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Zinc–Azatrane Complexes as Efficient Catalysts for the Conversion of Carbon Dioxide into Cyclic Carbonates

Benjamin Bousquet,^[a] Alexandre Martinez,^{*,[b]} and Véronique Dufaud^{*,[a]}

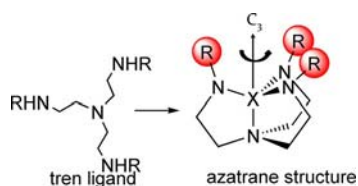
Three Zn complexes based on the N₄-tris(2-aminoethyl)amine (tren) chelating ligand and presenting a C₃-symmetrical axis were synthesized and successfully applied in the coupling of CO₂ with terminal and internal epoxides. These complexes proved to be efficient catalysts if associated with tetrabutylammonium iodide, even at a low catalyst loading (0.005 mol%) or at room temperature, and allowed the production of cyclic carbonates in good to high yields. Variation of the substitution pattern on the tren ligand was shown to impact the catalyst

performance greatly, and the highest turnover number (TON) (up to 11 200) was achieved with the less sterically hindered methyl-substituted Zn^{II}-azatrane complex. These binary Zn–azatrane/NBu₄I catalytic systems could be applied to a wide range of epoxide substrates, including the more challenging internal epoxides. Moreover, although soluble in the reaction medium, Zn–azatrane catalysts could be easily recovered and reused up to three times without any substantial loss in activity, proving their robustness under the reaction conditions.

Introduction

The development of catalytic processes that can control the outcome of a reaction continues to arouse interest from both academia and industry.^[1] Examination of the huge number of existing coordination complexes capable of catalyzing organic transformations in a highly efficient and selective way has revealed some privileged structures,^[2,3] including Schiff base,^[4,5] porphyrine-,^[6,7] and phosphoramidite-derived^[8] complexes, that have been successfully applied in numerous reactions.^[11] Among them, the conversion of carbon dioxide (CO₂) into cyclic carbonates by coupling with epoxides^[9–12] has emerged as a powerful tool to produce renewable chemicals from this greenhouse gas: indeed CO₂ is abundant, cheap, and nontoxic, and as such, it represents an ideal C₁ building block for the development of greener and safer alternatives to fossil-fuel-based resources and phosgene-based organic transformations.^[13,14] Nevertheless, the discovery of catalysts capable of converting carbon dioxide into fine chemical products, under mild operating temperatures and pressures, remains challenging because of its kinetic and thermodynamic stability. In general, active catalytic systems for this reaction involve the use of a metal complex in conjunction with a nucleophile, usually a halide anion, that can be either included within the same structure (monocomponent catalyst)^[15,16] or added separately (bicompo-

nent catalyst)^[17,18] during the catalytic reaction. In all of these catalytic systems, the metal-derived complex (the Lewis acid) and the nucleophile act cooperatively at the epoxide through oxygen-atom coordination and nucleophile ring opening, respectively. Some of the ligand scaffolds mentioned above have been used to build up transition-metal-based catalysts to incorporate CO₂ efficiently into cyclic carbonates. The most performing ligand–metal configurations include N₄-porphyrins,^[19–22] N₄-Schiff bases,^[23,24] N₂O₂-salen/salphen,^[25–28] and N₂O-substituted phenols^[29,30] associated with Al, Co, Fe, Mg, and Zn metals, amongst others. For instance, North et al. described the use of a very active bimetallic aluminum salen complex, either homogeneous^[31,32] or attached to a silica surface through ammonium linkages,^[33] that was able to operate at room temperature and atmospheric pressure of CO₂. Of particular interest to the present report are a series of studies by Kleij et al.^[34,35] on aluminum–aminotriphenolate- and vanadium–aminotriphenolate-based complexes, which showed unprecedented high activity if used in conjunction with tetrabutylammonium halide salts. These catalysts are structurally very similar in terms of geometry to the C₃ tris(2-aminoethyl)amine (tren) ligand coordinated to zinc, which forms the core of the catalyst system we report here. Indeed, tren derivatives are particularly attractive, as upon complexation with a metal or a heteroelement (B, P, Ga.) they can lead to azatrane structures, a well-known class of compounds that present unique features.^[36,37] The tren ligands usually bind in a tetradentate manner, involving both N₃ chelation of the aminoethyl moieties and coordination of the fourth neutral nitrogen donor atom in the apical position (Scheme 1). The simultaneous formation of three five-membered rings provides thermodynamic stability to the whole structure, thereby creating a sterically protected, threefold-symmetric “pocket” around the central element. In addition, the electronic and steric properties can



Scheme 1. Representation of the azatrane structure.

also be easily tuned notably by changing the auxiliary groups on the equatorial nitrogen atoms, thus allowing one to test for structure–activity relationships.

