

Robust zinc complexes bearing pyrrolidine based ligands as recyclable catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides.

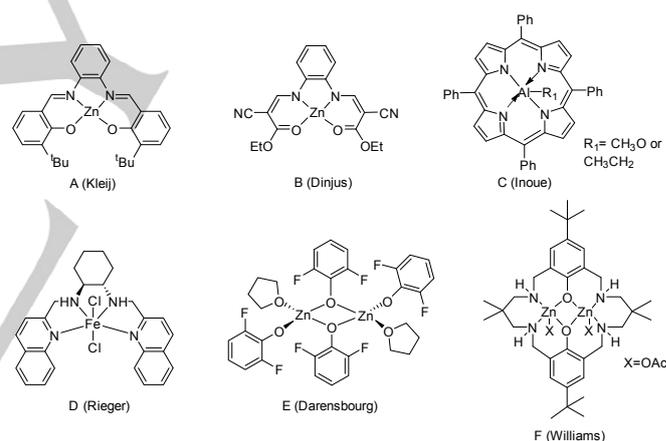
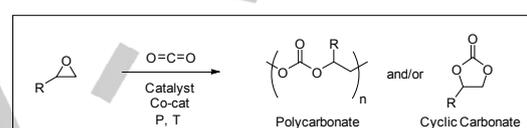
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Abstract: New zinc catalysts bearing the ligands **1-4** containing a pyrrolidine scaffold were synthesized and successfully tested in the coupling of CO₂ with terminal and internal epoxides, providing excellent activity and total selectivity to the corresponding cyclic carbonates, even for challenging substrates such as cyclohexene oxide, trans-1,2-epoxybutane and methyl epoxioleate. The **Zn-3/TBAI** catalytic system revealed as the most active of the series and its robustness was demonstrated through TON values up to 1840 for propylene oxide. The recycling of this catalytic system was also performed up to 5 times without relevant loss of activity using this substrate.

Introduction

Carbon dioxide (CO₂) is an abundant, inexpensive, non-toxic and widely available renewable carbon source. However, its use for the production of valuable chemicals is often hampered due to its thermodynamic stability.^{1,2} This issue can be overcome by the use of catalysts and/or highly reactive products such as epoxides or oxetanes. The development of chemical processes that can convert CO₂ into high added-value products is thus an important goal for scientists.³ One of the most successful processes for the use of CO₂ is the coupling with epoxides to produce polycarbonates and/or cyclic carbonates. This transformation avoids the use of phosgene as a reagent, which makes this process environmentally benign and 100% atom economical.⁴ Polycarbonates have various applications such as thermoplastics, packaging materials, etc. due to their inherent properties which include durability, heat resistance, strength, high transparency, electrical insulation and compatibility with other polymers.⁵⁻⁷ Cyclic carbonates can also be used for numerous applications such as polar aprotic solvents, additives, plasticizers, precursors for poly(carbonate) synthesis and more recently as useful intermediates in organic synthesis.⁸⁻¹⁰

The metal-free coupling of CO₂ with epoxides was shown to be kinetically disfavored due to the high energy barrier associated with this transformation.^{11,12} Catalytic systems for the coupling of CO₂ and epoxides include the combination of metal complexes with quaternary ammonium or phosphonium salts, halides or ionic liquids.⁴ The anion of these co-catalysts act as a nucleophile and ring-opens the epoxide or labilizes the *trans*-coordinated ligands.^{13,14}



Scheme 1. Successful catalysts reported for the formation of polycarbonates/cyclic carbonates from CO₂ and epoxides.

Since the pioneering work of Inoue and co-workers for the copolymerization of CO₂ with epoxides,¹⁵ an increasing number of homogeneous and heterogeneous catalysts have emerged in this area.^{10,16} The homogeneous catalysts can be employed alone when the ligand contains a nucleophile moiety or in combination with a co-catalyst which provides the nucleophilic species. To date, the most efficient catalysts involve aluminium,¹⁷ cobalt,¹⁸ iron,¹⁹ chromium²⁰ and zinc²¹ as the most suitable metals. Among those, Zn based complexes exhibit some advantages such as low toxicity, lower price and higher stability towards oxidation.⁴ The most common ligands reported for this process are based on Salen/Salphen and related ligands (N₂O₂),²²⁻²⁵ tetraarylporphyrins (N₄),²⁶ Schiff bases (N₄),²⁷ or substituted phenols and related ligands (N₂O/N₄O₂)^{28,29} (Scheme 1). In the formation of cyclic carbonates from CO₂ and epoxides catalyzed by Zn catalysts,

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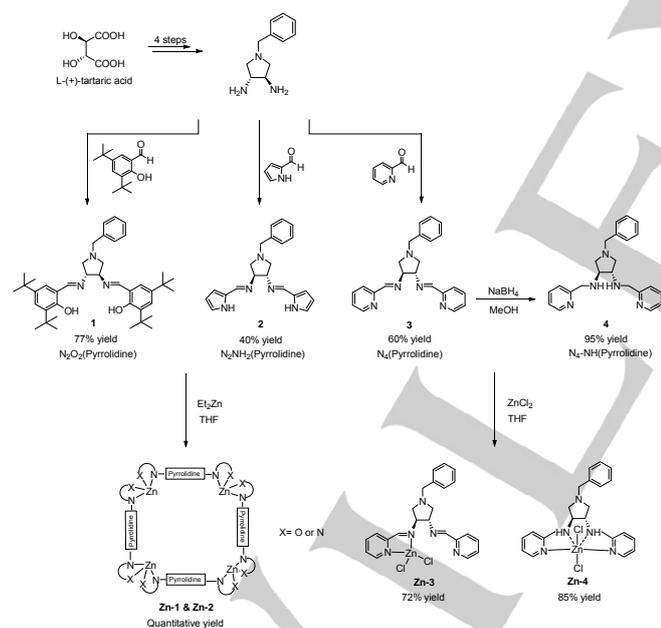
N_2O_2 ligands were shown to form highly active catalysts while $N_2(NH)_2$ and N_4 ligands are far less studied. To the best of our knowledge, only one study using Zn(II) complexes bearing N_4 ligands has been reported up to date.³⁰

Here, we report the synthesis and characterization of a series of zinc complexes bearing N_2O_2 , $N_2(NH)_2$ and N_4 ligands containing a pyrrolidine scaffold and their utilization in the coupling of CO_2 with a variety of epoxides.

Results and Discussion

Synthesis and characterization of zinc complexes.

The synthesis of the ligands N_2O_2 (**1**), $N_2(NH)_2$ (**2**), N_4 (**3**) and N_4-NH (**4**) was carried out by condensation of (*3R,4R*)-3,4-diamino-1-benzylpyrrolidine with two equivalents of the appropriate aldehyde to yield the corresponding compounds in moderate to good yields (see supporting information for synthetic details) (Scheme 2). It has to be mentioned that the chiral salen N_2O_2 (pyrrolidine) **1** has been synthesized by modifying a previously described procedure.³¹ The ligands **2-4** were characterized using NMR spectroscopy, IR spectroscopy, HRMS and Elemental Analysis (see supporting information).



Scheme 2. Synthesis of the ligands and related Zn(II) complexes **Zn-1-4** used in this study.

The corresponding air stable Zn(II) complexes were synthesized by reaction with Et_2Zn (for **Zn-1** and **Zn-2** complexes) or with $ZnCl_2/THF$ (for **Zn-3** and **Zn-4** complexes) (Scheme 2). In the 1H NMR spectra of the complexes **Zn-1** and **Zn-2**, the detected resonances indicated the formation of symmetric species.

