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New zinc/tetradentate N_4 ligand complexes: Efficient catalysts for solvent-free preparation of cyclic carbonates by CO_2 /epoxide coupling



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ABSTRACT

Tetra-nitrogenated Zn-Schiff-base complexes have been synthetized and studied by X-ray diffraction. The prepared Zn-N₄-ligands complexes could not follow the 18-electron rule. This property has allowed the complexes to be efficient in the coordination and activation of the substrates. The zinc complex of *N*,*N*^{*}-bis(2-p-tosylaminobenzylidene)-1,2-diaminecyclohexane, Zn(Cy-Ts) combined to tetra-butylammonium iodide (TBAI) in a ratio of 1:1, or to triethylamine, catalyzed efficiently the CO₂/epoxides coupling. These catalytic reactions were carried out without solvent at 120 °C under CO₂ pressure. Cyclic carbonates were selectively obtained with high yield up to 99% (TON up to 4900). Two plausible pathways of CO₂/epoxide coupling mechanism were proposed without halide intervention, where both reactants are activated by the same Zn metal center.

Introduction

The global demand for energy is continuously increasing because of the economic development. [1] The combustion of fossil fuels is often considered as one of the main sources of the CO_2 release in the atmosphere, which is considered as a primary greenhouse gas (GHG) that is periodically exchanged among the land surface, ocean, and atmosphere where a variety of creatures absorb and produce it daily. However, the processes of producing and consuming CO_2 must be balanced by nature. Thus, decreasing the emissions of anthropogenic greenhouse gases is becoming more urgent. Therefore, utilizing CO_2 , as an abundant renewable and non-toxic resource of C1 building blocks and its conversion into fuels and value-added chemicals emerge as active option not only used worldwide to convert an abundant available product into various valuable ones, but is also employed as a potential strategy to mitigate the CO_2 emissions and climate change, [2] energy crisis (i.e., fossil fuels depletion) [3], and the challenges in storage of energy [4].

The formation of cyclic organic carbonates, an important class of organic compounds, is among the most widely studied reactions in CO_2 catalysis, apart from the formation of linear carbonates and polycarbonates. [5] Carbonates are useful intermediates in organic synthesis, electrolytes in lithium ion batteries, green solvents, [6] plasticizers, [7] thickeners for cosmetics, [8] and important ingredients in

medicinal and agricultural industries. [9] Cyclic carbonates are produced from CO_2 by coupling with epoxides. This reaction, which can be called CO_2 /epoxide direct coupling, is fully atom-economical and constitute a sustainable and safer substitute to phosgene-based cyclic carbonate formation. [10] The basic transformations of carbon dioxide rely on its C==O polarization, with a partial negative charge (- 0.296) on its O atoms and a partial positive charge (+ 0.592) on its C center. [11] This polarization allows the attack of nucleophiles such as amines, halides, phenolates at its C center.

The more advanced chemical interactions of CO_2 are based on the coordination of the CO_2 triatomic molecules to catalysts. This can induce important changes in its chemical reactivity by altering both its molecular geometry (e.g., linear to more activated bent) and its electronic distribution (e.g., less electron-deficient carbon upon coordination). [11] Different catalysts have *hitherto* been investigated in the activation of the relatively stable CO_2 to realize indispensable catalytic reactions. Thus, finding new catalysts for converting carbon dioxide into fine chemicals under mild conditions remains an area of intensive research. To date, the effective catalytic systems for this reaction involve the use of ammonium, imidazolium, phosphonium, [12–14] salts combined or no to a metal complex, added or either included in. In the case of metal complexes, it is believed that the metal acts as a Lewis acid and activates the epoxide through oxygen donor coordination, thus

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allowing the nucleophile to react with the activated site. The literature has documented various metallic complexes of Mn, Cr, Fe, Co, Zn, Mg, and Al, which act as efficient catalysts for the CO_2 /epoxide coupling when complexed to ligand scaffolds such as N₄ porphyrins, [15] N₄ Schiff bases, [16] N₂O₂ Salfen and Salen Schiff bases, [17] N₄O₂ macrocyclic ancillary ligand, [18a] and phenol derivatives. [18b] On the other hand, metal-free organocatalysis has received unprecedented attention in recent years for its advantages of being inexpensive, stable, and not sensitive to air. [12,19]