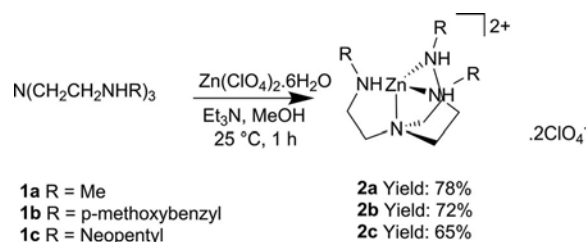
We recently reported on the use of azaphosphatrane (AZAP) structures as single-component organocatalysts for the coupling of CO₂ with various epoxides.^[38,39] Although purely organic catalysts generally require elevated temperatures and pressures to achieve sufficient conversion, the azaphosphatrane catalysts were able to operate at atmospheric pressure of CO₂ and a low catalyst loading (0.1 mol%) without the need for an additional co-catalyst or additives. Mechanistic insight based on kinetic studies showed that dual activation of both the epoxide and CO₂ took place at the same azaphosphatrane molecule, which was further supported by encapsulating the active site of AZAP in a hemicryptophane structure.^[40] Despite these promising results, it appears that this class of ligands has been underexploited, and no catalyst based on a metal–azatrane structure has been described for the conversion of CO₂ into cyclic carbonates.

Herein, we wish to report on the synthesis and characterization of a series of Zn^{II}–azatrane complexes of varying stereo-electronic properties and their utilization in the coupling of CO₂ with epoxides. In addition to being inexpensive and bio-relevant, several Zn complexes bearing N₂O₂ ligands,^[26,27,41] and two examples with N₄-donor ligands,^[42,43] have already proven their efficiency for the production of organic carbonates. To the best of our knowledge, no examples of a C₃-symmetric N₄-chelated Zn complex have been reported for this transformation.

As we shall see, Zn^{II}–azatrane complexes in conjunction with tetrabutylammonium iodide led to the formation of cyclic carbonates in good to high yields. These catalytic systems were still found to be active even at a low catalyst loading (0.005%) or at room temperature, providing high turnover numbers. Structure–activity relationships were evidenced, and the less sterically hindered Zn^{II}–azatrane catalyst was the most active. These Zn catalysts could be reused up to three times without any noticeable loss in activity, showing high stability under the reaction conditions.

Results and Discussion

Three N-substituted Zn^{II}–azatrane complexes bearing methyl (see compound **2a**), *p*-methoxybenzyl (see compound **2b**), and neopentyl (see compound **2c**) groups were readily prepared by mixing corresponding tren ligands **1a–c** with 1 equivalent of the Zn(ClO₄)₂ salt in MeOH at room temperature for 1 h in the presence of a catalytic amount of triethyla-



Scheme 2. Synthesis of Zn^{II}–azatrane complexes **2a–c**.

mine, as shown in Scheme 2. Complexes **2a–c** were isolated in good yields (65–78%) and were fully characterized by NMR spectroscopy (¹H and ¹³C) and HRMS analyses (see the Experimental Section). The ¹H NMR spectra of the tren ligands after complexation to the Zn center reveal the equivalence of the substituents on the three equatorial nitrogen atoms, as illustrated for complex **2a** (Figure S1, Supporting Information). This suggests that all the Zn^{II}–azatrane complexes feature C₃ symmetry in solution with respect to the NMR timescale. HRMS analyses indicate a [M–2ClO₄ + Cl]⁺ molecular fragment for all complexes **2a–c**. The presence of chloride ions could stem either from partial decomposition of the ClO₄[–] anion during analysis or from trace amounts of the chlorine anion present in the spectrometer, which could subsequently coordinate to the Zn center.

