[Zinc(II)(Pyridine-Containing Ligand)] Complexes as Single-Component Efficient Catalyst for Chemical Fixation of CO$_2$ with Epoxides

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Dedicated to Professor Franco Cozzi on the occasion of his 70th birthday. “Senatores boni viri, senatus mala bestia”

The reaction between epoxides and CO$_2$ to yield cyclic carbonates is efficiently promoted under solvent-free and relatively mild reaction conditions (0.5 mol% catalyst loading, 0.8 MPa, 125°C) by zinc(II) complexes of pyridine containing macrocyclic ligands (Pc–L pyridinophanes). The zinc complexes have been fully characterized, including X-ray structural determination. The [Zn(II)(Pc–L)]X complexes showed good solubility in several polar solvents, including cyclic carbonates. The scope of the reaction under solvent-free conditions has been studied and good to quantitative conversions with excellent selectivities have been obtained, starting from terminal epoxides. When solvent-free conditions were not possible (solid epoxides or low solubility of the catalyst in the oxirane) the use of cyclic carbonates as solvents has been successfully investigated. The remarkable stability of the catalytic system has been demonstrated by a series of consecutive runs.

Introduction

Carbon dioxide is the principal greenhouse gas, largely recognized as responsible for global warming and related climate changes, but it represents also an abundant C$_2$ source. It is naturally present in the atmosphere and it is produced on large scale by many human activities, sensitively enhancing its natural greenhouse effect. Limiting CO$_2$ emissions can only stem the problem but to solve it a circular economy based on carbon dioxide should be pursued. This means developing new and efficient carbon capture and utilization technologies to sequester the large quantities of CO$_2$ produced in industrial processes and to obtain high valuable products with low energy consumption. However, carbon dioxide is kinetically and thermodynamically stable and difficult to activate and use. Therefore, efficient CO$_2$ activation appears to be still a highly coveted target.

The synthesis of cyclic carbonates from carbon dioxide and epoxides is a 100% atom economical reaction and an attractive pathway for CO$_2$ utilization; it is a topic of great relevance in this field especially because cyclic carbonates have a great applicability in industrial processes. Cyclic carbonates are mainly employed as aprotic polar solvents, electrolytes in secondary batteries, monomers for polycarbonate based polymers and intermediates of fine chemicals.

In the last twenty years, to overcome the limitations inherent to homogeneous catalysts, such as stability and recovery issues, heterogeneous catalysts such as modified zéolithes, metal oxides, MOFs, supported catalysts, mesoporous materials, silica, cellulose and poly-ionic liquids (PILs) have been investigated. Heterogeneous catalytic systems seem to be an interesting option to develop a reusable and easily separable catalyst. However, heterogeneous catalysts are inherently more stable compared to homogeneous ones. This implies that all these catalysts suffer from low activity, thus requiring higher temperatures and pressures to display comparable results, so limiting a wide applicability.

According to the literature, the synthesis of cyclic carbonates from CO$_2$ and epoxide consists in three main steps: (i) the activation of the epoxide with the subsequent ring-opening by an external nucleophile; (ii) the CO$_2$ insertion into the oxygen anion intermediate; and (iii) the ring-closing reaction. Because CO$_2$ is a thermodynamically stable molecule, for an efficient coupling reaction to give cyclic carbonates the use of co-catalysts is needed in the ring opening of the epoxide and in reducing the activation energy of the CO$_2$ conversion.

Considering environmental compatibility and the high-efficiency catalytic conversion of CO$_2$, there is the strong need...
to develop green catalysts capable of high conversions and selectivities, especially under solvent-free conditions.\(^{[17]}\)

The development of new catalysts for a so crucial reaction, able to work at mild process conditions with good performance, that are also reusable and easily separable, is therefore of high industrial interest.

We have recently reported that iron(III) complexes of pyridine based 12 membered tetraaza macrocyclic ligands (Pc–L) are efficient catalyst for the epoxidation of alkenes with H\(_2\)O\(_2\) as the terminal oxidant and we have also disclosed that under certain conditions they are also suitable catalysts for the epoxide activation towards ring-opening with a nucleophile.\(^{[18]}\)

As a continuation of our studies on the catalytic activity of pyridinophane type macrocyclic ligands,\(^{[18–19]}\) we envisioned that Zn(II) complexes would be perfect candidates to promote a clean conversion of epoxides and CO\(_2\) in cyclic carbonates under mild reaction conditions and without the addition of any co-catalyst (Scheme 1). Herein we disclose our findings.

