vacuum.

Elemental analyses were recorded using an Elementar Vario EL III Analyzer. The infrared spectra were recorded using a ThermoFisher Nicolet 6700 spectrometer in the 400–4000 cm^{-1} region. The NMR (^1H, ^{13}C, and ^1H Dosy) spectra were recorded using a Bruker Ascend 400 spectrometer or an Agilent DD2-600 spectrometer. The crystal data were collected using a Bruker D8 Venture diffractometer (Mo Kα radiation, λ = 0.71073 Å) at 293 K. Data reduction was accomplished by the Bruker APEX program. The structures were solved by direct methods and refined by a full matrix least-squares technique based on F^2 using the SHELXL program. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically.

Experimental procedure

Synthesis of ligand precursor LH_3.[9a] 2,4-Di-*tert*-butylphenol (44.36 g, 215 mmol, 2.15 eq.), 37% aqueous formaldehyde (17.53 mL, 216 mmol, 2.16 eq.), 2-(2-aminoethoxy)ethanol (10.52 g, 100 mmol, 1.00 eq.) and toluene (200 mL) were added into a 500 mL round-bottomed flask that was equipped with a Dean–Stark trap and reflux condenser. The mixture was heated under reflux overnight which was tracked by TLC (10 : 1 petroleum ether : ethyl acetate). The crude product was purified by column chromatography with petroleum ether and ethyl acetate (60 : 1). The pure product was isolated as a white solid. Yield: 47.74 g, 88%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 2.2 Hz, 2H, ArH), 6.89 (d, J = 2.3 Hz, 2H, ArH), 3.86–3.79 (m, 2H, NCH_2CH_2), 3.74 (s, 4H, NCH_2Ar), 3.66–3.56 (m, 4H, CH_2OCH_2), 2.79–2.68 (m, 2H, CH_2OH), 1.39 (s, 18H, CH_3), 1.27 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 141.4, 136.3, 125.0, 123.8, 121.7 (Ar–C), 73.7, 68.9, 62.0 (NCH_2), 58.0, 52.1, 35.0, 34.3 (OCH_2), 31.8 ($C(CH_3)$), 29.8 ($C(CH_3)$).

General synthetic procedure of dinuclear rare earth metal complexes $RE_2L_2(THF)_n$ (1–4). The ligand precursor LH_3 (1.63 g, 3.00 mmol) was dissolved in dry THF (15 mL). The THF solution (10 mL) of $RECp_3(THF)$ [RE = Y, Yb, Nd, La] (3.00 mmol) was added and the mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure, and a large amount of powder was precipitated by adding hexane (10 mL). The powder was collected and redissolved at 120 °C in a mixture of THF (10 mL) and toluene (8 mL). The dilute solution was concentrated to saturation. After a few weeks, single crystals of the dinuclear complexes (**1–4**) were obtained at about 0 °C.

Yttrium complex Y_2L_2 (1). Yield: 1.69 g, 90%. Anal. calcd for $C_{68}H_{104}N_2O_8Y_2\cdot 3C_7H_8$: C, 69.78; H, 8.42; N, 1.83. Found: C, 69.73; H, 8.43; N, 1.82. ^1H NMR (400 MHz, THF-d_8): δ 7.05–7.01 (m, 4H, ArH), 6.79–6.78 (m, 4H, ArH), 4.18 (s, 4H, $ArCH_2N$), 3.69 (s, 8H, $ArCH_2NCH_2$), 3.45 (s, 8H, CH_2OCH_2), 2.75 (s, 4H, CH_2OH), 1.38 (s, 36H, $C(CH_3)_3$, 1.18 (s, 36H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, THF-d_8): δ 162.2, 135.6, 135.3, 124.9, 123.3 (Ar–C), 75.5 ($ArCH_2N$), 35.5, 34.1 (OCH_2), 32.1 ($C(CH_3)$), 30.6 ($C(CH_3)$). IR (selected absorbances, cm^{-1}): 2896 (–CH_2–), 1475 (–CH_3), 1202 (–C–O–C–), 1167 (–C–N–), 875 (Ar).

Ytterbium complex Yb_2L_2 (2). Yield: 1.75 g, 82%. Anal. calcd for: $C_{68}H_{104}N_2O_8Yb_2\cdot 2C_7H_8$: C, 61.25; H, 7.52; N, 1.74. Found: C, 61.20; H, 7.52; N, 1.73. IR (selected absorbances, cm^{-1}): 2949 (–CH_2–), 2897 (C–H), 1475 (–CH_3), 1368 (–C–O–C–), 1101 (–C–N–), 875 (Ar).

Neodymium complex $Nd_2L_2(THF)_2$ (3). Yield: 1.96 g, 87%. Anal. calcd for: $C_{76}H_{120}N_2O_{10}Nd_2$: C, 60.44; H, 8.01; N, 1.85. Found: C, 60.55; H, 8.06; N, 1.85. IR (selected absorbances, cm^{-1}): 2950 (–CH_2–), 1473 (–CH_3), 1279 (–C–O–C–), 1166 (–C–N–), 877 (Ar).

