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Synthesis of Oxazolidinones from Epoxides and Isocyanates Catalyzed by Rare-Earth-Metal Complexes

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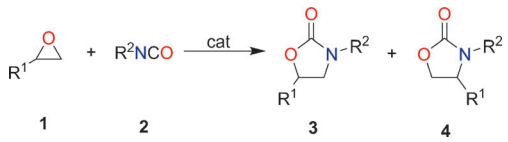
Rare-earth-metal complexes stabilized by an amino-bridged triphenolate ligand showed high efficiency in catalyzing the cycloaddition of isocyanates and epoxides in the presence of NBu_4I under mild conditions. This strategy is applicable to both terminal and disubstituted epoxides as well as various isocyanates, and tolerated different types of functional groups. Moreover, it is highly regio- and stereoselective, and afforded 3,5-disubstituted oxazolidinones as the only products in most cases in moderate to good yields.

Introduction

Oxazolidinones are important intermediates in organic synthesis. For instance, they are commonly used to prepare β-aminoalcohols,[1] and are valuable building blocks for polymers.[2] In addition, they also serve as precursors to antibacterial medicines such as *Staphylococcus aureus*, *Enterococcus faecium*, *Streptococcus pneumoniae*.[3,4] Hence, the construction of oxazolidinone frameworks is of significant importance.

Many efforts have been made to prepare oxazolidinones, which include reactions of carbon dioxide with β-aminoalcohols or aziridines,[5–11] oxidative carbonylation of β-aminoalcohols with CO/O_2,[12–16] and carbonylation of β-aminoalcohols with dialkyl carbonate.[17–19] Among them, the [3+2] addition of isocyanates to epoxides (Scheme 1) is a 100% atom-economic strategy, and has thus attracted substantial attention. Many catalytic systems have been reported to catalyze this transformation, including onium salts,[20] metal halides,[21–41] and Pd^0 species.[42,43] However, harsh conditions, such as high catalyst loadings (usually more than 10%),[26,29–31,33,37] and high temperature exceeding 160 °C[20] were usually required to get decent yields. Slow addition of isocyanates or large excess of epoxides was required to suppress the trimerization of isocyanates, which is a common side reaction.[22,24,27] Moreover, substrate scopes are largely limited to monosubstituted epoxides.[27–29]



Scheme 1. Formation of oxazolidinones from epoxides and isocyanates.

Very recently, North et al. reported a bimetallic Al-Salen complex which efficiently catalyzed the coupling of isocyanates and epoxides.[44] With 5 mol% catalyst, 33–100% conversions were achieved, and isomers of 3,4-disubstituted and 3,5-disubstituted oxazolidinones formed in varying ratios. Nguyen et al. reported a Cr^{III}–Salen complex that in the presence of a Lewis base catalyzed the oxazolidinone formation reactions in good yields of >90% with 3,5-disubstituted 2-oxazolidinones as the major products.[45]

Rare-earth-metal complexes are highly oxophilic, which makes them potentially useful in activating epoxides. Although some rare-earth-metal salts have been reported to catalyze the cycloaddition of isocyanates and epoxides, 10 mol%[31,32] or substoichiometric amounts[33] of catalyst were required. Our group has reported a series of rare-earth-metal complexes stabilized by a bridged poly(phenolate) ligand, which catalyzed the cycloaddition of carbon dioxide with both terminal and disubstituted epoxides under mild conditions and showed high activity and regioselectivity.[46] As both carbon dioxide and isocyanates are heterocumulenes,[27,30,37,47,48] we were prompted to explore the performance of rare-earth-metal complexes in catalyzing the reaction between isocyanates and epoxides.

Results and Discussion

Amino-bridged triphenolate ligands (LH_3) have been reported to be useful in stabilizing trivalent rare-earth metals, and their complexes have been applied in catalyzing various transformations, including the coupling of epoxides and carbon dioxide,[49,50] lactide polymerization,[51–54] and ethylene/propylene copolymerization.[55] The ligand precursor LH_3 was readily prepared according to a literature method.[56] Treating $LnCp_3(THF)$

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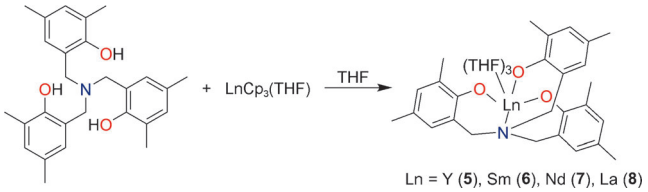


Scheme 2. Synthesis of complexes **5**–**8**.

(Ln = Y, Sm, Nd, La) with LH_3 in THF afforded four complexes isolated in 64–87% yields after 12 h reaction at room temperature (Scheme 2). ^{1}H NMR spectra of diamagnetic complexes **5** and **8** in [D_8]THF showed that all three phenolate moieties of the ligand gave rise to one set of signals, with the diastereotopic methylene protons resonating as two doublets at 3.98 and 2.62 ppm, respectively. Resonances assignable to THF molecules are also observed, suggesting the existence of coordinating THF molecules. The unambiguous identity of these complexes was confirmed by the solid-state structures of complexes **6**–**8** determined by X-ray diffraction on single crystals obtained from hexane/THF solution. All three complexes are isostructural with the structure of **7** depicted in Figure 1. Each

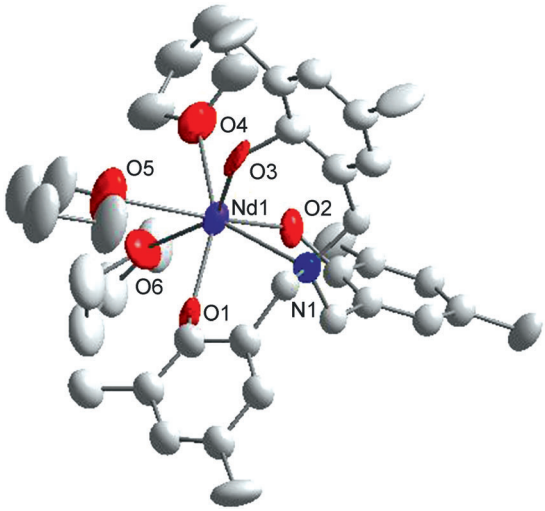


Figure 1. Molecular structure of complex **7**·3THF showing 50% probability ellipsoids. Solvent molecules and hydrogen atoms are omitted for clarity.

rare-earth-metal center is coordinated by four donors (O1, O2, O3, and N1) from the phenolate ligand, and three oxygen atoms from three THF molecules. The coordination geometry can be best described as orthorhombic.

