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Transformation of Carbon Dioxide into Oxazolidinones and Cyclic Carbonates Catalyzed by Rare-Earth-Metal Phenolates

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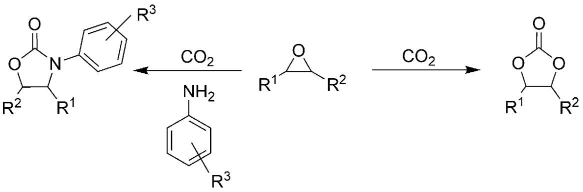
Rare-earth-metal complexes stabilized by amine-bridged tri(phenolato) ligands were developed, and their activities in catalyzing transformations of CO_2 were studied. A series of terminal epoxides and challenging disubstituted epoxides were converted into the respective cyclic carbonates in the presence of CO_2 in yields of 58 to 96%. In addition, these rare-earth-metal complexes also showed good activities in catalyzing three-component reactions of anilines, epoxides, and CO_2, which generated 5-substituted-3-aryl-2-oxazolidines in yields of 48 to 96%, as a useful strategy to construct oxazolidinones.

Carbon dioxide is a main greenhouse gas, and a reduction in CO_2 emission is becoming a global challenge. On the other hand, it is an important C1 building block and can be used in producing fine chemicals and fuels.[1] Fixation and transformation of CO_2 into value-added chemicals contribute to a greener and more sustainable chemical industry and are, thus, gaining increasing interest.

The transformation of CO_2 is, in general, challenging owing to its thermodynamic stable nature. A wide range of catalysts have thus been developed to overcome the kinetic limitations of CO_2 conversion.[2] Among them, rare-earth (RE)-metal complexes are finding more applications in fields including the copolymerization of CO_2 and epoxides[3] and the synthesis of cyclic carbonates[4] and carboxylic acids.[5] The cycloaddition of CO_2 and epoxides is a 100% atom-economic strategy to construct cyclic carbonates (Scheme 1).[6] Our group reported the first example of a rare-earth-metal complex catalyzed reaction of CO_2 with epoxides under mild conditions, which revealed the great potential of rare-earth-metal complexes in promoting transformations of CO_2.[4]



Scheme 1. Reactions of epoxides and CO_2.

Recently, we reported the synthesis of oxazolidinones from isocyanates, which are also heterocumulenes as CO_2, catalyzed by rare-earth-metal complexes.[7] A series of oxazolidinones were prepared under mild conditions from epoxides and isocyanates. Oxazolidinones are important heterocycles and may potentially find applications as HIV-1 protease inhibitors, antibiotics, and antidepressant drugs.[8] However, this strategy requires the handling of toxic isocyanates and is limited to the availability of isocyanates that are synthesized from amines and phosgene. Thus, a method for the preparation of oxazolidinones from more easily available amines that avoids the handling of highly toxic isocyanates will be greatly desirable. Gao et al. reported a three-component synthesis of oxazolidinones from CO_2, ethylene oxide, and amines catalyzed by binary ionic liquids (Scheme 1).[9] This method, however, requires high CO_2 pressures (25 bar; 1 bar = 0.1 MPa) and high temperatures (140 °C). To overcome these limitations, we herein report the application of rare-earth-metal complexes in catalyzing the three-component reaction. Milder reaction conditions [lower CO_2 pressure (10 bar) and temperature (95 °C)] and a broad substrate scope were achieved.

As a continuation of our investigation on rare-earth-metal mediated CO_2 transformations,[4,5] a series of rare-earth-metal complexes stabilized by amine-bridged tri(phenolato) ligands were prepared, and their activities were studied and compared. Complexes **1**–**4** were synthesized according to our previous report (Scheme 2).[7] Given that neodymium complex **3** performed best in catalyzing the synthesis of oxazolidinones from epoxides and isocyanates,[7] analogous complexes **5** and **6** bearing tri(phenolato) ligands with different substituents were synthesized by a similar strategy in yields of 70 and 56%, respectively. The solid-state structure of complex **5** (depicted in Figure S1 in the Supporting Information) was unambiguously confirmed by X-ray diffraction analysis of single crystals obtained from a hexane/THF solution. The neodymium center in complex **5** is coordinated by the phenolato L^2 ligand and three THF molecules, adopting an orthorhombic geometry.

