

Highly active and selective Zn(II)-NN'O Schiff base catalysts for the cycloaddition of CO₂ to epoxides

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Abstract

Mononuclear Zn(II) complexes with tridentate NN'O-donor base Schiff ligand *N*-(2-pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzaldimine (**1H**) combined with a co-catalyst are active for the cycloaddition of CO₂ and epoxides. They provide cyclic carbonates selectively even with the more hindered substrates such as cyclohexene oxide and methyl epoxyoleate. The best conditions were achieved running the reaction in expanded neat substrate in CO₂ as reaction media. The activity obtained for the cycloaddition of CO₂ to styrene oxide reached an initial TOF of 3733 h⁻¹. The solid state structures of [Zn(**1**)₂] and [Zn(**1**)(OAc)₂]_n were determined by X-ray diffraction methods. Relative stability of the species in solution was analysed by DFT calculations.

Keywords

Chemical fixation of carbon dioxide

Zinc(II) catalysts

Schiff base ligands

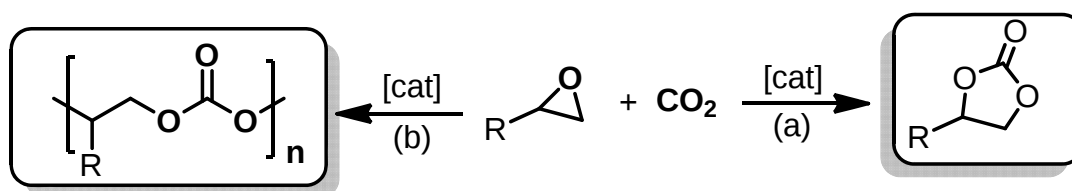
Epoxide

Cyclic carbonate

1. Introduction

Carbon dioxide is a renewable C₁-building block for the synthesis of organic chemicals such as carboxylic acids, esters, amides or lactones

[1]. The main drawback is its thermodynamic stability and kinetic inertness. To overcome this problem the use of catalysts or highly reactive substrates such as epoxides is required. Epoxides are known to react with carbon dioxide in the presence of catalysts to form cyclic carbonates or polycarbonates (Scheme 1) [2]. This process is an alternative to the classical method to obtain carbonates that involves highly toxic and hazardous phosgene and pyridine [3]. Cyclic carbonates present a wide range of applications as they can act as polar aprotic solvents, antifoam additives or plasticizers [3,4,5,6]. In addition, they are also used as raw materials for the synthesis of polyurethane and urea derivatives [7]. They can also be used for copolymerization with cyclic esters leading to biodegradable materials for biomedical applications [8]. The yearly market of organic carbonates was estimated in 2.6 Mt in 2014 [9]. The increasing demand of these products requires the development of more effective and selective catalysts at mild conditions.



Scheme 1. a) Cycloaddition and b) copolymerization of CO₂ and epoxides

Catalysts for the coupling of carbon dioxide and epoxides include halide, quaternary alkyl ammonium or phosphonium salts, as well as ionic liquids and metal complexes [2,7]. Halide, quaternary salts and ionic liquids are known to produce the most stable thermodynamic product, which is the cyclic carbonate [2], due to the higher reaction temperatures required in the absence of a Lewis acid [10]. On the other hand, metal complexes can catalyse the formation of polymer and/or cyclic carbonate products depending on the co-catalyst, substrate and reaction conditions used. N-heterocyclic amines, phosphines or anions derived from PPN⁺ (PPN⁺ = [Ph₃P=N=PPh₃]⁺) and ammonium salts [11], which act as nucleophiles, have been employed as co-catalysts [12]. In most cases, such binary catalytic systems, Lewis acid/nucleophile, lead to an enhanced activity at milder reaction conditions [13,14]. Outstanding examples of binary systems are the ones containing Al(III) salen complexes reported by North *et al.* [15] and the Al(III) aminotri(phenolate) complexes, developed by Kleij's group, leading to highly active catalysts at mild reaction conditions [16].

Among all metal complexes used as catalysts, Zn based derivatives have extensively been studied. The key issue in the fixation of CO₂ into carbonates was the discovery by Inoue and coworkers that Zn catalysts copolymerized CO₂ and epoxides to form polycarbonates [17]. As a matter of fact, one of the enzymes involved in the transformation of CO₂ into organic carbonates is a carbonic anhydrase, which contains a zinc cation in the active site [9]. Among the most efficient Zn(II) based catalysts are those containing Zn-phenoxides [18], Zn-pyridine [19], Zn- β -diiminates [20], dinuclear anilido-aldimino Zn complexes [21], Zn-NNONNO-complexes [22] and dinuclear Zn β -diketiminato complexes [23]. They produce polymerization products, specially starting from cyclohexene oxide (CHO) and propylene oxide. By contrast, catalysts based on Zn tetradentate NNOO-donor salen derived ligands [24,25,26] and tridentate NNN-donor ligands [13,27] produced selectively the cyclic carbonates.