With all four complexes in hand, we examined their performance in catalyzing reactions between phenylisocyanate and propylene oxide. No conversion was detected at all if the reaction was conducted in the presence of 0.3 mol% of the neodymium complex **7** at 80 °C after 18 h reaction in toluene (Table 1, entry 1). However, the addition of 0.3 mol% NBu_4Br led to a dramatically improved yield of 47% (entry 2). A similar finding was observed in the reaction of carbon dioxide and epoxides catalyzed by rare-earth-metal complexes.[46] Apparently,

Table 1. Reactions of propylene oxide with phenylisocyanate.[a]

Entry	Cat.	Cocat.	Solvent	T [°C]	Conc. [mmol mL^{-1}]	Yield [b] [%]
1	**7**	–	toluene	80	2.14	0
2	**7**	NBu_4Br	toluene	80	2.14	47
3	–	NBu_4Br	toluene	80	2.14	23
4	**7**	NBu_4Br	toluene	60	2.14	33
5	**7**	NBu_4Br	toluene	18	2.14	0
6[c]	**7**	NBu_4Br	toluene	80	2.14	37
7[d]	**7**	NBu_4Br	toluene	80	2.14	52
8	**7**	NBu_4Br	bromo-benzene	80	2.14	44
9	**7**	NBu_4Br	xylene	80	2.14	43
10	**7**	NBu_4Br	cyclic carbonate	80	2.14	7
11	**7**	NBu_4Br	solvent free	80	–	18
12	**7**	NBu_4Br	toluene	80	1.07	63
13	**7**	NBu_4Br	toluene	80	0.71	81
14	**7**	NBu_4Br	toluene	80	0.54	86
15	**5**	NBu_4Br	toluene	80	0.71	72
16	**6**	NBu_4Br	toluene	80	0.71	69
17	**8**	NBu_4Br	toluene	80	0.71	80
18	**7**	NBu_4I	toluene	80	0.71	87
19	**7**	PPNCl[e]	toluene	80	0.71	37
20[f]	**7**	NBu_4I	toluene	80	0.71	91
21[g]	**7**	NBu_4I	toluene	80	0.71	93
22[h]	**7**	NBu_4I	toluene	80	0.71	98

[a] Reaction conditions, unless otherwise stated: propylene oxide (0.3 mL, 4.28 mmol), phenylisocyanate (0.47 mL, 4.28 mmol), 0.3 mol% catalyst, 0.3 mol% cocatalyst, 18 h; [b] Determined by ^{1}H NMR spectroscopy; [c] 12 h reaction time; [d] 24 h reaction time; [e] bis(triphenylphosphine)-iminium chloride; [f] 0.3 mol% catalyst, 0.67 mol% cocatalyst; [g] 0.3 mol% catalyst, 1 mol% cocatalyst; [h] 0.5 mol% catalyst, 1 mol% cocatalyst.

ammonium halide plays a crucial role in initiating the reaction of epoxides with rare-earth metals. A control experiment revealed that NBu_4Br alone was also active and gave rise to a 23% yield (entry 3), which is approximately half of the result obtained from the combination of complex **7** and NBu_4Br (entry 2). Ring-opening of epoxides by the halides and subsequent addition reaction with isocyanate has also been observed by Speranza and Peppel.[20] In the presence of rare-earth-metal complexes, coordination to metal centers activates epoxides towards ring-opening, which were readily attacked by the nucleophilic reagent X^- to produce the requisite metal alkoxide intermediate. On the other hand, no oxazolidinone formed in the absence of halide, because the ring-opening of epoxides did not proceed. In contrast, no cocatalyst was required for the bimetallic aluminum–salen catalytic system, which may be attributed to the existence of a Lewis basic oxygen atom that bridges the two Al centers.[44] 3,5-Disubstituted oxazolidinone **3a** was isolated as the only product, suggesting that the β-cleavage of epoxides at the less hindered carbon atom predominates. Different reaction conditions were then screened in the presence of both **7** and NBu_4Br. Lowering the reaction temperature to 60 °C led to a lower yield of 33% (entry 4), and no conversion was detected at 18 °C (entry 5). 18 h proved to be the optimal reaction time as shortening it