Compared to the spectra of the ligands, the higher chemical shift observed for the $CH=N$ moiety and the absence of broad OH/NH signals suggested the coordination of the ligands through the imine and phenoxo groups. Similarly, in the corresponding IR spectra, the absence of a strong absorption band in the $\nu(O-H)$ region (ca 3600 cm^{-1} for **Zn-1** complex) and $\nu(N-H)$ region (ca 3400 cm^{-1} for **Zn-2** complex), and the shift to lower frequencies of the $\nu(C=N)$ stretching band ($\nu(C=N)_{\text{free ligand}} = 1625\text{ cm}^{-1}$, $\nu(C=N)_{\text{complex}} = 1598\text{ cm}^{-1}$ for **Zn-1** complex) and ($\nu(C=N)_{\text{free ligand}} = 1633\text{ cm}^{-1}$, $\nu(C=N)_{\text{complex}} = 1579\text{ cm}^{-1}$ for **Zn-2**) confirmed a tetradentate coordination mode for both ligands. Importantly, the mass spectra (HRMS) of these complexes revealed the formation of tetrameric species of formula $[Zn_4(L)_4]$. This result was confirmed when crystals of **Zn-1** suitable for X-ray diffraction were obtained by vapor diffusion from EtOH in hexane at room temperature (Figure 1).

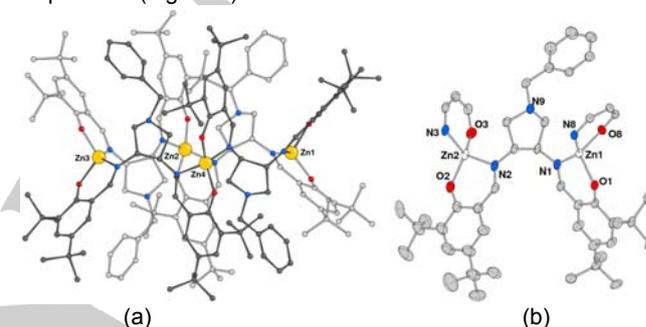


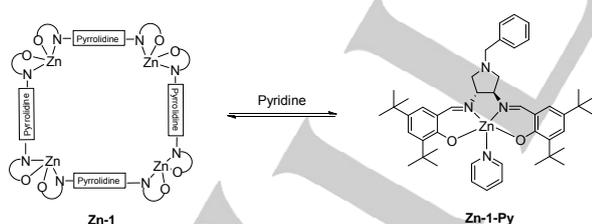
Figure 1. a) Crystal structure of the tetranuclear complex $[Zn_4(\mathbf{1})_4]$ (only disordered groups at higher occupancy are shown); b) Detail of $[Zn_4(\mathbf{1})_4]$ showing the ligand coordinated to zinc atoms Zn1 and Zn2 (probability ellipsoids at 40%; solvent molecules and H atoms are omitted for clarity and only a partial labelling scheme is illustrated).

The complex $[Zn_4(\mathbf{1})_4]$ forms a cyclic tetrameric aggregate where the two N,O moieties of each ligand coordinate to two Zn atoms. The metals, located at a mean distance of 6.75 \AA , afford a rhomboid arrangement with intermetallic angles of ca. 70 and 110° . The ligands are arranged in such a way that the benzylpyrrolidine moieties are located alternatively above and below the mean plane through the metal atoms, so that the complex presents a pseudo S_2 -symmetry. Each Zn(II) atom, chelated by two salicylaldimine N,O donors from different ligands, exhibits a slightly distorted tetrahedral geometry with close comparable Zn-O and Zn-N bond distances (Table 1) that vary in the range $1.893(4)$ - $1.921(3)$ and $2.000(3)$ - $2.034(3)$ \AA , respectively. The chelating O-Zn-N bond angles average at ca. 97.0° . All these data are within the range detected in other salicylaldimine tetranuclear zinc complexes reported in the literature.^{32,33} Nevertheless, few examples can be found in which two zinc metal atoms are bound to one ligand,³³ which is indeed our case scenario. This fact was attributed by Harder and co-workers to the rigidity of the backbone used.

Table 1. Selected Bond distances (Å) and Angles (deg) for [Zn₄(1)₄].

Bond lengths			
Zn(1)-O(1)	1.918(3)	Zn(2)-O(2)	1.903(3)
Zn(1)-O(8)	1.921(3)	Zn(2)-O(3)	1.900(3)
Zn(1)-N(1)	2.000(3)	Zn(2)-N(2)	2.021(3)
Zn(1)-N(8)	2.008(3)	Zn(2)-N(3)	2.030(3)
Bond angles			
O(1)-Zn(1)-N(1)	96.50(11)	O(2)-Zn(2)-N(2)	96.75(13)
O(8)-Zn(1)-N(8)	95.09(12)	O(3)-Zn(2)-N(3)	96.24(14)
O(1)-Zn(1)-O(8)	111.87(12)	O(2)-Zn(2)-O(3)	123.85(14)
O(1)-Zn(1)-N(8)	111.39(11)	O(2)-Zn(2)-N(3)	115.31(15)
O(8)-Zn(1)-N(1)	106.17(12)	O(3)-Zn(2)-N(2)	116.77(14)
N(1)-Zn(1)-N(8)	135.46(12)	N(2)-Zn(2)-N(3)	108.14(13)

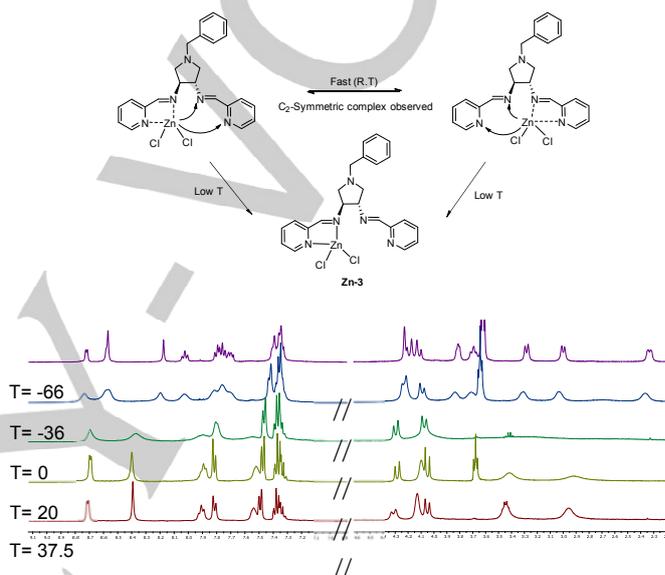
In order to test the stability of such tetrameric structure, a sample of **Zn-1** was dissolved in pyridine-*d*₅ and a ¹H-NMR spectrum was recorded. Two sets of signals were detected in a 1:10 ratio, indicating that two species were present under these conditions. The major product was characterized by NMR and MS (ESI-TOF) (see supporting information) and identified as the mononuclear complex **Zn-1-Py** (Scheme 3) containing a pyridine ligand coordinated to the zinc atom. Similar species were previously detected by Kleij and co-workers for a Zn(II) complex containing salphen ligands.³⁴ The minor product was attributed to unreacted **Zn-1** tetranuclear complex.