North et al. have reported a very active bimetallic complex of Al [20], acting either in homogeneous catalysis or supported on silica in heterogeneous catalysis. This complex has allowed the first example of CO_2 insertion into terminal epoxides under mild conditions, permitting to carry out the first mechanistic study of the reaction. [20a] The authors have also demonstrated that the amine, generated from the ammonium, plays a crucial role in the mechanism cooperatively with the halide, which will be discussed in details in the present paper (vide infra). This observation represents a key step to understand this reaction well and to further develop adequate catalytic systems. Later, Basset, Kühn and their collaborators have performed a detailed mechanistic study and proposed a mechanism in which the amine acts as the nucleophile on CO_2 in the absence of any role of the halide. [21]

The majority of studies have focused on using an ammonium salt as an activator used in high ratio in conjunction with Lewis acid complexes. However, this strategy (high ratio of the ammonium with respect to the metal complex) does not allow the judicious evaluation of the activity of the metallic complexes.

Very recently, new zinc complexes have been described as effective catalysts for CO₂/epoxide coupling under conditions that are free of ammonium salt but including amine functionalities instead. [22]

In the present paper, we report the synthesis of N₄-Schiff basesbased zinc complexes comprising sulfonamides functions and N₄-tetraamines and their evaluation in carbon dioxide/epoxides coupling. The three ligands are derived from Salen-like N₄-Schiff base that we have already reported. [23] The actual interest of present report is the synthesis of new Zn-based complexes and the series of catalytic studies described using these complexes using ammonium salt only in a stoichiometric amount with the zinc complexes. Zn exhibits some advantages over other metals such as low toxicity, low price, and high stability towards oxidation. [6] Zinc complexes do not follow the 18electron rule, but Zn complexes with 22 electrons are possible with low field ligands.

Experimental section

Chemicals

All the chemicals and solvents were purchased from Sigma-Aldrich (analytical grade) and used as received without prior treatment. CO_2 gas used is of 99.995% purity from air liquide.

Method and techniques

¹H NMR spectra were recorded on Bruker spectrometers (250, 300 and 400 MHz). Samples were prepared in $CDCl_3$ or $DMSO-d_6$, chemical shifts (δ) are expressed in ppm and are measured by referring to the residual solvent as references: 7.26 ppm for $CDCl_3$ and 2.50 ppm for $DMSO-d_6$.

GC–MS analysis was realized on GCMS-QP2010 Plus, SHIMADZU instrument equipped with DB5MS column (length 30 m, internal diameter 0.25 mm, film $0.25 \,\mu$ m). Program of temperature: 60 °C (hold time 1 min), then ramp at 10 °C.min⁻¹ to reach 220 °C (hold time 1 min), and finally 10 °C.min⁻¹ to reach 280 °C (hold time 1 min). Injector temperature 280 °C, interface and ion source temperature 280 °C, EI ionization on MS, 70 eV.

GC- MS and NMR are enclosed in the supplementary materials.

Ligands and zinc complexes synthesis

The Schiff base ligands (*trans*)-H₂CyTs (L1) and (*trans*)-H₂CyTf (L2) were synthesized according to the procedure we already reported, [23] and (*trans*)-CyTA-NH₂ (L3) was prepared according to the procedure already reported in the literature. [24]

[Zn(trans)-CyTs] (C1)

To a mixture of (*trans*)-H₂CyTs (**L1**) (1 g, 1.59 mmol) in MeOH (40 mL), Zn(AcO)₂.2H₂O (0.4 g, 1.82 mmol) was added. The reaction mixture was heated at reflux for 1 h. A copious amount of precipitate was formed, collected, and washed with methanol, isolated yield = 78%. Yellow crystals obtained in CH₂Cl₂/MeOH were suitable for X-ray diffraction study. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ (ppm) = 8.6 (s, 2H, HC = N), 7.7 (d, 4H, Ar), 7.6 (d, 4H, Ar), 7.3 (t, 2H, Ar), 7.2 (m, 6H, Ar), 6.9 (t, 2H, Ar), 3.5 (m, 2H, HCN), 2.25 (s, 3 H), 1.95 (m, 4H, Cy) and 1.5 (m, 4H, Cy). MS-ESI: in positive mode: m/ z = 691 for [M+H]⁺, 729 for [M + AcCN]⁺ and 730 for [M + AcCN + H]⁺. CCDC number: 1841123.

