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[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)X(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_1 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.[1] 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.[2] 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;[3] it is a topic of great relevance in this field especially because cyclic carbonates have a great applicability in industrial processes.[4] Cyclic carbonates are mainly employed as aprotic polar solvents, electrolytes in secondary batteries, monomers for polycarbonate based polymers and intermediates of fine chemicals.[5]

In the last twenty years, to overcome the limitations inherent to homogeneous catalysts, such as stability and recovery issues, heterogeneous catalysts such as modified zeolites,[6] metal oxides,[7] MOFs,[8] supported catalysts,[9] mesoporous materials,[10] silica,[11] cellulose[12] and poly-ionic liquids (PILs)[13] 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.[14]

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.[15] 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.[16]

Considering environmental compatibility and the high-efficiency catalytic conversion of CO_2, there is the strong need

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to develop green catalysts capable of high conversions and selectivities, especially under solvent-free conditions.[17]

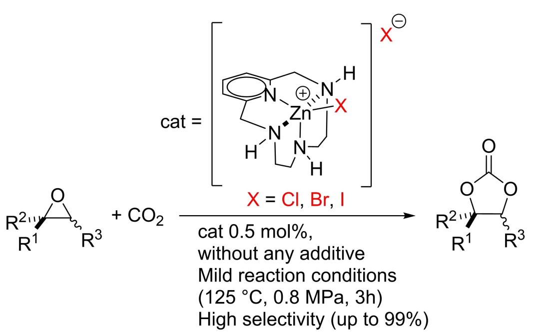
The development of new catalysts for a so crucial reaction, able to work at mild process conditions with good performance, that are also reusable and easily separable, is therefore of high industrial interest.

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_2O_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]

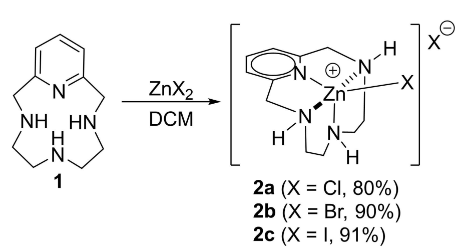
As a continuation of our studies on the catalytic activity of pyridinophane type macrocyclic ligands,[18–19] we envisioned that Zn(II) complexes would be perfect candidates to promote a clean conversion of epoxides and CO_2 in cyclic carbonates under mild reaction conditions and without the addition 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-diyl*bis*(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



Scheme 1. Cycloaddition of CO_2 and epoxides catalyzed by [Zn^{II}(X)(Pc–L)]X complexes reported in this work.



Scheme 2. Synthetic route used to obtain zinc complexes **2a–c**.

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 [Zn^{II}(X)(Pc–L)]$^+$ (with X=Cl, Br, 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 (+ + +) 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

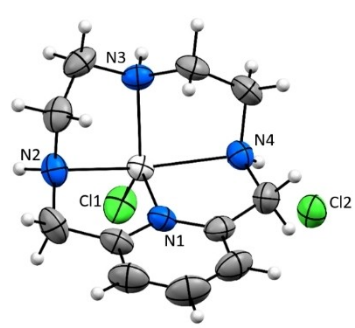


Figure 1. Molecular structure of the complex [Zn(II)(Cl)(Pc–L)]Cl·1.5H_2O, **2a** (50% probability thermal ellipsoids). Selected bond lengths (Å):): Zn–N1 2.063(1), Zn–N2 2.214(2), Zn–N3 2.053(1), Zn–N4 2.220(1), Zn–Cl1 2.2139(5). Water molecules have been omitted for clarity. Full crystal structure data of **2a** are reported in the Supporting Information.

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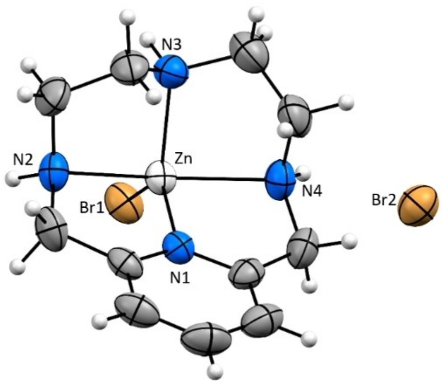


Figure 2. Molecular structure of the complex [Zn(II)(Br)(Pc–L)]Br·H_2O, **2 b** (50 % probability thermal ellipsoids). Selected bond lengths (Å): Zn–N1 2.058(2), Zn–N2 2.264(3), Zn–N3 2.050(3), Zn–N4 2.181(3), Zn–Br1 2.3516(5). The water molecule has been omitted for clarity. Full crystal structure data of **2 b** are reported in the Supporting Information.