Lanthanum complex $La_2L_2(THF)_2$ (4). Yield: 2.02 g, 90%. Anal. calcd for $C_{76}H_{120}N_2O_{10}La_2$: C, 60.87; H, 8.07; N, 1.87. Found: C, 60.75; H, 8.15; N, 1.86. ^1H NMR (400 MHz, THF-d_8): δ 7.15 (d, J = 2.6 Hz, 4H, ArH), 6.90 (d, J = 2.8, Hz, 4H, ArH), 4.18 (t, J = 4.7 Hz, 4H, $ArCH_2N$), 4.05 (d, 4H, J = 12.0 Hz, $ArCH_2N$), 3.61–3.59 (m, 8H, CH_2), 3.53 (t, J = 4.4 Hz, 4H, NCH_2CH_2O), 3.27 (t, 4H, J = 5.6 Hz, NCH_2CH_2O), 3.14 (d, J = 12.2 Hz, 4H, OCH_2CH_2O), 2.73 (t, J = 5.1 Hz, 4H, OCH_2CH_2O), 1.77–1.67 (m, 8H, CH_2), 1.47 (s, 36H, $C(CH_3)_3$), 1.27 (s, 36H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, THF-d_8): δ 164.1, 136.4, 135.9, 127.2, 126.1, 124.4 (Ar–C), 78.1, 72.4, 68.8, 66.0 ($ArCH_2N$), 65.0 (NCH_2), 53.1, 36.4, 35.0 (OCH_2), 33.0 ($C(CH_3)$), 31.7 ($C(CH_3)$). IR (selected absorbances, cm^{-1}): 2951 (–CH_2–), 1473 (–CH_3), 1280 (–C–O–C–), 1166 (–C–N–), 876 (Ar).

General synthetic procedure of $Zn(OAc)_2$-bridged heterometallic rare earth metal–zinc complexes (5 and 6). The ligand precursor **LH_3** (0.548 g, 1.00 mmol) was dissolved in dry THF (15 mL). The THF solution (10 mL) of $RECp_3$(THF) [RE = Nd, Sm] (1.00 mmol) was added and the mixture was stirred for 12 h at 50 °C. $Zn(OAc)_2$ (0.092 g, 0.50 mmol) was added into the mixture, which gave a clear solution after a 24 h reaction at 50 °C. The solvent was removed under reduced pressure, and a large amount of powder was precipitated by adding hexane (15 mL). The powder was collected and redissolved in a mixture of THF (3 mL) and hexane (3 mL). After a few days, the crystals of the heterometallic complexes (**5–6**) were obtained at about 0 °C.

Samarium–zinc complex $Sm_2ZnL_2(OAc)_2$ (THF)$_2$ (5). Yield: 0.217 g, 20%. Anal. calcd for: $C_{80}H_{126}N_2O_{14}Sm_2Zn$: C, 56.26; H, 7.55; N, 1.64. Found: C, 57.09; H, 7.42; N, 1.54. IR (selected absorbances, cm^{-1}): 2948 ($-CH_2-$), 2876 ($-CH_2-$), 1565(C=O), 1473 ($-CH_3$), 1201 (–C–O–C–), 1165 (–C–N–), 876 (Ar).

Neodymium–zinc complex $Nd_2ZnL_2(OAc)_2$ (THF)$_2$ (6). Yield: 0.212 g, 25%. Anal. calcd for: $C_{80}H_{126}N_2O_{14}Nd_2Zn$: C, 56.66; H, 7.61; N, 1.65. Found: C, 57.10; H, 7.41; N, 1.70. IR (selected absorbances, cm^{-1}): 2950 ($-CH_2-$), 2866 ($-CH_2-$), 1563(C=O), 1473 ($-CH_3$), 1201 (–C–O–C–), 1166 (–C–N–), 875 (Ar).

General synthetic procedure of $Zn(OBn)_2$-bridged heterometallic rare earth metal–zinc complexes $RE_2ZnL_2(OBn)_2(THF)_2$ (7–11). $ZnEt_2$ (1 M in hexane, 1.50 mmol, 1.50 mL) and $PhCH_2OH$ (1 M in THF, 3.00 mmol, 3.00 mL) were mixed and stirred for 4 h to give a suspension. The mixture of $RECp_3$(THF) [RE = Y, Yb, Sm, Nd, La] (3.00 mmol) and **LH_3** (3.00 mmol) in 20 mL of THF was added into the suspension, which gave a clear solution after 24 h reaction at 50 °C. The solvent was removed under reduced pressure. The resulting solids were dissolved in THF (5 mL) and hexane (8 mL). After the filtration and removal of the solvent, heterometallic complexes **7–11** were obtained.