Catalytic Zn(II) systems with NN'O-donor ligands have been less extensively studied. The tridentate ligands may offer different possibilities to stabilize the intermediate species. In fact, NN'O-ligands with pyridino/amino-imino-phenolato functionalities have been found to form tetracoordinate, pentacoordinate and hexacoordinate species using one or two ligands per metal center [28]. Furthermore the formation of higher coordinative saturated species may benefit the selective formation of the cyclic carbonates by promoting the back-biting mechanism [29]. Complexes with pyridine-imine-phenolate NN'O-donor ligands (Figure 1) [30,31] have been successfully applied as catalysts in aluminium(III) catalyzed ethylene polymerization [32] and in calcium(II) and zinc(II) catalyzed ring-opening polymerization of cyclic monomers [33,34,28f]. Cu(II) complexes with dimethylamine-imine-phenolate NN'O-ligands have been reported to be active in the copolymerization of CHO/CO₂ [35]. We recently reported that a Cr(III) complex with ligand **1H** (Figure 1) in the presence of a co-catalyst was an active catalysts for the copolymerization of CHO/CO₂ as well as for the cycloaddition of CO₂/propylene and styrene oxides [14]. The proposed structure for this chromium complex involved one ligand acting as tridentate and another as bidentate, [Cr(κ^3N,N,O)(κ^2N,O)Cl]. Using this catalyst and dimethylaminopyridine (DMAP) as co-catalyst, the reaction of CHO with CO₂ produced mixtures of poly(cyclohexenecarbonate) and cyclic carbonate. In order to improve the conversion and selectivity obtained with this Cr(III) based catalytic system, we decided to prepare analogous catalysts with Zn(II) for the following reasons: a) they could stabilize mononuclear complexes with different coordination numbers, therefore they would

favour the dissociation of the carbonate growing chain thus selectively forming the cyclic carbonate; b) Zn(II) catalysts have shown high activity at milder conditions than Cr(III) ones; c) the softer Lewis acid character of the Zn(II) d^{10} complex compared to the Cr(III) one [36] may decrease the strength of M-O bond, leading to the selective formation of the cyclic carbonate [10]; d) the higher lability of Zn(II) compared to Cr(III) complexes towards the substitution reaction may favour the dissociation of the carbonate growing chain; e) the pyridine moieties may act as a pendant group and could replace the growing chain, favouring the backbiting mechanism, which yield the cyclic product.

Thus, here we report the synthesis and catalytic activity of Zn(II) complexes with ligand **1H** (Figure 1) in the coupling reaction of CO₂ and different epoxides. The catalytic activity of a Zn(II) complex with ligand **2H** (Figure 1) has also been studied for comparative purposes. In addition, a set of calculations based on density functional theory methods (DFT) were also performed on Zn(II) complexes with **1H** in order to confirm computationally the hypotheses suggested by the experimental results.

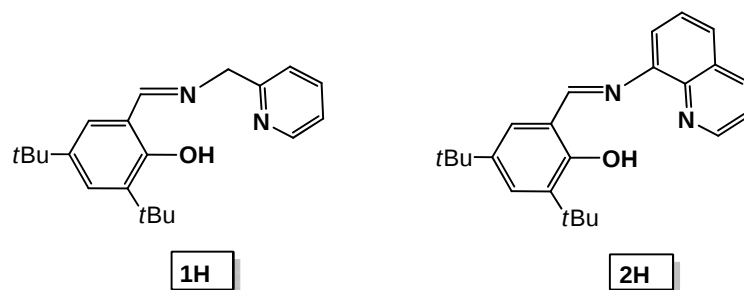


Figure 1. NN'O- Schiff base ligands **1H** and **2H**.

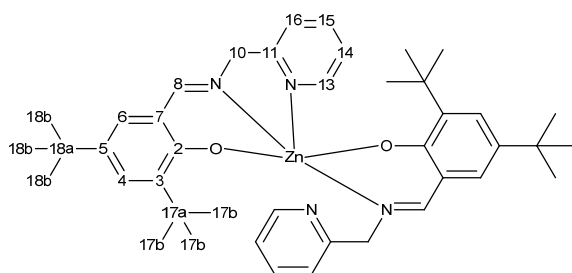
2. Experimental

2.1. General comments

1H was prepared following described procedures [30]. Epoxides were dried over CaH₂, distilled and stored under inert atmosphere except 1,2-epoxyhexane and 1,2-epoxydodecane and epichlorohydrin, which were purchased at Sigma-Aldrich and used as received. Solvents were purified by the system Braun MB SPS-800 and stored under nitrogen atmosphere. Carbon dioxide (SCF Grade, 99.999 %, Air Products) was used introducing an oxygen/moisture trap in the line (Agilent). IR spectra were recorded on a Midac Grams/386 spectrometer in ATR (range 4000-600) cm⁻¹ or KBr range (4000-400 cm⁻¹). UV-visible spectra were recorded on a UV-3100PC spectrophotometer. NMR spectra were recorded at 400 MHz Varian, with tetramethylsilane (¹H NMR and ¹³C

NMR) as internal standards. MALDI-TOF measurements of complexes were performed in a Voyager-DE-STR (Applied Biosystems) instrument equipped with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. α -cyano-4-hydroxycinnamic acid (CHCA) was used as matrix when indicated. The matrix was dissolved in THF at a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$. The complex was dissolved in MeOH ($50 \text{ mg}\cdot\text{L}^{-1}$). The matrix and the samples were premixed in the ratio 1:1 (matrix:sample) and then the mixture was deposited ($1 \mu\text{L}$) on the target. For each spectrum 100 laser shots were accumulated. Electrospray ionization mass spectra (ESI-MS) were obtained with an Agilent Technologies mass spectrometer. Typically, a dilute solution of the compound in the indicated solvent (1:99) was delivered directly to the spectrometer source at $0.01 \text{ mL}\cdot\text{min}^{-1}$ with a Hamilton microsyringe controlled by a single-syringe infusion pump. The nebulizer tip operated at 3000–3500 V and 250°C , and nitrogen was both the drying and a nebulising gas. The cone voltage was 30 V. Photochemical reactions were performed using a Philips HPL-N 125 W high-pressure mercury lamp, which can be purchased at most commercial lighting stores. Elemental analyses were performed at the *Serveis Tècnics de Recerca* from the *Universitat de Girona* (Spain). High-pressure NMR experiment (HP NMR) was carried out in a 10-mm-diameter sapphire tube with a titanium cap equipped with a Teflon/polycarbonate protection [37].