Results and Discussion

Preparation of the zinc complexes. We recently reported the straightforward synthesis of macrocycle 1\(^{[20]}\) in good overall yield by treatment of \(N,N',N''\)-tritosyl-diethylenetriamine with pyridine-2,6-diylibis(methylene) dimethanesulfonate, followed by the hydrolysis in strong mineral acids of the tosyl protecting groups.\(^{[19a]}\) Zinc complexes 2a–c were obtained by slowly adding the metal salt to a stirred dichloromethane (DCM) solution of the macrocyclic ligand (Scheme 2). A small defect of the zinc salt was used to avoid the presence of free metal salt in the final product, being the excess of ligand easily removable by simple washing of the crystalline metal complex with DCM. The choice of the different halogen anions was made in order to assess their different reactivity in the nucleophilic ring opening of the epoxide in the catalytic tests.

The metal complexes showed a good solubility in different polar media. They were fully characterized by NMR spectroscopy, MS spectrometry and elemental analyses. All experimental evidences are in perfect agreement with the proposed structures. \(^1\)H NMR data in DMSO-\(d_6\) are consistent with an apparent Cs symmetry of the structure in solution, with two signals for each couple of equivalent methylene groups.

It should be noted that by changing from chlorine to bromine, the nature of the counteranion affected the NMR spectra in DMSO-\(d_6\) only to a minor extent, whilst this is not the case when the bulkier iodine is used, indicating that a slight different geometry of the donor atoms in the macrocyclic skeleton is imposed by steric crowding. The MS (ESI) analyses clearly showed that in all complexes only one halogen was coordinated to the metal center, confirming the saline nature of the complexes (see Supporting Information, page S3).

For all complexes, 2a, 2b and 2c, single crystals suitable for X-ray crystallography were grown. Although the refinement left no doubt about the validity of the structural model of complex 2c, it was not possible to obtain satisfactory R values and as a consequence the full crystal structure determination for 2c is not reported here. Therefore, structural details and geometrical parameters will be given for complexes 2a and 2b (Figure 1 and Figure 2, respectively). The overall solid-state structures of compounds 2a, 2b and 2c are different. However, they share some features like the same molecular geometry for the cationic complex \([\text{Zn}^\text{II}(X)(\text{Pc–L})]^+\) (with \(X=\text{Cl}, \text{Br}, \text{I}\)). Four nitrogen atoms of the macrocycle and a monodentate \(X^–\) ligand form a distorted square pyramidal environment around the Zn(II) ion, while an additional \(X^–\) anion balances the positive charge in the second coordination sphere. The macrocycle adopts a cis-folded (\(+\,+\,+\,+\) or \(+\,+\,+\,-\) conformation with the metal atom that is displaced from the N4 macrocyclic cavity.\(^{[21]}\) This arrangement and all the structural parameters are comparable to those of similar complexes which have been already reported in the

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\text{Scheme 1. Cycloaddition of CO}_2\text{ and epoxides catalyzed by [Zn}^\text{II}(X)(\text{Pc–L})]X\text{ complexes reported in this work.}
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\text{Scheme 2. Synthetic route used to obtain zinc complexes 2a–c.}
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\text{Figure 1. Molecular structure of the complex [Zn(II)(Cl)(Pc–L)]Cl \cdot 1.5H}_2\text{O, 2a (50\% probability thermal ellipsoids). Selected bond lengths (Å): Zn–N1 2.063(1), Zn–N2 2.214(2), Zn–N3 2.053(1), Zn–N4 2.220(1), Zn–C1 2.2139(5). Water molecules have been omitted for clarity. Full crystal structure data of 2a are reported in the Supporting information.}
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have a quantitative esteem of the deviation from ideal square-pyramidal (continuum between the two ideal geometries, it appears that reaction of CO with styrene oxide by the Zn(salphen)/TBAX (TBAX = halogen anion and a free coordination site on the zinc. To verify this hypothesis we tested all metal complexes both in the presence and in the absence of TBAX salts as co-catalysts and results are summarized in Table 1.