Yttrium–zinc complex $Y_2ZnL_2(OBn)_2(THF)_2$ (7). Yield: 2.18 g, 87%. Anal. calcd for: $C_{90}H_{134}N_2O_{10}Y_2Zn\cdot 4.5C_4H_{10}O_2$: C, 62.22; H, 8.65; N, 1.34. Found: C, 62.25; H, 8.62; N, 1.34. ^1H NMR (600 MHz, THF-d_8): δ 7.62 (s, 3H, Ar*H*), 7.32–7.28 (m, 4H, Ar*H*), 7.22 (s, 5H, Ar*H*), 7.10 (s, 1H, Ar*H*), 6.91 (s, 3H, Ar*H*), 6.84 (s, 2H, Ar*H*), 5.32 (dd, *J* = 14.5, 55.0 Hz, 4H, PhC*H*$_2$O), 4.36–4.34 (m, 1H, NC*H*$_2$CH$_2$O), 4.22–4.08 (m, 8H, ArC*H*$_2$N), 3.65–3.64 (m, 4H, C*H*$_2$–THF), 3.55–3.50 (m, 3H, NC*H*$_2$CH$_2$O), 3.09 (s, 4H, NCH$_2$C*H*$_2$O), 3.02–2.85 (m, 4H, OC*H*$_2$CH$_2$O), 2.74–2.65 (m, 4H, OCH$_2$C*H*$_2$O), 1.80–1.76 (m, 4H, C*H*$_2$–THF), 1.60–1.56 (m, 18H, C(C*H*$_3$), 1.30–1.19 (m, 54H, C(C*H*$_3$)$_3$). ^{13}C NMR (151 MHz, THF-d_8): δ 161.2, 145.8, 135.8, 135.2, 134.8, 134.6, 127.7, 125.2, 124.4, 124.1, 122.9, 122.7 (Ar–*C*), 74.5, 70.1 (Ar*C*H$_2$N), 67.6, 67.2 (*C*H$_2$O*C*H$_2$), 65.3, 64.4 (N*C*H$_2$CH$_2$), 52.1 (O*C*H$_2$Ar), 34.8, 34.3, 33.4 (*C*H$_2$O), 31.4 (C(*C*H$_3$)), 29.9, 29.0 (*C*(CH$_3$)), 25.4 (*C*H$_2$*C*H$_2$). IR (selected absorbances, cm^{-1}): 2989 ($-CH_2-$), 1602 (C–H(Ph)), 1475 (CH_2), 1301 (–C–O–C–), 1168 (–C–N–), 874 (Ar).

Ytterbium–zinc complex $Yb_2ZnL_2(OBn)_2(THF)_2$ (8). Yield: 2.22 g, 80%. Anal. calcd for: $C_{90}H_{134}N_2O_{10}Yb_2Zn$: C, 58.51; H, 7.31; N, 1.52. Found: C, 58.63; H, 7.37; N, 1.52. IR (selected absorbances, cm^{-1}): 2900 ($-CH_2-$), 1602 (C–H(Ph)), 1475 ($-CH_3$), 1202 (–C–O–C–), 1166 (–C–N–), 876 (Ar).

Samarium–zinc complex $Sm_2ZnL_2(OBn)_2(THF)_2$ (9). 2.08 g, 77%. Anal. calcd for: $C_{90}H_{134}N_2O_{10}Sm_2Zn$: C, 59.98; H, 7.49; N, 1.55. Found: C, 59.97; H, 7.50; N, 1.88. IR (selected absorbances, cm^{-1}): 2900 ($-CH_2-$), 1602 (C–H(Ph)), 1475 ($-CH_3$), 1199 (–C–O–C–), 1166 (–C–N–), 875 (Ar).

Neodymium–zinc complex $Nd_2ZnL_2(OBn)_2(THF)_2$ (10). Yield: 2.05 g, 76%. Anal. calcd for: $C_{90}H_{134}N_2O_{10}Nd_2Zn$: C, 60.39; H, 7.55; N, 1.57. Found: C, 60.59; H, 7.56; N, 1.56. IR (selected absorbances, cm^{-1}): 2900 ($-CH_2-$), 1602 (C–H(Ph)), 1474 ($-CH_3$), 1201 (–C–O–C–), 1166 (–C–N–), 877 (Ar).

Lanthanum–zinc complex $La_2ZnL_2(OBn)_2(THF)_2$ (11). Yield: 2.17 g, 81%. Anal. calcd for: $C_{90}H_{134}N_2O_{10}La_2Zn$: C, 60.76; H, 7.59; N, 1.57. Found: C, 60.83; H, 7.57; N, 1.53. ^1H NMR (600 MHz, THF-d_8): δ 7.60 (s, 4H, Ar*H*) 7.35–7.30 (m, 4H, Ar*H*), 7.25–7.18 (m, 6H, Ar*H*), 6.99 (s, 4H, Ar*H*), 5.33 (s, 4H, PhC*H*$_2$O), 4.20–4.05 (m, 8H, ArC*H*$_2$N), 3.71 (m, 4H, C*H*$_2$–THF), 3.56 (s, 4H, NC*H*$_2$C*H*$_2$O), 3.10 (s, 8H, C*H*$_2$OC*H*$_2$), 2.74 (s, 4H, C*H*$_2$O), 1.87–1.80 (m, 4H, C*H*$_2$–THF), 1.58 (s, 8H, C(C*H*$_3$)$_3$), 1.35 (s, 56H, C(C*H*$_3$)$_3$). ^{13}C NMR (151 MHz, THF-d_8): δ 164.4, 163.8, 147.5, 136.6, 129.6, 127.5, 126.8, 126.4, 124.8 (Ar*C*), 77.5, 72.7 (Ar*C*H$_2$N), 69.1 (*C*H$_2$O*C*H$_2$), 67.2, 66.3 (N*C*H$_2$CH$_2$), 52.4 (Ar*C*H$_2$O), 36.6, 36.4, 35.3 (*C*H$_2$O), 33.4 (C(*C*H$_3$)), 31.6, 31.1 (*C*(CH$_3$)), 27.2 (*C*H$_2$*C*H$_2$). IR (selected absorbances, cm^{-1}): 2875 ($-CH_2-$), 1602 (C–H(Ph)), 1473 ($-CH_3$), 1205 (–C–O–C–), 1167 (–C–N–), 878 (Ar).