[Zn(trans)-CyTf] (C2)

To a mixture of (*trans*)-H₂CyTf (**L2**) (500 mg, 0.855 mmol) in MeOH (30 mL), Zn(AcO)₂.2H₂O (210 mg, 0.96 mmol) was added. The reaction mixture was heated at reflux for 1 h. A copious amount of precipitate was formed, collected, and washed with methanol, isolated yield = 75%. Yellow crystals obtained in CH₂Cl₂/MeOH were suitable for X-ray diffraction study. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ (ppm) = 8.43 (s, 2H, HC = N), 7.75 (m, 2H, Ar-H), 7.5 (m, 2H, Ar-H), 7.43 (m, 2H, Ar-H), 7.2 (m, 2H, Ar-H), 3.55 (m, 2H, CH-N), 2.53 (m, 2H, CH₂), 2.15 (m, 2H, CH₂), 1.5-1.4 (m, 4H, CH₂). ¹⁹F NMR (CDCl₃, 300 MHz, 25 °C): δ (ppm) = -76.14 (s, 6 F, CF₃). MS-ESI: in positive mode, m/z = 685 for [M + AcCN]⁺ and 686 for [M + AcCN+H]⁺. CCDC number: 1841180.

Zn[(trans)-CyTA-NH₂](AcO)Cl (C3)

To a solution of (trans-CyTA-NH2) (L3) (0.3 g, 0.93 mmol) in MeOH (40 mL), Zn(AcO)₂.2H₂O (220 g, 1.002 mmol) was added. The reaction mixture was heated at reflux for 2 h. Solvent was eliminated using a rotatory evaporator. The yellow precipitate was washed with brine. The solid was dried under vacuum, isolated yield = 65%. Yellow crystals obtained in CH₂Cl₂/pentane were suitable for X-ray diffraction study. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ (ppm) = 7.1-6.8 (m, 8H, Ar-H), 5.3 (broad s, 4H, NH₂), 4 (m, 2H, H₂C-NH), 3.85 (m, 2H, H₂C-NH), 2.85 (broad s, 2H, NH) 2.52 (m, 1H, CH-N of cyclohexyl), 2.3 (m, 1H, CH-N of cyclohexyl), 1.7 (s, 3H, OCOCH₃), 1.7-0.8 (m, 8H, cyclohexyl). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ (ppm) = 179.14 (C = O), 141.76 (Ar-Cq), 130.3 (Ar-CH), 129.24 (Ar-CH), 126.5 (Ar-Cq), 122.76 (Ar-CH), 120.84 (Ar-CH), 60.08 (CH-N), 48 (CH2-N), 30.5 (CH2), 24.5 (CH2) and 23.24 (CH₃). MS-ESI: in positive mode, m/z = 424 (75%) and 426 (25%) of [Zn(trans-CyTA-NH₂)Cl + H⁺], in negative mode m/z = 558(75%) and 560 (25%) of [Zn(trans-CyTA-NH₂)(AcO)Cl + AcCN + 2H₂O -H]⁺. CCDC number: 1841124.

X-ray crystallographic study

A suitable crystal was selected and mounted on a Xcalibur kappageometry diffractometer [25a] equipped with an Atlas CCD detector and using Mo radiation ($\lambda = 0.71073$ Å).

Intensities were collected at 150 K by means of the CrysalisPro software. [25a] Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software. [25a] An analytical absorption correction was applied using the modeled faces of



Scheme 1. General synthesis of the N₄ Schiff base ligands and complexes.

the crystal. [25b] The resulting set of *hkl*was used for structure solution and refinement. The structures were solved by direct methods with SIR97, [25c] and the least-square refinement on F² was achieved with the CRYSTALS software. [25d] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93-0.98 Å, O–H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Experimental details are shown in Scheme 1. CCDC-1841123, CCDC-1841124 and CCDC-1841180 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road].

Catalytic procedure

Reactions of CO_2 with different epoxides were carried out in a small stainless-steel batch reactor (autoclave of 43 mL of inner volume) equipped with a magnetic bar. The autoclave initially containing air was charged with CO_2 , so the real CO_2 amount present is slightly less than calculated. During reaction, autoclave was immersed in oil bath with thermocouple and placed on a magnetic stirrer with temperature-controlled hotplate.

In a typical reaction, styrene oxide (SO) (2.1 g, 17.5 mmol), tetrabutylammonium iodide (TBAI) (1.06 mg, 0.00289 mmol) and the Zn complex (2 mg, 0.00289 mmol) were placed into the autoclave, which was then charged with 10 bars of CO₂ (\approx 17.8 mmol) charged at 25 °C. The reaction mixture was heated to the designated temperature (70–140 °C) and magnetically stirred for duration of time (6–24 h). Then, the reactor was cooled at 0 °C in an ice-water bath and then depressurized slowly to release carefully the remaining CO₂.

For the catalytic tests with triethylamine (TEA), a neat mother solution of SO and TEA was prepared with a ratio of TEA/Zn-complex equal to 20 since the smallest precise quantity of TEA that can be measured is $50 \,\mu$ L (0.36 mmol).