**Scheme 3.** Reactivity of the tetrameric **Zn-1** complex in pyridine.

The zinc complexes **Zn-3** and **Zn-4** were synthesized in THF by reaction of the ligands **3** and **4** in the presence of ZnCl₂ at room temperature and isolated as orange powders in yields over 70%. Interestingly, 12 signals were detected in the ¹H NMR spectrum of complex **Zn-3** at room temperature, indicating the formation of a C₂-symmetric complex. Furthermore, 7 of these resonances in both the aromatic and the aliphatic regions were broad,

suggesting a fluxional behavior for this complex. These signals were attributed to the pyridine moiety at 8.70, 7.89 and 7.52 ppm, the C=N fragment (8.40 ppm), and three signals at 4.20, 3.42, 2.92 ppm corresponding to the CH- and CH₂- protons of the pyrrolidine backbone (Figure 2).

To clarify the structure of the complex, NMR spectra was recorded at low temperature (-66 °C) where new signals were detected (Figure 2). The 7 broad set of signals that appeared at room temperature were split into two sets of signals in all cases, indicating that the ligand was not symmetrically coordinating to the Zn centre.

**Figure 2.** ¹H-NMR spectra of **Zn-3** complex in CD₂Cl₂ at various temperatures (°C).

In the IR spectrum of complex **Zn-3**, two bands were detected in the ν(C=N) region at 1644 and 1597 cm⁻¹. The band at 1644 cm⁻¹ was attributed to an uncoordinated imino group whereas the band at 1597 cm⁻¹ was assigned to an imine moiety coordinated to Zn. This result was thus in agreement with the NMR observations. To gain information on the coordination of the chloride atoms in this complex, the molar conductivity of **Zn-3** was recorded (0.001 M in THF) and the obtained value (Λ_M = 0.062 Ω⁻¹·cm²·mol⁻¹) indicated the coordination of the chloride atoms to the zinc centre.

In view of these results, it can be concluded that a rapid exchange between the two “arms” of the ligand (one coordinated to Zn and one uncoordinated) occurs at room temperature, leading to the detection of a C₂-symmetric complex. At low temperature, this exchange process is slowed down and resonances for both the coordinated and uncoordinated arms were detected (Figure 2). X-ray diffraction of the mononuclear Zn (II) complex [Zn(**3**)Cl₂] confirmed this hypothesis where the metal presents a distorted trigonal bipyramidal coordination geometry. An Ortep view of the

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complex is shown on Fig.3 and relevant bond lengths and angles are listed in Table 2.

The ligand acts as a tridentate species with pyridine N(1) and amine nitrogen N(3) occupying the axial positions in the TBP geometry, and the two chlorides and the imine nitrogen N(2) are located in the equatorial plane. Remarkably, the imine nitrogen donor appears to be bound more strongly to Zn than the pyridine (Zn-N(2) of 2.0619(19) vs Zn-N(1) of 2.202(2) Å), while the pyrrolidine nitrogen N(3) has a significantly weaker interaction with the zinc atom (Zn-N(3) of 2.388(2) Å), nevertheless providing a stabilizing effect around the metal centre (Figure 3).

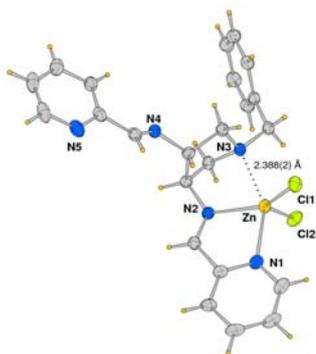


Figure 3. Crystal structure for [Zn(3)Cl₂] with probability ellipsoids drawn at the 50% level. Only a partial labelling scheme is illustrated for clarity.

The N(1)-Zn-N(3) bond angle of 150.11(7)° and data of Table 2 give indication of the distortions from the ideal values around the coordination sphere due to the requirements to accomplish the formation of two five-membered rings.

Table 2. Selected Bond distances (Å) and Angles (deg) for [Zn(3)Cl₂].

Bond lengths			
Zn-N(1)	2.202(2)	Zn-Cl(1)	2.229(7)
Zn-N(2)	2.062(19)	Zn-Cl(2)	2.247(7)
Zn-N(3)	2.388(2)		
Bond angles			
N(1)-Zn-N(2)	76.00(8)	N(2)-Zn-Cl(1)	123.30(6)
N(2)-Zn-N(3)	74.18(7)	N(2)-Zn-Cl(2)	116.01(6)
N(1)-Zn-N(3)	150.11(7)	N(3)-Zn-Cl(1)	97.21(5)
N(1)-Zn-Cl(1)	97.31(6)	N(3)-Zn-Cl(2)	94.68(5)
N(1)-Zn-Cl(2)	100.15(6)	Cl(1)-Zn-Cl(2)	120.55(3)

Recently, Yang and co-workers reported a series of Zn(II) complexes containing similar N₄ ligands and showed that the

rigidity of the diamine backbone played a crucial role in the structure of the resulting complexes.³⁵ With flexible or semi-flexible backbones such as 1,4-diaminobutane or 1,2-cyclohexanediamine, the formation of dinuclear Zn(II) complexes of type [Zn₂(L)Cl₄] was observed, whereas with more rigid backbones such as 1,2-phenylenediamine, mononuclear complexes of type [Zn(L)Cl₂], with only one imino and pyridine nitrogen bound to the metal center, were obtained. This suggests that our pyrrolidine backbone acts as a rigid backbone, leading to the formation of the mononuclear complex [Zn(3)Cl₂] with only one imine and pyridine nitrogen atoms bound to the metal centre. The ¹H-NMR spectrum of complex **Zn-4** showed the expected signals when both the pyridine and the NH- groups are coordinated to the zinc atom. Mass spectrum (HRMS) exhibited a molecular peak at m/z = 472.1262 corresponding to the mononuclear species [ZnCl₂(4)] (calc for C₂₃H₂₇N₅ClZn m/z = 472.1241 [M-Cl]⁺). In addition, the molar conductivity of **Zn-4** (0.001M in DMSO, λ_M = 16.05 Ω⁻¹·cm²·mol⁻¹) confirmed the coordination of the chloride atoms to the zinc metal. This complex was therefore identified as [Zn(N,N-4)(Cl)₂] (Scheme 2).

Catalytic test using Zn(II) complexes for the coupling of CO₂ with epoxides

Complexes **Zn1-4** were tested as catalysts in the coupling of CO₂ with 1,2-epoxyhexane as model substrate. The effect of the nature of the co-catalyst, catalyst/co-catalyst ratio, pressure and temperature were particularly looked at. Based on reported data, the initial conditions were 30 atm CO₂, 80 °C and 0.2 mol% catalyst in neat substrate for 16h. These results are summarized in Table 3. Under these conditions, no catalytic activity was observed using **Zn-1** alone (Entry 1). With the addition of TBAF or TBACl, low conversions were obtained (Entries 2 and 3). However, using TBABr or TBAI as co-catalysts (Entries 4 and 5), an increase in conversion up to 73% was observed. The observed activity trend: iodide (73%) > bromide (50%) > chloride (12%) can be explained by the increased nucleophilicity of the anion, as previously reported.¹ Nonetheless, the use of 4-dimethylaminopyridine (DMAP) as co-catalyst did not provide any conversion (Entry 6). This could be due to the formation of a stable N₂O₂-Zn-DMAP complex, as previously suggested by the groups of Rieger³⁷ and Zhang³⁸ for similar systems. Optimization of the catalyst/co-catalyst ratio (Entries 5, 7 and 8) showed that a cat/cocat ratio of 1/2 provided the most active catalytic system with a conversion of 83% (Entry 7) into the corresponding cyclic carbonate. Importantly, low conversion towards the cyclic carbonate product was achieved using 0.4 mol% of TBAI alone (39%).