General procedure for the reaction of CO_2 with epoxides. Epoxide (10 mmol), catalyst (0.05 mmol), and Bu_4NBr (tetrabutylammonium bromide) (0.2 mmol) were placed in a 5 mL flask. A balloon filled with CO_2 was connected to the flask, and the mixture was stirred at 25 °C for 24 h. The conversion of an epoxide to a cyclic carbonate was determined by ^1H NMR spectroscopy. The product was purified by flash chromatography (hexane and ethylene acetate). Cyclic carbonates **12a–l** are known compounds, and spectroscopic data are consistent with those reported in the literature.[3–5]

4-Butyl-1,3-dioxolan-2-one:.[5d] ^1H NMR (400 MHz, $CDCl_3$) δ 4.72–4.64 (m, 1H, C*H*O), 4.50 (t, *J* = 8.8 Hz, 1H, OC*H*$_2$), 4.05 (t, *J* = 8.2 Hz, 1H, OC*H*$_2$), 1.86–1.76 (m, 1H, C*H*$_2$), 1.70–1.63 (m, 1H, C*H*$_2$), 1.37–1.29 (m, 4H, C*H*$_2$), 0.91 (t, *J* = 6.8 Hz, 3H, C*H*$_3$).

*4-Phenyl-1,3-dioxolan-2-one (**12b**).*[5d] ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.44 (m, 3H, Ar*H*), 7.38–7.36 (m, 2H, Ar*H*), 5.68 (t, *J* = 8.5 Hz, 1H, OC*H*$_2$), 4.80 (t, *J* = 8.7 Hz, 1H, OC*H*$_2$), 4.35 (t, *J* = 8.6 Hz, 1H, OC*H*).

*4-(4-Bromophenyl)-1,3-dioxolan-2-one (**12c**).*[5m] ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.23 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.62 (t, *J* = 8.5 Hz, 1H, OC*H*), 4.78 (t, *J* = 7.5 Hz, 1H, OC*H*$_2$), 4.28 (t, *J* = 9.3 Hz, 1H, OC*H*$_2$).

*4-(4-Chlorophenyl)-1,3-dioxolan-2-one (**12d**).*[5d] ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.29 (d, *J* = 8.5 Hz, 2H, Ar*H*), 5.64 (t, *J* = 8.7 Hz, 1H, OC*H*), 4.78 (t, *J* = 8.6 Hz, 1H, OC*H*$_2$), 4.28 (t, *J* = 8.6 Hz, 1H, OC*H*$_2$).

*4-(Methoxymethyl)-1,3-dioxolan-2-one (**12e**).*[5d] ^1H NMR (400 MHz, $CDCl_3$) δ 4.79–4.76 (m, 1H, OC*H*), 4.45 (t, *J* = 8.3 Hz, 1H, OC*H*$_2$), 4.32–4.29 (m, 1H, OC*H*$_2$), 3.61–3.48 (m, 2H, OC*H*$_2$O), 3.35 (s, 3H, OC*H*$_3$).

*4-(Phenoxymethyl)-1,3-dioxolan-2-one (**12f**).*[5n] ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.3 Hz, 2H, Ar*H*), 7.00 (t, *J* = 7.0

Hz, 1H, Ar*H*), 6.90 (d, *J* = 7.7 Hz, 2H, Ar*H*), 5.03–5.02 (m, 1H, OC*H*), 4.64–4.54 (m, 2H, OC*H*$_2$), 4.26–4.13 (m, 2H, OC*H*$_2$).

*(2-Oxo-1,3-dioxolan-4-yl)-methyl 4-(tert-butyl)benzoate (**12g**).*[17] ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.46 (d, *J* = 8.7, 2H, Ar*H*), 5.03–5.00 (m, 1H, OC*H*), 4.62–4.60 (m, 1H, OC*H*$_2$), 4.58–4.54 (m, 2H, OC*H*$_2$), 4.51–4.39 (m, 1H, OC*H*$_2$), 1.32 (s, 9H, C(C*H*$_3$)$_3$).

*4-(Propoxymethyl)-1,3-dioxolan-2-one (**12h**).*[18] ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.82–4.77 (m, 1H, OC*H*), 4.48 (t, *J* = 8.4, 1H, OC*H*$_2$), 4.39–4.36 (m, 1H, OC*H*$_2$), 3.68–3.60 (m, 2H, C*H*$_2$O), 3.57–3.48 (m, 2H, OCH$_2$), 1.56–1.51 (m, 2H, C*H*$_2$CH$_2$), 1.37–1.32 (m, 2H, CH$_2$C*H*$_2$), 0.90 (t, *J* = 7.1 Hz, 3H, C*H*$_3$).

*4-((Allyloxy)methyl)-1,3-dioxolan-2-one (**12i**).*[5d] ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.92–5.82 (m, 1H, C*H*═CH$_2$), 5.31–5.21 (m, 2H, CH═C*H*$_2$), 4.82–4.80 (m, 1H, OC*H*), 4.50 (t, *J* = 8.4 Hz, 1H, OC*H*$_2$), 4.48–4.38 (m, 1H, OC*H*$_2$), 4.11–4.10 (m, 2H, OC*H*$_2$), 3.71–3.60(m, 2H, OC*H*$_2$).