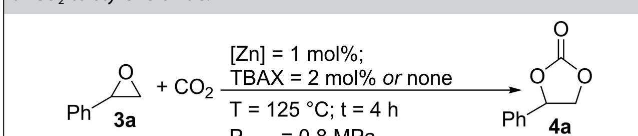
literature.[22] For both complexes **2 a** and **2 b**, the shortest Zn–N bond length is that with the N3 donor atom (2.053 Å for complex **2 a** and 2.050 Å for complex **2 b**). The Zn–X bond distance varies consistently with the X– anion size (2.2139 Å for Zn–Cl and 2.3516 Å for Zn–Br).

To better describe the geometry of the $[Zn^{II}(X)(Pc–L)]^+$ five-coordinated system, the τ-value was calculated. $\tau = (\beta - \alpha)/60$, 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[23] in order to have a quantitative esteem of the deviation from ideal square-pyramidal ($\tau = 0$) or trigonal-bipyramidal geometry ($\tau = 1$). 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 **2 b** tends to approach closely the square-pyramidal ($\tau = 0.26$), complex **2 a** is slightly more distorted away from it ($\tau = 0.35$).

Optimization of the zinc-catalyzed cyclic carbonate synthesis. At the outset, we decided to compare the catalytic activity of our zinc complexes **2 a**–**c** in the cycloaddition reaction of CO_2 with styrene oxide **3 a** 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 CO_2 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 **2 a**–**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 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,[25] 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 **2 a** 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).[26] Better results were obtained with complex **2 c**, 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 **2 b**, whose presence in combination with TBAB gave the best selectivity and conversion (entry 4, Table 1). Noteworthy, complex **2 b** 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 **4 a** was easily isolated in almost quantitative yield (99 %) and excellent purity by simple filtration followed by precipitation with *n*-hexane. No reaction

Table 1. Screening of the [Zn(II)(X)(Pc–L)]X, **2 a**–**c**, catalyzed cycloaddition of CO_2 to styrene oxide.[a]



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

[a] Reaction conditions: neat, 250 μL of **3 a** (2.19 mmol), [Zn] = 1 mol %, TBAX = 2 mol %, at 125 °C; P(CO_2) = 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 ($mol_{3a(converted)} \cdot mol_{cat}^{-1} \cdot$ reaction time^{-1}).

was observed when using ligand **1** as the catalyst, nor with $ZnCl_2$ 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 CO_2 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 $mol_{3a} \cdot mol_{cat}^{-1} \cdot reaction\ time^{-1}$ (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).

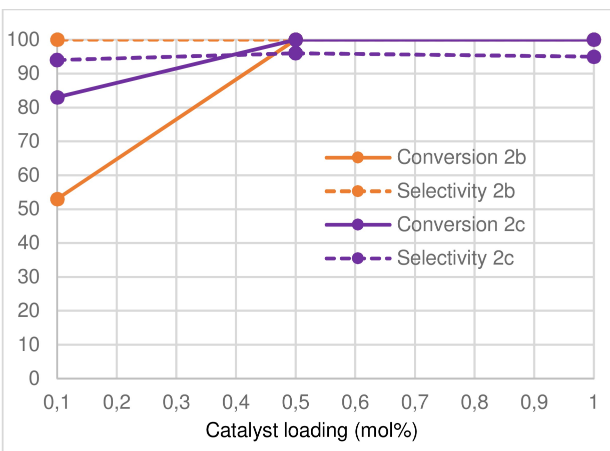


Figure 3. Conversion *vs* selectivity at different catalyst loading with complexes **2b** and **2c**. Reaction conditions: neat, 250 μL of **3a** (2.19 mmol), at 125 °C; $P(CO_2) = 0.8$ MPa; reaction time = 3 h.

Table 2. Dependence of the temperature in [Zn(II)(X)(Pc–L)]X, **2b**, catalyzed cycloaddition of CO_2 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%; $P(CO_2) = 0.8$ MPa; reaction time = 4 h. [b] Conversions and selectivities determined by ^1H NMR using 1,3,5-trimethylbenzene as internal standard. [c] Turnover frequency ($mol_{3a(converted)} \cdot mol_{cat}^{-1} \cdot reaction\ time^{-1}$). [d] The catalyst was previously dissolved in 250 μL of dimethyl sulfoxide.