Table 3. Screening of co-catalysts for the coupling of CO₂ with epoxides catalyzed by **Zn-1**.^[a]

Entry	Cocat	Cat/Cocat ratio	Conv. (%) ^[b]	TON ^[c]
1	-	-	0	-
2	TBAF	1/1	24	120
3	TBACl	1/1	12	60
4	TBABr	1/1	50	250
5	TBAI	1/1	73	365
6	DMAP	1/1	0	-
7	TBAI	1/2	83	415
8	TBAI	1/5	85	425

[a] Reaction conditions: Zn-1=0.2 mol%, T=80 °C, PCO₂=30 bar, time=16 h, 1,2-epoxyhexane 24.89 mmols (3ml); [b] measured by ¹H-NMR; [c] mol of substrate converted/mol of catalyst.

The effect of the temperature and pressure was also examined obtaining an optimal CO₂ pressure of 30 bar and 80 °C of temperature (see supporting information for details).

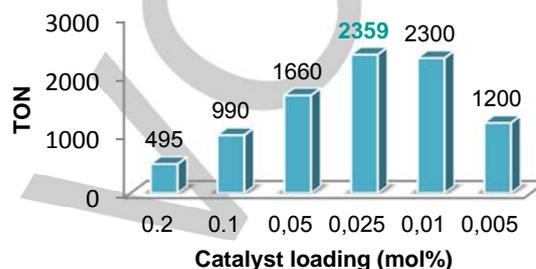
Then, the catalytic performance of complexes **Zn-2**, **Zn-3** and **Zn-4** was investigated and compared to that of **Zn-1** under the optimized conditions: T=80 °C, PCO₂=30 bar, ratio cat/cocat=0.2/0.4 mol% and time=16h (Table 4). Interestingly, both systems containing a tetranuclear complex (Entry 1 and 2) behaved identically, providing 83% conversion to the corresponding cyclic carbonate while the **Zn-3**/TBAI system displayed the highest activity of the series.

Table 4. Coupling of CO₂ with epoxides catalyzed by Zn-1-4/TBAI.^[a]

Entry	Cat	Conv. (%) ^[b]	TON ^[c]
1	Zn-1	83	415
2	Zn-2	83	415
3	Zn-3	>99(83) ^[d]	495(1660)
4	Zn-4	>99(75) ^[d]	495(1500)

[a] Reaction conditions: T=80 °C, PCO₂=30 bar, ratio cat/cocat=0.2/0.4 mol% respect to the substrate, cocat=TBAI, time=16 h, 1,2-epoxyhexane 24.89 mmols (3ml); [b] measured by ¹H-NMR; [c] mol of substrate converted/mol of catalyst; [d] at 0.05 mol% catalyst loading.

In order to exploit the potential of the **Zn-3** complex, an optimization of the catalyst loading, amount of co-catalyst used, time and pressure was performed (Table 5). Reducing the catalyst loading up to 0.025 mol% a maximum TON of 2319 was achieved (Figure 4). It is also important to note that increasing the reaction time up to 60h, a TON of 4500 was reached at 0.01mol% of catalyst loading which indicates that the **Zn-3** complex is highly robust. A maximum TOF of 480 h⁻¹ was obtained at 0.05 mol% of catalyst loading (value calculated at 24% conversion).

**Figure 4.** Optimization of TOF (h⁻¹) using **Zn-3**/TBAI catalytic system. Reaction conditions: ratio catalyst/co-catalyst 1:2 in all cases, T=80 °C, PCO₂=30 bar, time=16 h.

The optimal catalyst/co-catalyst ratio revealed to be 1:2 (Entry 2) as no improvement was achieved when the ratio was increased up to 1:5 (Entry 3). Increasing the temperature from 80 to 100 °C provided a slightly higher conversion (92%, Entry 4) whereas at 60 °C, a clear decrease of activity was observed (16%, Entry 6). Performing the reaction at 50 bar of CO₂ pressure (Entry 7) did not improve the activity of the catalyst while a decrease in activity was observed using 20 or 10 bar (Entries 8 and 9). Importantly, low conversion was observed using 0.1 mol% of TBAI alone (32%).

Table 5. Optimization of the amount of co-catalyst, temperature and pressure for the coupling of CO₂ with epoxides catalyzed by **Zn-3**/TBAI.^[a]

Entry	Cat/Cocat (mol%) ^[b]	Temp. (°C)	PCO ₂ (bar)	Conv. (%) ^[c]	TON ^[d]
1	0.025/0.025	80	30	34	1359
2	0.025/0.05	80	30	59	2359
3	0.025/0.125	80	30	60	2399
4	0.05/0.1	100	30	92	1840
5	0.05/0.1	80	30	83	1660
6	0.05/0.1	60	30	26	520
7	0.05/0.1	80	50	83	1660
8	0.05/0.1	80	20	70	1400
9	0.05/0.1	80	10	68	1360

[a] Reaction conditions: Catalyst: **Zn-3**, cocat=TBAI, time=16 h, 1,2-epoxyhexane 24.89 mmols (3ml); [b] mol% respect to the substrate [c] measured by ¹H-NMR; [d] mol of substrate converted/mol of catalyst.

In order to investigate the scope and limitations of these new zinc complexes, the **Zn-3**/TBAI system was tested as catalyst for a variety of terminal and internal epoxides/oxetanes, including challenging substrates such as styrene oxide, cyclohexene oxide, trans-2,3-epoxybutane and methyl epoxioleate (Figure 5).¹⁰ Exclusive formation of the cyclic carbonate product was observed by NMR spectroscopy for all substrates.

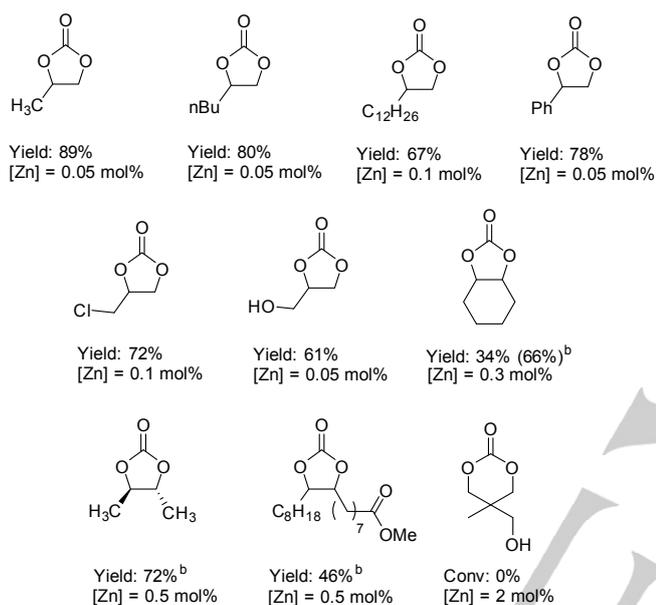


Figure 5. [a] Reaction conditions: Catalyst: **Zn-3**, cocat= TBAI, ratio cat/cocat= 1:1, T=80 °C, PCO₂=30 bar, time=16 h. Selectivity towards the cyclic carbonate product was >99% in all cases, determined by ¹H-NMR in CDCl₃ except for glycidol (determined in DMSO-d₆). Yield determined using mesitylene as internal standard. [b] Using TBABr as co-catalyst.

For terminal epoxides, the **Zn-3**/TBAI catalytic system exhibited moderate to high activity with yields (67–89%). For alkyl substituted epoxides, the activity depended on the steric hindrance induced by the substituents (Me > nBu > C₁₂H₂₆). The **Zn-3**/TBAI catalytic system also provided high yield for styrene oxide (78%), which is higher than that obtained with the recently reported **Zn-N₄**/TBABr systems.³⁰ In addition, high TON was obtained when propylene oxide (1840) was the substrate. Good yields were also obtained using epichlorohydrin (72% using 0.1 mol% catalyst) and glycidol (61% using 0.05 mol% catalyst) as substrates.