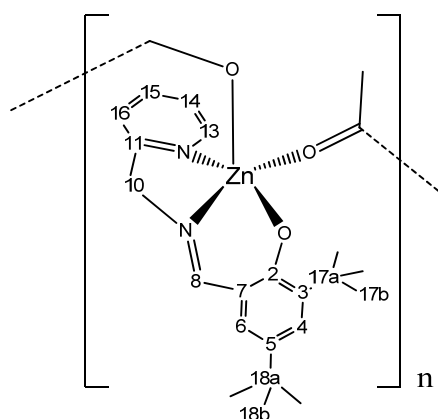
2.2. Syntheses of bis(N-(2-pyridylmethyl)-3,5-di-*tert*-butylsalicylaldimino)zinc(II) [$\text{Zn}(\mathbf{1})_2$] (**1a**)



To a solution of ligand **1H** (400 mg, 1.23 mmol) in MeOH (38 mL), NaOH (49.3 mg, 1.23 mmol) was added. After 10 min stirring, a solution of ZnI_2 (196.3 mg, 0.615 mmol) in MeOH (5 mL) was added. The yellow mixture was stirred for 4.5 h at r.t. The resulting solution was dried under vacuum. Cold diethyl ether was added and a white solid appeared and was separated by filtration. The filtrate yellow solution was dried under vacuum, washed with deionised water, filtered off and dried under vacuum to

obtain a yellow solid, 357.4 mg (Yield 74 %). The solid was stable while kept under nitrogen atmosphere at low temperature. Anal. Calcd. for $C_{42}H_{54}N_4O_2Zn \cdot 0.5H_2O$ (720.8): C 70.0, H 7.6, N 7.8; found C 69.8, H 7.5, N 7.9. ESI Calcd. for $C_{42}H_{54}N_4O_2ZnNa$ m/z : 733.3430 $[M+Na]^+$, found m/z : 733.3436. UV-vis (MeOH, $2.56 \cdot 10^{-5}$ M) $\lambda(nm)$ (ϵ , $L \text{ mol}^{-1} \text{ cm}^{-1}$): 227.0 (42900), 252 sh (26000), 265 sh (26000), 269 sh (25000), 331 (5130), 390.0 (7100). Selected IR bands (ATR, $\nu \text{ cm}^{-1}$): 2948 m, 2895 m, 2866 m, 1616 $\nu(C=N)$ s, 1527 m, 1432 m, 1411 m, 1329 $\nu(C-O)$ m, 1254 m, 1200 m, 1158 s, 1049 m, 834 m, 790 m, 752 m, 636 m. 1H NMR (400 MHz, toluene- d_8): δ 1.40 (s, 9H, CH_3), 1.67 (s, 9H, CH_3), 4.15 (d, 1H, CHH , $J=16.0$ Hz), 4.23(d, 1H, CHH , $J=16.0$ Hz), 6.36 (m, 1H, $(CH)^{14}$, $J = 7.4$ Hz, $J = 5.0$ Hz, $J = 0.9$ Hz), 6.56 (d, 1H, $(CH)^{16}$, $J = 7.8$ Hz), 6.73 (dt, 1H, $(CH)^{15}$, $J = 7.7$ Hz, $J = 1.8$ Hz), 6.82 (d, 1H, $(CH)^6$, $J = 2.7$ Hz), 7.59 (d, 1H, $(CH)^4$, $J = 2.7$ Hz), 7.75 (s, 1H, $CH=N$), 8.27 (d, 1H, $(CH)^{13}$, $J = 4.1$ Hz); ^{13}C NMR (75.43 MHz, $CDCl_3$): δ 30.1 (CH_3 , $C^{17b}tBu$), 31.7 ($CH_3, C^{18b}tBu$), 34.0 ($C, C^{17a}tBu$), 35.9 ($C, C^{18a}tBu$), 62.3($C^{10}H_2$), 118.0(C^2), 121.7 (C^{16}), 122.0 (C^{14}), 129.3 (C^4), 132.9 (C^6), 136.6 (C^3), 141.8 (C^{15}), 148.4 (C^5), 157.0 (C^{11}), 171.1 (C^7), 171.3 (C^6).

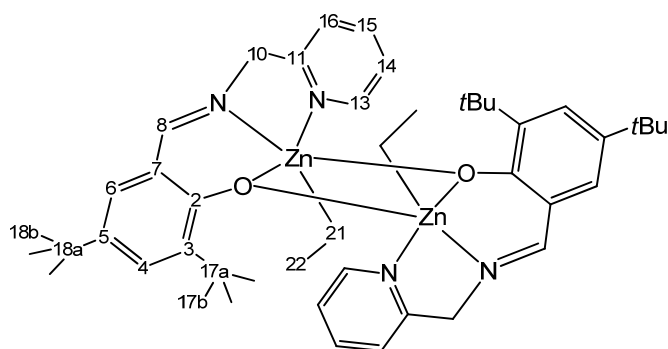
2.3. Synthesis of poly[N-(2-pyridylmethyl)-3,5-di-*tert*-butylsalicylaldimino]zinc(II)- μ -(acetato-O,O) [$Zn(1)(OAc)_2$] $_n$ (**1b**)