As it can be seen from data reported in the table and according to literature, TBAX alone can efficiently promote the cycloaddition reaction, with only slight differences depending on the nature of the halide. Under the selected reaction conditions, TBAB is the most active catalyst (>99% of conversion, TOF > 12 h⁻¹, entry 5, Table 1), whilst TBACl is the most selective (99% selectivity, entry 2 Table 1). It should be pointed out, however, that at lower catalytic loadings, quaternary ammonium salts are less efficient and with 1 mol% of TBAB the observed conversion was only 60% (Table S1). Moreover, two problems arise with the use of these reagents. First, they are very hygroscopic, so the reactions need strict anhydrous conditions. Second, the presence of organic counterparts make trickier the purification step, which requires demanding column chromatography. Although complex 2a alone is a competent catalyst, it demonstrated to be less active than TBACl (compare entries 3 and 2, Table 1) and even when employed in combination with TBACl, only moderate beneficial effect has been observed, mainly in terms of conversion (compare entry 1 and 3, Table 1) [23]. Better results were obtained with complex 2b, where very similar conversion and selectivity were observed (entries 8 and 9, Table 1). Conversely, the use of the binary catalytic system seemed to decrease slightly the selectivity (entry 7, Table 1). Better results were observed with complex 2b, whose presence in combination with TBAB gave the best selectivity and conversion (entry 4, Table 1). Noteworthy, complex 2b alone gave the best TOF observed (25 h⁻¹), with quantitative conversion and full selectivity (entry 6, Table 1). It should be pointed out that in the absence of the ammonium salt the styrene carbonate 4a was easily isolated in almost quantitative yield (99%) and excellent purity by simple filtration followed by precipitation with n-hexane. No reaction

To better describe the geometry of the [Zn(n)(X)(Pc-L)]⁺ five-coordinated system, the τ-value was calculated. τ = (β-α)/60, where β and α (°) are the largest angles in the system, those that define the basal plane of a square-pyramid. The τ-value was first introduced by Addison and colleagues[24] in order to have a quantitative estimation of the deviation from ideal square-pyramidal (τ = 0) or trigonal-bipyramidal geometry (τ = 1). In the current study, β and α refer to N2–Zn–N4 and X–Zn–N1 bond angles respectively and N3 represents the axial ligand. Considering that both complexes under investigation lie in the continuum between the two ideal geometries, it appears that while complex 2b tends to approach closely the square-pyramidal (τ = 0.26), complex 2a is slightly more distorted away from it (τ = 0.35).

Optimization of the zinc-catalyzed cyclic carbonate synthesis. At the outset, we decided to compare the catalytic activity of our zinc complexes 2a–c in the cycloaddition reaction of CO₂ with styrene oxide 3a with that of quaternary ammonium halides, which are well known to exhibit good activities in carbon dioxide fixation with epoxides.[15] Very efficient binary catalytic systems composed by Zn complexes and ammonium salts have been reported and a detailed DFT study of the mechanism of the cycloaddition reaction of CO₂ to epoxides by the Zn(salphen)/TBAX (TBAX = tetra-n-butylammonium halide) has been reported by Bo and co-workers.[24] The presence of both Lewis acid and nucleophile in the binary catalytic system makes the ring-opening process, which is often considered the rate-determining step, less energetically demanding. Our consideration was that, due to their coordination geometry, metal-complexes 2a–c were perfectly suited to act as bifunctional systems, possessing an outer sphere nucleophilic halogen anion and a free coordination site on the zinc. To verify

![Figure 2. Molecular structure of the complex (ZnIII)(Br)(Pc–L)Br·H₂O, 2b](Image 85x581 to 252x724)

Table 1. Screening of the [Zn(n)(X)(Pc–L)]X, 2a–c, catalyzed cycloaddition of CO₂ to styrene oxide.abc

| Entry | Catalyst | TBAX | Selectivity [%] | Conversion [%] | TOF [h⁻¹] |
|-------|----------|------|----------------|---------------|------------|
| 1     | 2a       | TBAI | 95             | 90            | 11         |
| 2     | –        | TBAI | 99             | 97            | 12         |
| 3     | 2a       | –    | 92             | 78            | 19.5       |
| 4     | 2b       | TBAI | > 99           | > 99          | > 12       |
| 5     | –        | TBAI | 91             | > 99          | > 19       |
| 6     | 2b       | –    | > 99           | > 99          | > 25       |
| 7     | 2c       | TBAI | 93             | 96            | 12         |
| 8     | –        | TBAI | 98             | 95            | 12         |
| 9     | 2c       | –    | 97             | 97            | 24         |