Then, internal epoxides were tested as substrates. Cyclohexene oxide was converted into the corresponding cyclic carbonate in 66% yield using the **Zn-3**/TBABr catalytic system. Compared to the **Zn-salphen**/TBAI system reported by Kleij²¹ and co-workers (37% CHC, at 80 °C, 80 bar, 2.5 mol% catalyst loading and 3h), the **Zn-3**/TBABr catalytic system operates at lower CO₂-pressure

(30 bar) and lower catalyst loading (0.3 mol%), although longer reaction times are needed (16h). Regarding the tetrabutylammonium halides (TBAI and TBABr) tested for cyclohexene oxide, TBABr showed in this case higher conversion towards the cyclic carbonate. This can be explained due to the fact that bulky epoxides (such as cyclohexene oxide), once activated by the metal center, can be easily opened by the co-catalyst (halide) which need to fulfill these criteria: high nucleophilicity, good leaving group ability and small size. In this respect, bromide showed the best compromise for all these statements and thus displayed a higher activity. This trend has also been observed before.¹⁹ For more challenging substrates such as trans-2,3-epoxybutane, a 72% yield towards the corresponding cyclic carbonate product was achieved at 0.5 mol% of catalyst loading. It has to be also highlighted the 46% yield (at 0.5mol% of catalyst loading) obtained for the methyl epoxioleate, which derives from a natural product. Nonetheless, no conversion was obtained for the more challenging substrate 3-methyl-2-oxetanemethanol.

To evaluate the robustness of the catalytic system, a typical recycling experiment was carried out with propylene oxide as substrate using the **Zn-3**/TBAI catalytic system (reaction conditions: 3ml of epoxide, catalyst loading = 0.1 mol%, at 80 °C, 30 bar of CO₂, 16h, five consecutive runs). After the catalytic experiment, the propylene carbonate was separated by vacuum distillation and the catalyst was directly used for the next catalytic cycle. The minimal loss of the catalyst observed during the recycling experiments was compensated by adjusting the amount of propylene oxide used in order to uphold the epoxide:catalyst ratio unchanged (1000:1). Practically full conversion was maintained for the first two cycles after which a small decrease was observed (92%) but also preserved up to the fifth cycle (Figure 6).

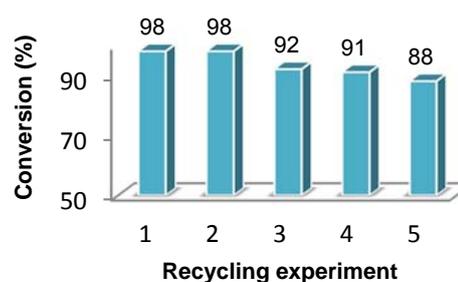


Figure 6. Recycling experiment using the **Zn-3**/TBAI catalytic system. Reaction conditions: 3ml of propylene oxide, 0.1 mol% catalyst, T=80 °C, PCO₂=30 bar, time=16 h.

These promising results indicate the robustness and reusability of this catalytic system without relevant loss of neither activity nor selectivity for the coupling of carbon dioxide with epoxides.

The proposed mechanistic cycle for the **Zn-3** complex is shown in figure 7. We proposed an initial coordination of the epoxide to the **Zn-3** forming the penta-coordinated **Zn-3**-substrate. Next, the

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ring-opening of the epoxide by the nucleophile (iodide) takes place producing a zinc-alkoxide intermediate which reacts with CO₂ to form a carbonate complex through insertion of CO₂ into the Zn-O bond. Finally, ring-closing and regeneration of the catalyst by coordination of another molecule of epoxide takes place.

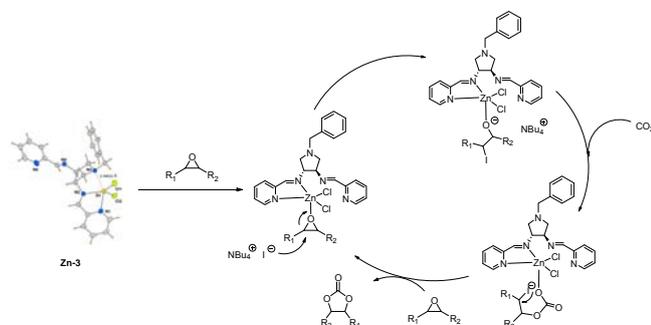


Figure 7. Proposed mechanism for the formation of the cyclic carbonate from the mononuclear complex **Zn-3**.

Conclusions

New mono- and tetra-nuclear zinc complexes bearing N₂O₂, N₂(NH)₂ and N₄ ligands **1-4** containing a pyrrolidine scaffold were synthesized and fully characterized. These complexes were successfully tested in the coupling of CO₂ with terminal and internal epoxides with tetrabutylammonium iodide (TBAI) as co-catalyst, providing excellent activity and total selectivity to the corresponding cyclic carbonates. The **Zn-3**/TBAI catalytic system revealed to be the most active of the series obtaining a TON up to 2359 using 1,2-epoxyhexane as substrate. Terminal epoxides were converted into the corresponding cyclic carbonates in good to high yields (67% to 89%) and even for styrene oxide, which is usually a challenging substrate, the **Zn-3**/TBAI catalytic system provided high yield (78%). Additionally, the robustness of the catalyst was demonstrated with TON values up to 1840 for propylene oxide and recycling of this catalytic system could be performed up to 5 times without relevant loss of activity. Internal epoxides were also successfully converted into the corresponding cyclic carbonates, reaching a 66% yield for cyclohexene oxide at 0.3 mol% catalyst loading. More sterically hindered substrates such as trans-2,3-epoxybutane and methyl epoxioleate were also selectively transformed with 72% and 46% yield, respectively. It should be highlighted that this is the highest conversion obtained for trans-2,3-epoxybutane using Zn(II) complexes.^{9,21,23}

Experimental Section

Synthesis of the ligands 1-4.

(1): 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.245g, mmol) was added to 4ml of toluene containing activated molecular sieves. Then, (3*S*,4*S*)-3,4-

diamino-1-benzylpyrrolidine (0.1g, mmol) was added to the mixture. This solution was allowed to stir overnight at 90 °C. The reaction was filtered through a pad of celite and evaporated to dryness. To this crude solid, methanol was added and the product precipitates. Then, the product was filtered and washed further with methanol. Evaporation to dryness afforded a yellow solid in 77% yield. **¹H-NMR** (CDCl₃, 400 MHz, δ in ppm): δ = 13.42 (s, 2H, -OH), 8.17 (s, 2H, -N=CH), 7.29-7.14 (m, 7H, Ar-), 6.92 (d, 2H, *J*=4Hz, Ar-), 3.87 (quint, 2H, *J*=4Hz, -CH), 3.62 (s, 2H, -CH₂-Ph), 3.01 (dd, 2H, *J*=4 & 8Hz, -CH₂), 2.82 (dd, 2H, *J*=4 & 8Hz, -CH₂), 1.34 (s, 18H, ^tBu, -CH₃), 1.16 (s, 18H, ^tBu, -CH₃). **¹³C-NMR** (CDCl₃, 100.6 MHz, δ in ppm): δ = 166.3 (C=N), 157.9 (C-OH), 140.2 (-C-), 138.4 (-C-), 136.6 (-C-), 128.8 (Ar-), 128.3 (Ar-), 127.2 (Ar-), 127.1 (Ar-), 126.2 (Ar-), 117.6 (-C-), 75.4 (-CH-), 60.3 (-CH₂), 60.1 (CH₂-Ph, -CH₂), 35.0 (-C-), 34.1(-C-), 31.4 (-CH₃) 29.4 (-CH₃). **IR** (KBr pellet): ν_{C=N}= 1625cm⁻¹. **ESI-HRMS**: Calculated for **C₄₁H₅₇N₃O₂**: Exact: (M: 623.4524, [M+H]⁺: 624.4524); Experimental ([M+H]⁺: 624.4509). **Elemental Analysis**: Calculated for **C₄₁H₅₇N₃O₂**: C, 78.93; H, 9.21; N, 6.73; Found: C, 78.26; H, 9.16; N, 6.41.