In a first series of experiments, screening of the reaction parameters was undertaken to delineate the optimal conditions for the Zn^{II}–azatrane complexes to function efficiently. The coupling of 1,2-epoxyhexane with CO₂ to produce 1-hexene carbonate (EC) was chosen as a benchmark reaction, and **2a** was first evaluated in combination with tetrabutylammonium iodide (*n*Bu₄NI) as a co-catalyst in neat substrate under the following conditions: **2a** (0.25 mol%), *n*Bu₄NI (0.4 mol%), 110 °C, and CO₂ (10 bar, 1 bar = 0.1 MPa). In all of the cases studied, complete selectivity towards the cyclic carbonate was observed. Detailed catalytic protocols and analyses of the crude mixtures by ¹H NMR spectroscopy (Figure S2) are displayed in the Experimental Section and Supporting Information, respectively. The time-dependent reaction profile of **2a** is provided in Figure S3. One can see that the reaction with **2a** proceeded rapidly, achieving up to 79% yield¹ in EC after 3 h and full conversion after 6 h. To allow for the observation of subtle effects among the different Zn^{II}–azatrane catalysts, the other parameters were assessed using a time of 3 h, as this time period allowed sufficient and differentiable conversion of the 1,2-epoxyhexane substrate. The effect of the reaction temperature on the catalytic performance of **2a** was then investigated, as the temperature can impact both the reaction rate and the solubility of CO₂ in the reaction medium. The results shown in Figure S4 reveal that the reaction temperature strongly affected the catalyst reactivity, as only a trace amount of the EC prod-

¹ All yields in this article were determined by integration of clearly identified product signals in the NMR spectrum in the presence of an internal standard (mesitylene). For protocols for the purification of cyclic carbonates at the gram scale, see Luis Martínez-Rodríguez et al.^[46]

uct was detected at 50 °C, whereas increasing the temperature from 80 to 130 °C led to a marked increase in the yield of EC with nearly full conversion at 130 °C. As working at too high a temperature involves a high energy input, which is not attractive from a green perspective, 110 °C was considered as a suitable reaction temperature with the production of 1-hexene carbonate in 79% yield after 3 h. The activation energy for EC formation derived from the kinetic data at variable temperatures (Figure S5) was found to be $(43 \pm 4.2) \text{ kJ mol}^{-1}$, which compares well with the values reported in the literature for the coupling of CO₂ with various epoxides by using Zn^[44] and other metal^[45] complexes. The pressure of CO₂ is also a key parameter to explore, as it may dramatically impact the conversion of epoxides into cyclic carbonates. As shown in Figure S6, our catalytic system, **2a**/*n*Bu₄Ni, exhibited no activity at 1 bar of CO₂, as only a trace amount of the EC product was detected by ¹H NMR spectroscopy. However, increasing the CO₂ pressure further to 5 and 10 bar led to a steady increase in the EC yield up to a maximum of 79% at 10 bar, after which the yield decreased slightly with increasing pressure. Thus, a pressure of 10 bar seemed to be ideal for **2a** to operate efficiently. If binary catalysts are at stake, another parameter that may affect reactivity is the relative molar ratio between the two catalyst components. Figure S7 shows the dependence of the EC yield on the concentration of the *n*Bu₄Ni co-catalyst while keeping the concentration of catalyst **2a** (0.25 mol%) constant. Using a 1:1 molar ratio of **2a**/*n*Bu₄Ni led to poor activity with an EC product yield of only 9% after 3 h. However, increasing the amount of *n*Bu₄Ni slightly from 1 to 1.6 equivalents with respect to **2a** significantly impacted the reaction, and a yield of 79% was attained within the same timeframe. Increasing the quantity of the *n*Bu₄Ni co-catalyst further to 2 and 3 equivalents led to additional improvements in activity, achieving 87 and 95% yield, respectively.

The nature of the nucleophile is also a crucial parameter to consider, as it is involved in the first step of the catalytic cycle, that is, opening of the epoxide ring. To investigate the effect of the halide anion of the ammonium salt co-catalyst, we chose to use a 1:1.6 molar ratio of **2a**/*n*Bu₄NX under the previously optimized conditions to differentiate minor reactivity changes between the binary catalytic systems. The results are displayed in Table 1.