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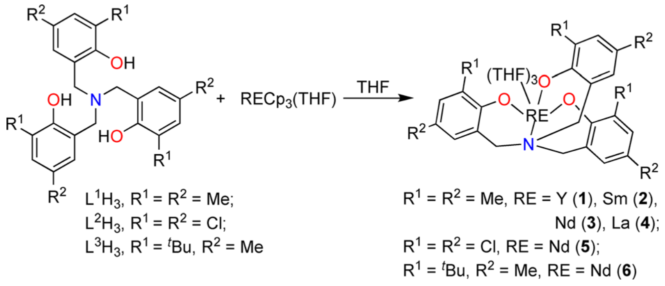
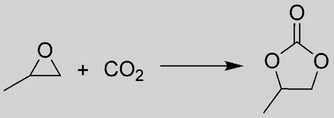


Scheme 2. Synthesis of complexes **1–6**. Cp = η^5-cyclopentadienyl.

Prior to studying the three-component reaction, the activities of complexes **1–6** in catalyzing the two-component reaction between CO_2 and propylene oxide (PO) were assessed, and the results are summarized in Table 1. A preliminary study with complexes **1–4** (0.1 mol%) in the presence of NBu_4I (0.5 mol%) as a co-catalyst under CO_2 (10 bar) pressure at 100 °C generated propylene carbonate in yields of 64 to 82%, and complexes **3** and **4** bearing metal ions of larger ionic radii were the most active (Table 1, entries 1–4). Complex **3** was employed for further condition screening. The reaction was conducted at a lower CO_2 pressure of 6 bar, which, however, led to a significantly lower yield of 69% (Table 1, entry 5). On the other hand, raising the pressure was not helpful in improving the yield (Table 1, entries 6 and 7). Different co-catalysts were tested, and the combination of complex **3** with NBu_4Br proved to be most effective (Table 1, entries 3, 8–10). Consistent with previous reports, halides of good nucleophilic and leaving abilities were crucial in opening of the epoxide ring and subsequent cycloaddition.[10] In comparison, complex **3** or NBu_4Br alone did not lead to good results (Table 1, entries 11 and 12). On the basis of this finding, the ratio of complex **3**/NBu_4Br was examined and 1:6 proved to be optimal (Table 1, entries 3, 13–14).

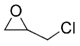
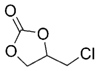
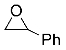
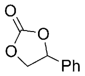
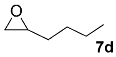
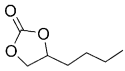
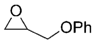
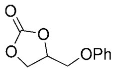
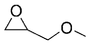
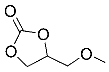
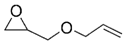
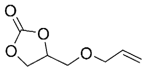
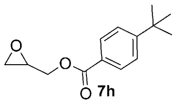
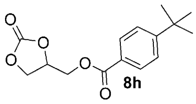
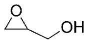
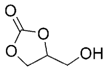
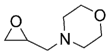
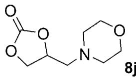
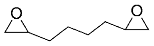
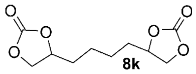
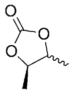
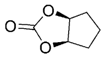
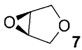
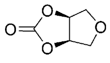
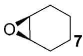
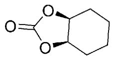
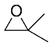
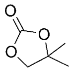
Table 1. Screening of conditions for the reaction of propylene oxide (PO) with CO_2.[a]