(2): Pyrrole-2-carboxyaldehyde (197.8mg, 2.08 mmol) was added to 8ml of dry and degassed toluene containing activated molecular sieves. Then, (3*R*,4*R*)-3,4-diamino-1-benzylpyrrolidine (0.2g, 1.04mmol) was added to the mixture. Finally, few drops of acetic acid were added to the reaction mixture and the solution was allowed to stir overnight at 90°C. The reaction was filtered through a pad of celite and evaporated to dryness to obtain a brown syrup. This syrup was triturated repeatedly with diethylether. After filtration, the organic solution was concentrated to dryness in order to afford the product as a bright orange-red powder in 40% yield. **¹H-NMR** (CDCl₃, 400 MHz, δ in ppm): δ = 7.92 (s, 2H, N=CH), 7.38-7.24 (m, 5H, Ar-), 7.01 (s, 2H, Pyrrole), 6.55 (d, 2H, *J*=4Hz, Pyrrole), 6.23 (t, 2H, *J*=4Hz, Pyrrole), 3.92 (quint., 2H, *J*=4Hz, -CH-), 3.77 (d, 1H, *J*=12Hz, -CH₂-Ph), 3.69 (d, 1H, *J*=12Hz, -CH₂-Ph), 3.08 (dd, 2H, *J*=4 & 8Hz, -CH₂-), 2.83 (dd, 2H, *J*=4 & 8Hz, -CH₂-). **¹³C-NMR** (CDCl₃, 100.6 MHz, δ in ppm): δ = 151.63 (N=CH-), 138.04 (-C-), 128.99 (Ar-), 128.88 (-C-), 128.26 (Ar-), 127.14 (Ar-), 123.51 (Pyrrole, -CH-), 116.49 (Pyrrole, -CH-), 110.29 (Pyrrole, -CH-), 74.81 (-CH-), 60.09 (-CH₂-), 60.00 (-CH₂-). **IR** (KBr pellet): ν_{NH}= 3170cm⁻¹ ν_{C=N}= 1633cm⁻¹. **ESI-HRMS**: Calculated for **C₂₁H₂₃N₅**: Exact: (M: 345.2014; [M+H]⁺: 346.2014); Experimental ([M+H]⁺: 346.2026). **Elemental Analysis**: Calculated for **C₂₁H₂₃N₅·5CH₂Cl₂**: C, 40.55; H, 4.32; N, 9.09; Found: C, 40.48; H, 3.98; N, 9.59.

(3): 2-Pyridinecarboxyaldehyde (0.198ml, 2.08 mmol) was added to 7ml of dry and degassed toluene containing activated molecular sieves. Then, (3*R*,4*R*)-3,4-diamino-1-benzylpyrrolidine (0.2g, 1.04mmol) was added to the mixture which was allowed to stir overnight at 90°C. The reaction was filtered through a pad of celite and evaporated to dryness. To this crude solid, diethylether (2ml) was added and a white solid precipitate. The solution was filtered and evaporated. The residue was washed with hexane until the washings were colourless. The solid was dried to afford the product as a pale orange powder in 60% yield. **¹H-NMR** (CD₂Cl₂, 400 MHz, δ in ppm): δ = 8.57 (d, 2H, *J*=4Hz, *o*-Py), 8.25 (s, 2H, N=CH), 8.03 (d, 2H, *J*=4Hz, *m*-Py), 7.74 (t, 2H, *J*=8Hz, *m*-Py), 7.41-7.24 (m, 7H, Ar-), 4.09 (quint., 2H, *J*=4Hz, -CH-), 3.77 (d, 1H, *J*=12Hz, -CH₂-Ph), 3.74 (d, 1H, *J*=12Hz, -CH₂-Ph), 3.12 (dd, 2H, *J*=4 & 8Hz, -CH₂-), 2.90 (dd, 2H, *J*=4 & 8Hz, -CH₂-). **¹³C-NMR** (CD₂Cl₂, 100.6 MHz, δ in ppm): δ = 162.96 (N=CH-), 155.07 (Py, -C-), 149.86 (*o*-Py, CH-), 136.57 (-C-), 136.89 (*m*-Py, CH-), 129.39 (Ar-), 128.76 (Ar-), 127.50 (Ar-), 125.27 (*p*-Py, CH-), 121.56 (*m*-Py, CH-), 76.38 (-CH-), 60.79 (-CH₂-), 60.74 (-CH₂-). **IR** (KBr pellet): ν_{C=N}= 1644cm⁻¹. **ESI-HRMS**: Calculated for **C₂₃H₂₃N₅**: Exact: (M: 369.2026; [M+H]⁺: 370.2026); Experimental ([M+H]⁺: 370.2026). **Elemental Analysis**: Calculated for **C₂₃H₂₃N₅**: C, 74.77; H, 6.27; N, 18.96; Found: C, 74.41; H, 5.82; N, 18.56.

(4): **3** (50mg, 0.135mmol) was dissolved in 5ml of dry methanol and placed in an ice bath (0°C). Then, NaBH₄ (25.5mg, 0.675mmol) was added

dropwise. The reaction was stirred at room temperature for 16h and H₂O (0.5ml) was added. The mixture was extracted with CH₂Cl₂ (3ml×3). The combined organic layers were dried over anhydrous MgSO₄ and evaporation under vacuum afforded the product as a pale yellow viscous liquid in 95% yield. **¹H-NMR** (CD₂Cl₂, 400 MHz, δ in ppm): δ = 8.51 (d, 2H, *J*=8Hz, *o*-Py), 7.63 (t, 2H, *J*=8Hz, *m*-Py), 7.33-7.30 (m, 5H, Ar-), 7.28-7.21 (m, 2H, Ar-), 7.15 (dd, 2H, *J*=4 & 8Hz, Ar-), 3.86 (d, 2H, *J*=12Hz, CH₂-NH), 3.82 (d, 2H, *J*=12Hz, CH₂-NH), 3.58 (s, 2H, CH₂-Ph), 3.06 (quint, 2H, *J*=4Hz, -CH-), 2.84 (dd, 2H, *J*=4 & 8Hz, -CH₂-), 2.41 (dd, 2H, *J*=4 & 8Hz, -CH₂-), 2.10 (sh, 2H, NH-). **¹³C-NMR** (CD₂Cl₂, 100.6 MHz, δ in ppm): δ = 160.67 (Py, -C-), 149.59 (*o*-Py, -CH-), 139.79 (-C-), 136.77 (*m*-Py, -CH-), 129.23 (Ar-), 128.66 (Ar-), 127.32 (Ar-), 122.68 (Ar-), 122.30 (Ar-), 64.96 (-CH-), 60.82 (-CH₂-), 60.46 (-CH₂-), 54.08 (CH₂-NH, -CH₂-). **IR** (KBr pellet): ν_{NH}= 3311cm⁻¹ ν_{C=N}= 1593cm⁻¹. **ESI-HRMS**: Calculated for C₂₃H₂₇N₅: Exact: (M: 373.2333, [M+H]⁺: 374.2333); Experimental ([M+H]⁺: 374.2339).