*4,4-Dimethyl-1,3-dioxolan-2-one (**12j**).*[5d] ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.15 (s, 2H, OC*H*$_2$), 1.53 (s, 6H, C*H*$_3$).

*cis-Tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one (**12k**).*[5d] ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.11 (s, 2H, OC*H*$_2$), 2.29–2.19 (m, 2H, C*H*$_2$), 1.87–1.73 (m, 2H, C*H*$_2$), 1.71–1.68 (m, 2H, C*H*$_2$).

*cis-Hexahydrobenzo[d][1,3]dioxol-2-one (**12l**).*[5d] ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.72–4.68 (m, 2H, C*H*O), 1.95–1.84 (m, 4H, C*H*$_2$), 1.68–1.56 (m, 2H, C*H*$_2$), 1.48–1.40 (m, 2H, C*H*$_2$).

*cis-5-Vinylhexahydrobenzo[d][1,3]dioxol-2-one (**12m**).*[5d] ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.75–5.66 (m, 1H, C*H*═CH$_2$), 5.06–4.99 (m, 2H, C*H*), 4.80–4.61 (m, 2H, CH═C*H*$_2$), 2.32–2.16 (m, 2H, C*H*$_2$), 1.65–1.51(m, 2H, C*H*$_2$), 1.41–1.15(m, 2H, C*H*$_2$), 1.11–1.24 (m, 1H, C*H*).

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) R. A. Sheldon, Green and sustainable manufacture of chemicals from biomass: state of the art, *Green Chem.*, 2014, **16**, 950; (*b*) M. Aresta, A. Dibenedetto and A. Angelini, Catalysis for the valorization of exhaust carbon: from CO$_2$ to chemicals, materials, and fuels. Technological use of CO$_2$, *Chem. Rev.*, 2014, **114**, 1709; (*c*) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, Transformation of carbon dioxide with homogeneous transition-metal catalysts: a molecular solution to a global challenge, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510; (*d*) C. Maeda, Y. Miyazaki and T. Ema, Recent progress in catalytic conversions of carbon dioxide, *Catal. Sci. Technol.*, 2014, **4**, 1482; (*e*) A. Otto, T. Grube, S. Schiebahn and D. Stolten, Closing the loop: captured CO$_2$ as a feedstock in the chemical industry, *Energy Environ. Sci.*, 2015, **8**, 3283; (*f*) K. Sekine and T. Yamada, Silver-catalyzed carboxylation, *Chem. Soc. Rev.*, 2016, **45**, 4524; (*g*) T. Sakakura, J. C. Choi and H. Yasuda, Transformation of carbon dioxide, *Chem. Rev.*, 2007, **107**, 2365; (*h*) G. Fiorani, W. Guo and A. W. Kleij, Sustainable conversion of carbon dioxide: the advent of organocatalysis, *Green Chem.*, 2015, **17**, 1375; (*i*) 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; (*j*) R. R. Shaikh, S. Pornpraprom and V. D'Elia, *ACS Catal.*, 2018, **8**, 419.

2 (*a*) B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, Organic carbonates as solvents in synthesis and catalysis, *Chem. Rev.*, 2010, **110**, 4554; (*b*) C. Beattie, M. North and P. Villuendas, Proline-catalysed amination reactions in cyclic carbonate solvents, *Molecules*, 2011, **16**, 3420; (*c*) K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, *Chem. Rev.*, 2004, **104**, 4303; (*d*) V. Besse, F. Camara, C. Voirin, R. Auvergne, S. Caillol and B. Boutevin, Synthesis and applications of unsaturated cyclocarbonates, *Polym. Chem.*, 2013, **4**, 4545; (*e*) W. S. Guo, J. Gýnzalez-Fabra, N. A. G. Bandeira, C. Bo and A. W. Kleij, A metal–free synthesis of N–aryl carbamates under ambient conditions, *Angew. Chem., Int. Ed.*, 2015, **54**, 11686.

3 (*a*) B. H. Xu, J. Q. Wang, J. Sun, Y. Huang, J. P. Zhang, X. P. Zhang and S. J. Zhang, Fixation of CO$_2$ into cyclic carbonates catalyzed by ionic liquids: a multi-scale approach, *Green Chem.*, 2015, **17**, 108; (*b*) A. Tlili, E. Blondiaux, X. Frogneux and T. Cantat, Reductive functionalization of CO$_2$ with amines: an entry to formamide, formamidine and methylamine derivatives, *Green Chem.*, 2015, **17**, 157; (*c*) X. B. Lu and D. J. Darensbourg, Cobalt catalysts for the coupling of CO$_2$ and epoxides to provide polycarbonates and cyclic carbonates, *Chem. Soc. Rev.*, 2012, **41**, 1462; (*d*) J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings, *Green Chem.*, 2015, **17**, 1966; (*e*) C. Martín, G. Fiorani and A. W. Kleij, Recent advances in the catalytic preparation of cyclic organic carbonates, *ACS Catal.*, 2015, **5**, 1353; (*f*) P. P. Pescarmona and M. Taherimehr, Challenges in the catalytic synthesis of cyclic and polymeric carbonates from epoxides and CO$_2$, *Catal. Sci. Technol.*, 2012, **2**, 2169; (*g*) M. North and R. Pasquale, Mechanism of cyclic carbonate synthesis from epoxides and CO$_2$, *Angew. Chem., Int. Ed.*, 2009, **48**, 2946; (*h*) R. Zhang, L. Wang, C. Xu, H. Yang, W. Chen, G. Gao and W. Li, Anion-induced 3d-4f lumines-