The conversion, selectivity, and identification of the products were determined by the NMR of a sample of the produced mixture dissolved in deuterated solvent CDCl₃. The reaction products were also analyzed by GCMS. NMR Spectra are compared with already reported data [17f]. For the resorcinol diglycidyl ether carbonate, we carried out MS and NMR analyses that were not previously described. MS, NMR and X-ray spectra are enclosed in the supplementary materials.

Calculation of conversion

Conversions were calculated from the proton NMR spectra of the crude reaction mixtures. As presented in the next equation, the conversion is the ratio of the integral [Int.H_A(carbonate)] of the H_A peak of the generated carbonate to the sum of the integrals of H_A [Int.H_A(epoxide) + Int.H_A(carbonate)] of both peaks of the epoxide and carbonate, multiplied by 100. It is worth noting that the calculation can also be carried out by employing the integrals of H_B or H_C instead of H_A.

$$Conv. = \frac{Int. H_A(carbonate)}{Int. H_A(epoxide) + Int. H_A(carbonate)} x100$$

We did not use an internal standard such as mesitylene or dicholorotoluene in this study because of the inconvenience of such procedures for two main reasons: the substrate is used in a high ratio with respect to the catalyst and the internal standard affects the solubility of the ammonium salt, the activity of the catalytic system, and the purification. Thus, using an external standard seemed unnecessary especially since the analysis was carried out on the raw products where all constituents were soluble in the NMR solvent.

Results and discussion

Syntheses of ligands

The Schiff bases **L1** and **L2** were synthesized following the procedures we have already reported. [23a] The tetra-amine ligand **L3** was prepared by the reduction of the corresponding Schiff base **L0** in ethanol using sodium tetraborate NaBH₄ under reflux for one hour achieving an excellent yield of 97%, following already reported procedure. [24]

Synthesis of complexes

Complexes **C1** and **C2** were prepared according to a procedure we have already described for nickel and cobalt complexes [23] by the reactions between divalent zinc acetate dihydrate $Zn(OAC)_2.2H_2O$ and the corresponding Schiff bases **L1** and **L2** in methanol at 50 °C for one hour. The complexes were precipitated in methanol and obtained with high purities and very good yields (**C1** (78%) and **C2** (75%)) by simple filtration of the cold suspensions. The samples of the complexes for X-ray diffraction were crystallized in CH₂Cl₂/MeOH (Fig. 1).

Complex C3 was prepared using the same reaction procedure between divalent zinc acetate dihydrate $Zn(OAc)_2.2H_2O$ and the corresponding tetra-amine ligand L3 in methanol at 50 °C for one hour. The



Fig. 1. Part of ¹H NMR in CDCl₃ obtained for a raw reaction mixture showing three peaks of styrene carbonate and three peaks associated to styrene oxide starting material at the left (63% conversion).

product was obtained after evaporation of methanol and washing by saturated solution of brine (NaCl) leading to a solid compound in the form of white foam after drying (65% yield). The sample for X-ray diffraction was crystallized in CH_2Cl_2 /pentane.

The ORTEP views of the complexes are shown in Fig. 2. In complexes C1 and C2, the N-donor atoms of the imine groups were coordinated to the zinc center, while the N-donor atoms of the sulfonamide groups were deprotonated and covalently bonded to the zinc center.

In complex **C1**, the Zn-O (5) and Zn-O (5ⁱ) distances are equal to 2.774 Å, which can be considered as coordination bonds (Fig. 2A). However, the Zn-O distances in complex **C2** are close to 2.8 Å where the oxygen atoms are not coordinated to zinc. This may be due to the presence of strong electron-withdrawing group as CF_3 , which causes a decrease in the basicity of the oxygen atoms.

The X-ray analysis, NMR, and mass spectra of the complex C3 reveal the formation of a penta-coordinated complex where zinc was found to coordinate to the tetradentate ligand L3 and to the acetate, with a chloride anion closely present. A similar complex derived from L3 and Cu(II)OTf₂ was already reported by Fonseca et al. [24]. In our case, the presence of a chloride atom is most likely arising from the substitution of the acetate by a chloride from the NaCl solution used to wash the raw complex powder. In C3, four N-donor atoms were found all coordinated to the zinc center as L-type ligands; each by its lone pair of electrons. Moreover, the O-donor atom of the acetate was shown to be covalently bonded to zinc, while Zn-Cl bond length was found to be 3.88 Å, which is too long to be considered as a covalent bond but rather ionic one where chloride is the counter anion of zinc cation (for more details see supplementary materials). Zn complex C3 has 22 valence electrons and does not follow the 18-electron rule, since Zn is a transition metal of the class 3d and the ligands are of weak-field type.