Synthesis of the zinc complexes Zn1-4.

(Zn-1): Diethyl zinc (1M in hexane) (0.32ml, 0.32mmol) was added to a solution of **1** (0.2g, 0.32mmol) in 6ml of THF. The solution was allowed to stir at room temperature for 16h and a colour change from yellow to bright yellow was observed. The product was isolated after evaporation to dryness in quantitative yield. **¹H-NMR** (CD₂Cl₂, 400 MHz, δ in ppm): δ = 7.60 (s, 2H, -N=CH), 7.48 (d, 2H, *J*=4Hz, Ar-), 7.26-7.18 (m, 5H, Ar-), 6.55 (d, 2H, *J*=4Hz, Ar-), 4.39 (quint, 2H, *J*=8Hz, -CH), 3.60 (d, 1H, *J*=12Hz, CH₂-Ph), 3.48 (d, 1H, *J*=12Hz, CH₂-Ph), 2.93 (t, 2H, *J*=8Hz, -CH₂), 2.72 (t, 2H, *J*=8Hz, -CH₂), 1.46 (s, 18H, -CH₃), 1.27 (s, 18H, -CH₃). **¹³C-NMR** (CD₂Cl₂, 100.6 MHz, δ in ppm): δ = 173.86 (C=N), 168.85 (C-O), 142.15 (-C-), 139.44 (-C-), 136.38 (-C-), 131.42 (Ar-), 129.82 (Ar-), 128.76 (Ar-), 128.72 (Ar-), 127.46 (Ar-), 117.62 (-C-), 69.27 (N-CH), 60.83 (CH₂-Ph, -CH₂), 59.49 (-CH₂), 35.97 (-C¹Bu, -C-), 34.39 (-C¹Bu, -C-), 31.72 (-CH₃), 29.83 (-CH₃). **IR** (KBr pellet): ν_{C=N}= 1598cm⁻¹. **ESI-HRMS**: Calculated for (C₄₁H₅₅N₃O₂)₄Zn₄: Exact: (M: 2741.4343; [M+Na]⁺: 2764.4241); Experimental ([M+Na]⁺: 2764.4218). **Elemental Analysis**: Calculated for (C₄₁H₅₅N₃O₂)₄Zn₄·0.5CH₂Cl₂: C, 68.30; H, 7.74; N, 5.76; Found: C, 68.87; H, 7.68; N, 5.62.

(Zn-1-Py): 0.7ml of pyridine-d₅ was added to a 20mg of the Zn-1 complex which was shake it for 2 h at room temperature. **¹H-NMR** (Py-d₅, 400 MHz, δ in ppm): δ = 8.26 (s, 2H, -N=CH), 7.81 (d, 2H, *J*=4Hz, Ar-), 7.35-7.24 (m, 5H, Ar-), 7.10 (d, 2H, *J*=4Hz, Ar-), 4.68 (quint, 2H, *J*=8Hz, -CH), 3.58 (d, 1H, *J*=12Hz, CH₂-Ph), 3.29 (d, 1H, *J*=12Hz, CH₂-Ph), 2.88 (t, 2H, *J*=8Hz, -CH₂), 2.71 (t, 2H, *J*=8Hz, -CH₂), 1.77 (s, 18H, -CH₃), 1.38 (s, 18H, -CH₃). **¹³C-NMR** (Py-d₅, 100.6 MHz, δ in ppm): δ = 175.26 (C=N), 169.18 (C-O), 141.98 (Ar-, -C-), 139.64 (Ar-, -C-), 136.53 (Ar-, -C-), 131.34 (Ar-), 131.28 (Ar-), 129.18 (Ar-), 129.10 (Ar-), 127.82 (Ar-), 199.0 (Ar-, -C-), 69.64 (N-CH), 61.06 (CH₂-Ph, -CH₂), 59.93 (-CH₂), 36.39 (-C¹Bu, -C-), 34.68 (-C¹Bu, -C-), 32.15 (-CH₃), 30.36 (-CH₃). **ESI-HRMS**: Calculated for C₄₆H₅₅D₅N₄O₂Zn: Exact: (M: 769.4322; [M+O+H]⁺: 786.4427); Experimental ([M+O+H]⁺: 786.4357).

(Zn-2): Diethyl zinc (1M in hexane) (0.29ml, 0.29mmol) was added to a solution of **2** (0.1g, 0.29mmol) in 6ml of THF. The solution was stirred at room temperature for 16h and a colour change from yellow to bright yellow was observed. The product was isolated in quantitative yield after evaporation to dryness. **¹H-NMR** (CD₂Cl₂, 400 MHz, δ in ppm): δ = 7.31-7.17 (m, 7H, Ar- & C=N), 7.07 (s, 2H, *o*-Pyrrole), 6.70 (d, 2H, *J*=4Hz, *p*-Pyrrole), 6.37 (dd, 2H, *J*=4 & 8Hz, *m*-Pyrrole), 3.76 (t, 2H, *J*=4Hz, -CH-), 3.62 (d, 1H, *J*=12Hz, CH₂Ph), 3.43 (d, 1H, *J*=12Hz, CH₂Ph), 2.91 (t, 2H, *J*=8Hz, -CH₂-), 2.58 (t, 2H, *J*=8Hz, -CH₂-). **¹³C-NMR** (CD₂Cl₂, 100.6 MHz, δ in ppm): δ = 160.67 (C=N), 139.20 (-C-), 137.36 (-C-), 135.91 (*o*-Pyrrole, -CH-), 128.90 (Ar-), 128.75 (Ar-), 127.50 (Ar-), 119.40 (*p*-Pyrrole, -CH-),

113.69 (*m*-Pyrrole, -CH-), 68.49 (-CH-), 60.78 (CH₂Ph), 58.36 (-CH₂-). **IR** (KBr pellet): ν_{C=N}= 1579cm⁻¹. **ESI-HRMS**: Calculated for (C₂₁H₂₁N₅)₄Zn₄: Exact: (M: 1628.4354; [M+H]⁺: 1629.4499); Experimental ([M+H]⁺: 1629.4426). **Elemental Analysis**: Calculated for (C₂₁H₂₁N₅)₄Zn₄·4CH₂Cl₂·C₄H₈O: C, 42.45; H, 4.54; N, 8.53; Found: C, 43.20; H, 3.87; N, 8.72.