cent coordination clusters: structural characteristics and chemical fixation of CO_2 under mild conditions, *Dalton Trans.*, 2018, **47**, 7159; (*i*) A. Monassier, V. D'Elia, M. Cokoja, H. Dong, J. D. A. Pelletier, J. M. Basset and F. E. Kühn, Synthesis of cyclic carbonates from epoxides and CO_2 under mild conditions using a simple, highly efficient Niobium-based catalyst, *ChemCatChem*, 2013, **5**, 1321; (*j*) M. Cozzolino, K. Press, M. Mazzeo and M. Lamberti, Carbon dioxide/epoxide reactions catalyzed by bimetallic salalen aluminum complexes, *ChemCatChem*, 2016, **8**, 455; (*k*) H. Wang, Z. Zhang, H. Wang, L. Guo and L. Li, Metal β-diketonate complexes as highly efficient catalysts for chemical fixation of CO_2 into cyclic carbonates under mild conditions, *Dalton Trans.*, 2019, **48**, 15970; (*l*) O. Sodpiban, S. D. Gobbo, S. Barman, V. Aomchad, P. Kidkhunthod, S. Ould-Chikh, A. Poater, V. D'Elia and J. M. Basset, Synthesis of well-defined yttrium-based Lewis acids by capturing a reaction intermediate and catalytic application for cycloaddition of CO_2 to epoxides under atmospheric pressure, *Catal. Sci. Technol.*, 2019, **9**, 6152.

4 (*a*) C. Maeda, Y. Miyazaki and T. Ema, Recent progress in catalytic conversions of carbon dioxide, *Catal. Sci. Technol.*, 2014, **4**, 1482; (*b*) A. Otto, T. Grube, S. Schiebahn and D. Stolten, Closing the loop: captured CO_2 as a feedstock in the chemical industry, *Energy Environ. Sci.*, 2015, **8**, 3283; (*c*) A. Banerjee, G. R. Dick, T. Yoshino and M. W. Kanan, Carbon dioxide utilization via carbonate-promoted C-H carboxylation, *Nature*, 2016, **531**, 215; (*d*) G. Centi and S. Perathoner, Opportunities and prospects in the chemical recycling of carbon dioxide to fuels, *Catal. Today*, 2009, **148**, 191; (*e*) A. Cai, W. Guo, L. Martínez-Rodríguez and A. W. Kleij, Palladium-catalyzed regio- and enantioselective synthesis of allylic amines featuring tetrasubstituted tertiary carbons, *J. Am. Chem. Soc.*, 2016, **138**, 14194; (*f*) L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, Isocyanate-free routes to polyurethanes and poly (hydroxy urethane)s, *Chem. Rev.*, 2015, **115**, 12407; (*g*) T. Jose, S. Cañellas, M. A. Pericàs and A. W. Kleij, Polystyrene-supported bifunctional resorcinarenes as cheap, metal-free and recyclable catalysts for epoxide/CO_2 coupling reactions, *Green Chem.*, 2017, **19**, 5488; (*h*) M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing and C. Detrembleur, Organocatalyzed coupling of carbon dioxide with epoxides for the synthesis of cyclic carbonates: catalyst design and mechanistic studies, *Catal. Sci. Technol.*, 2017, **7**, 2651; (*i*) C. Kohrt and T. Werner, Recyclable bifunctional polystyrene and silica gel-supported organocatalyst for the coupling of CO_2 with epoxides, *ChemSusChem*, 2015, **8**, 2031; (*j*) H. Buettner, J. Steinbauer and T. Werner, Synthesis of cyclic carbonates from epoxides and carbon dioxide by using bifunctional one-component phosphorus-based organocatalysts, *ChemSusChem*, 2015, **8**, 2655; (*k*) X. Wu, C. Chen, Z. Guo, M. North and A. C. Whitwood, Metal- and halide-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide, *ACS Catal.*, 2019, **9**, 1895; (*l*) Y. D. Li, D. X. Cui, J. C. Zhu, P. Huang, Z. Tian, Y. Y. Jia and P. A. Wang, Bifunctional phase-transfer catalysts for fixation of CO_2 with epoxides under ambient pressure, *Green Chem.*, 2019, **21**, 5231; (*m*) Á. Mesías-Salazar, J. Martínez, R. S. Rojas, F. Carrillo-Hermosilla, A. Ramos, R. Fernández-Galán and A. Antiñolo, Aromatic guanidines as highly active binary catalytic systems for the fixation of CO_2 into cyclic carbonates under mild conditions, *Catal. Sci. Technol.*, 2019, **9**, 3879.