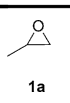
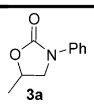
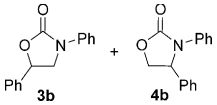
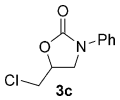
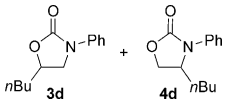
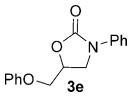
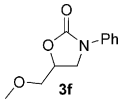
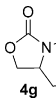
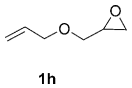
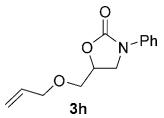
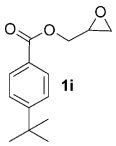
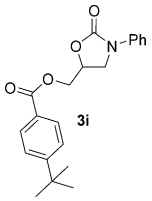
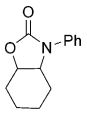
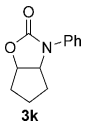
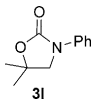
to 12 h led to a reduced yield of 37% (entry 6), whereas prolonging it to 24 h resulted in a 5% increase only (entry 7). Reactions conducted in xylene and bromobenzene afforded the desired product **3a** in similar yields (entries 8–9), whereas a significantly lower yield of 7% was obtained from that in cyclic carbonate (entry 10). Notably, 18% of **3a** was isolated if the reaction was conducted neat, although 72% of PhNCO was transformed into the byproduct resulting from its trimerization (entry 11). Apparently, the undesired trimerization can be suppressed in this catalytic system by simply diluting the reaction mixture, which thus avoids the need to add large excess of epoxides or to add isocyanates portionwise.[22,24,27] To identify the optimal concentration for oxazolidinone formation, different amounts of toluene were screened. The results reveal a raise of the yield from 18% to 86% if the solvent volume increased from 0 to 8 mL (entries 11–14). Complexes of different metal centers and different Lewis acidities were also tested under identical conditions. **5** and **6** bearing rare-earth metals of small ionic radii led to lower yields of 72 and 69%, respectively, whereas **7** and **8** showed better activities and gave rise to yields of 81% and 80%, respectively (entries 15–17). This may be explained by the larger open coordination sphere of the larger rare-earth metals which may be helpful for activation of propylene oxide. Different cocatalysts including NBu_4I and bis(triphenylphosphine)iminium chloride (PPNCl) were also tested, and NBu_4I proved to be the optimal choice (entries 18–19). Studies on different loadings of catalyst and cocatalyst revealed that 0.5 mol% of **7** and 1 mol% of NBu_4I were the best combination, and led to an almost quantitative yield (entries 20–22).

With the optimal reaction conditions, the scope of substrates was explored. Epoxides bearing a phenyl (**1b**), chloromethyl (**1c**), or *n*-butyl (**1d**) group were converted to the corresponding oxazolidinones in 82–89% yields (Table 2, entries 2–4). Reaction with epoxides carrying ether groups (**1e** and **1f**) also proceeded straightforwardly without deactivating the catalyst, and afforded the desired products in the same yield of 93% (entries 5–6). In comparison, control experiments in the absence of complex **7** resulted in oxazolidinones in less than 30% yields (entries 2 and 5), which further confirms that rare-earth-metal complexes play a crucial role in catalyzing this transformation.

Notably, glycidol **1g** bearing an unprotected hydroxyl group, which might poison the rare-earth-metal complex, was also converted to the desired product **4g** in a good yield of 73% (entry 7). Other functional groups, including an alkene (**1h**) and an ester group (**1i**), were also tolerated under the established conditions, and corresponding oxazolidinones were isolated in 83% and 72%, respectively (entries 8–9).

3,5-Disubstituted oxazolidinones formed almost exclusively in most cases, revealing excellent regioselectivity of this strategy. The reaction with styrene oxide yielded both 3,5-diphenyloxazolidinone **3b** and 3,4-diphenyloxazolidinone **4b** in the ratio of 2.1:1, the latter of which resulted from the favorable ring-opening at the benzylic position.[44] A mixture of 3,5-disubstituted and 3,4-disubstituted oxazolidinones in 9:1 ratio was also observed from the reaction with 1,2-epoxyhexane **1d**.

Table 2. Formation of oxazolidinones from epoxides and phenylisocyanate catalyzed by complex **7**.[a]

Entry	Epoxide	Product	Yield [%][b]	3:4[c]
1	 **1a**	 **3a**	72	1:0
2	 **1b**	 **3b** + **4b**	89[d] (26[e])	2.1:1
3	 **1c**	 **3c**	86	1:0
4	 **1d**	 **3d** + **4d**	82[f]	9:1
5	 **1e**	 **3e**	93[d] (15[e])	1:0
6	 **1f**	 **3f**	93[f]	1:0
7	 **1g**	 **4g**	73	0:1
8	 **1h**	 **3h**	83[f]	1:0
9	 **1i**	 **3i**	72	1:0
10	 **1j**	 **3j**	28	–
11	 **1k**	 **3k**	69[f,g]	–
12	 **1l**	 **3l**	95[f]	1:0

[a] Reactions conditions, unless otherwise stated: oxides (conc. = 0.71 mmol mL^{-1}), 0.5 mol% catalyst, 1.0 mol% NBu_4I, 18 h, 80 °C; [b] Isolated yield; [c] Determined by ^{1}H NMR spectroscopy; [d] The same amount of NBu_4Br was used instead of NBu_4I; [e] In the absence of **7**; [f] 1.0 mol% catalyst and 2.0 mol% NBu_4I were used; [g] The *cis*-fused structure was determined by X-ray diffraction analysis on single crystals.

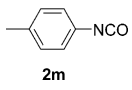
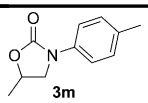
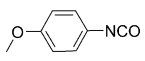
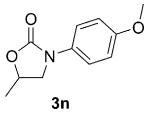
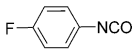
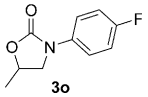
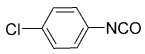
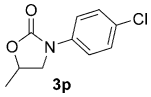
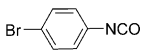
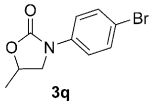
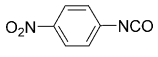
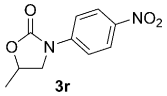
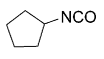
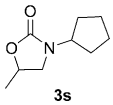
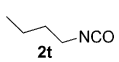
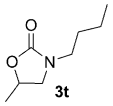
3,4-Disubstituted oxazolidinone from glycidol **1g** was obtained as the only product, which is consistent with previous reports

that isocyanates first react with the hydroxyl group followed by intramolecular reaction with epoxide.[44,57–61]

Nonterminal epoxides have been reported to be challenging substrates for this transformation.[27,28,29,44] In our system, *cis*-cyclohexene oxide (**1j**) and *cis*-cyclopentene oxide (**1k**) were transformed to corresponding oxazolidinones in 28 and 69% yields, respectively. ^{1}H NMR spectra show the existence of single diastereomers, and the solid state structure of **3k** was determined by X-ray diffraction analysis on single crystals, which proves that the two rings are *cis*-fused to each other (Supporting Information, Figure S3). It is thus conceivable that the formation of **3k** underwent a double inversion process,[44] which results in the retention of the epoxide stereochemistry. This finding is consistent with the result from the coupling of cyclohexene oxide and cyclopentene oxide with CO_2 catalyzed by rare-earth-metal complexes and NBu_4I.[46] In the presence of higher loading of catalyst and cocatalyst, 1,2-dimethylepoxide (**1l**) reacted with PhNCO and yielded **3l** in 95%.