To a solution of **1H** (109 mg, 0.335 mmol) in dry methanol (10 mL) was added a solution of $Zn(OAc)_2$ (61 mg, 0.335 mmol) in methanol (10 mL). The mixture was refluxed for 4h and then cooled to room temperature. The solid precipitated from the reaction mixture and was filtered and washed with methanol, diethyl ether and dried in vacuum. Light brown solid, 82 mg (Yield 55 %). Anal. Calcd. for $(C_{23}H_{30}N_2O_3Zn \cdot 0.5H_2O)_n$ ($n=1$, 456.8): C 60.5, H 6.8, N 6.1; found C 60.5, H 6.4, N 6.1. ESI MS calc for $(C_{23}H_{30}N_2O_3Zn)_n$ m/z : $n=2$ $C_{44}H_{57}N_4O_4Zn_2$, 833.2957 $[M_2-OAc]^+$;

found 833,2958. Selected IR bands (KBr, ν cm^{-1}): 3449 m, 2959 m, 2905m, 1642 $\nu(\text{C}=\text{N})$ s, 1557 s, 1439 m, 1347 $\nu(\text{C}-\text{O})$ w, 1274 w, 1162 m, , 499 $\nu(\text{Zn}-\text{N})$ w, 409 $\nu(\text{Zn}-\text{O})$ w. ^1H NMR (400 MHz, CD_2Cl_2): δ 1.29 (br, 18H, *t*Bu), 1.87 (br, 3H, $\text{CH}_3\text{-OAc}$), 4.90 (br, 2H, $(\text{CH}_2\text{N})^{10}$), 6.92 (br, 1H, $(\text{CH})^6$), 7.23 (br, 1H, $(\text{CH})^{14}$) 7.33-7.35 (br, 2H, $(\text{CH})^{4,16}$), 7.81 (br, 1H, $(\text{CH})^{15}$), 8.41 (br, 1H, $(\text{CH}=\text{N})^8$), 8.80 (br, 1H, $(\text{CH})^{13}$). ^{13}C NMR (75.43 MHz, CD_2Cl_2): δ 23.3 ($\text{CH}_3\text{-OAc}$), 29.2 (CH_3), 31.2 (CH_3), 33.6 (C, *t*Bu), 35.2 (C, *t*Bu), 58.5 ($\text{CH}_2\text{-N}$), 117.4 (C^2), 121.9 ($\text{C}^{6,4}$), 123.3 ($\text{C}^{14,16}$), 128.6 (C^5), 138.6 (C^{15}), 140.9 (C^3), 149.0 (C^{13}), 156.1 (C^{11}), 170.2 ($\text{CH}=\text{N}$, C^7), 179.7 (CO-OAc).

2.4. Synthesis of bis[N-(2-pyridylmethyl)-3,5-di-*tert*-butylsalicylaldimino)-ethyl]zinc(II) [$\text{ZnEt}(\mathbf{1})_2$] (**1c**)



A solution of ZnEt_2 (1.0 mL, 1.0 mmol, 1M in hexane) was added to a stirred solution of **1H** (66 mg, 0.2 mmol) in dry hexane (3 mL). The resulting solution was stirred at room temperature for 2 hours. A yellow product precipitated from the reaction mixture and was collected by filtration, washed with cold diethyl ether and dried in vacuum. Yellow solid, 127 mg (Yield 75%). MALDI-TOF (CHCA) calc for $\text{C}_{46}\text{H}_{68}\text{N}_4\text{O}_2\text{Zn}_2$ m/z : 875.3557 $[\text{M}+4\text{H}+\text{K}]^+$, found m/z : 875.3743. ^1H NMR (400 MHz, CDCl_3): δ 0.89 (br, 6H, $(\text{CH}_3)^{22}\text{-Et}$, $^3J = 6.6$ Hz), 1.23 (br, 4H, $(\text{CH}_2)^{22}\text{-Et}$), 1.43 (s, 18H, *t*Bu), 1.74 (s, 18H, *t*Bu), 4.23 (s, 4H, $(\text{CH}_2\text{N})^{10}$), 6.33 (pst, 2H, $(\text{CH})^{15}$), 6.52 (d, 2H, $(\text{CH})^{16}$, $^3J = 7.2$ Hz), 6.70 (pst, 2H, $(\text{CH})^{14}$), 6.89 (d, 2H, $(\text{CH})^6$, $^4J = 2.4$ Hz), 7.67 (d, 2H, $(\text{CH})^4$, $^4J = 2.4$ Hz), 7.81 (s, 2H, $(\text{CH}=\text{N})^8$), 8.26 (d, 2H, $(\text{CH})^{13}$, $^3J = 4.4$ Hz); ^{13}C NMR (75.43 MHz, CDCl_3): δ 14.4 (CH_3)²²-Et, 23.1 (CH_2)²²-Et, 30.1 (CH_3), 31.9 (CH_3), 34.0 (C, *t*Bu), 36.0 (C, *t*Bu), 62.3 ($\text{CH}_2\text{-N}$), 118.1 (C^2), 121.7 (C^{16}), 122.1 (C^{14}), 128.9 (C^4), 129.4 (C^6), 133.1 (C^5), 136.7 (C^{15}), 141.9 (C^3), 148.5 (C^{13}), 156.9 (C^{11}), 171.2 (C^7), 171.4 ($\text{CH}=\text{N}$).