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 CO_2 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 CO_2 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 CO_2 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 ^1H 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, $P(CO_2) =$ 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

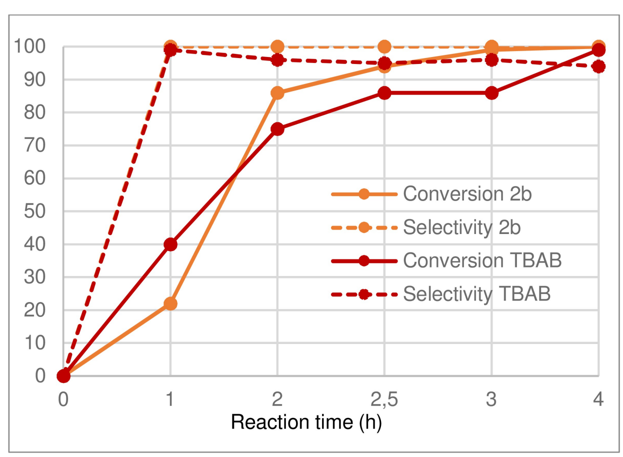


Figure 4. Conversion *vs* selectivity at different reaction times with complexes **2b** and TBAB. Reaction conditions: neat, 250 μL of **3a** (2.19 mmol), [Zn(II)(Br)(Pc–L)]Br, **2b** (1 mol%) or TBAB (2 mol%), at 125 °C.

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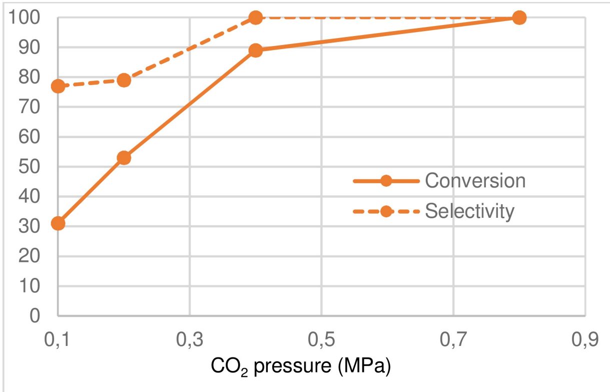


Figure 5. Conversion *vs* selectivity at different CO_2 pressures. Reaction conditions: neat, 250 μL of **3 a** (2.19 mmol), [Zn(II)(Br)(Pc–L)]Br, **2 b** (1 mol %), at 125 °C; reaction time = 3 h.

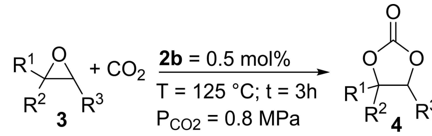
(method B, see Supporting Information for details). We choose PC due to its high polarity and non-toxic nature, and because we previously notice that the complex solubility was improved during the course of the reaction, when the cyclic carbonate is formed. Table 3 summarizes the results obtained. Conversion and selectivities reported have been calculated by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethylbenzene as internal standard, but products can be easily isolated after the reaction and when necessary purified by column chromatography (see Supporting Information). An excellent correlation between isolated and ^{1}H NMR calculated yield has been found in all cases.

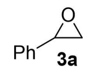
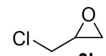
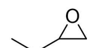
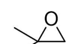
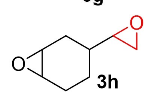
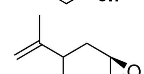
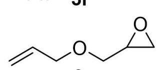
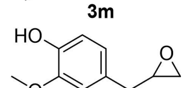
Reactive epoxide such as (+/−)-epichlorohydrin **3 b**, due to electronegative effect of its substituent that facilitated the nucleophilic attack to open the epoxide ring,[27] gave quantitative yield of cyclic carbonate (entry 2, Table 3). On the other hand, the low solubility of complex **2 b** in alkyl epoxides even at high temperatures caused a drop in the reaction yield, whose effect is more pronounced on increasing chain length, as exemplified by the difference between propylene oxide and 1,2-hexene oxide (compare entry 3 with entry 7 in Table 3). However, as cited above, complex **2 b** 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 **2 b** is insoluble in chlorinated solvents and precipitates quantitatively. A simple filtration, followed by evaporation of chloroform under reduced pressure yielded pure **4 c** 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), **3 f**, we were not able to