Entry	Catalyst	Co-catalyst	P_{CO_2} [bar]	T [°C]	Yield[b,c] [%]
1	**1**	NBu_4I	10	100	74
2	**2**	NBu_4I	10	100	76
3	**3**	NBu_4I	10	100	82
4	**4**	NBu_4I	10	100	80
5	**3**	NBu_4I	6	100	69
6	**3**	NBu_4I	20	100	81
7	**3**	NBu_4I	30	100	83
8	**3**	NBu_4Br	10	100	90
9	**3**	$NOct_4Br$	10	100	85
10	**3**	PPNCl	10	100	77
11	–	NBu_4Br	10	100	13
12	**3**	–	10	100	trace
13[d]	**3**	NBu_4Br	10	100	54
14[e]	**3**	NBu_4Br	10	100	93
15[e]	**5**	NBu_4Br	10	100	98
16[e]	**5**	NBu_4Br	10	85	96
17[f]	**5**	NBu_4Br	10	85	93
18[g]	**5**	NBu_4Br	10	85	88
19[g]	**6**	NBu_4Br	10	85	55
20[f,h]	**5**	NBu_4Br	10	85	80

[a] Reaction conditions: catalyst (0.1 mol%), co-catalyst (0.5 mol%), neat, 1 h. Oct = *n*-octyl. [b] Determined by ^1H NMR spectroscopy. [c] Selectivity for the cyclic carbonate product was > 99%. [d] Catalyst (0.1 mol%), NBu_4Br (0.1 mol%). [e] Catalyst (0.1 mol%), NBu_4Br (0.6 mol%). [f] Catalyst (0.067 mol%), NBu_4Br (0.4 mol%). [g] Catalyst (0.05 mol%), NBu_4Br (0.3 mol%). [h] 0.5 h.

Table 2. Scope of the reaction of epoxides with CO_2.[a]

Entry	Substrate		Product		Yield[b,c] [%]
1		**7b**		**8b**	95
2		**7c**		**8c**	83[d] (46[e])
3		**7d**		**8d**	77[d]
4		**7e**		**8e**	93
5		**7f**		**8f**	96
6		**7g**		**8g**	94 (41[e])
7		**7h**		**8h**	72
8		**7i**		**8i**	58[d]
9		**7j**		**8j**	75[d]
10		**7k**		**8k**	88[f]
11		**7l**		**8l**	72[g,h]
12		**7m**		**8m**	89[g]
13		**7n**		**8n**	83[i]
14		**7o**		**8o**	86[g]
15		**7p**		**8p**	91[g]

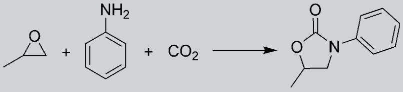
[a] Reaction conditions: complex **5** (0.067 mol%), NBu_4Br (0.4 mol%), neat, 24 h, CO_2 (1 bar), 85 °C. [b] Yield of isolated product. [c] Selectivity for the cyclic carbonate product was > 99%. [d] Complex **5** (0.1 mol%), NBu_4Br (0.6 mol%). [e] In the absence of **5**. [f] Complex **5** (0.1 mol%), NBu_4Br (0.6 mol%), 36 h. [g] CO_2 (10 bar), complex **5** (0.067 mol%), NBu_4Br (0.4 mol%). [h] 6:1 dr. [i] CO_2 (10 bar), complex **5** (0.1 mol%), NBu_4Br (0.6 mol%).

To study the influence of ancillary ligands, complex **5** was tested, and a near-quantitative yield of 98% was obtained (Table 1, entry 15). The presence of electron-withdrawing chloro substituents in ligand L^2 makes the neodymium center in **5** more Lewis acidic, which may result in enhanced activity. Lowering the temperature to 85 °C gave a similar yield (Table 1, entry 16). Evaluation of the catalyst loading revealed that >90% yield was still obtained at a low catalyst loading of 0.067 mol% (Table 1, entries 16–18). For comparison, under identical conditions, the reaction catalyzed by complex **6** led to a significantly lower yield of 55% (Table 1, entry 19). An attempt to conduct the reaction for a shorter time of 0.5 h resulted in a decreased yield of 80% (Table 1, entry 20).