2.5. X-ray crystallography

Diffraction data for the structures reported were collected on a Smart CCD 1000 Bruker diffractometer system with Mo K α radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing and scaling of the data sets were carried out using programs Bruker Smart and Bruker Saint. All the structures were solved by *SIR97* [38] and refined by *Shelxl9* [39] and the molecular graphics with *ORTEP-3 for Windows* [40]. All the calculations were performed using the *WinGX* publication routines [41]. Crystallographic data are collected in Table S1 (Supplementary Information).

2.6. Catalysis

General procedure for the synthesis of cyclic carbonates

The catalytic tests were carried out in a 100 mL Berghof or 25 mL Parr reactor, which were previously kept under vacuum 4 h at 100 °C. After cooling, a solution under inert atmosphere containing the catalyst dissolved in neat distilled substrate and the co-catalyst, when indicated, was injected into the reactor. The autoclave was pressurized with CO₂ and then heated to the desired temperature to reach the final pressure. After the reaction time, the reactor was cooled to room temperature with an ice bath and slowly depressurized through a dichloromethane trap. The % conversion was determined by ¹H NMR spectroscopy of the crude mixture by integral ratio between alkene oxide and cyclic carbonate. The work-up was as follow depending on the substrate. Purification in the case of the styrene carbonate was performed by extraction with hexane to remove the styrene oxide. The remaining solid was evaporated and diluted in CH₂Cl₂ and passed through a silica pad to remove the catalyst. The dichloromethane solution was evaporated to obtain the NMR spectroscopically pure styrene carbonate as a white solid. The purification of propylene carbonate was performed removing the propylene epoxide by vacuum evaporation and the remaining oily residue was diluted in dichloromethane and passed through a silica pad to remove the catalyst. Typical procedure for cyclohexene oxide: the final crude was dissolved in dichloromethane, the solvent was evaporated and the residue dried in vacuum at 100 °C for 3 hours to remove excess of cyclohexene oxide and subsequently it was analysed by ¹H NMR spectroscopy. % *cis/trans* cyclohexylcarbonate ratio was calculated from the integral ratio between the –CH– signals of the *cis*-isomer ($\delta = 4.63$ ppm) and the *trans*-isomer ($\delta = 3.90$ ppm). % *cis/trans* ratio of the carbonated methyloleate (methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate) was calculated from the integral ratio between

the –CH– signals of the *cis*-isomer ($\delta = 4.61$ ppm) and the *trans*- isomer ($\delta = 4.22$ ppm) [53].

2.7. HP NMR experiments

The HP NMR tube was filled under N₂ with the mixture of **1a** (0.15 mmol), tetrabutylammonium bromide (TBAB) (0.15 mmol) and toluene-d₈ (1.8 mL). The tube was pressurised to 10 atm of CO₂ and heated to 60 °C and the ¹H NMR spectra were then recorded.

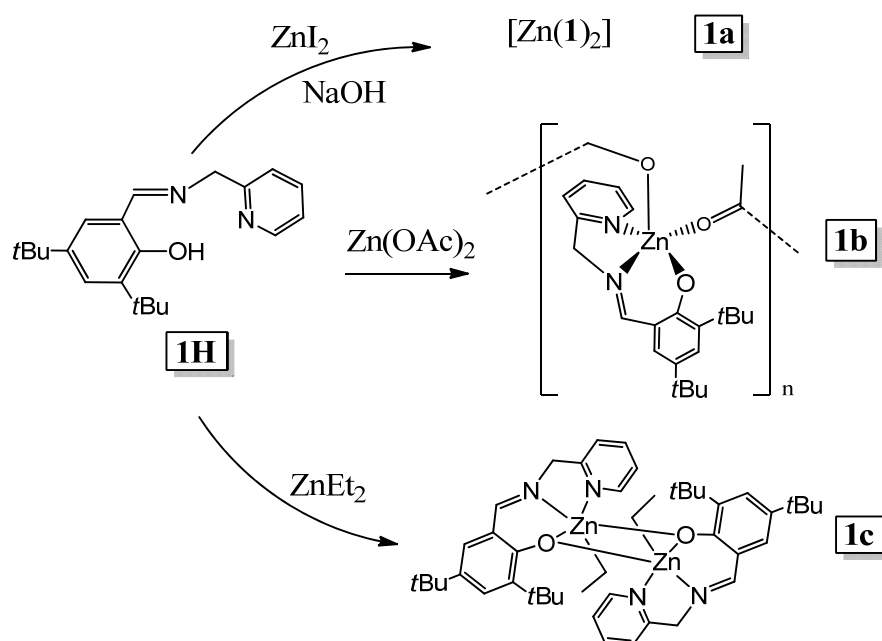
2.8. Computational details

DFT calculations were run with the Gaussian 09 package [42] using the M06 functional to include dispersion effects and to account for the possible π -stacking interactions of the pyridine rings. A 6-31G (d,p) basis set with LANL2TZ (Los Alamos National Laboratory 2 double z) pseudo potential for the zinc atom was used. The optimized geometries were verified as true minima by frequency calculations and the zero-point vibrational energy was added to the absolute energies. The solvent environment of toluene was simulated using the polarizable continuous model (IEF-PCM). Relaxed linearly interpolated reaction paths were obtained between species of interest.