The X-ray diffraction shows that the zinc metal complexes: (1) can still coordinate to more ligands even after attaining 18 valence electrons (**C1** and **C3**; Fig. 2A & C); (2) exhibit a good oxophilicity as shown in Fig. 2A, the Zn center is coordinated to two neighboring oxygen

atoms; (3) the Zn center, as in C3, retaining its acetate ligand to get 22 valence electrons. Thus, the zinc complex is a good Lewis acid and an oxophile, these characteristics rationalize the Zn complex activity in the CO_2 /epoxide coupling.

Catalysis: CO₂/epoxides coupling

The synthesis of cyclic carbonates using the Zn complexes for the coupling of CO_2 with styrene oxide as the model substrate was studied. The effects of the ammonium salt, halide, complex/ammonium salt ratio, temperature, CO_2 pressure and reaction time were examined since these parameters affect the conversion and the selectivity towards the formed carbonates.

Preliminary tests of CO₂/styrene oxide coupling

The polar solvents initially thought necessary for this reaction are toxic like DMF or DCM. Working without such solvents has been proven to be effective and highly suitable for green chemistry processing and synthesis. Carrying out this reaction under solvent-free conditions is due to the low solubility of CO_2 in conventional solvents where the epoxide or cyclic carbonate produced can act as the solvent.

Calò et *al.* have realized the reaction in a mixture of molten salts TBAB/TBAI (1:1/ w:w) in an almost stoichiometric ratio with the epoxide under an atmosphere of carbon dioxide. [12] In a free solvent medium, we first realized the reaction with a catalytic amount of TBAI (0.0165 mol %) at 100 °C under a CO_2 pressure of 10 bars in a stainless-steel batch reactor. A conversion of 34% was obtained (Table 1, entry 1). The resulting carbonate was obtained after crystallization in a solution of NaOH (1 N) in order to eliminate the unreacted epoxides as water-soluble diols. As a control experiment, we performed a blank test without the TBAI, i.e., the styrene oxide only under 10 bars CO_2 pressure at 100 °C, no reaction was observed at all (Table 1, entry 2), demonstrating the importance of the ammonium (amine source) in this catalytic reaction.



Fig. 2. ORTEP views of the complexes C1 (A), C2 (B) and C3 (C).

Table 1

Preliminary catalytic tests on the CO_2 /styrene oxide coupling catalyzed by Zn-complex C1.

Cal= C1/(TBA) (1.1): SO(Cal= 6055)							
Entry	Ammonium Salt	Zn-complex	Conversion (%)*	TON**			
L	TBAI	None	34	2059			
2	None	None	0	0			
3	None	C1	0	0			
1	TBAI	C1	60	3633			
5	TBACl	C1	17	1029			
5	TBABr	C1	28	1695			

Complex **C1** (0.00289 mmol), TBAX (0.00289 mmol), Styrene oxide (2.1 g, 17.5 mmol), CO₂ (\approx 17.8 mmol). CO₂/styrene oxide \approx 1.02. *Conversion is calculated from ¹H NMR spectrum. **TON according to catalytic system 1/1 complex/Ammonium Salt. *TON* = $\frac{nb \text{ of mol of formed carbonate}}{nb \text{ of mol of Complex (or of TBAX)}}$.

Then, we started our study to evaluate the catalytic activity of our synthetized complexes. Specifically, a catalytic amount of C1 (0.0165 mol %) complex with styrene oxide under 10 bars of CO_2 did not achieve the desired chemical transformation (Table 1, entry 3). When TBAI was used in a stoichiometric ratio with C1, the reaction was processed with a conversion of 60%, and the TON was found to increase from 2059 with the TBAI alone to 3633 with this combination (Table 1, entry 4). Next, we tested TBACl and TBABr using the same conditions as TBAI, lower activities were observed achieving a conversion of 17% (TON = 1029) and 28% (TON = 1695), respectively (Table 1, entries 5 & 6).

Temperature and pressure effects

To evaluate the temperature effect, we realized several catalytic tests at different temperatures (Table 2) employing the same conditions firstly used in our study. The yield decreased remarkably from 60% (at 100 °C) to 12% when the reaction was performed at 70 °C (entries 1 & 2). In contrast, the yield increased to 68% at 120 °C (entry 3). It was also found to increase to 81% at 140 °C (entry 4) although traces of side products started to appear, probably arising from the degradation of epoxide starting materials.