(Zn-3): Zinc dichloride (73.8mg, 0.54mmol) in THF (4ml) was added to a solution of **3** (0.2g, 0.54mmol) in THF. The reaction mixture was stirred at room temperature for 16h and evaporated under vacuum. Then, the residue was re-dissolved in DCM (2ml) and diethylether (4ml) was added to the mixture in order to precipitate the product. The obtained orange solid was filtered and further washed with diethylether (3x3ml). The product was isolated in 72% yield after drying under vacuum. **¹H-NMR** (CD₂Cl₂, 400 MHz, δ in ppm, at -65°C): δ = 8.73 (d, 1H, *J*=4Hz, coordinated *o*-Py), 8.58 (bs, 2H, uncoordinated *o*-Py & coordinated C=N), 8.18 (s, 1H, uncoordinated C=N), 8.05 (t, 1H, *J*=8Hz, *p*-Py), 7.81-7.69 (m, 4H, -Py), 7.39-7.35 (m, 6H, Ar-), 4.23 (s, 1H, -CH-), 4.20 (d, 1H, *J*=12Hz, CH₂Ph), 4.12 (d, 1H, *J*=12Hz, CH₂Ph), 3.81 (s, 1H, -CH-), 3.69 (t, 1H, *J*=8Hz, -CH₂), 3.29 (d, 1H, *J*=8Hz, -CH₂), 3.00 (d, 1H, *J*=12Hz, -CH₂), 2.33 (d, 1H, *J*=8Hz, -CH₂). **¹³C-NMR** (CD₂Cl₂, 100.6 MHz, δ in ppm, at -65°C): δ = 162.82 (uncoordinated C=N), 158.27 (coordinated C=N), 152.94 (-C-), 149.52 (uncoordinated *o*-Py), 149.30 (coordinated *o*-Py), 144.98 (-C-), 140.00 (*p*-Py, -CH-), 136.79 (-Py, -CH-), 132.97 (-C-), 131.44 (Ar-), 129.21 (Py-), 127.95 (Ar-), 127.65 (Ar-), 126.98 (Py, -CH-), 125.34 (Py, -CH-), 121.33 (Py, -CH-), 73.82 (-CH-), 69.86 (-CH-), 55.77 (-CH₂), 55.12 (-CH₂Ph), 54.47 (-CH₂). **IR** (KBr pellet): ν_{C=N}= 1644cm⁻¹ (uncoordinated C=N) & 1597cm⁻¹ (coordinated C=N). **Conductivity** (0.001M in THF)= 0.062Ω⁻¹·cm·mol⁻¹. **ESI-HRMS**: Calculated for C₂₃H₂₃N₅Cl₂Zn: Exact: (M: 503.0622; [M-Cl]⁺: 468.0933); Experimental ([M-Cl]⁺: 468.0928). **Elemental Analysis**: Calculated for C₂₃H₂₃N₅Cl₂Zn·0.5CH₂Cl₂: C, 51.49; H, 4.41; N, 12.78; Found: C, 52.36; H, 4.27; N, 12.98.

(Zn-4): Triethylamine (1ml, excess) was added to a solution of **4** (0.1g, 0.27mmol) in 4ml of THF. Then, zinc dichloride (36.9mg, 0.27mmol) in THF (2ml) was added to the solution. The reaction was stirred at room temperature for 16h during which an orange solid precipitated. The obtained solid was filtered and washed with THF (3x3ml). The product was isolated in 85% yield after drying under vacuum. **¹H-NMR** (DMSO-d₆, 400 MHz, δ in ppm): δ = 8.94 (d, 2H, *J*=4Hz, *o*-Py), 8.04 (t, 2H, *J*=8Hz, *p*-Py), 7.57 (t, 2H, *J*=8Hz, *m*-Py), 7.52 (d, 2H, *J*=8Hz, *m*-Py), 7.29-7.19 (m, 5H, -Ar), 4.48 (bs, 2H, -NH), 4.26 (dd, 2H, *J*=4&16Hz, -CH₂), 3.95 (d, 2H, *J*=16Hz, -CH₂), 3.65 (d, 1H, *J*=12Hz, CH₂Ph), 3.50 (d, 1H, *J*=12Hz, CH₂Ph), 2.83 (s, 2H, -CH₂NH), 2.43 (bs, 4H, -CH₂NH & -CH). **¹³C-NMR** (DMSO-d₆, 100.6 MHz, δ in ppm): δ = 155.49 (Py, -C-), 148.38 (*o*-Py, -CH-), 139.63 (*p*-Py, -CH-), 139.04 (-C-), 128.71 (Ar-), 128.41 (Ar-), 127.12 (Ar-), 124.52 (*m*-Py, -CH-), 123.72 (*m*-Py, -CH-), 60.25 (-CH₂Ph), 59.48 (-CH-), 53.08 (-CH₂NH), 48.34 (-CH₂-). **IR** (KBr pellet): ν_{NH}= 3221cm⁻¹, ν_{C=N}= 1607cm⁻¹. **Conductivity** (0.001M in DMSO)= 16.05 Ω⁻¹·cm·mol⁻¹. **ESI-HRMS**: Calculated for C₂₃H₂₇N₅Cl₂Zn: Exact: (M: 507.0935; [M-Cl]⁺: 472.1241); Experimental ([M-Cl]⁺: 472.1262). **Elemental Analysis**: Calculated for C₂₃H₂₅N₅Zn·1.5CH₂Cl₂: C, 46.18; H, 4.75; N, 10.99; Found: C, 45.98; H, 5.02; N, 10.55.

General catalytic procedure

The catalytic tests were carried out in a 100 mL Berghoff or 25 mL Parr reactor, which were previously kept under vacuum for 2 h (in the case of Zn-3, the catalyst was placed into the autoclave prior to vacuum). Then, a solution containing the catalyst, the epoxide substrate and the co-catalyst were injected into the reactor under inert atmosphere. The autoclave was then pressurized with CO₂ and heated at the appropriate temperature.

After the reaction, the system was cooled down with an ice bath and slowly depressurized through a dichloromethane trap.

General procedure for recycling experiments

The recycling experiments were carried out in a 100 mL Berghoff reactor containing the catalyst (**Zn-3**), which was previously kept under vacuum 2 h at room temperature. Then, the substrate (propylene oxide) and the co-catalyst (TBAI) were injected into the reactor under inert atmosphere. The autoclave was then pressurized with CO₂ and heated to reach the desired pressure (reaction conditions: 3ml of epoxide, catalyst loading = 0.1 mol%, ratio cat:co-cat 1:2, at 80°C, 30bar of CO₂, 16h). Once the reaction was finished, the reactor was cooled down with an ice bath and slowly depressurized through a dichloromethane trap. After each catalytic experiment, the propylene carbonate was separated by vacuum distillation and the catalyst was directly used for the next catalytic cycle (five consecutive runs).

X-ray crystallography

Data collections of structures reported were carried out at the X-ray diffraction beamline of the Elettra Synchrotron, Trieste (Italy), using the rotating crystal method with a monochromatic wavelength of 0.7000 Å, on a Pilatus detector. Measurements were performed at 100(2) K using a nitrogen stream cryo-cooler. Cell refinement, indexing and scaling of the data set were performed using the CCP4 package,³⁹ and programs Denzo and Scalepack.⁴⁰ The structure was solved by direct methods and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.⁴¹ The electron density map of **Zn-1** shows four disordered n-C₆H₁₄ molecules, the atoms of which were fixed at half occupancy (for a total of 2 molecules) and isotropically refined with restrained bond distances. Some positionally disorder groups were detected in the tetranuclear **Zn-1** complex: a benzyl group (attached to a pyrrolidine) and a phenyl ring with one *t*-butyl group were found disordered over two positions (refined occupancies of 0.61/0.39 and 0.56/0.44, respectively). Finally another *t*-butyl group was split over two positions with half occupancy each. All the calculations were performed using the WINGX SYSTEM, Ver 2013.3.⁴²

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FULL PAPER

Robust zinc catalysts bearing ligands containing a pyrrolidine scaffold were synthesized, characterized and successfully tested in the coupling of CO₂ with terminal and internal epoxides, providing excellent activity and total selectivity to the corresponding cyclic carbonates, even for challenging substrates. The recycling of one of these catalytic systems was also performed up to 5 times without relevant loss of activity.

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Robust zinc complexes bearing pyrrolidine based ligands as recyclable catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides.