Besides epoxides, various arylisocyanates bearing either an electron-donating or electron-withdrawing *para*-substituent were also tested, and the results are summarized in Table 3. In general, reactions with electron-rich substrates worked better, which generated oxazolidinones in 85–89% yields (entries 1–2). Although the catalyst loadings were increased, electron-deficient arylisocyanates led to lower yields of 57–82% (entries 3–6). Moreover, 5-substituted 2-oxazolidinone isomers formed exclusively in all cases. Rare-earth-metal complexes proved limited in catalyzing the reaction with aliphatic isocyanates, as almost no conversion was detected for cyclohexylisocyanate (entries 7–8).

Table 3. Formation of oxazolidinones from propylene oxide and isocyanates catalyzed by complex **7**.[a]

Entry	Isocyanate	Product	Yield [%][b]	3:4[c]
1	 **2m**	 **3m**	89	1:0
2	 **2n**	 **3n**	85	1:0
3	 **2o**	 **3o**	67[d]	1:0
4	 **2p**	 **3p**	82[d]	1:0
5	 **2q**	 **3q**	68[d]	1:0
6	 **2r**	 **3r**	57[e]	1:0
7	 **2s**	 **3s**	trace	–
8	 **2t**	 **3t**	trace	–

[a] Reactions conditions, unless otherwise stated: oxides (conc. = 0.71 mmol mL^{-1}), 0.5 mol% catalyst, 1.0 mol% NBu_4I, 18 h, 80 °C; [b] Isolated yield; [c] Determined by ^{1}H NMR spectroscopy; [d] 1.0 mol% catalyst, 2.0 mol% NBu_4I; [e] 2.0 mol% catalyst, 4.0 mol% NBu_4I, 95 °C.

Conclusions

Rare-earth-metal complexes stabilized by an amino-bridged triphenolate ligand were prepared, which showed high activity towards the cycloaddition of isocyanates and epoxides. Various terminal and disubstituted epoxides and arylisocyanates were studied, and oxazolidinones were isolated in generally moderate to good yields in the presence of 0.5–2.0 mol% catalyst and 1.0–4.0 mol% NBu_4I as a cocatalyst. Good regioselectivity was achieved and the 3,5-disubstituted isomers formed exclusively in most cases. The *cis*-configuration of substrates was retained after reaction, revealing an excellent stereoselectivity. Further investigations on the tuning of the structure of the ligands and complexes to search for catalysts of enhanced activities are ongoing in our laboratory.

Experimental Section

Oxides, isocyanates, and onium salts were commercially available. Hexane, toluene, and THF were freshly distilled after heating to reflux over sodium/benzophenone ketyl prior to use. The ligand precursor LH_3 was prepared according to the previous literature.[56] Standard Schlenk techniques were applied to synthesize rare-earth-metal complexes **5**–**8**. Elemental analysis was performed with a CarloErba EA-1110 instrument. The IR spectra were performed with a Nicolet-550 FT-IR spectrometer. NMR (^{1}H, ^{13}C, ^{19}F) spectra were recorded on a Unity Varian AC-400 spectrometer. The structures of rare-earth-metal complexes **6** (CCDC 1038013), **7** (CCDC 1038014), **8** (CCDC 1038015) were detected by X-ray single-crystal diffractometry. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Procedure for the synthesis of rare-earth-metal complexes 5–8

Complex **5**: A 2 mL volume of THF solution of LH_3 (0.8380 g, 2.00 mmol) was added to a 4 mL volume of THF solution of $Y(C_5H_5)_3(THF)$ (0.7126 g, 2.00 mmol). After stirring for 12 h at RT, the reaction mixture was concentrated under vacuum. THF (2 mL) was added to extract the residue, and the solid that remained insoluble was removed after centrifugation. To the THF solution, hexane (4 mL) was added. Yellow crystals were obtained after several days from the THF/hexane solution at RT (0.9228 g, 1.28 mmol, 64%). IR (KBr pellet): $\tilde{\nu}$ = 3380 (s), 2910 (w), 1606 (s), 1469 (s), 1378 (s), 1340 (s), 1306 (s), 1250 (s), 1151 (s), 1049 (s), 850 (s), 801 (s), 752 (s), 640 (s), 631 (s), 625 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}NO_6Y$: C 63.55, H 6.90, N 1.78, Y 12.46; found: C 63.90, H 7.54, N 1.94, Y 12.32; ^{1}H NMR ([D$_8$]THF, 400 MHz): δ = 6.70 (s, 3H, ArH), 6.61 (s, 3H, ArH), 3.98 (d, J = 11.32 Hz, 3H, ArC*H*HN), 3.69–3.63 (m, THF), 2.65 (d, J = 11.32 Hz, 3H, ArCH*H*N), 2.14 (s, 9H, CH_3),

2.10 (s, 9H, CH_3), 1.85–1.80 ppm (m, THF) (owing to the exchange of coordinating THF with [D_8]THF, correct integration is not possible). ^{13}C NMR ([D_8]THF, 100 MHz): 160.5, 129.5, 128.1, 123.5, 123.2, 121.5 (Ar-C), 60.4 ($ArCH_2N$), 19.6, 16.8 (CH_3).