Table 2

Temperature effect on the CO₂/styrene oxide coupling catalyzed by Zn-complex C1.

Entry	T (°C)	P CO ₂ (bar)	CO ₂ /SO ratio	t (h)	Yield (%)	TON	Final TOF (h ⁻¹)
1	70	10	≈ 1.02	24	12	727	30
2	100	10	≈ 1.02	24	60	3633	151
3	120	10	≈ 1.02	24	68	4118	171
4	140	10	≈ 1.02	24	81*	4905	204
5	120	5	≈ 0.50	6	24	1453	242
6	120	10	≈ 1.02	6	32	1938	323
7	120	15	≈ 1.52	6	33	1998	333

Complex C1 (0.00289 mmol), TBAI (0.00289 mmol), Styrene oxide (2.1 g, 17.5 mmol), 0.0165 mol% of catalyst = C1/TBAI (1:1). Yield Calculated from ¹H NMR spectrum. * 81% is the yield of styrene carbonate.

The effect of CO_2 pressure on this coupling reaction is also studied by performing reaction on the same conditions and on the best temperature chosen for our study (120 °C) but at shorter time (6 h) for well comparison. Working at 10 or 15 bars doesn't almost affect reaction yield because CO_2 amount present is sufficient and then TON is conserved approximately (Table 2, entries 6&7), whereas working at 5 bars ($CO_2/SO = 0.5$) less yield was attained (24%) since there is deficiency in CO_2 quantity. Probably the solubilized quantity of CO_2 is the only to be affected by CO_2/SO ratio variation.

Reaction time

In order to obtain a complete conversion and then prevent the purification of the product, we proceeded to determine the reaction time. We firstly tried to double the catalytic loading (0.033 mol%) at 120 °C, the reaction was complete after 24 h with a TON of 3027 (Table 3, entry 1). Under the same conditions, the reaction was found to be complete after 18 h (Table 3, entry 2). Decreasing the reaction time further was found to lead to an incomplete conversion (83% and 64% NMR yields) and the TON was 2513 and 1938 after 13 h and 6 h of reaction, respectively. Obviously, higher TOFs were reached; 193 h⁻¹ and 323 h⁻¹ after 13 h and 6 h, respectively (Table 3, entries 4 &5), which can be explained by the exponential variation of the reaction rate with time. When the catalyst load was decreased to 0.022 mol% in an 18 h reaction time, a TON of 3315 was gained but with a lower yield of 73% (Table 3, entry 3).

Reactions catalyzed with different catalytic systems (Zn-complex/TBAI)

With the optimal conditions in hand, we set out to examine the catalytic activity of the other two Zn complexes **C2** and **C3**. The **C2** complex comprising CF_3 groups in the sulfonamide functionalities showed a lower activity (TON = 2513) than the **C1** holding tosyl groups (Table 4, entry 2). This might be probably due to the stability of the **C1** complex and its geometry maintained by pi-stacking interactions of the toluene rings of tosyl groups in addition to the electronic effect.

Table 3

Reaction stopping at different reaction times of $CO_2/styrene$ oxide coupling catalyzed by Zn-complex C1.

t (h)	Mole % Cat (SO/Cat ratio)	Yield (%)	TON	Final TOF (h^{-1})
24	0.033 (3027)	100	3027	At least 126
18	0.033 (3027)	100	3027	At least 168
18	0.022 (4541)	73	3315	184
13	0.033 (3027)	83	2513	193
6	0.033 (3027)	64	1938	323
	t (h) 24 18 18 13 6	t (h) Mole % Cat (SO/Cat ratio) 24 0.033 (3027) 18 0.033 (3027) 18 0.022 (4541) 13 0.033 (3027) 6 0.033 (3027)	t (h) Mole % Cat (SO/Cat ratio) Yield (%) 24 0.033 (3027) 100 18 0.032 (3027) 100 18 0.022 (4541) 73 13 0.033 (3027) 83 6 0.033 (3027) 64	t (h) Mole % Cat (SO/Cat ratio) Yield (%) TON 24 0.033 (3027) 100 3027 18 0.032 (3027) 100 3027 18 0.022 (4541) 73 3315 13 0.033 (3027) 83 2513 6 0.033 (3027) 64 1938

Complex **C1** (0.00289 mmol), TBAI (0.00289 mmol), Styrene oxide (1.05 g, 8.75 mmol), CO₂ (10 bars, \approx 17.8 mmol). CO₂/styrene oxide \approx 2.03. Catalyst = **C1**/TBAI (1:1), T = 120 °C. Yield was calculated from ¹H NMR spectrum.