Table 1. Influence of the halide anion on the coupling of CO₂ with 1,2-epoxyhexane using **2a**/*n*Bu₄NX binary catalytic systems.^[a]

| Entry | Catalyst | Co-catalyst | Yield [%] |
|-------|-----------|------------------------------|-----------|
| 1 | 2a | – | 0 |
| 2 | – | <i>n</i> Bu ₄ Ni | 20 |
| 3 | – | <i>n</i> Bu ₄ NBr | 12 |
| 4 | – | <i>n</i> Bu ₄ NCl | 16 |
| 5 | 2a | <i>n</i> Bu ₄ Ni | 79 |
| 6 | 2a | <i>n</i> Bu ₄ NBr | 50 |
| 7 | 2a | <i>n</i> Bu ₄ NCl | 6 |

[a] Reaction conditions: 1,2-epoxyhexane (10 mmol), CO₂ (10 bar), 110 °C, 3 h, **2a** (0.25 mol%), *n*Bu₄NX (0.4 mol%). Yields were determined by ¹H NMR spectroscopy by using mesitylene as an internal standard.

Under these conditions, one can see that **2a** alone was not active (Table 1, entry 1) and that the reactions performed with the tetrabutylammonium halides but without **2a** proceeded very modestly with yields below 20% (Table 1, entries 2–4). Contrarily to what was observed with *n*Bu₄Ni, the association of **2a** with *n*Bu₄NBr and *n*Bu₄NCl resulted in lower yields. These marked differences in reactivity mirror the nucleophilicity and leaving ability of the anions, which is, under solventless conditions, I[–] > Br[–] > Cl[–]. Surprisingly, combining **2a** with *n*Bu₄NCl gave rise to a decrease in the yield with respect to the corresponding ammonium used alone (6 vs. 16% yield), whereas a significant gain in activity was observed in the other cases. The interaction between the chlorine anion (hard Lewis base) and the zinc catalyst (hard Lewis acid) could account for the decrease in activity of this binary system. The *n*Bu₄Ni co-catalyst was thus chosen to pursue our catalytic studies, as it showed the highest activity if combined to **2a**.

The effect of the substitution patterns of the Zn-azatrane catalysts on the catalytic performance was then investigated by using binary catalytic system **2a–c**/*n*Bu₄Ni under the optimized conditions. As shown in Table 2 (entries 1–3), Zn^{II}-azatrane complexes bearing *p*-methoxybenzyl (see complex **2b**) and neopentyl (see complex **2c**) groups both exhibited lower activity than methyl-substituted complex **2a** (65 vs. 79%), but the overall performance of all three Zn-azatrane catalysts at this short reaction time (3 h) remained very good with turnover numbers (TONs) up to 316. The gain in activity of approximately 23% obtained with **2a** (105 vs. 85/87 h^{–1}) could be correlated to the lower steric hindrance of the methyl groups around the Zn center, thus promoting the coordination and activation of the epoxide at the Lewis acid site. To explore further the structural dependence in terms of catalyst efficiency and to develop more environmentally friendly catalysts, the catalyst and nucleophile loadings were reduced by a factor of 50 to 0.005 mol% for Zn-azatranes **2a–c** and by a factor of 16 to 0.025 mol% for *n*Bu₄Ni. Under these low-loading conditions, one can see that Zn catalysts **2a–c** all exhibited high efficiency and robustness with TONs ranging from 5400 to 11 200 after 24 h of reaction (Table 2, entries 4–6). Notably, *n*Bu₄Ni alone at a 0.025 mol% loading showed very low activity (7% yield; Table 2, entry 7). The best results were obtained with the binary system **2a**/*n*Bu₄Ni, the activity of which was approximately twofold higher than that of catalysts **2b** and **2c** (467 vs. 225–250 h^{–1}). Here again, the lower steric hindrance around the Zn catalytic center in **2a** could account for this enhanced reactivity, highlighting the importance of the available space above the Lewis acidic site to synergistically activate the epoxide. Relative to that shown by other N₄-chelated Zn catalysts, Zn-azatrane catalysts **2a–c** showed better performance in the coupling of CO₂ with epoxyhexane with, in the case of best catalyst **2a**, turnover frequencies (TOFs) on average 47 and 6 times higher than those obtained with Zn-bpb^[42] [bpb = *N,N*-bis-(2-pyridinecarboxamide)-1,2-benzene, TOF: 10 h^{–1}, 80 °C, 20 h, 50 bar, Zn/*n*Bu₄NBr = 0.2/0.2] and Zn-pyrrolidine-based catalysts^[43] (TOF: 75 h^{–1}, 80 °C, 20 h, 35 bar, Zn/*n*Bu₄Ni = 0.005/0.1), respectively. The activation of CO₂ at room temperature is highly challenging and few catalytic systems are able to ach-