Complex **6** was synthesized in analogy to complex **5** from $Sm(C_5H_5)_3(THF)$ (0.8340 g, 2.00 mmol). After removal of solvent in vacuum, THF (2 mL) was added to extract the residue, and the solid that remained insoluble was removed after centrifugation. Yellow crystals were obtained after several days from the THF solution at RT (1.2518 g, 1.60 mmol, 80%). IR (KBr pellet): $\tilde{\nu}$ = 3390 (s), 2916 (w), 1610 (s), 1478 (s), 1386 (s), 1365 (s), 1307 (s), 1263 (s), 1160 (s), 1054 (s), 855 (s), 810 (s), 760 (s), 660 (s), 630 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}NO_6Sm$: C 59.81, H 6.95, N 1.79, Sm 19.20; found: C 59.46, H 6.89, N 1.88, Sm 18.85.

Complex **7** was synthesized in analogy to complex **5** from $Nd(C_5H_5)_3(THF)$ (0.8228 g, 2.00 mmol). After removal of solvent in vacuum, THF (2 mL) was added to extract the residue, and the solid that remained insoluble was removed after centrifugation. Blue crystals were obtained after several days from the THF solution at RT (1.3196 g, 1.70 mmol, 85%). IR (KBr pellet): $\tilde{\nu}$ = 3411 (s), 2918 (w), 1613 (s), 1478 (s), 1383 (s), 1346 (s), 1310 (s), 1258 (s), 1160 (s), 1056 (s), 858 (s), 800 (s), 759 (s), 641 (s), 624 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}NO_6Nd$: C 58.88, H 6.84, N 1.84, Nd 18.90; found: C 60.28, H 7.00, N 1.80, Nd 18.56.

Complex **8** was synthesized in analogy to complex **5** from $La(C_5H_5)_3(THF)$ (0.8126 g, 2.00 mmol). After removal of solvent in vacuum, THF (2 mL) was added to extract the residue, and the solid remained insoluble was removed after centrifugation. Colorless crystals were obtained after several days from the THF solution at RT (1.3414 g, 1.74 mmol, 87%). IR (KBr pellet): $\tilde{\nu}$ = 3425 (s), 2914 (w), 1610 (s), 1478 (s), 1384 (s), 1306 (s), 1257 (s), 1160 (s), 1053 (s), 857 (s), 802 (s), 762 (s), 613 (s), 603 cm^{-1} (s); elemental analysis calcd (%) for $C_{39}H_{54}NO_6La$: C 60.93, H 6.69, N 1.82, La 18.07; found: C 60.58, H 6.84, N 1.84, La 18.82; ^1H NMR ([D_8]THF, 400 MHz): δ = 6.70 (s, 3H, ArH), 6.61 (s, 3H, ArH), 3.96 (d, J = 11.32 Hz, 3H, Ar*CH*HN); 3.68–3.62 (m, THF), 2.63 (d, J = 11.32 Hz, 3H, ArCH*H*N), 2.14 (s, 9H, CH_3), 2.12 (s, 9H, CH_3), 1.85–1.80 ppm (m, THF) (owing to the exchange of coordinating THF with [D_8]THF, correct integration is not possible); ^{13}C NMR ([D_8]THF, 100 MHz): δ = 161.4, 130.2, 128.8, 123.5, 121.2(Ar-C), 60.4($ArCH_2N$), 19.5, 16.6 ppm (CH_3).

General procedure for the synthesis of oxazolidinones

Complex **7** (0.0167 g, 0.0215 mmol) and cocatalyst (0.0138 g, 0.0429 mmol) were added to a 10 mL flask equipped with a magnetic stirring bar under dry argon atmosphere, to which toluene (6–8 mL) was added. Epoxide (4.2872 mmol) and isocyanate (4.2872 mmol) were added to the above stirred solution before heating the solution to 80 °C for 18–24 h. After the reaction, the resulting mixture was cooled to RT. The conversion and selectivity were analyzed by ^1H NMR spectroscopy on one drop of the mixture. The solvent of the mixture was removed in vacuum. The desired compound was purified by column chromatography (eluent: ethyl acetate: petroleum ether = 1: 20).

5-Methyl-3-phenyloxazolidin-2-one (**3a**):[27,30,37,44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, J = 8.0 Hz, 2H, ArH), 7.40 (t, J = 7.6 Hz, 2H, ArH), 7.15 (t, J = 7.4 Hz, 1H, ArH), 4.85–4.75 (m, 1H, CH), 4.14 (t, J = 8.4 Hz, 1H, CH_2), 3.65 (dd, J = 8.3, 7.4 Hz, 1H, CH_2), 1.56 ppm (d, J = 6.2 Hz, 3H, CH_3); m/z (ESI-TOF): calcd for $C_{10}H_{11}NO_2H^+$: 178.0868, found: 178.0864; calcd for $C_{10}H_{11}NO_2Na^+$: 200.0687, found: 200.0691; calcd for $(2\times C_{10}H_{11}NO_2)Na^+$: 377.1478, found: 377.1484.

3,5-Diphenyloxazolidin-2-one (**3b**):[27,44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.61–7.35 (m, 9H, ArH), 7.18 (tt, J = 7.4, 1.1 Hz, 1H, ArH), 5.67 (dd, J = 8.4, 8.2 Hz, 1H, CH), 4.42 (t, J = 8.8 Hz, 1H, CH_2), 3.99 ppm (dd, J = 8.8, 7.6 Hz, 1H, CH_2); m/z (ESI-TOF): calcd for $C_{15}H_{13}NO_2Na^+$: 262.0844, found: 262.0842; calcd for $(2\times C_{15}H_{13}NO_2)Na^+$: 501.1790, found: 501.1805.

3,4-Diphenyloxazolidin-2-one (**4b**):[27,44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.45–7.20 (m, 9H, ArH), 7.06 (tt, J = 7.4, 1.1 Hz, 1H, ArH), 5.39 (dd, J = 8.7, 6.0 Hz, 1H, CH), 4.78 (t, J = 8.7 Hz, 1H, CH_2), 4.20 ppm (dd, J = 8.6, 6.0 Hz, 1H, CH_2); m/z (ESI-TOF): calcd for $C_{15}H_{13}NO_2Na^+$: 262.0844, found: 262.0844; calcd for $(2\times C_{15}H_{13}NO_2)Na^+$: 501.1790, found: 501.1800.