[a] Reaction conditions: neat, 250 μL of 3a (2.19 mmol), [Zn] = 1 mol%, TBAX = 2 mol%, at 125 °C; P(CO₂) = 0.8 MPa; reaction time = 4 h. [b] Conversions and selectivities determined by ¹H NMR using 1,3,5-trimethylbenzene as internal standard. [c] Turnover frequency (molcat⁻¹·h⁻¹).
was observed when using ligand 1 as the catalyst, nor with ZnCl₂ alone (Table S1).

Encouraged by these preliminary results, we decided to optimize the reaction conditions with complexes 2b and 2c in order to maintain high conversions and selectivities under milder reaction conditions. First we decreased the catalyst loading, maintaining the CO₂ pressure of 0.8 MPa, the temperature at 125 °C and the reaction time set at three hours (for full experimental details see Supporting Information, page). Results are summarized in Figure 3.

The selectivity does not seem to be affected by the catalyst loading while the conversion starts to suffer below 0.5 mol%. Complex 2c maintains a good activity even at very low catalyst loading and with a remarkable TOF of 277 mol₃ _CO₂·mol⁻¹·reaction time⁻¹ (83% conversion with 0.1 mol% catalyst loading in 3 h). Despite the catalyst loading, higher selectivities were always observed with complex 2b. With this complex, in all cases, the desired cyclic carbonate 4a was obtained as the only reaction product. Noteworthy, an almost quantitative conversion (99%) with complete selectivity (>99%) towards 4a was obtained with 0.5 mol% loading of the [Zn(II)(Br)(Pc-L)]Br, 2b, complex.

We next monitored the effect of the temperature and, especially with complex 2b, we observed a dramatic drop in the conversion at lower temperatures (Table 2). We supposed that this drop-in conversion was most probably due to the lower solubility of the metal complexes in the neat epoxide 3a at lower temperatures. To overcome this problem, we added 250 μL of DMSO to the reaction mixture and, as expected, even at 75 °C a 39% conversion with good selectivity for compound 4a was obtained (entry 4, Table 2).

Since the best results in terms of selectivity were always obtained with the cheaper bromide complex, we decided to complete the optimization of the reaction conditions only using complex 2b. We next looked at the reaction outcome at different times under fixed catalyst loading (1 mol%), temperature (125 °C) and CO₂ pressure (0.8 MPa). Then we compared these results with those obtained under otherwise identical conditions but using 2 mol% of TBAB instead of 2b as catalyst (Figure 4). We were pleased to find that the Zn complex 2b alone outperforms the quaternary ammonium salt by being more active and more selective.

Finally, we investigated the effect of CO₂ pressure on conversion and selectivity, and we disclosed that the catalytic activity was retained also at very low pressures (Figure 5). In fact, even charging the autoclave under CO₂ at atmospheric pressure (0.101 MPa) at 125 °C, we observed a moderate conversion (31%) in just 3 h, with a good selectivity (77%). It should be noted that, at such low conversion the errors we introduce in measuring the yield in 4a is quite high. In fact, in the 'H NMR we just observe the starting epoxide and the target cyclic carbonate.

**Scope of 2b-catalysed cyclic carbonates synthesis.** With these results in our hand, we decided to study the scope of the reaction by using complex 2b under the optimized reaction conditions (0.5 mol% of the zinc complex at 125 °C, P(CO₂) = 0.8 MPa; reaction time = 3 h). Whenever this was possible, reactions were carried out in neat epoxide (250 μL); on the other hand, in the case of solid epoxides (stilbene oxide, 3l) or in cases where we found a very low solubility of 2b in the reaction media, 125 μL of propylene carbonate (PC) were added.