3. Results and discussion

3.1. Synthesis and characterization of **1a-c**

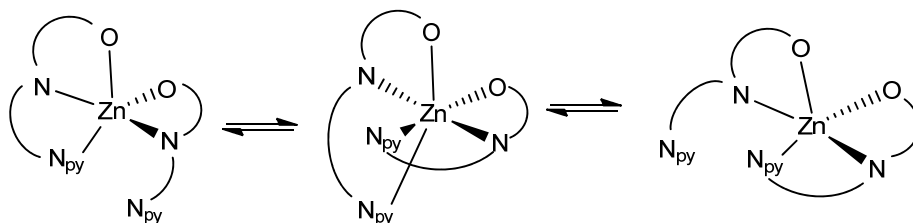
N-(2-Pyridyl)methyl-2-hydroxy-3,5-di-*tert*-butylbenzalimine (**1H**) was synthesized following previously described procedures by condensation of 3,5-di-*tert*-butyl salicylaldehyde and 2-methylaminopyridine [30]. Reaction of **1H** with ZnI₂ in methanol in the presence of a base (NaOH) produced a yellow solid, **1a** (Scheme 2), which was stable in solid and solution under inert atmosphere. However it slowly turned red under air and UV-irradiation, especially in solution, maybe due to phenolate oxidation processes [43].



Scheme 2. Reaction of **1H** with Zn(II) precursors.

The absence of a strong absorption in the IR spectrum of **1a** at the $\nu(\text{O-H})$ region (*ca* 3600 cm^{-1}) and the shift to low energy of the band assigned to the stretching $\nu(\text{C=N})$ ($\Delta\nu = \nu(\text{C=N})_{\text{free ligand}} - \nu(\text{C=N})_{\text{complex}} = 20\text{ cm}^{-1}$) pointed to the coordination through both the phenolate fragment and the imine group. Mass spectrum (ESI) showed a peak at m/z 711.3616 corresponding to the mononuclear species $[\text{Zn}(\mathbf{1})_2]$ (calc for $\text{C}_{42}\text{H}_{54}\text{N}_4\text{O}_2\text{Zn}$ m/z : 711.3756 $[\text{M}+\text{H}]^+$). The electronic spectrum of **1a** in MeOH showed absorptions at 260 and 331 nm associated with the ligand $\pi \rightarrow \pi^*$ and C=N transitions as well as bands at 227 and 390 nm attributed to charge-transfer bands [44]. The pattern observed in the ^1H NMR spectrum in toluene- d_8 of **1a** in the region δ 6-10 ppm corresponded to equivalent imino, pyridino and phenolato coordinated fragments. All signals were assigned by 2D NMR experiments (COSY, HMQC, HMBC and NOESY, Supplementary Information). Nevertheless, the X-ray structure of crystals of **1a**, obtained from a MeOH solution, showed a five-coordinate environment around the Zn(II) centre with one ligand acting as tridentate and another one as bidentate, $[\text{Zn}(\mathbf{1}-\kappa^3\text{N},\text{N}',\text{O})(\mathbf{1}-\kappa^2\text{N}',\text{O})]$ (see X-Ray diffraction structure of complex **1a** below). It was previously proposed in the literature the formation of $[\text{Zn}(\mathbf{1}-\kappa^3\text{N},\text{N}',\text{O})_2]$ from $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in methanol as solvent in the presence of NEt_3 [28e] or from $[\text{Zn}(\text{N}(\text{SiMe}_3)_2)_2]$ in THF [28f] but the solid structure was not reported in either case. The observation in the ^1H NMR spectrum of **1a** in toluene- d_8 of only one set of equivalent signals in the aromatic region can be explained by a fluxional process, which

may proceed through six-coordinate species as observed for similar complexes (Scheme 3) [13]. The signals corresponding to free ligand (3 %) were also observed in the ^1H NMR spectrum. The presence of free ligand may be related with partial decomposition of the complex due to hydrolysis. VT ^1H NMR spectra of **1a** in toluene- d_8 under nitrogen atmosphere at temperatures from -80 to 80 $^\circ\text{C}$ (see Supplementary Information) clearly indicated that the equilibrium was fast even at -80 $^\circ\text{C}$ since no splitting of signals was observed.



Scheme 3. Fluxional process proposed in solution for complex **1a**.

In order to gain insight into the experimental results, a computational study based on DFT calculations was performed (see computational details below) comparing the different stability of the tetra-, penta- and hexacoordinate species. Calculations modelled the complexes in a toluene solution as environment, where the NMR experiments were recorded. Modelling of the crystal was not carried out given the complexity of the calculation and its more limited interest from the reactivity point of view. All results are collected in Table 1 and the most stable structures for each coordination number are shown in Figure 2. Several isomers were found for each coordination number, with *mer* configuration in all cases of hexa- and pentacoordinate species. *Fac* isomers for the six-coordinate species were explicitly looked for, but the optimization process always ended up in *mer* isomers. This is in accord with the reported observation that rigid imine ligands accommodate better in a meridional mode in a Fe(III) octahedral complex.⁴⁴

The tetracoordinate species (Table 1) are significantly less stable than the other geometries, so their presence as long-lived species can be discarded, although they might participate in the catalytic cycle. On the other hand, the small energy differences between hexa- and some of the penta-coordinate species clearly indicate that in solution a coexistence of such species is possible. These results are not necessarily contradictory with the observed X-ray five-coordinate structure of **1a**. The small stabilization of the

six-coordinate species in solution can be easily compensated by more adequate packing factors for the pentacoordinate species in the crystal structure.