5 (*a*) W. Clegg, R. W. Harrington, M. North and R. Pasquale, Cyclic carbonate synthesis catalysed by bimetallic aluminium-salen complexes, *Chem. – Eur. J.*, 2010, **16**, 6828; (*b*) J. Meléndez, M. North and R. Pasquale, Synthesis of cyclic carbonates from atmospheric pressure carbon dioxide using exceptionally active aluminium(salen) complexes as catalysts, *Eur. J. Inorg. Chem.*, 2007, **21**, 3323; (*c*) M. North and C. Young, Bimetallic aluminium(acen) complexes as catalysts for the synthesis of cyclic carbonates from carbon dioxide and epoxides, *Catal. Sci. Technol.*, 2011, **1**, 93; (*d*) M. North and C. Young, Reducing the cost of production of bimetallic aluminium catalysts for the synthesis of cyclic carbonates, *ChemSusChem*, 2011, **4**, 1685; (*e*) C. Beattie, M. North, P. Villuendas and C. Young, 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; (*f*) J. A. 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; (*g*) A. Buchard, M. R. Kember, K. G. Sandemanb and C. K. Williams, A bimetallic iron(III) catalyst for CO_2/epoxide coupling, *Chem. Commun.*, 2011, **47**, 212; (*h*) S. F. Yin and S. Shimada, Synthesis and structure of bismuth compounds bearing a sulfur-bridged bis(phenolato) ligand and their catalytic application to the solvent-free synthesis of propylene carbonate from CO_2 and propylene oxide, *Chem. Commun.*, 2009, **9**, 1136; (*i*) Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda and K. Mashima, Efficient cyclic carbonate synthesis catalyzed by zinc cluster systems under mild conditions, *Catal. Sci. Technol.*, 2012, **2**, 509; (*j*) L. Wang, C. Xu, Q. Han, X. Tang, P. Zhou, R. Zhang, G. Gao, B. Xu, W. Qin and W. Liu, Ambient chemical fixation of CO_2 using a highly efficient heterometallic helicate catalyst system, *Chem. Commun.*, 2018, **54**, 2212; (*k*) G. Bresciani, M. Bortoluzzi, F. Marchetti and G. Pampalon, Iron(III) N,N- dialkylcarbamate-catalyzed formation of cyclic carbonates from CO_2 and epoxides under ambient conditions by dynamic CO_2 trapping as carbamato ligands, *ChemSusChem*, 2018, **11**, 2737; (*l*) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North and R. S. Rojas, Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates, *ChemCatChem*, 2018, **10**, 2271; (*m*) J. Steinbauer, A. Spannenberg and T. Werner, An in *situ* formed Ca^{2+}-crown ether complex and its use in CO_2-fixation reactions with terminal and internal epoxides, *Green*

Chem., 2017, **19**, 3769; (*n*) H. B. Vignesh and K. Muralidharan, Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl) iminomethyl}pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis, *Dalton Trans.*, 2013, **42**, 1238; (*o*) Y. Chen, P. Xu, M. Arai and J. Sun, Cycloaddition of carbon dioxide to epoxides for the synthesis of cyclic carbonates with a mixed catalyst of layered double hydroxide and tetrabutylammonium bromide at ambient temperature, *Adv. Synth. Catal.*, 2019, **361**, 335; (*p*) L. He, K. J. Nath and Q. Lin, Robust multivariate metal-porphyrin frameworks for efficient ambient fixation of CO_2 to cyclic carbonates, *Chem. Commun.*, 2019, **55**, 412; (*q*) C. K. Ng, R. W. Toh, T. T. Lin, H. K. Luo, T. S. A. Hor and J. Wu, Metal-salen molecular cages as efficient and recyclable heterogeneous catalysts for cycloaddition of CO_2 with epoxides under ambient conditions, *Chem. Sci.*, 2019, **10**, 1549; (*r*) P. Yingcharoen, C. Kongtes, S. Arayachukiat, K. Suvarnapunya, S. V. C. Vummaleti, S. Wannakao, L. Cavallo, A. Poater and V. D'Elia, Assessing the pK_a -dependent activity of hydroxyl hydrogen bond donors in the organocatalyzed cycloaddition of carbon dioxide to epoxides: experimental and theoretical study, *Adv. Synth. Catal.*, 2019, **361**, 366; (*s*) N. Liu, Y. F. Xie, C. Wang, S. J. Li, D. Wei, M. Li and B. Dai, Cooperative multifunctional organocatalysts for ambient conversion of carbon dioxide into cyclic carbonates, *ACS Catal.*, 2018, **8**, 9945; (*t*) Y. Kim, K. Hyun, D. Ahn, R. Kim, M. H. Park and Y. Kim, Efficient aluminum catalysts for the chemical conversion of CO_2 into cyclic carbonates at room temperature and atmospheric CO_2 pressure, *ChemSusChem*, 2019, **12**, 4211.

6 (*a*) L. Wang, R. Zhang, Q. Han, C. Xu, W. Chen, H. Yang, G. Gao, W. Qin and W. Liu, Amide-functionalized heterometallic helicate cages as highly efficient catalysts for CO_2 conversion under mild conditions, *Green Chem.*, 2018, **20**, 5311; (*b*) G. Wang, C. Xu, L. Wang and W. Liu, Highly efficient 3d/4d-4f coordination polymer catalysts for carbon dioxide fixation into cyclic carbonates, *Dalton Trans.*, 2018, **47**, 12711.

7 L. Y. Qu, I. Rosal, Q. Y. Li, Y. R. Wang, D. Yuan, Y. M. Yao and L. Maron, Efficient CO_2 transformation under ambient condition by heterobimetallic rare earth complexes: experimental and computational evidences of a synergistic effect, *J. CO_2 Util.*, 2019, **33**, 413.

8 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 CO_2 and epoxides, *Inorg. Chem.*, 2019, **58**, 8775.