![Figure 3. Conversion vs selectivity at different catalyst loading with complexes 2b and 2c. Reaction conditions: neat, 250 μL of 3a (2.19 mmol), at 125 °C, P(CO₂) = 0.8 MPa; reaction time = 3 h.](image1)

![Figure 4. Conversion vs selectivity at different reaction times with complexes 2b and TBAB. Reaction conditions: neat, 250 μL of 3a (2.19 mmol), [Zn(II)(Br)(Pc-L)]Br, 2b (1 mol%) or TBAB (2 mol%), at 125 °C.](image2)

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**Table 2.** Dependence of the temperature in [Zn(II)(X)(Pc-L)]X, 2b, catalyzed cycloaddition of CO₂ to styrene oxide.[a]

| Entry | T [°C] | Selectivity[b] [%] | Conversion[b] [%] | TOF[c] [h⁻¹] |
|-------|--------|---------------------|-------------------|-------------|
| 1     | 100    | 61                  | 30                | 15          |
| 2     | 75     | 10                  | 10                | 5           |
| 3[d]  | 100    | 97                  | 58                | 29          |
| 4[d]  | 75     | 82                  | 39                | 19.5        |

[a] Reaction conditions: neat, 250 μL of 3a (2.19 mmol), 2b = 0.5 mol%; P(CO₂) = 0.8 MPa; reaction time = 4 h. [b] Conversions and selectivities determined by 'H NMR using 1,3,5-trimethylbenzene as internal standard. [c] Turnover frequency (molₓ(autox)·mol⁻¹·reaction time⁻¹). [d] The catalyst was previously dissolved in 250 μL of dimethyl sulfoxide.
and selectivities reported have been calculated by the NMR method (method B, see Supporting Information for details). We choose PC due to its high polarity and non-toxic nature, and because it is very soluble in more polar cyclic carbonates even at room temperature. Thus, if the complex solubility was improved (method B), the reaction product can be isolated in almost quantitative yield. On the other hand, the reactions of 1,1- and 1,2-disubstituted epoxides failed to give the desired cyclic carbonates (entries 9 and 10, Table 3). However, cyclic carbonate 19 seemed to be due to the high volatility of 1,1-dimethyloxirane (entries 9 and 10, Table 3). A very low conversion (15%), and selectivity (40%) beside some unidentified by-products. However, as cited above, complex 2b is very soluble in more polar cyclic carbonates even at room temperature. Thus, if the metal complex was dissolved previously in PC, high conversions with excellent selectivities were restored even with alkyl epoxides (entries 4, 6 and 8, Table 3).

Worth to note, when the reaction product is the same as the cyclic carbonate employed as the solvent, as is the case of entry 4, Table 3, the reaction product can be isolated in almost quantitative yield and very high purity by addition of chloroform to the reaction mixture because complex 2b is insoluble in chlorinated solvents and precipitates quantitatively. A simple filtration, followed by evaporation of chloroform under reduced pressure yielded pure 4c in almost quantitative yield.

On the other hand, the reactions of 1,1- and 1,2-disubstituted epoxides failed to give the desired cyclic carbonates (entries 9–13, Table 3). Actually, in the case of 1,1-dimethyloxirane (1,2-epoxy-2-methyl propane), 3f, we were not able to determine the conversion of the starting product because we noticed a high loss in weight of the sample even when pre-dissolving the catalyst in propylene carbonate. This result seemed to be due to the high volatility of 1,1-dimethyloxirane that evaporated, at least in part, under the reaction conditions (entries 9 and 10, Table 3). A very low conversion (15%), and only prior dissolution of the catalyst in propylene carbonate, was observed in the case of cyclohexene oxide (entry 12, Table 3). However, cyclic carbonate 4g was obtained with a modest selectivity (40%) beside some unidentified by-products. The strong preference for the cycloadition reaction of CO$_2$ towards terminal vs. internal double bonds was further demonstrated in the case of 4-vinylcyclohexene dioxide 3h,

![Figure 5. Conversion vs selectivity at different CO$_2$ pressures. Reaction conditions: neat, 250 μL of 3a (2.19 mmol), [Zn(II)(Br)(PC–L)]Br, 2b (1 mol %), at 125 °C; reaction time = 3 h.](image)