To explore the scope of the epoxides, a series of terminal and disubstituted epoxides were tested, and the results are summarized in Table 2. Notably, under 1 bar of CO_2, terminal epoxides bearing chloro, aryl, alkyl, ether, ester, hydroxy, and morpholinyl substituents were converted expediently into the respective cyclic carbonates in yields ranging from 58 to 96% yields (Table 2, entries 1–9). 1,2,7,8-Diepoxyoctane reacted with CO_2 (2 equiv.) and generated the corresponding dicarbonate in 88% yield (Table 2, entry 10). Reactions of more challenging disubstituted epoxides[6c,10a,11] required a higher pressure of 10 bar, and the respective cyclic carbonates were isolated in good yields of 72 to 91% (Table 2, entries 11–15). It is thus conclusive that rare-earth-metal phenolates show good activities and functional-group tolerance for a broad range of substrates. Similar performances were observed for rare-earth-metal complexes stabilized by ethylenediamine-bridged tetra(phenolato) ligands.[4] For substrate **7l** comprised of 86% *trans* and 14% *cis* isomers, respective cyclic carbonate **8l** comprising 89% *trans* and 11% *cis* configurations was obtained, which suggested that the configurations are retained during the transformation.[10a,12] Carbonates **8m–o** derived from internal *cis*-epoxides **7m–o** were determined to be *cis* configured after comparison with literature data.[12,13] Two background reactions involving the use of **7c** and **7g** were conducted in the absence of complex **5**, and the yields dropped by 37% (Table 2, entry 2) and 53% (Table 2, entry 6), respectively, which is indicative of the imperative role of rare-earth-metal complexes in this reaction.

Inspired by the good performance of rare-earth-metal tri(phenolate) complexes in catalyzing the cycloadditions of epoxides and CO_2, we examined their activities in catalyzing three-component reactions involving PO, aniline, and CO_2 (Table 3). An initial study with complex **3** in the presence of NBu_4Br as co-catalyst formed desired product **10a**, 5-methyl-3-phenyl-2-oxazolidinone, in a trace amount after a reaction time of 18 h, and a large amount of propylene carbonate was formed as a byproduct (Table 3, entry 1). Given that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) works as a CO_2 activator by forming zwitterionic adducts,[14] the addition of DBU was tested, which resulted in an dramatic increase in the yield to 72%

Table 3. Screening of the conditions for the reaction of propylene oxide (PO), aniline, and CO_2.[a]



Entry	Catalyst	Co-catalyst	PO/PhNH$_2$/Catalyst/Co-catalyst	Additive	Additive/PhNH$_2$	*t* [h]	Yield[b] [%]
1	**3**	NBu_4Br	1000:100:1:1	–	–	18	trace
2	**3**	NBu_4Br	1000:100:1:1	DBU	1:1	18	72
3	**3**	NBu_4Br	1500:100:1:1	DBU	1:1	18	89
4	**3**	NBu_4Br	2000:100:1:1	DBU	1:1	18	94
5	**3**	NBu_4Br	2000:100:1:1	DBU	1:1	12	96
6	**3**	NBu_4Br	2000:100:1:1	DBU	1:1	9	92
7	**3**	NBu_4Br	2000:100:1:1	DBU	1:1	6	52
8[c]	**3**	NBu_4Br	2000:100:1:1	DBU	1:1	9	43
9	**3**	NBu_4Br	3000:150:1:1	DBU	1:1	9	74
10	**3**	NBu_4Br	3000:150:1:1	TMEDA	1:1	9	6
11	**3**	NBu_4Br	3000:150:1:1	Et_3N	1:1	9	45
12	**3**	NBu_4Br	3000:150:1:1	DABCO	1:1	9	8
13	**3**	NBu_4Br	3000:150:1:1	DBU	7:10	9	99
14	**3**	NBu_4Br	3000:150:1:1	DBU	5:10	9	85
15	**3**	NBu_4Br	3000:150:1:1	DBU	1:10	9	66
16	**3**	NBu_4Br	2400:400:1:1	DBU	7:10	9	67
17[d]	**3**	NBu_4Br	2400:400:1:1	DBU	7:10	9	58
18	**3**	NBu_4I	2400:400:1:1	DBU	7:10	9	55
19	**3**	PPNCl	2400:400:1:1	DBU	7:10	9	49
20	**1**	NBu_4Br	2400:400:1:1	DBU	7:10	9	55
21	**2**	NBu_4Br	2400:400:1:1	DBU	7:10	9	60
22	**4**	NBu_4Br	2400:400:1:1	DBU	7:10	9	58
23	**5**	NBu_4Br	2400:400:1:1	DBU	7:10	9	73
24	**5**	NBu_4Br	4000:400:1:1	DBU	7:10	9	84
25	**5**	NBu_4Br	6000:400:1:1	DBU	7:10	9	95

