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Catalytic production of cyclic carbonates mediated by lanthanide phenolates under mild conditions;

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Readily available lanthanide complexes stabilized by a bridged poly(phenolate) ligand have been used for the first time as efficient catalysts for the insertion of CO_2 into epoxides to generate cyclic carbonates with high activity, high selectivity, and a wide substrate scope under mild conditions.

Carbon dioxide (CO_2) is an abundant, non-toxic, and renewable C_1 building block in synthetic chemistry, and chemical fixation of CO₂ has received considerable attention as it is consistent with the requirement of green chemistry and sustainability.¹ Among all methods to transform CO₂, the coupling with epoxides (Scheme 1) has attracted much interest due to its 100% atom efficiency. Moreover, the resulting cyclic carbonates have found wide applications as excellent aprotic polar solvents, 2^{2a} fine chemical intermediates (e.g., to prepare diols and methanol)^{2b-d} and valuable raw materials to produce polycarbonates which are useful as engineering thermoplastics in sheets, food packings and adhesives.^{2e} To date, a variety of promising catalysts, especially organometallic complexes, have been studied extensively to catalyze this transformation.³ Among them, transition metal⁴ (e.g., Zn, Cr, Co, and Fe) and main-group metal⁵ (e.g., Al) complexes have been widely reported. However, most catalysts suffer from some limitations such as requiring harsh reaction conditions and displaying narrow substrate scopes. 3b,c,4c,e Therefore, it is still a challenge to develop catalytic systems which can conduct this transformation under mild conditions (e.g., ideally atmospheric pressure) with high efficiency (at low catalyst loadings) for a broad range of substrates (especially for internal epoxides).

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Scheme 1 Synthesis of cyclic carbonates from epoxides and CO₂.

Recently, important progress has been achieved in this area. North *et al.* reported bimetallic aluminium–Salen complexes which catalyzed the cycloaddition of CO_2 with monosubstituted epoxides at atmospheric pressure with 2.5 mol% catalyst loading to give 34–98% yields.^{5b,c} Kleij *et al.* reported an aluminum complex stabilized by an amino bridged triphenolate ligand, which catalyzed this transformation for both mono- and disubstituted epoxides with 0.05–0.1% catalyst loading at 10 bar CO_2 pressure to give 40–99% vields.^{5g}

Lanthanide metals are oxyphilic, and many of their complexes possess unusually high Lewis acidity, properties which are expected to benefit the activation of epoxides and the subsequent coupling with CO2. 3c,4c,5g However, lanthanide-based complexes have seldom been applied in this area. To the best of our knowledge, only two examples have been reported involving simple lanthanide salts SmOCl and Sc(OTf)₂,⁶ which required either supercritical CO_2^{6a} or 20 bar CO₂ at 120 °C.^{6b} Since ligands largely influence the catalytic properties of lanthanide complexes, the introduction of a suitable ligand is expected to be an efficient method to improve their catalytic performance. A bridged poly(phenolate) ligand with multiple coordination sites will stabilize the electrophilic lanthanide centre, and may also give rise to complexes with enhanced catalytic activities. Hence, we developed four new lanthanide complexes bearing a bridged tetra(phenolate) ligand, which were found to be efficient in catalysing the coupling reaction of CO₂ to epoxides with high activity, high selectivity, and a wide substrate scope under relatively mild conditions.

The ligand precursor ethylenediamine-bridged tetra(phenol) (LH₄) was easily prepared according to a literature method.⁷ Reactions of LH₄ with Ln(C₅H₅)₃(THF) (Ln = Yb, Y, Sm, Nd) in THF for 4 hours at 25 °C afforded the corresponding lanthanide complexes

^b The Institute of Low Carbon Economy, Suzhou 215123, People's Republic of China † Electronic supplementary information (ESI) available: An initial TOF study, the experimental section, copies of ¹H NMR spectra of cyclic carbonate products, variable-temperature ¹H NMR spectra of complex 2, and crystallographic data for complexes 1–4, and solid state structures of complexes 1–4. CCDC 977124-977127. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc02065k



1–4 [Ln = Yb(1), Y(2), Sm(3), Nd(4)] in good yields (75–80%) (Scheme 2). Solid state structures of complexes **1–4** (ESI^{\dagger}) reveal that complexes **1** and **2** are isostructural, in which the central metal ions are six-coordinated with five donors from the ligand as well as one oxygen atom from THF with one pendent phenol moiety. However, for complexes **3** and **4** with larger ionic radii, the oxygen atom of phenol is bound to the lanthanide centres.