| Table 3. Substrate scope of the [Zn(II)(Br)(PC–L)]Br, 2b, catalysed cycloaddition of CO$_2$ to epoxides$^{[a]}$ |
|---|---|---|---|
| Entry | Substrate | Selectivity$^{[b]}$ (%) | Conversion$^{[c]}$ (%) | TOF$^{[d]}$ [h$^{-1}$] |
| 1 | 3a | >99 | >99 | >66 |
| 2 | 3b | >99 | >99 | >66 |
| 3 | 3c | 74 | >99 | >66 |
| 6$^{[e]}$ | 3d | 96 | 97 | 65 |
| 10$^{[f]}$ | 3e | 15 | 26 | 17 |
| 9 | 3f | – | n.d. | – |
| 11$^{[g]}$ | 3g | 40 | 15 | 10 |
| 13 | 3h | 99 | 25 | 17 |
| 14$^{[h]}$ | 3h | >99 | 80 | 53 |
| 15 | 3i | – | 7 | 5 |
| 16$^{[i]}$ | 3j | – | 0 | – |
| 17 | 3k | >99 | 98 | 65 |
| 18 | 3l | >99 | 71 | 47 |

[a] Reaction conditions: neat, 250 μL of 3, 2b = 0.5% at 125 °C; P(CO$_2$) = 0.8 MPa; reaction time = 3 h. [b] Conversions and selectivities determined by $^1$H NMR using 1,3,5-trimethylbenzene as internal standard. [c] Turnover frequency (mol products/mol cat reaction time $^{-1}$). [d] Complex 2b was dissolved in 125 μL of propylene carbonate.

![Image](image)
where only the terminal exocyclic epoxide highlighted in red reacted to give in good yields 4-(7-oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one, 4h (entries 13 and 14, Table 3).

No reaction was observed with sterically hindered internal epoxides such as cis-limonene 1,2-oxide, 3l, or trans-stilbene, 3i (entries 15 and 16 Table 3).

Unsaturated cyclic carbonates are currently gaining increasing attention both from academic and industrial communities as reactive monomers for copolymerization reactions, since they allow for a good control in terms of spontaneous cross-linking reactions.\[^{28}\]\ When we reacted allyl glycidyl ether, 3m, we were pleased to find an almost quantitative formation of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether, 4m (entry 17, Table 3).

To demonstrate further the tolerability of electron-donating substituents, eugenol epoxide 3n was converted in a satisfying 71% yield into the corresponding cyclic carbonate (entry 18, Table 3). To the best of our knowledge, cyclic carbonate 4n was never characterized before, but it can be considered as an interesting building block for eugenol-based non-isocyanate polyurethane from renewable resources.\[^{29}\]

**Catalyst recovery and recycle.** The stability and recyclability of a catalyst are of fundamental importance for practical application. In order to gain insights to the catalyst stability and its potential reuse, two different tests were conducted under the optimized reaction conditions (2b \(= 0.5 \text{ mol\% at } 125 \degree\text{C; } \text{P(CO)}_2 = 0.8 \text{ MPa; reaction time } = 3 \text{ h}.\) As we already pointed out, at the end of the reaction, dilution with chlorinated solvent allows for the precipitation of the zinc complex that can be collected by filtration as a white solid. In order to set up a more reproducible procedure, we performed the reaction on 2.5 mL of styrene oxide, 3a. We noticed a scale up effect, probably due to a less efficient stirring in the reaction vessel, and the conversion was only of 86%, but again the only product formed was styrene carbonate 4a (> 99% selectivity). At the end of the catalytic reaction, 4 mL of chloroform were added and the solid metal complex 2b (76%) was recovered by filtration followed by a double washing with 2 mL of chloroform (see Supporting Information for details). The \(^1\text{H NMR\ spectrum of the recovered solid is perfectly consistent with the starting complex [Zn(II)(Br)(Pc-

\[2b\])Br, 2b, catalyzed cycloaddition of CO\(_2\) to styrene oxide.\[^{2d}\]\ Table 4. Recyclability of the [Zn(II)(Br)(Pc-

\[2b\])Br, 2b, catalyzed cycloaddition of CO\(_2\) to styrene oxide.\[^{2d}\]\

| Run | Selectivity \[^{2l}\] [\%] | Conversion \[^{2l}\] [\%] | TOF \[^{2i}\] [h\(^{-1}\)] | TON \[^{2i}\] |
|-----|-----------------|-------|-------|-------|
| 1   | > 99            | > 99  | > 66  | 200   |
| 2   | > 99            | 95    | 63    | 390   |
| 2*  | n.d.            | n.d.  | n.d.  | n.d.  |
| 4   | > 99            | 88    | 59    | 756   |