Table 3. Substrate scope of the [Zn(II)(Br)(Pc–L)]Br, **2 b**, catalysed cycloaddition of CO_2 to epoxides[a]



Entry	Substrate	Selectivity[b] [%]	Conversion[b] [%]	TOF[c] [h⁻¹]
1	 **3a**	> 99	> 99	> 66
2	 **3b**	> 99	> 99	> 66
3	 **3c**	74	> 99	> 66
4[d]		> 99	> 99	> 66
5	 **3d**	19	42	28
6[d]		96	97	65
7	 **3e**	15	26	17
8[d]		94	99	66
9	 **3f**	–	n.d.	–
10[d]		–	n.d.	–
11	 **3g**	–	0	–
12[d]		40	15	10
13	 **3h**	99	25	17
14[d]		> 99	80	53
15	 **3i**	–	7	5
16[d]	 **3l**	–	0	–
17	 **3m**	> 99	98	65
18	 **3n**	> 99	71	47

[a] Reaction conditions: neat, 250 μL of **3**, **2 b** = 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 ($mol_{3a(converted)} \cdot mol_{cat}^{-1} \cdot$reaction time^{-1}). [d] Complex **2 b** was dissolved in 125 μL of propylene carbonate.

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 **4 g** was obtained with a modest selectivity (40 %) beside some unidentified by-products. The strong preference for the cycloaddition reaction of CO_2 towards terminal *vs.* internal double bonds was further demonstrated in the case of 4-vinylcyclohexene dioxide **3 h**, 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, **4 h** (entries 13 and 14, Table 3).

No reaction was observed with sterically hindered internal epoxides such as *cis*-limonene 1,2-oxide, **3 i**, or *trans*-stilbene, **3 l** (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, **3 m**, we were pleased to find an almost quantitative formation of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether, **4 m** (entry 17, Table 3).

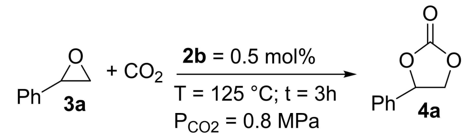
To demonstrate further the tolerability of electron-donating substituents, eugenol epoxide **3 n** was converted in a satisfying 71 % yield into the corresponding cyclic carbonate (entry 18, Table 3). To the best of our knowledge, cyclic carbonate **4 n** was never characterized before, but it can be 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 (**2 b** = 0.5 mol % at 125 °C; P(CO_2) = 0.8 MPa; reaction time = 3 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, **3 a**. 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 **4 a** (> 99 % selectivity). At the end of the catalytic reaction, 4 mL of chloroform were added and the solid metal complex **2 b** (76 %) was recovered by filtration followed by a double washing with 2 mL of chloroform (see Supporting Information for details). The ^{1}H NMR spectrum of the recovered solid is perfectly consistent with the starting complex [Zn(II)(Br)(Pc–L)]Br, **2 b**, while the elemental analysis showed a slightly higher content of carbon than expected.

Bearing in mind that our metal complex is more soluble in cyclic carbonate than in the starting epoxide, we next decided to restore a catalytic cycle without isolating the catalyst but just adding fresh styrene oxide and charging again the reaction vessel under CO_2 pressure. Results of four catalytic cycles are summarized in Table 4.

Only at the fourth run, we observed a decrease in catalytic activity, but again this result might be due to a less efficient stirring due to the increased solvent volume or even to a higher dilution of the catalyst. In any case, a remarkable TON of 756 mol of styrene oxide per mole of catalyst was achieved.

Table 4. Recyclability of the [Zn(II)(Br)(Pc–L)]Br, **2 b**, catalyzed cycloaddition of CO_2 to styrene oxide.[a]



Run	Selectivity[b] [%]	Conversion[b] [%]	TOF[c] [h^{-1}]	TON[d]
1	> 99	> 99	> 66	200
2	> 99	95	63	390
3[e]	n.d.	n.d.	n.d.	n.d.
4	> 99	88	59	756

[a] Reaction conditions: neat, 250 μL of **3 a**, **2 b** = 0.5 mol % at 125 °C; P (CO_2) = 0.8 MPa; reaction time = 3 h. At each run 250 μL of **3 a** were added. [b] Conversions and selectivities determined by ^{1}H NMR using 1,3,5-trimethylbenzene as internal standard. [c] Turnover frequency ($mol_{3a(converted)} \cdot mol_{cat}^{-1} \cdot$ 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 **2 b**, 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 °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