The ¹H NMR spectrum of diamagnetic yttrium complex 2 recorded at 25 °C shows only broad signals. At temperature lower than -10 °C, splitting of the broad signals occurred as indicated by variable-temperature ¹H NMR spectra, suggesting a certain degree of fluctionality of this system (ESI[†]).

The cycloaddition of CO_2 to propylene oxide was first examined using 0.2 mol% of 1–4 and 0.4 mol% of NBu₄I as a co-catalyst under

Table 1Catalytic synthesis of cyclic carbonate via insertion of CO_2 topropylene oxide (1a) catalysed by complexes $1-4^a$

Entry	Cat.	$T(^{\circ}C)$	$P_{\rm CO_2}$ (bar)	Co-cat.	$\operatorname{Conversion}^{b,c}(\%)$	$\operatorname{TOF}^{d}\left(\mathbf{h}^{-1}\right)$
1	1	85	10	NBu ₄ I	64	320
2	2	85	10	NBu ₄ I	66	330
3	3	85	10	NBu ₄ I	93	465
4	4	85	10	NBu ₄ I	92	460
5	4	70	10	NBu ₄ I	88	440
6	4	55	10	NBu ₄ I	70	350
7	4	30	10	NBu ₄ I	31	155
8	4	85	20	NBu ₄ I	93	465
9	4	85	7	NBu_4I	87	435
10	4	85	7	NBu_4Br	83	415
11	4	85	7	NBu ₄ Cl	64	320
12	4	85	7	NOc ₄ Br	83	415
13	4	85	7	_	0	0
14	—	85	7	NBu ₄ I	7	
15^e	4	85	7	NBu ₄ I	76	380
16^f	4	85	7	NBu ₄ I	92	460
17^g	4	85	7	NBu ₄ I	90	450
18^h	4	85	7	NBu ₄ I	65	1970
19^i	4	85	7	NBu ₄ I	40	4000

 a Reactions conditions: 0.2 mol% catalyst, 0.4 mol% co-catalyst, 1 h. b Determined by $^1\mathrm{H}$ NMR spectroscopy. c Selectivity for the cyclic carbonate product were all >99%. d mol **1a**/mol **4**/h. e 0.2 mol% of NBu₄I. f 0.8 mol% of NBu₄I. g 1.2 mol% of NBu₄I. h 0.033 mol% catalyst and 0.132 mol% of NBu₄I were used. i 0.01 mol% catalyst and 0.04 mol% of NBu₄I were used.

solvent-free conditions. From the results listed in Table 1, it can be seen that cyclic carbonates formed in good to excellent yields and >99% selectivities in the presence of 10 bar CO₂ after 1 h reaction at 85 °C (Table 1, entries 1-4). Moreover, lanthanide complexes 3 and 4 with larger ionic radii showed higher activities (entries 1-4). This can be attributed to the open coordination sphere of the larger lanthanide metal, which facilitates the coordination of the propylene oxide. Reactions at different temperatures revealed that the best result was obtained at 85 °C (entries 4-7). CO₂ at higher pressure led to similar results (entries 4 and 8), whereas lowering the pressure to 7 bar resulted in only 6% drop in yield (entry 9). Further attempts to conduct the reaction at the ideal atmospheric pressure, however, failed, as propylene oxide with a boiling point of 34 °C mainly evaporated into the balloon at 85 °C and did not participate in the coupling reaction. Different co-catalysts have also been tested with NBu₄I being the best performer (entries 9-12). The co-existence of the lanthanide complex and NBu₄I proved to be essential for this transformation, as neither complex 4 nor NBu₄I alone could catalyze this reaction to give satisfactory yields (entries 13 and 14). After screening different loadings of the catalyst as well as the co-catalyst, 0.2 mol% of 4 and 0.8 mol% of NBu₄I proved to be the best combination. Lowering the catalyst loading to 0.01 mol% resulted in a moderate yield of 40% and a good TOF of 4000 (entry 19).