[a] Reaction conditions: 95 °C, CO_2 (10 bar). TMEDA = *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine, DABCO = 1,4-diazabicyclo[2.2.2]octane. [b] Determined by GC. [c] 80 °C. [d] CO_2 (6 bar).

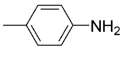
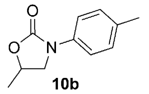
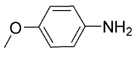
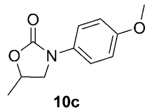
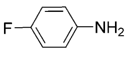
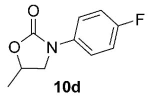
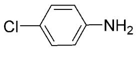
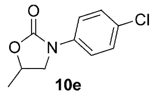
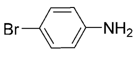
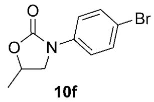
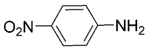
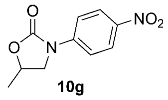
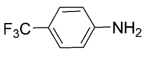
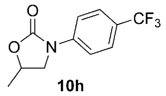
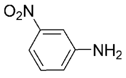
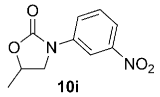
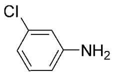
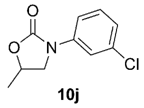
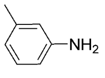
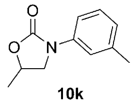
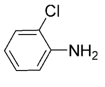
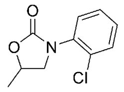
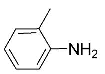
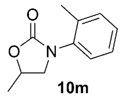
(Table 3, entry 2). To gain better yields of the oxazolidinones, a large excess amount of PO was essential. Increasing the ratio of PO to aniline led to a significant increase in the yield (89 and 94%; Table 3, entries 3 and 4). Optimization of the reaction time suggested 9 h to be sufficient (Table 3, entries 4–7). A relatively high temperature of 95 °C was crucial, as only a moderate yield of 43% was obtained at 80 °C (Table 3, entry 8). In an attempt to reduce the catalyst loading, a good yield of 74% was achieved with a PO/$PhNH_2$/catalyst ratio of 3000:150:1 (Table 3, entry 9). Different additives were screened, and DBU remained the optimal choice (Table 3, entries 9–12). Adjustment of the ratio of DBU to aniline suggested that 7:10 was the most effective (Table 3, entries 9, 13–15), as evidenced by the near-quantitative yield (Table 3, entry 13). A further increase in the substrate/catalyst ratio to 400:1 resulted in a reduced yield of 67% (Table 3, entry 16), and the reaction proceeded moderately at a lower CO_2 pressure of 6 bar (Table 3, entry 17). Different co-catalysts were screened, and NBu_4Br proved to be the best performer (Table 3, entries 16, 18, and 19).

Under identical conditions, the performances of complexes **1**–**5** were studied and compared, and the reaction catalyzed by complex **5** bearing a more Lewis acidic metal center gave the best yield (Table 3, entries 16, 20–23), which is consistent with the observation of the rare-earth-metal catalyzed cycloaddition of epoxides and CO_2 (see above). Increasing the amount of PO led to an improved yield of 95% (Table 3, entries 23–25).