5-Chloromethyl-3-phenyloxazolidin-2-one (**3c**):[27,44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, J = 7.9 Hz, 2H, ArH), 7.42 (t, J = 7.5 Hz, 2H, ArH), 7.19 (t, J = 7.3 Hz, 1H, ArH), 4.95–4.85 (m, 1H, CH), 4.20 (t, J = 8.9 Hz, 1H, CH_2), 4.00 (dd, J = 8.9, 5.8 Hz, 1H, CH_2), 3.87–3.7 ppm (m, 2H, CH_2Cl); m/z (ESI-TOF): calcd for $C_{10}H_{10}ClNO_2Na^+$: 234.0298, found: 234.0298; calcd for $(2\times C_{10}H_{10}ClNO_2)Na^+$: 445.0698, found: 445.0709.

5-Butyl-3-phenyloxazolidin-2-one (**3d**):[44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, J = 7.8 Hz, 2H, ArH), 7.40 (t, J = 7.5 Hz, 2H, ArH), 7.15 (tt, J = 7.3, 2.0 Hz, 1H, ArH), 4.70–4.61 (m, 1H, CH), 4.10 (t, J = 8.5 Hz, 1H, CH_2), 3.68 (dd, J = 8.6, 7.2 Hz, 1H, CH_2), 1.94–1.83 (m, 1H, CH_2), 1.81–1.71 (m, 1H, CH_2), 1.59–1.50 (m, 1H, CH_2), 1.48–1.38 (m, 3H, CH_2), 0.97 ppm (t, J = 7.0 Hz, 3H, CH_3); m/z (ESI-TOF): calcd for $C_{13}H_{17}NO_2Na^+$: 242.1157, found: 242.1158; calcd for $(2\times C_{13}H_{17}NO_2)Na^+$: 461.2416, found: 461.2428.

4-Butyl-3-phenyloxazolidin-2-one (**4d**):[44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.48–7.37 (m, 4H, ArH), 7.21 (tt, J = 7.2, 1.8 Hz, 1H, ArH), 4.56 (t, J = 8.4 Hz, 1H, CH), 4.48–4.39 (m, 1H, CH_2), 4.16 (dd, J = 8.4, 5.4 Hz, 1H, CH_2), 1.83–1.72 (m, 1H, CH_2), 1.65–1.53 (m, 1H, CH_2), 1.40–1.20 (m, 4H, CH_2), 0.89 ppm (t, J = 6.9 Hz, 3H, CH_3); m/z (ESI-TOF): calcd for $C_{13}H_{17}NO_2H^+$: 220.1138, found: 220.1125; calcd for $C_{13}H_{17}NO_2Na^+$: 242.1157, found: 242.1149; calcd for $(2\times C_{13}H_{17}NO_2)Na^+$: 461.2416, found: 461.2426.

5-Phenoxymethyl-3-phenyloxazolidin-2-one (**3e**):[27,37,44,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, J = 8.6 Hz, 2H, ArH), 7.40 (t, J = 8.6 Hz, 2H, ArH), 7.30 (t, J = 7.4 Hz, 2H, ArH), 7.16 (tt, J = 7.3, 1.8 Hz, 1H, ArH), 7.00 (tt, J = 7.4, 1.8 Hz, 1H, ArH), 6.91 (d, J = 7.8 Hz, 2H, ArH), 5.03–4.95 (m, 1H, CH), 4.25–4.18 (m, 3H, CH_2), 4.08 ppm (dd, J = 8.9, 5.9 Hz, 1H, CH_2); m/z (ESI-TOF): calcd for $C_{16}H_{15}NO_3Na^+$: 292.0950, found: 292.0951; calcd for $(2\times C_{16}H_{15}NO_3)Na^+$: 561.2002, found: 561.2018.

5-Methoxymethyl-3-phenyloxazolidin-2-one (**3f**): White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, J = 8.7 Hz, 2H, ArH), 7.39 (t, J = 7.4 Hz, 2H, ArH), 7.15 (m, 1H, ArH), 4.83–4.74 (m, 1H, CH), 4.07 (t, J = 8.8 Hz, 1H, CH_2), 3.93 (dd, J = 8.7, 6.4 Hz, 1H, CH_2), 3.66 (d, J = 4.6 Hz, 2H, OCH_2), 3.45 ppm (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.5, 138.1, 129.0, 123.9, 118.0, 73.1, 71.3, 59.5, 47.2 ppm. IR (KBr): $\tilde{\nu}$ = 3101, 3074, 3048, 3019, 2994, 2948, 2929, 2865, 2830, 1738, 1702, 1596, 1493, 1414, 1226, 1129, 1066, 1047, 755, 689, 585, 505 cm^{-1}. m/z (ESI-TOF): calcd for $C_{11}H_{13}NO_3Na^+$: 230.0793, found: 230.0799; calcd for $(2\times C_{11}H_{13}NO_3)Na^+$: 437.1688, found: 437.1700.

4-Hydroxymethyl-3-phenyloxazolidin-2-one (**4g**): White solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.53–7.37 (m, 4H, ArH), 7.23 (tt, J = 7.3, 1.2 Hz, 1H, ArH), 4.60–4.45 (m, 3H, CH, CH_2O), 3.90–3.65(m, 2H,

CH_2OH), 1.83 ppm (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 156.1$, 136.2, 129.3, 125.4, 122.0, 64.4, 60.5, 57.5 ppm. *m/z* (ESI-TOF): calcd for $C_{10}H_{11}NO_3H^+$: 194.0817, found: 194.0820; calcd for $C_{10}H_{11}NO_3Na^+$: 216.0635, found: 216.0628; calcd for $(2\times C_{10}H_{11}NO_3)Na^+$: 409.1376, found: 409.1375.