To study the scope of the cycloaddition, a series of monosubstituted terminal epoxides bearing an alkyl, aryl, halogen, alkenyl, hydroxyl, ether, morpholine or ester substituent were tested. Since they all have relatively high boiling points, the reactions were conducted at atmospheric pressure (balloon) under solvent-free conditions. To our delight, all monosubstituted epoxides were commendably converted to the corresponding cyclic carbonates in moderate to excellent yields (60 to 97%) (Table 2, entries 1-9). Notably, substrates containing substituents which might coordinate to the lanthanide centre and deactivate the catalyst (such as 1c, 1f, and 1j) also yielded the corresponding cyclic carbonates in 60-95% yields.^{5g} These results suggest that complex 4 not only had broad functional group toleration but also showed good catalytic performance even under atmospheric pressure. Furthermore, bulky/ internal epoxides, which were generally considered as substrates of low reactivity, 3c,4c-e,5c,g were also tested, and all of them were transformed into the corresponding cyclic carbonates in 66–97% yields at elevated pressure (10 bar CO₂) after prolonged reaction time (entries 10-13). The background reactions without complex 4 ceteris paribus have also been studied for selected substrates including both terminal (1d) and non-terminal (1n) epoxides. The yields dropped by around 60%, which strongly suggests the imperative role of lanthanide complexes to attain good yields (entries 3 and 13). Moreover, for substrate 11 comprised of 78% trans and 22% cis isomers, the corresponding carbonate 21 with trans and cis configurations formed in approximately the same ratio, revealing that the configuration was retained during the transformation (entry 11). Similarly, cis-carbonates 2m and 2n were obtained exclusively from cis-configured internal epoxides 1m and 1n (entries 12 and 13). This finding is consistent with previous reports that the substrate configuration is retained,^{4d,5f} whereas a recent

Table 2 Synthesis of various cyclic carbonates catalysed by complex 4 and $\mathsf{NBu}_4\mathsf{I}^a$

Entry	Substrate	Product	$\operatorname{Yield}^{b,c}(\%)$
1	0Cl 1b	0 0 Cl 2b	95
2		0 0 0 0 0 0	96
3	O _{Ph} 1d	O O Ph 2d	93 (35 ^d)
4	01e	0 0 0 2e	97
5	OOH ^{1f}	O O O O O O O O O S f	60
6	01g	0 0 2g	84
7			85
8	O 1i OPh	O O OPh	95
9	O N 1j		95
10	⁰ ∕∕ 1k	0 0 0 2k	97 ^e
11	0 11 ^r		66 ^{<i>e</i>,<i>g</i>}
12	0 1m	0 0 2m	84 ^{<i>e</i>,<i>h</i>}
13	0 1n	0 0 2n	75 (31 ^{<i>d</i>}) ^{<i>e,h</i>}

^{*a*} Reaction conditions: 0.2 mol% catalyst, 0.8 mol% NBu₄I, 24 h, 1 bar CO_2 (balloon), 85 °C. ^{*b*} Isolated yield. ^{*c*} Selectivity for the cyclic carbonate were all >99%. ^{*d*} Conversions in the absence of 4. ^{*e*} 0.8 mol% NBu₄Br, 45 h, 10 bar CO_2 was used for **1k–n**. ^{*f*} 78% *trans* and 22% *cis* isomers. ^{*g*} 81% *trans* and 19% *cis* isomers. ^{*h*} Only *cis*-carbonate products are formed.

report shows that the stereochemistry can be controlled by the co-catalyst loading and other factors.^{4g}

To further evaluate the Ln-based catalyst 4, the initial TOF which was considered as a measurement for the potential of a catalyst^{5h} was then studied under atmospheric pressure using **1b** as a benchmark substrate. A good initial TOF of 220 h⁻¹ was obtained within 1 h (Table S1, ESI[†]). However, the TOF decreased along with the increase of the conversion, mainly because of the obviously

decreased concentration of the substrate. In addition, reasonable TOF values were obtained for **1c** (180 h⁻¹) and **1e** (175 h⁻¹). Thus, our system achieves good initial TOFs at atmospheric pressure,^{4f,5f} while a much higher initial TOF value of 36 000 h⁻¹ has been reported by Kleij *et al.* under 10 bar CO₂.^{5g}

Overall, complex 4 is among the most active catalysts that catalyze the formation of cyclic carbonates from CO_2 and a broad range of epoxides with a low catalyst loading under relatively low pressure compared with other catalytic systems.³ Both terminal and non-terminal substrates bearing different types of functional groups were transformed into cyclic carbonates in good yields. It is also noteworthy that all substrates were used as received without prior removal of either oxygen or moisture, implying that lanthanide complex 4 is relatively robust. These results strongly suggest that organolanthanide complexes have great potential as catalysts for chemical fixation of CO_2 , which provides some new insights for designing efficient organometallic catalysts in this field. Further studies of these lanthanide complexes on the transformation of CO_2 are in process in our laboratory.

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