On the basis of the optimization results, the scopes of the epoxides and amines were studied to construct oxazolidinones with different substituents (Tables 4 and 5). A series of anilines bearing either electron-donating or electron-withdrawing substituents in the *para* positions were conveniently converted into the corresponding oxazolidinones in yields of 76 to 92% (Tables 4, entries 1–7), with the exception of *p*-anisidine (Tables 4, entry 2), possibly because of deactivation of the catalyst with coordinating oxygen atoms. Reactions of anilines with *meta* substituents, including nitro, chloro, and methyl groups, also proceeded, and led to the desired oxazolidinones in yields of 72, 76, and 48%, respectively (Tables 4, entries 8–10). However, no product was isolated with substrates bearing *ortho* substituents, regardless of the electron-donating or electron-withdrawing nature (Tables 4, entries 11 and 12). Comparing the three-component reaction with the two-component reaction of epoxides and isocyanates, comparable yields were generally obtained.[7] However, the latter is restricted to aryl isocyanates bearing *para* substituents owing to the availability of substituted aryl isocyanates. Thus, the three-component reaction not only employs easily available substrates but also provides a synthetic route to a broader range of oxazolidinones.

Reactions of different epoxides were also studied, and moderate yields were obtained from monosubstituted epoxides bearing alkyl, ether, alkenyl, or phenyl groups (Table 5, entries 1–6). 5-Phenyl aryloxazolidinone **10 r** formed exclusively as the only product, showing the high regioselectivity of this strategy. In comparison, a mixture of 5- and 4-phenyl aryloxazolidinones was formed in a ratio of 2.1:1 from the two-component reaction of styrene oxide with phenyl isocyanate.[7] Reaction of the disubstituted epoxide 1,2-epoxy-2-methylpropane proceeded sluggishly and generated the desired oxazolidinone in < 10% yield, which is significantly lower than that obtained through the two-component reaction.[7] These two methods are thus complementary to each other and provide access to a diverse set of oxazolidinones.

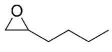
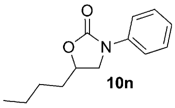
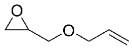
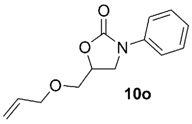
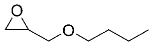
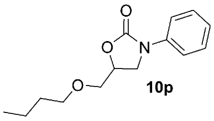
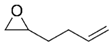
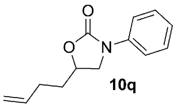
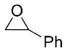
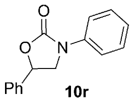
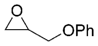
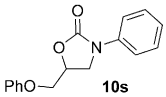
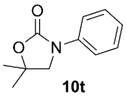
Table 4. Scope of the reaction of propylene oxide (PO), aniline, and CO_2.[a]

Entry	Amine	Product	Yield[b] [%]
1	 **9b**	 **10b**	86
2	 **9c**	 **10c**	56
3	 **9d**	 **10d**	76
4	 **9e**	 **10e**	85
5	 **9f**	 **10f**	91
6	 **9g**	 **10g**	86
7	 **9h**	 **10h**	92
8	 **9i**	 **10i**	72
9	 **9j**	 **10j**	76
10	 **9k**	 **10k**	48
11	 **9l**	 **10l**	trace
12	 **9m**	 **10m**	trace

[a] Reaction conditions: propylene oxide (PO) (5.75 mL, 82.2 mmol), aniline (5.48 mmol), 95 °C, CO_2 (10 bar), complex **5** (12.3 mg, 0.0137 mmol), NBu_4Br (4.4 mg, 0.0137 mmol), 9 h, DBU (0.57 mL, 3.84 mmol). [b] Yield of isolated product.

A preliminary study to investigate the reaction mechanism was conducted by treating propylene carbonate (15-fold

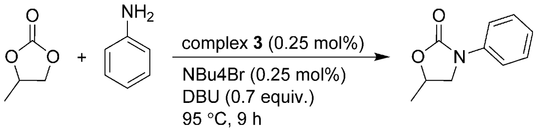
Table 5. Scope of the reaction of epoxides, aniline, and CO_2.[a]

Entry	Epoxide	Product	Yield[b] [%]
1	 **9n**	 **10n**	57
2	 **9o**	 **10o**	62
3	 **9p**	 **10p**	45
4	 **9q**	 **10q**	54
5	 **9r**	 **10r**	46
6	 **9s**	 **10s**	68
7	 **9t**	 **10t**	< 10