Table 4

Catalytic activities of the catalytic systems containing C1, C2, C3 and TBAI catalyzed CO₂/styrene oxide coupling.

Entry	Catalytic System	Cat % (SO/Cat ratio)	TBAI % (SO/TBAI ratio)	Yield %	t (h)	TON
1	C1/TBAI (1:1)	0.033 (3027)	0.033 (3027)	100	18	3027
2	C2/TBAI (1:1)	0.033 (3027)	0.033 (3027)	83	18	2513
3	C3/TBAI (1:1)	0.033 (3027)	0.033 (3027)	50	18	1513
4	TBAI alone (0:1)	-	0.033 (3027)	73	18	2210
5*	TBAI alone (0:1)	-	0.0165 (6055)	27	6	1635
6*	C1/TBAI (1:1)	0.0165	0.0165 (6055)	32	6	1938
		(6055)				
7*	TBAI alone (0:2)**	-	0.033 (3027)	37	6	1116
8*	C1/TBAI (1:2)**	0.0165 (6055)	0.033 (3027)	60	6	3633

Complex **C1, C2 or C3** (0.00289 mmol), TBAI (0.00289 mmol), Styrene oxide (1.05 g, 8.75 mmol), CO₂ (10 bars, \approx 17.8 mmol). CO₂/styrene oxide \approx 2.03, T = 120 °C. * Styrene oxide (2.1 g, 17.5 mmol), CO₂/styrene oxide \approx 1.02 ** TBAI (0.00578 mmol). Yield calculated from ¹H NMR spectrum.

In fact, the CF₃ group in the **C2** complex is an electron withdrawing group that has caused a decrease in the length of the two bonds S–O (around 1.431 Å), as compared to those of the tosyl groups (1.438 Å) in the **C1** complex. On the other hand, the **C3** complex, positively charged with 22 electrons, conduced to the lowest activity that is even lower than the one obtained with the TBAI alone (Table 4, entries 3&4). This might be due to the presence of a chloride anion, which could be exchanged with the iodide of TBAI.

To better understand **C1** complex activity that seems the most efficient with respect to the two other complexes studied, we varied the amount of co-catalyst TBAI to be double with respect to the complex (Table 4, entries 7&8). Comparing the activity of **C1** when performing CO_2 /epoxide coupling reaction at 6 h with **C1**/TBAI (1:1) and (1:2) ratios, a doubling of yield from 32 to 60% respectively is observed (TON of 3633 when TBAI is amount is doubled). However doubling TBAI amount without **C1** intervention doesn't reveal the same effect. That is expected due to the increase of nucleophile amount which plays a crucial role in this coupling.

Scope of terminal epoxides

A scope of six terminal epoxides was subjected to the CO₂/epoxide coupling reaction catalyzed by the best catalytic system C1/TBAI of this study. The reaction with 1-hexene oxide, which has a butyl group as an inductive donor group on the epoxide ring (Table 5, entry 2), resulted in a 10% yield with a TON of 303. In contrast, the glycidyl phenyl ether, the glycidol, and resorcinol di-glycidyl ether with the epoxide function substituted to inductive withdrawing groups, conduced to a full conversion under same conditions with a TON of 3027, similarly to the styrene oxide (Table 5, entries 1, 3, 4 & 6). The present oxygen atoms might have facilitated the interactions between the substrates and the catalyst. CO₂ has a strong affinity towards electron-donating functionalities [6]. Lastly, 1-Chloro-2,3-epoxypropane (Epichlorihydrin) bearing the chloride electron withdrawing group yielded 16% with a TON of 515 (Table 5, entry 5). Thus, the epoxides having additional oxygen atoms which facilitate the interaction with the catalyst seem to be important substrates in the scope of the reaction catalyzed by the zinc complexes.

Rationalization

Many researchers believed for a long time that the key step of the CO_2 /epoxide coupling mechanism is the opening of the epoxide ring by the halide of the ammonium salt. North et *al.* [20a] have introduced the role of amine generated in situ from ammonium salts. They have

Table 5

Cyclic carbonates produced from CO₂/epoxides coupling catalyzed by C1/TBAI catalytic system.



Complex C1 (0.00289 mmol), TBAI (0.00289 mmol), Styrene oxide (1.05 g, 8.75 mmol), CO₂ (10 bars, \approx 17.8 mmol). CO₂/ oxide \approx 2.03. Yield and selectivity were determined by ¹H NMR in CDCl₃ (except for glycidol in DMSO) and by GCMS.