5-Allyoxymethyl-3-phenyloxazolidin-2-one (**3h**):[27] Yellow syrup. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.58$ (d, $J = 8.8$ Hz, 2H, ArH), 7.40 (t, $J = 7.5$ Hz, 2H, ArH), 7.16 (tt, $J = 7.4$, 2.0 Hz, 1H, ArH), 5.90–5.84 (m, 1H, CH=CH_2), 5.35–5.21 (m, 2H, CH=CH_2), 4.85–4.75 (m, 1H, CH), 4.14–4.06 (m, 3H, CH_2, OCH_2), 3.97 (dd, $J = 8.8$, 6.3 Hz, 1H, OCH_2), 3.77–3.68 ppm (m, 2H, OCH_2); *m/z* (ESI-TOF): calcd for $C_{13}H_{15}NO_3H^+$: 234.1130, found: 234.1132; calcd for $C_{13}H_{15}NO_3Na^+$: 256.0950, found: 256.0957; calcd for $(2\times C_{13}H_{15}NO_3)Na^+$: 489.2002, found: 489.2022.

(2-Oxo-3-phenyloxazolidin-5-yl)methyl 4-(*tert*-butyl)benzoate (**3i**): White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.93$ (d, $J = 8.6$ Hz, 2H, ArH), 7.55 (d, $J = 7.8$ Hz, 2H, ArH), 7.45–7.35 (m, 4H, ArH), 7.15 (tt, $J = 7.4$, 1.8 Hz, 1H, ArH), 5.03–4.94 (m, 1H, CH), 4.63–4.52 (m, 2H, CH_2), 4.21 (t, $J = 9.0$ Hz, 1H, CH_2), 3.94 (dd, $J = 9.04$, 6.0 Hz, 1H, CH_2), 1.32 ppm (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.5$, 157.9, 155.0, 138.0, 129.8, 129.2, 126.3, 125.7, 124.2, 118.4, 70.5, 64.9, 46.9, 35.8, 31.0 ppm. IR (KBr): $\tilde{\nu} = 3065$, 3046, 2962, 2906, 2871, 1741, 1717, 1604, 1502, 1408, 1276, 1222, 1124, 1079, 979, 850, 774, 750, 705, 686, 669 cm^{-1}. *m/z* (ESI-TOF): calcd for $C_{21}H_{23}NO_4Na^+$: 376.1525, found: 376.1518; calcd for $(2\times C_{21}H_{23}NO_4)Na^+$: 729.3152, found: 729.3155.

cis-3-Phenylhexahydrobenzooxazolidin-2-one (**3j**):[27,44] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.51$ (d, $J = 8.6$ Hz, 2H, ArH), 7.39 (t, $J = 7.4$ Hz, 2H, ArH), 7.18 (tt, $J = 7.4$, 1.0 Hz, 1H, ArH), 4.73–4.66 (m, 1H, CH), 4.29 (q, $J = 6.4$ Hz, CH), 2.22–2.10 (m, 1H, CH_2), 2.10–1.98 (m, 1H, CH_2), 1.90–1.78 (m, 1H, CH_2), 1.70–1.50 (m, 4H, CH_2), 1.38–1.25 ppm (m, 1H, CH_2); *m/z* (ESI-TOF): calcd for $C_{13}H_{15}NO_2Na^+$: 240.1000, found: 240.1002; calcd for $(2\times C_{13}H_{15}NO_2)Na^+$: 457.2104, found: 457.2115.

cis-3-Phenylcyclopenteneoxazolidin-2-one (**3k**):[28] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.57$ (d, $J = 8.9$ Hz, 2H, ArH), 7.36–7.42 (m, 2H, ArH), 7.15 (tt, $J = 7.4$, 2.1 Hz, 1H, ArH), 5.09–5.03 (m, 1H, CH), 4.81–4.73 (m, 1H, CH), 2.25–2.13 (m, 1H, CH_2), 2.03–1.95 (m, 1H, CH_2), 1.87–1.67 ppm (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 155.2$, 137.3, 129.2, 124.2, 119.8, 78.6, 61.1, 34.0, 31.7, 22.2 ppm. IR (KBr): $\tilde{\nu} = 2965$, 2920, 2850, 1738, 1718, 1701, 1685, 1654, 1637, 1600, 1560, 1541, 1508, 1491, 1458, 1397, 1262, 1093, 1036, 801, 760, 694, 515 cm^{-1}. *m/z* (ESI-TOF): calcd for $C_{12}H_{13}NO_2Na^+$: 226.0844, found: 226.0845; calcd for $(2\times C_{12}H_{13}NO_2)Na^+$: 429.1790, found: 429.1799.

5,5-Dimethyl-3-phenyloxazolidin-2-one (**3l**):[27] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.53$ (d, $J = 8.7$ Hz, 2H, ArH), 7.37 (t, $J = 7.4$ Hz, 2H, ArH), 7.13 (tt, $J = 7.4$, 2.1 Hz,1H, ArH), 3.77 (s, 2H, CH_2), 1.56 ppm (s, 6H, CH_3); *m/z* (ESI-TOF): calcd for $C_{11}H_{13}NO_2H^+$: 192.1025, found: 192.1022; calcd for $C_{11}H_{13}NO_2Na^+$: 214.0844, found: 214.0848; calcd for $(2\times C_{11}H_{13}NO_2)Na^+$: 405.1790, found: 405.1800.

3-(4-Methylphenyl)-5-methyloxazolidin-2-one (**3m**):[27] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.43$ (d, $J = 8.6$ Hz, 2H, ArH), 7.19 (d, $J = 8.2$ Hz, 2H, ArH), 4.85–4.73 (m, 1H, CH), 4.11 (t, $J = 8.5$ Hz, 1H, CH_2), 3.62 (dd, $J = 8.6$, 7.0 Hz, 1H, CH_2), 2.35 (s, 3H, CH_3), 1.55 ppm (d, $J = 6.2$ Hz, 3H, CH_3); *m/z* (ESI-TOF): calcd for $C_{11}H_{13}NO_2H^+$: 192.1025, found: 192.1024; calcd for $C_{11}H_{13}NO_2Na^+$: 214.0844, found: 214.0850; calcd for $(2\times C_{11}H_{13}NO_2)Na^+$: 405.1790, found: 405.1802.