300 or 400 MHz spectrometers. Chemical shifts (δ) are expressed in ppm and they are reported relative to TMS. The coupling constants (*J*) are expressed in hertz (Hz). The ^{1}H NMR signals of the compounds described in the following were attributed by 2D NMR techniques. Assignments of the resonances in ^{13}C NMR were made by using the APT pulse sequence, HSQC and HMBC techniques. Catalytic tests were analyzed by ^{1}H NMR spectroscopy: the reaction crude was diluted in chloroform and analyzed by ^{1}H NMR, after the addition of an internal standard (ISTD). Low resolution MS spectra were recorded with instruments equipped with ESI/ion trap sources. The values are expressed as mass-charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. Syntheses of the ligand and zinc complexes are described in the experimental section. X-ray data collection for the crystal structure determination was carried out by using Bruker Smart APEX II CCD diffractometer with the Mo K radiation (λ = 0.71073) at 296 K.

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 × 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 mol %, 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 CO_2 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 ^{1}H NMR spectroscopy by using 1,3,5-trimethylbenzene (0.11 eq.) as the internal standard. **Method B**: In a 2.5 mL glass liner equipped with a screw cap and glass wool, the catalyst (0.5 mol %) and the epoxide (250 μL) were added and they were suspended in propylene carbonate (125 μL) as the solvent. The vessel was transferred into a 250 mL stainless-steel autoclave; three vacuum-nitrogen cycles were performed and CO_2 was charged at room temperature (0.8 MPa). The autoclave was placed in a preheated oil bath (125 °C) and let react under stirring (for 2 to 4 hours), then it was cooled at room temperature in an ice bath and it was slowly vented. The crude was treated with chloroform (700 μL) and a sample (150 μL) was analyzed by ^{1}H NMR spectroscopy by using 1,3,5-trimethylbenzene (0.11 eq.) as the internal standard.

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 $3.4° < 2\theta < 52.7° < \theta < 22.7$ for **2a** and $3.9° < 2\theta < 52.7°$ for **2b**. The frames were integrated and corrected for Lorentz-polarization effects with the Bruker SAINT software package1073 Å) by the ω-scan method, within the limits $3.4° < 2\theta < 52.7° < \theta < 22.7$ for **2a** and $3.9° < 2\theta < 52.7°$ for **2b**. The frames were integrated and corrected for Lorentz-polarization effects with the Bruker SAINT 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 Fo^2 and ΔF synthesis with SHELXL-97[33] within the WinGX interface.[34]

Crystal data for **2a**: $(C_{11}H_{18}ClN_4Zn)^+$ $(Cl)^-\cdot 3/2H_2O$, triclinic space group $P\bar{1}$ (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) Å. D_c = 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 θ_{max} = 26.369°, was 6179 of which 3277 were unique (R_{int} = 0.0098); 3144 were 'observed' with $I > 2\sigma(I)$. Final *R*-values: wR_2 = 0.0579 and R_1 = 0.0229 for all data; R_1 = 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 $\bar{1}$, 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 *i*) of its oxygen atom. The two sites, O1 A and O1B, share the same hydrogens 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 U_{iso} = 1.2 U_{eq}. The hydrogen atoms (H12 and H13) attached to O1 A and O1B were located from a difference Fourier map and refined isotropically, whereas it was not possible to determine the position of the hydrogens bound to O2. Restrains were applied to the distances between the oxygen and 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 in order to obtain a reasonable value for the H–O–H angle.

Crystal data for **2b**: $(C_{11}H_{18}BrN_4Zn)^+$ $(Br)^-\cdot H_2O$ triclinic space group $P\bar{1}$ (n° 2), Z = 2, a = 8.3278(8), b = 9.2464(9), c = 10.631(1) Å, α = 81.269(1), β = 89.239(1), γ = 89.991(1)°, V = 809.0(1) Å^3. D_c = 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 θ_{max} = 26.368°, was 6583 of which 3317 were unique (R_{int} = 0.0124); 2786 were 'observed' with $I > 2\sigma(I)$. Final *R*-values: wR_2 = 0.0744 and R_1 = 0.0355 for all data; R_1 = 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 U_{iso} = 1.2 U_{eq}. 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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