* In 1 mL of acetonitrile as solvent. 0.033 mol% epoxide function = > TON was calculated according to that.

proposed that the amine forms a carbamate with CO₂, which in turn reacts with the opened epoxide by the halide, all activated on the bimetallic complex conducing by cyclisation to the cyclic carbonate. It is really important to identify if the presence of an ammonium salt acts as amine generator or halide generator too. Recently, Basset, Kühn and their collaborators [21] have carried out a mechanistic study utilizing dimethylaminopyridine (DMPA) or NBu₄Br as a co-catalyst of NbCl₅. They have shown that the reaction with DMAP proceeds effectively, proving that this reaction can occur without a halide. Zinc catalysts containing free amine functions catalyzed the CO₂-epoxide coupling free of co-catalyst. [22] These investigations encouraged us to examine the reaction with other co-catalysts, particularly using other halide salts (NaI and KI) free of nitrogenated derivatives (ammonium) as well as using an amine source free of halides (TEA as simple amine).

We conducted the described catalytic tests. When NaI or KI was added to the reaction mixture of styrene oxide with the zinc complex **C1**, no reaction was observed. Whereas, when using TEA as nucleophile instead of TBAI, the catalytic activity is clearly improved with 76% yield and 4600 TON (Table 6, entry 3).

We believe now that the halide does not play its executive role by epoxide opening, but by leaving the ammonium cation to be decomposed into the nucleophilic amine as shown. [20–21] Thus, a better leaving group can lead easier to this fact with the following order of halides (iodide > bromide > chloride). The ammonium ion also plays the role of an activator by weak bond interactions as Van der Waals forces as documented in organocatalysis, since it has catalyzed the $CO_2/$ epoxides coupling even in the absence of Lewis acids (Scheme 1).

Based on the mechanistic studies reported by the groups of M.

Table 6

Evaluation of the role of amine (free of halide) as the co-catalyst with **C1** in the carbon dioxide/epoxide coupling.

	CO2 (10 Cat. (0.001 120°C	0 bars) 65 m ol%) , 18 h	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	t.= 6055
Entry	Co-Cat.	C1/Co-Cat. ratio	Yield %	TON
1 2	TBAI KI or Nai	1	48 0	2907 0
3	TEA	0.05	76	4600

Complex C1 (0.00289 mmol), TBAI (0.00289 mmol), Styrene oxide (2.1 g, 17.5 mmol), CO2 (10 bars, \approx 17.8 mmol), CO2/styrene oxide \approx 1.02. TEA (50 µL, 0.36 mmol).

North, of J. M. Basset, and of F. E. Kühn, we propose a mechanism (Scheme 2) with two possible pathways with our zinc complex C1 as the Lewis acid catalyst and amine as the co-catalyst. Keeping in mind that zinc complex we developed, could has 18 to 22 electrons valency, as we showed by X-ray study, and then could activate CO_2 and epoxide in the same time to form one intermediate with both molecules. In pathway 1, the epoxide, coordinated to Zn, is opened by the amine, forming adduct **II**, followed by CO_2 insertion and finally by a nucleophilic attack from the oxygen of the negatively charged metal complex to release a carbonate and regenerate both parts of the catalyst, the amine and the zinc complex.



Scheme 2. Proposed mechanistic cycles: pathway 1 begins with ring opening of epoxide while pathway 2 involves firstly the formation of carbamate.

In pathway 2, carbon dioxide activated by the zinc complex reacts with the amine and forms adduct **IV**, followed by the epoxide insertion and nucleophilic attack from the oxygen of the negatively charged metal complex to release the carbonate and regenerate the catalyst.

Conclusion

Carbonates represent an important class of organic compounds. Their synthesis from CO_2 is a promising research area as a substitute of toxic phosgene and a method to advance the valorization of CO_2 , as the major greenhouses gas, by its conversion into value-added organic materials of industrial interest.

Zn-N₄-Schiff bases complexes combined to TBAI or triethylamine were able to catalyze efficiently the synthesis of cyclic carbonates in presence of CO_2 in a free-solvent medium. The efficiency of the catalytic system is controlled by: the presence of a nucleophile generator, electron-donating/ withdrawing ability of the substituents of the Schiff base ligands, and the catalytic conditions such as CO_2 pressure, temperature, co-catalyst, and catalytic loading.

As perspectives of this work, we look to prepare other metal complexes based on our N_4 -Schiff base ligand (H_2CyTs) and prepare a related heterogeneous catalyst for this reaction.

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Appendix A. Supplementary data

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