Table 2. Influence of the structural features of the catalyst on the coupling of CO₂ with 1,2-epoxyhexane by using the **2a**-c/*n*Bu₄Ni binary catalytic system.^[a]

| Entry | Catalyst | Catalyst loading [mol %] | <i>n</i> Bu ₄ Ni [mol %] | <i>T</i> [°C] | <i>t</i> [h] | Yield [%] | TON | TOF [h ⁻¹] |
|-------|-----------|--------------------------|-------------------------------------|---------------|--------------|-----------|--------|------------------------|
| 1 | 2a | 0.25 | 0.4 | 110 | 3 | 79 | 316 | 105 |
| 2 | 2b | 0.25 | 0.4 | 110 | 3 | 64 | 256 | 85 |
| 3 | 2c | 0.25 | 0.4 | 110 | 3 | 65 | 260 | 87 |
| 4 | 2a | 0.005 | 0.025 | 110 | 24 | 56 | 11 200 | 467 |
| 5 | 2b | 0.005 | 0.025 | 110 | 24 | 27 | 5400 | 225 |
| 6 | 2c | 0.005 | 0.025 | 110 | 24 | 30 | 6000 | 250 |
| 7 | – | – | 0.025 | 110 | 24 | 7 | – | – |

[a] Reaction conditions: 1,2-epoxyhexane (10 mmol), CO₂ (10 bar). Yields were determined by ¹H NMR spectroscopy by using mesitylene as an internal standard. Turnover number (TON) and turnover frequency (TOF) values are based on the Zn catalyst.

ieve the conversion of CO₂ under such mild conditions. We were pleased to observe that complex **2a** retained some catalytic activity at room temperature to afford the cyclic product in 12% yield after a period of 24 h by using the following conditions: **2a** (2 mol %), *n*Bu₄Ni (1 mol %), CO₂ (10 bar), and 1,2-epoxyhexane (10 mmol). The activity was much lower with **2b** and **2c** (4 and 2% yield, respectively), underlining the better catalytic efficiency of **2a**, in agreement with the results obtained at low loadings (Table 2, entries 4–6).

As **2a**/*n*Bu₄Ni appears to be the most efficient system, its applicability to other epoxides was investigated under the optimized conditions. As clearly observed from Table 3, **2a** was applicable to a variety of terminal and internal epoxides, affording exclusively the corresponding cyclic carbonate products in good to high yields. Monosubstituted terminal epoxides were readily converted within a 3 h timeframe into their related carbonates with yields ranging from 75 to 95%, whereas a longer reaction time (24 h) was necessary to achieve sufficient conversion for more challenging disubstituted and terminal 1,2-epoxy-2-methylpropane (55% yield) and for sterically hindered cyclohexene oxide and cyclopentene oxide (23 and 67% yield, respectively), both obtained with full retention of configuration (*cis* > 99%). Although the reaction conditions reported in the literature are slightly different from ours to provide meaningful comparison, our binary **2a**/*n*Bu₄Ni catalytic system compares favorably with other N₄-chelated Zn catalysts,^[42,43] exhibiting, in most cases, greater efficiency for the conversion of terminal and even internal epoxides than the Zn-bpb catalyst reported recently by Adolph et al.^[42]

The reuse of metallic catalysts is also an important issue to investigate from economical and practical use viewpoints. The reusability of **2a** and **2b** was thus examined under the optimized reaction conditions by using 1,2-epoxyhexane as a model substrate over three catalytic cycles. Although homogeneous in nature, azatrane complexes **2a** and **2b** could be readily recovered from the reaction mixture by precipitation in diethyl ether before use in a subsequent run. For each catalytic run, fresh epoxide and the *n*Bu₄Ni co-catalyst, in the appropriate molar ratio, were introduced in the reactor along with