Table 1. Relative energies of the different isomers located computationally for complex **Zn1a** in toluene

Coordination	Isomer ^{a)}	ΔE (kcal/mol)	Population	%
6	6-mer1	0.00	1.000	94
	6-mer2	1.84	0.044	4
	6-mer3	2.28	0.021	2
5	5-mer1	3.74	0.002	0.2
	5-mer2	6.18	0.000	0
	5-mer3	7.14	0.000	0
	5-mer4	7.47	0.000	0
	5-mer5	10.50	0.000	0
4	4-iso1	12.86	0.000	0
	4-iso2	15.24	0.000	0

^{a)} See the geometries of all the isomers at Figure 2, Figure 5 and Supplementary Information

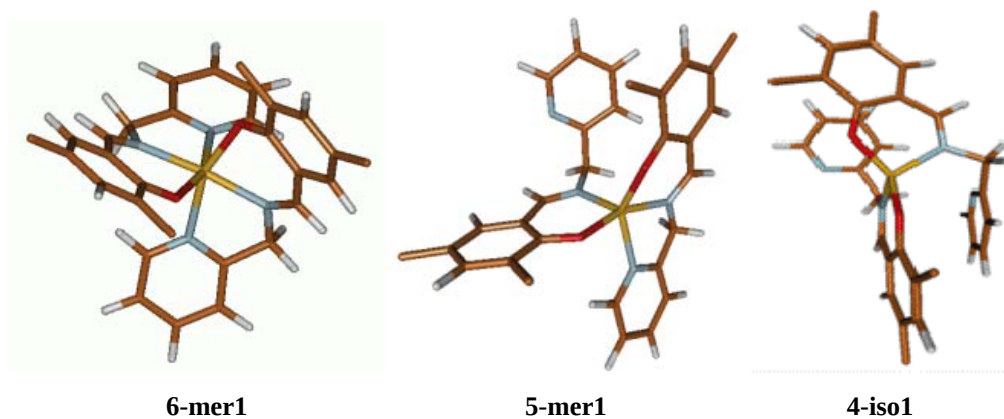


Figure 2. Geometries of the most stable minima located at DFT level, for complex **1a** in toluene for the different coordination numbers. *Tert*-butyl groups and H atoms have been omitted for clarity.

To corroborate that the interconversion in solution between hexa- and pentacoordinate species is feasible, the isomerization path of the fluxional process between equivalent **5-mer1** isomers and between species **6-mer1** and **5-mer1** (Scheme 3) was looked for. Unfortunately it was not possible to locate the transition states of these reactions. Instead, relaxed linearly interpolated reaction paths were calculated and upper limits of the energies of the corresponding transition states were obtained. Employing this methodology, it was found that the barrier for the fluxional process (**5-mer1**→**5-mer1**) was significantly higher (10 kcal/mol) than that of the isomerization **6-mer1**→**5-mer1** (3 kcal/mol). We can assume, then, that the fluxional process in solution proceeds via the most stable hexacoordinate species, which is the major species (Scheme 3).

In order to avoid the presence of strong coordinating anions such as chloride, the acetate salt of Zn(II) was used as a complex precursor. Thus, treatment of **1H** with Zn(OAc)₂ in absence of a base under reflux during 4 hours produced a light brown powder (**1b**, Scheme 2). The MALDI-TOF mass spectra and elemental analysis agreed with the formulation [Zn(**1**)(OAc)]_n. The infrared spectrum of **1b** confirmed the coordination of the ligand through the imine ($\Delta\nu = -6\text{ cm}^{-1}$) [45]. The presence of two strong bands at the IR spectrum of **1b** at 1557 and 1414 cm⁻¹ ($\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ $\Delta\nu = 143\text{ cm}^{-1}$) is in agreement with a bridging coordination of the acetate ion [46,47]. The ¹H NMR spectrum of compound **1b** exhibited broad signals. The upfield shifted signal of the methyl group from the acetate and the imine also confirmed the coordination of these ligands. The ¹³C NMR spectrum was assigned by ¹H-¹³C HSQC and ¹H-¹³C HMBC NMR experiments (see Supplementary Information).

Alkyl Zn(II) have been proved to be excellent catalyst precursors for fixation of CO₂ [20,48a]; therefore an ethyl zinc derivative was also prepared. Reaction of **1H** with 5 equivalents of diethylzinc in dry hexane at room temperature caused the evolution of ethane affording a yellow solid, **1c** (Scheme 2). This compound was unstable in solution in air, and it was characterized by mass spectrometry and NMR spectroscopy under inert atmosphere. In the MALDI-TOF mass spectra of **1c** appeared the molecular ion peak corresponding to a dimeric species [Zn(Et)(**1**)]₂. The ¹H and ¹³C NMR spectra of **1c** (C₆D₆, Supplementary Information) showed the signals attributed to the ethyl group bound to the zinc(II) [48] at δ 0.87 ppm, (broad, CH₂) and the signals corresponding to the bound ligand.

3.2. X-Ray diffraction structures of **1a** and **1b**

The structure of **1a** contains one Zn(II) atom in a pentacoordinate environment bound to two deprotonated ligands (Figure 3). One of the ligands acts as a tridentate κ^3N,N',O -donor, coordinating through the O(1) (phenol), N(2) (imino) and N(1) (pyridino) and occupying the square plane. The other ligand coordinates as a bidentate $\kappa^2N'O$ -donor by the O(2) (phenolato) and the N(4) (imino) while the pyridino nitrogen N(3) remains non coordinated (distance Zn(1)⋯N(3) 4.418 Å). The N(4) occupies the axial position of the square-pyramid. The phenolato O(2) is *trans* to the coordinated imino group N(2). The distortion of the 5-coordinate environment can be described by the τ -factor [49] (Figure 4). The low value of $\tau = 0.03$ for **1a** is indicative of a square-pyramidal distortion rather than a distorted trigonal bipyramid geometry ($\tau = 0$ for a perfect square-pyramidal geometry while $\tau = 1$ for a trigonal bipyramidal one).