[a] Reaction conditions: epoxide (82.2 mmol), aniline (0.5 mL, 5.48 mmol), 95 °C, CO_2 (10 bar), complex **5** (12.3 mg, 0.0137 mmol), NBu_4Br (4.4 mg, 0.0137 mmol), 9 h, DBU (0.57 mL, 3.84 mmol). [b] Yield of isolated product.

excess) with aniline under catalytic conditions (Scheme 3), and 5-methyl-3-phenyl-2-oxazolidinone was detected in 34% yield (by GC) along with unreacted propylene carbonate. This finding implies that the formation of the cyclic carbonate followed by reaction with aniline might be one of the pathways leading to oxazolidinone formation.

In summary, rare-earth-metal complexes stabilized by amine-bridged tri(phenolato) ligands were developed to catalyze transformations of CO_2. A series of terminal epoxides were treated with CO_2 under atmospheric pressure to generate cyclic carbonates in yields of 58 to 96%. More challenging disubstituted epoxides were also converted into cyclic carbonates in yields of 72 to 91% at a relatively higher pressure of 10 bar. In addition, rare-earth-metal complexes showed good activities in catalyzing three-component reactions of epoxides, amines, and CO_2 (10 bar) to generate a series of 5-substituted-3-aryl-2-oxazolidines with yields in the 48–96% range. These results prove the great application of rare-earth-metal complexes in mediating CO_2 transformations, adding value to the utilization of CO_2. One main drawback of the three-component approach is the necessity for a large excess amount of the epoxides with respect to the amine (15-fold excess in this study), which requires further optimization to improve atom efficiency. More investigations on rare-earth-metal mediated CO_2 transformations are in progress in our laboratory.



Scheme 3. Reaction of propylene carbonate with aniline.

Experimental Section

General procedure for the three-component reaction: The reaction was performed in a 300 mL stainless-steel Parr reactor with a stirring bar inside and a needle valve for injection. In a typical reaction, complex **5** (12.3 mg, 0.0137 mmol), NBu_4Br (4.4 mg, 0.0137 mmol), epoxide (82.2 mmol), aniline (5.48 mmol), and DBU (3.84 mmol) were introduced into the predried reactor. The reactor was pressurized to 10 bar with CO_2 and heated at 95 °C for 9 h. Upon completion of the reaction, the mixture was cooled to room temperature, and the pure product was isolated by column chromatography (EtOAc/petroleum ether 1:30). The structure was confirmed by comparison with literature data.[7,9]

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Keywords: carbon dioxide fixation · cyclic carbonates · oxazolidinones · rare earths · multicomponent reactions

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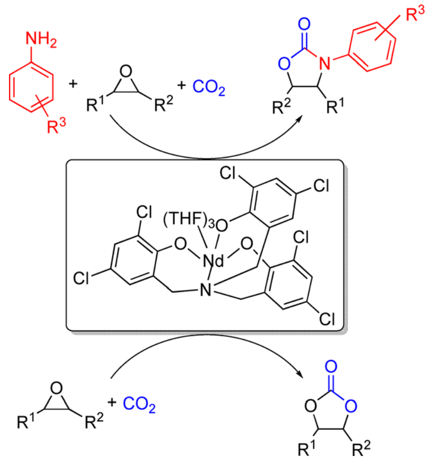
A rare find: Rare-earth-metal complexes stabilized by amine-bridged tri(phenolato) ligands are active in catalyzing transformations of CO_2. A series of terminal and disubstituted epoxides are converted into cyclic carbonates in yields of 58 to 96%. In addition, these rare-earth-metal complexes show good activities in catalyzing the three-component reaction of anilines, epoxides, and CO_2, which provides a useful strategy to prepare oxazolidinones.



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Transformation of Carbon Dioxide into Oxazolidinones and Cyclic Carbonates Catalyzed by Rare-Earth-Metal Phenolates