Table 3. Substrate scope in the coupling of CO₂ with various terminal and internal epoxides catalyzed by **2a**/*n*Bu₄Ni.^[a]

| | | |
|--------------------|--------------------|--------------------|
| | | |
| Yield: 79% 3 h | Yield: 87% 3 h | Yield: 75% 3 h |
| | | |
| Yield: 95% 3 h | Yield: 75% 3 h | Yield: 55% 24 h |
| | | |
| Yield: 23% 24 h | Yield: 67% 24 h | |

[a] Reaction conditions: epoxide (10.0 mmol), **2a** (0.25 mol %), *n*Bu₄Ni (0.4 mol %), 110 °C, CO₂ (10 bar). Yields were determined by ¹H NMR spectroscopy by using mesitylene as an internal standard.

spent catalyst **2a** or **2b**, and the reaction was launched for a duration of 3 h. The yields of the EC product after three repeated runs for both azatrane catalysts are shown in Figure 1. Interestingly, no significant loss in catalytic activity was observed with **2b** over three runs, emphasizing the stability of this catalyst under the reaction conditions and the viability of the recovering method. In the case of **2a**, the high initial activity achieved with this catalyst was maintained for the first two cycles, after which a slight decrease was observed. We believe that higher steric hindrance around the Zn site correlates with catalyst stability by maintaining the azatrane structure intact, thus protecting the Lewis acidic center.

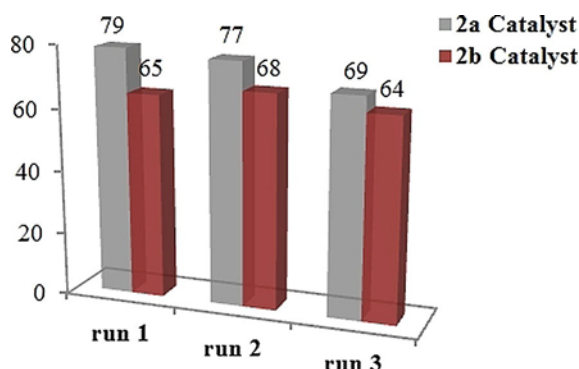


Figure 1. Recyclability of catalysts **2a** and **2b** after a 3 h period. Reaction conditions: 1,2-epoxyhexane (10 mmol), catalyst **2a** or **2b** (0.25 mol %), *n*Bu₄NI co-catalyst (0.4 mol %), 110 °C, CO₂ (10 bar).

Conclusions

Three N₄-chelated Zn complexes based on the tris(2-aminoethyl)amine (tren) scaffold were synthesized and successfully tested as catalysts in the coupling of CO₂ with epoxides to produce cyclic carbonates. Under the optimized reaction conditions (110 °C, 10 bar CO₂, 3 h), all three tripodal Zn-azatrane complexes associated with a *n*Bu₄NI co-catalyst exhibited good to high activity within this short reaction timeframe with yields and turnover numbers (TONs) up to 79% and 316, respectively. Performing the reactions at a low catalyst loading (0.005 mol %) or at room temperature evidenced that less sterically hindered methyl-substituted Zn^{II}-azatrane **2a** was the most efficient catalyst of the series, highlighting the importance of the accessibility of the Lewis acid site to synergistically activate the epoxide. With binary catalyst system **2a**/*n*Bu₄NI, TONs as high as 11 200 could be achieved, an activity far superior to that reported for other N₄-chelated Zn complexes (i.e., Zn-pyrrolidine-based catalyst). We also showed that **2a**/*n*Bu₄NI could be applied to a wide range of epoxide substrates, converting terminal epoxides into their corresponding carbonates in high yields (75 to 95%) in only 3 h, whereas a longer reaction period (24 h) was required in the case of internal and more sterically congested epoxides to attain satisfactory conversion (27 to 67%). Finally, the Zn-azatrane complexes could be reused up to three times without any substantial loss in activity, underlining their robustness under the reaction conditions. Current work concentrates on optimizing the design of solid catalysts derived from the Zn-azatrane motif towards higher recycling capacities and on the introduction of chirality to develop high-value added enantioselective pathways by using CO₂ as a raw reagent.