9 (*a*) J. Weil, R. T. Mathers and Y. D. Y. L. Getzler, Lactide cyclopolymerization by an alumatrane-inspired catalyst, *Macromolecules*, 2012, **45**, 1118; (*b*) H. Ouyang, K. Nie, D. Yuan, Y. Zhang, D. M. Cui and Y. M. Yao, A convenient method to prepare random LA/CL copolymers from poly(L-lactide) and ε-caprolactone, *Sci. China: Chem.*, 2018, **61**, 708; (*c*) Q. Sun, P. Chen, Y. Wang, Y. Luo, D. Yuan and Y. M. Yao, Addition of C-H bonds of pyridine derivatives to alkenes catalyzed by zirconium complexes bearing amine-bridged bis-(phenolato) ligands, *Inorg. Chem.*, 2018, **57**, 11788.

10 J. Qin, B. Xu, Y. Zhang, D. Yuan and Y. M. Yao, Cooperative rare earth metal-zinc based heterometallic catalysts for copolymerization of CO_2 and cyclohexene oxide, *Green Chem.*, 2016, **18**, 4270.

11 (*a*) B. Antalek, Using pulsed gradient spin echo NMR for chemical mixture analysis: How to obtain optimum results, *Concepts Magn. Reson.*, 2002, **14**, 225; (*b*) K. L. Kondo and P. Maris, Diffusion and scaling behavior of polymer-surfactant aggregates, *Phys. Rev. Lett.*, 1995, **74**, 3624; (*c*) R. Evans, Z. Deng, A. K. Rogerson, A. S. McLachlan, J. J. Richards, M. Nilsson and G. A. Morris, Quantitative interpretation of diffusion-ordered NMR Spectra: can we rationalize small molecule diffusion coefficients, *Angew. Chem., Int. Ed.*, 2013, **52**, 3199; (*d*) W. Li, G. Kagan, H. Yang, C. Cai, R. Hopson, D. A. Sweigart and P. G. Williard, Physically separated references for diffusion coefficient-formula weight (D-FW) analysis of diffusion-ordered NMR spectroscopy (DOSY) in water, *Org. Lett.*, 2010, **12**, 2698; (*e*) L. Wang, W. Amelung and S. Willbold, Diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY-NMR): a novel tool for identification of phosphorus compounds in soil extracts, *Environ. Sci. Technol.*, 2017, **51**, 13256; (*f*) P. Garca-lvarez, R. E. Mulvey and J. A. Parkinson, "$LiZn(TMP)_3$", a zincate or a turbo–lithium amide reagent? DOSY NMR spectroscopic evidence, *Angew. Chem., Int. Ed.*, 2011, **50**, 9668.

12 The average crystalline radius between a maximum value $R_{\max} = 13.1$ Å, which corresponds to the longest distance from the centroid of the molecule, and a minimum value $R_{\min} = \sqrt[3]{\frac{3V}{4\pi}} = 10.8\,\mathring{A}$ derived from the molecular volume $V = 4816$ $\mathring{A}^3$.

13 (*a*) C. Diebold, P. Mobian, C. Huguenard, L. Allouche and M. Henry, Spontaneous symmetry breaking during self-assembly of a double stranded biphenolate-based Ti(IV)-helicate, *Inorg. Chem.*, 2010, **49**, 6369; (*b*) J. C. Bruyere, D. Specklin, C. Gourlaouen, R. Lapenta, L. F. Veiros, A. Grassi, S. Milione, L. Ruhlmann, C. Boudon and S. Dagorne, Cyclic(alkyl)(amino) carbene (CAAC)-supported Zn alkyls: synthesis, structure and reactivity in hydrosilylation catalysis, *Chem. – Eur. J.*, 2019, **25**, 8061.

14 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.

15 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, High activity and switchable selectivity in the synthesis of cyclic and polymeric cyclohexene carbonates with iron amino triphenolate catalysts, *Green Chem.*, 2013, **15**, 3083.

16 (*a*) X. D. Lang, Y. C. Yu and L. N. He, Zn-salen complexes with multiple hydrogen bonding donor and protic ammonium bromide: bifunctional catalysts for CO_2 fixation with epoxides at atmospheric pressure, *J. Mol. Catal. A: Chem.*, 2016, **420**, 208; (*b*) P. Patel, B. Parmar, R. I. Kureshy, N. H. Khan and E. Suresh, Amine-functionalized Zn(II) MOF as an efficient multifunctional catalyst for CO_2 utilization and sulfoxidation reaction, *Dalton Trans.*, 2018, **47**, 8041; (*c*) F. Castro-Gómez, G. Salassa, A. W. Kleij and C. Bo, A DFT study on the mechanism of the cycloaddition reaction of CO_2 to epoxides catalyzed by Zn (salphen) complexes, *Chem. – Eur. J.*, 2013, **19**, 6289; (*d*) Y. Xie, T. T. Wang, R. X. Yang, N. Y. Huang, K. Zou and W. Q. Deng, Efficient fixation of CO_2 by a zinc-coordinated conjugated microporous polymer, *ChemSusChem*, 2014, **7**, 2110; (*e*) 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.

17 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 CO_2 and epoxides at atmospheric pressure, *Inorg. Chem.*, 2017, **56**, 4568.

18 S. Bhunia, R. A. Molla, V. Kumari, S. M. Islam and A. Bhaumik, Zn(II) assisted synthesis of porous salen as an efficient heterogeneous scaffold for capture and conversion of CO_2, *Chem. Commun.*, 2015, **51**, 15732.