3-(4-Methoxyphenyl)-5-methyloxazolidin-2-one (**3n**):[30,45] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.44$ (d, $J = 9.1$ Hz, 2H, ArH), 6.92 (d, $J = 9.1$ Hz, 2H, ArH), 4.84–4.74 (m, 1H, CH), 4.10 (t, $J = 8.4$ Hz, 1H, CH_2), 3.82 (s, 3H, OCH_3), 3.61 (dd, $J = 8.6$, 7.1 Hz, 1H, CH_2), 1.54 ppm (d, $J = 6.2$ Hz, 3H, CH_3); *m/z* (ESI-TOF): calcd for $C_{11}H_{13}NO_3H^+$: 208.0974, found: 208.0978; calcd for $C_{11}H_{13}NO_3Na^+$: 230.0793, found: 230.0799; calcd for $(2\times C_{11}H_{13}NO_3)Na^+$: 437.1688, found: 437.1706.

3-(4-Fluorophenyl)-5-methyloxazolidin-2-one (**3o**): White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.55$–7.47 (m, 2H, ArH), 7.14–7.05 (m, 2H, ArH), 4.85–4.76 (m, 1H, CH), 4.12 (t, $J = 8.4$ Hz, 1H, CH_2), 3.63 (dd, $J = 8.6$, 7.1 Hz, 1H, CH_2), 1.56 ppm (d, $J = 6.2$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 160.4$, 158.0, 154.9, 134.5, 120.0(d, $J = 5.8$ Hz), 115.8(d, $J = 22.4$ Hz), 69.5, 52.4, 20.7 ppm. ^{19}F NMR ($CDCl_3$): $\delta = -118.7$ ppm (s); IR (KBr): $\tilde{\nu} = 3080$, 2950, 2930, 2889, 1742, 1514, 1403, 1360, 1223, 1119, 1068, 834, 751, 644, 555, 510 cm^{-1}. *m/z* (ESI-TOF): calcd for $C_{10}H_{10}FNO_2H^+$: 196.0768, found: 196.0770; calcd for $C_{10}H_{10}FNO_2Na^+$: 218.0593, found: 218.0589.

3-(4-Chlorophenyl)-5-methyloxazolidin-2-one (**3p**):[37] White solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.51$ (d, $J = 9.0$ Hz, 2H, ArH), 7.35 (d, $J = 9.0$ Hz, 2H, ArH), 4.87–4.77 (m, 1H, CH), 4.11 (t, $J = 8.4$ Hz, 1H, CH_2), 3.62 (dd, $J = 8.6$, 7.1 Hz, 1H, CH_2), 1.56 ppm (d, $J = 6.3$ Hz, 3H, CH_3); *m/z* (ESI-TOF): calcd for $C_{10}H_{10}ClNO_2H^+$: 212.0478, found: 212.0474; calcd for $C_{10}H_{10}ClNO_2Na^+$: 234.0298, found: 234.0293; calcd for $(2\times C_{10}H_{10}ClNO_2)Na^+$: 445.0698, found: 445.0693.

3-(4-Bromophenyl)-5-methyloxazolidin-2-one (**3q**): Yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.52$–7.43 (m, 4H, ArH), 4.86–4.77 (m, 1H, CH), 4.11 (t, $J = 8.4$ Hz, 1H, CH_2), 3.61 (dd, $J = 8.6$, 7.1 Hz, 1H, CH_2), 1.56 ppm (d, $J = 6.2$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 154.7$, 137.5, 132.0, 119.6, 116.7, 69.6, 51.7, 20.6 ppm. IR (KBr): $\tilde{\nu} = 3035$, 2940, 2870, 1735, 1718, 1685, 1654, 1637, 1590, 1508, 1490, 1414, 1398, 1219, 1126, 1063, 823, 764, 642 cm^{-1}. *m/z* (ESI-TOF): calcd for $C_{10}H_{10}BrNO_2H^+$: 255.9973, found: 255.9969; calcd for $C_{10}H_{10}BrNO_2Na^+$: 277.9793, found: 277.9785.

5-Methyl-3-(4-nitrophenyl)oxazolidin-2-one (**3r**):[27] Yellow solid. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.27$ (d, $J = 9.4$ Hz, 2H, ArH), 7.74 (d, $J = 9.4$ Hz, 2H, ArH), 4.94–4.84 (m, 1H, CH), 4.22 (t, $J = 8.6$ Hz, 1H, CH_2), 3.71 (dd, $J = 8.8$, 7.1 Hz, 1H, CH_2), 1.60 ppm (d, $J = 6.3$ Hz, 3H, CH_3); *m/z* (ESI-TOF): calcd for $C_{10}H_{10}N_2O_4H^+$: 223.0719, found: 223.0712; calcd for $C_{10}H_{10}N_2O_4Na^+$: 245.0538, found: 245.0535; calcd for $(2\times C_{10}H_{10}N_2O_4)Na^+$: 467.1180, found: 467.1186.

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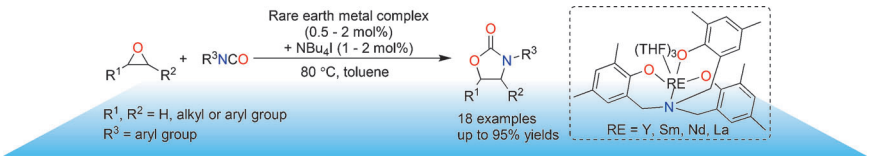
Synthesis of Oxazolidinones from Epoxides and Isocyanates Catalyzed by Rare-Earth-Metal Complexes



Does Kepler-186f count as a rare earth? Rare-earth-metal complexes stabilized by an amino-bridged triphenolate ligand are highly active in catalyzing the cycloaddition of isocyanates and epoxides. Under mild conditions, various terminal and disubstituted epoxides as well as arylisocyanates are transformed into corresponding oxazolidinones with moderate to good yields and good regio- and stereoselectivity.