Experimental Section

General

The commercial reagents Zn(ClO₄)₂·6H₂O and tren (**1a**) were purchased from Aldrich Chemicals and were used without further purification. Solvents were dried by using standard methods and

were stored over activated 4 Å molecular sieves. Depending on the experiments, ¹H NMR and ¹³C NMR spectra were recorded with a Bruker Avance 300 spectrometer at 300.1 and 75.48 MHz, respectively, or a Bruker Avance HD III 400 spectrometer at 400.1 and 100.6 MHz, respectively. Chemical shifts were referenced to tetramethylsilane. Mass spectral analyses were performed with a Nermag R10-10C for exact mass. Compounds **1b** and **1c** were synthesized according to literature procedures.^[47]

Synthesis and characterization of Zn^{II}-azatrane complexes **2a–c**

In a Schlenk flask, equimolar amounts of tren ligands **1a–c** and Zn(ClO₄)₂·6H₂O were solubilized in methanol (1 mL) and stirred for 1.5 h at room temperature. After the evaporation of methanol, obtained complexes **2a–c** were washed with small portions of diethyl ether, resolubilized in acetonitrile, and reprecipitated by the drop-wise addition of diethyl ether. Complexes **2a–c** were obtained as crystalline powders and dried under vacuum at room temperature.

2a: Yield: 78%; ¹H NMR (300.1 MHz, CD₃OD, 298 K): δ = 2.52 (m, 4H), 2.34 (s, 3H), 1.92 ppm (m, 1H); ¹³C NMR (100.6 MHz, CD₃OD, 298 K): δ = 32.34, 46.55, 50.39 ppm; HRMS (ESI): *m/z*: calcd for C₉H₂₄ClN₄Zn: 287.0975 [*M*–2ClO₄+Cl]⁺; found: 287.0975.

2b: Yield: 72%; ¹H NMR (300.1 MHz, CDCl₃, 298 K): δ = 1.70–2.07 (m, 2H), 2.57–2.78 (m, 2H), 3.68 (s, 3H), 6.56 (m, 2H), 7.29 ppm (m, 2H); ¹³C NMR (100.6 MHz, CD₃CN, 298 K): δ = 53.18, 47.90, 51.57, 54.39, 113.92, 130.46, 130.75, 159.95 ppm; HRMS (ESI): *m/z*: calcd for C₃₀H₄₂ClN₄O₃Zn: 605.2231 [*M*–2ClO₄+Cl]⁺; found: 605.2227.

2c: Yield: 65%; ¹H NMR (300.1 MHz, CD₃OD, 298 K): δ = 1.10 (s, 9H), 2.78 (s, 2H), 2.90 (t, 2H), 3.07–3.21 ppm (m, 2H); ¹³C NMR (100.6 MHz, CD₃CN, 298 K): δ = 27.09, 32.66, 46.18, 49.63, 59.71 ppm; HRMS (ESI): *m/z*: calcd for C₂₁H₄₈ClN₄Zn: 455.2890 [*M*–2ClO₄+Cl]⁺; found: 455.2853.

Catalytic procedure

In a typical experiment, 1,2-epoxyhexane (10.0 mmol), Zn^{II}-azatrane complex **2** (0.25 mol %), and *n*Bu₄NX (X = Cl, Br, I; 0.40 mol %) were loaded into a 25 mL stainless autoclave. The reactor was flushed (3×) at room temperature with CO₂ (99.99%, 5 bar) to remove air from the vessel before it was charged to 10 bar of CO₂ and the temperature was raised to 110 °C. After the desired reaction time, the reactor was cooled with an ice bath to stop the reaction, and finally, the excess amount of CO₂ was carefully released. The crude mixture was analyzed by ¹H NMR spectroscopy by using mesitylene as an internal standard. A typical ¹H NMR spectrum of the crude reaction mixture is provided in the Supporting Information (Figure S2).

Recycling procedure

In the recycling experiment, used catalyst **2a** or **2b** was fully recovered from the reaction mixture by precipitation with diethyl ether. After separation by filtration and careful washing with diethyl ether (3×2 mL), the spent catalyst was dried at 50 °C overnight in an oven and then reused for another run, maintaining the molar ratio of epoxide and the *n*Bu₄NI co-catalyst as described above for a typical test.

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