\[^{a}\] Reaction conditions: neat, 250 \muL of 3a, 2b = 0.5 mol\% at 125 \degree\text{C; } \text{P(CO)}_2 = 0.8 \text{ MPa; reaction time } = 3 \text{ h}. At each run 250 \muL of 3a were added. \[^{b}\] Conversions and selectivities determined by \(^1\text{H NMR\ using 1,3,5-trimethylbenzene as internal standard. \[^{c}\] Turnover frequency (mol\text{converted}_\text{cat} \cdot \text{mol}_\text{cat}^{-1} \cdot \text{reaction time }^{-1}). \[^{d}\] Moles of styrene oxide converted per mole of catalyst. \[^{e}\] Due to the experimental setup (see Supplementary Information), we were not able to determine the conversion of the 3rd run without altering the yield of the 4th.

**Conclusion**

In summary, we have shown that well-defined pentacoordinated Zn(II) complexes of basic Pc–L macrocyclic ligands are efficient catalyst, without the need of any Lewis base as co-catalyst, for the cycloaddition of CO\(_2\) to epoxide under solvent-free conditions and under mild reaction conditions. The bifunctional nature of the catalyst is assured by the peculiar geometry imposed by the tetracoordinate ligand to the cationic Zn(II) complex. The best catalytic performances have been obtained by using complex 2b, which can be conveniently prepared in high yields starting from cheap and available reagents. The metal complexes are easier to handle and far less hygroscopic than quaternary ammonium salts. Moreover, at the end of the reaction, they can be simply filtered off, thus allowing for the isolation of cyclic carbonates in high yields and excellent purities by simple recrystallization. Remarkably, quantitative conversions of terminal epoxides with full selectivity towards the cyclic carbonate have been obtained without the need of any co-catalyst at 0.8 MPa in 3 h at 125 \degree\text{C, with a 0.5 mol\% of catalyst loading.}

Finally, the reusability of the metal complex has been assessed by restoring the catalytic cycle for four consecutive runs. Based on these results, we think that among the several homogeneous catalytic systems reported in the last years for the synthesis of cyclic carbonates by cycloaddition of CO\(_2\) to epoxides, the pyridine containing macrocyclic Zn(II) halide complexes represent a considerable case of study and surely deserve the development in further applications.

**Experimental Section**

All the reactions that involved the use of reagents sensitive to oxygen or to moisture were carried out under an inert atmosphere employing standard Schlenk techniques. All chemicals and solvents were commercially available and used as received except where specified. NMR spectra were recorded at room temperature with
General procedure for the synthesis of Zn(II) complexes. A zinc (II) salt (0.65 mmol) was slowly added to a solution of ligand 1 (0.1340 g, 0.75 mmol) in DCM (20.0 mL). The mixture was left to react at room temperature for 1.5 hours. The reaction mixture was then filtered over a Büchner and washed with DCM (5.0 mL x 2), with cold MeOH (few drops), and again with DCM (5.0 mL). The product was recovered as a white powder and it was dried under vacuum (see Supporting Information for details).

General catalytic procedures. Method A: In a 2.5 mL glass liner equipped with a screw cap and glass wool, the catalyst (0.1, 0.5 or 1 mmol, see Table captions) and the epoxide (250 μL) were added. The vessel was transferred into a 250 mL stainless-steel autoclave; three vacuum-nitrogen cycles were performed and CO₂ was charged at room temperature (0.1, 0.2, 0.4 or 0.8 MPa). The autoclave was placed in a preheated oil bath (at 75 or 100 or 125 °C) and it was let to react under stirring (for 2 to 4 hours), then it was cooled at room temperature in an ice bath and slowly vented. The crude was treated with chloroform (700 μL) and a sample (150 μL) was analyzed by ¹H NMR spectroscopy by using the APT pulse sequence, HSQC and HMBC techniques.

Procedure for the isolation of styrene carbonate, 4a. At the end of the reaction, after venting the autoclave, 700 μL of DCM were added, the reaction mixture was filtered then n-hexane (30.0 mL) was added and the vessel was stored at 4 °C overnight. A white precipitate fell off that was collected and dried under reduced pressure (99% yield).

Crystal structure determination. Prismatic colorless crystals of the compound 2a suitable for X-ray analysis were grown by slow evaporation from an aqueous solution at room temperature while prismatic colorless crystals of the compound 2b were obtained from slow evaporation of mother liquor after purification process. Single crystal X-ray diffraction experiments were performed on a Bruker Smart APEX II diffractometer with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) by the ω-scan method, within the limits 3.4° < 2θ < 52.7° < 0° < 22.7° for 2a and 3.9° < 2θ < 52.7° for 2b. The frames were integrated and corrected for Lorentz-polarization effects with the Bruker SAIANT software package[30] by the ω-scan method, within the limits 3.4° < 2θ < 52.7° < 0° < 22.7° for 2a and 3.9° < 2θ < 52.7° for 2b. The frames were integrated and corrected for Lorentz-polarization effects with the Bruker SAIANT software package[30]. The intensity data were then corrected for absorption by using SADABS.[31] No decay correction was applied. The structure of both the compounds in this study was solved by direct methods (SIR-97)[32] and refined by iterative cycles of full-matrix least-squares on Fo² and ΔF synthesis with SHELXL-97[33] within the WinGX interface.[34]

Crystal data for 2a: (C₁₅H₁₅Cl₂N₃)⁺ (Cl⁻)⁻· 3/2H₂O; triclinic space group P1 (n° 2), Z = 2, a = 7.8000(4), b = 8.9923(7), c = 12.1580(9) Å, α = 78.255(1), β = 88.493(1), γ = 75.167(1)°, V = 806.79(1) Å³. Dᵣ = 1.517 g cm⁻³, F(000) = 380, T = 298(2) K, μ(Mo–Kα) = 1.855 mm⁻¹. Total number of reflections recorded, to θmax = 26.369°, was 6179 of which 3277 were unique (Rint = 0.0098); 3144 were ‘observed’ with I > 2σ(I). Final R-values: wR2 = 0.0579 and R1 = 0.0229 for all data; R1 = 0.0216 for the ‘observed’ data. All atoms are in general position. A water molecule (oxygen atom O2) is located very close to a cell vertex (site symmetry 1, Wyckoff letter a) and refined with an occupancy of 0.5. A second water molecule is present that shows a disorder over two positions (site symmetry 1, Wyckoff letter b) of its oxygen atom. The two sites, O1 A and O1B, share the same hydrogen and were refined with a sof of 0.5. The hydrogen atoms of the ligand were placed in geometrically calculated positions and then refined using a riding model based on the positions of the parent atoms with Uiso = 1.2 Ueq. The hydrogen atoms (H12 and H13) of the O1 A and O1B water molecules. A restrain was applied to the H12···H13 distance as well as the hydrogen atoms (H1 W and H2 W) were located from a difference Fourier map and refined isotropically, whereas it was restrained to a target value in order to obtain a reasonable value for the H–O bonding.

Crystal data for 2b: (C₁₅H₁₄BrNa₂N₂)⁺ (Br⁻)⁻· H₂O; triclinic space group P1 (n° 2), Z = 2, a = 8.3278(8), b = 9.2466(9), c = 10.6311(1) Å, α = 81.26(1)°, β = 89.23(1)°, γ = 89.991(1)°, V = 809.01(1) Å³. Dᵣ = 1.845 g cm⁻³, F(000) = 444, T = 298(2) K, μ(Mo–Kα) = 6.454 mm⁻¹. Total number of reflections recorded, to θmax = 26.368°, was 6583 of which 3317 were unique (Rint = 0.0124); 2786 were ‘observed’ with I > 2σ(I). Final R-values: wR2 = 0.0744 and R1 = 0.0355 for all data; R1 = 0.0275 for the ‘observed’ data. All atoms are in general position. The hydrogen atoms of the ligand were placed in geometrically calculated positions and then refined using a riding model based on the positions of the parent atoms with Uiso = 1.2 Ueq. The hydrogen atoms of the water molecule (H1 W and H2 W) were located from a difference Fourier map and refined isotropically. Their distance to the oxygen atom O was restrained to be equal within a standard deviation of 0.02. Furthermore, the distance H1 W–H2 W was restrained to a target value in order to retain a reasonable value for the H–O–H angle.

Deposition Numbers 2064861 (for 2a), and 2064860 (for 2b) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carbon dioxide fixation · Cyclic carbonates · Cycloaddition · Pyridine containing macrocyclic ligands · Zinc complexes

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