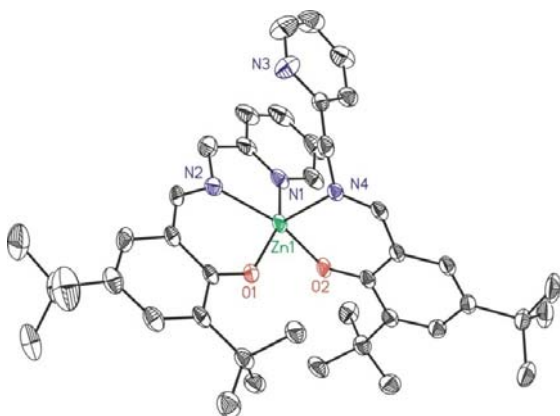
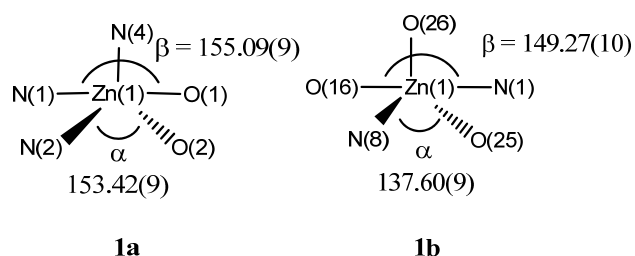


Figure 3. X-ray diffraction molecular structure of **1a**. H atoms are omitted for clarity. Thermal ellipsoids are depicted at 50 % probability.



$$\tau(\mathbf{1a}) = \frac{\beta - \alpha}{60} = 0.03 \quad \tau(\mathbf{1b}) = \frac{\beta - \alpha}{60} = 0.19$$

Figure 4. Angles α and β and τ factor for complexes **1a** and **1b**.

Bond distances Zn-O (1.976 (2) and 1.9785 (19) Å), Zn-N (pyridino) (2.152(3) Å) and Zn-N (imino) (2.086(2) and 2.033(2) Å) in complex **1a** lay in the range observed for analogous N,N',O-donor ligands (Table 2) [28a-c,28e,28g-h]. The N(imino)-C bond lengths of the imino group C=N (1.454(3) and 1.457(4) Å) are in the range of the ones reported for Zn-N(imino) complexes [28a,28c,28e].

The observed X-ray geometry of **1a** can be compared with those of the pentacoordinate isomers obtained computationally, in spite that the X-ray structure is in a crystal and the calculation is modelled in a toluene solution environment. The different minima localized at the DFT level correspond to different orientations of the non-coordinated pyridine moiety due to the free rotation around the C-N(imino) and CH₂-C(pyridino) single bonds. Rotation around the C-N(imino) bond determines the possible approach of the two pyridine rings to favour π -stacking, which will be also determined by the mutual orientation of the rings, given by the rotation around the CH₂-C(pyridino) bond. In isomer **5-mer3** (Figure 5) the rings do not face each other and in **5-mer5** (Figure 5) both rings are almost perpendicular. In **5-mer1** (Figure 2) the pyridine ring is parallel to the phenyl ring, while in **5-mer2** and **5-mer4** (Figure 5) both pyridine rings are facing each other. In the last isomers, the average C-C distances between rings are 3.823, 4.226 and 4.613 Å for **5-mer2**, **5-mer4** and **5-mer1** respectively. It indicates that the largest π -stacking must occur for isomer **5-mer2**.

The rotation around the C-C bond also modifies the position of the N(3) atom relative to the Zn centre, thus controlling the possibility of the Zn-N(3) bond formation to yield the hexacoordinate species and the fluxional process in solution. The Zn-N(3) distance varies between 3.657 Å (in **5-mer1**) to 4.619 Å (in **5-mer4**).

The computational geometry most similar to the X-ray structure observed is **5-mer2** (Figure 5), one of the most stable pentacoordinate isomers (Table 1). Comparison of selected bond lengths and angles shows a very satisfactory agreement, taken into account the different environments of the experimentally determined geometry (crystal) and the computed one (solution) (less than a 2 % of average error in bond distances and

a 5 % of average error for angles, see Table S2 in Supplementary Information). This agreement assesses the validity of the computational results.

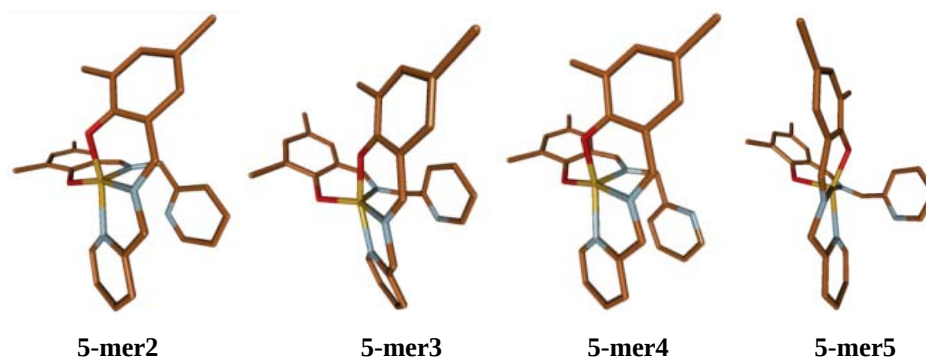


Figure 5. Geometries of the minima located at DFT level, for pentacoordinate species of complex **1a** in toluene. *Tert*-butyl groups and H atoms have been omitted for clarity.

For **1b**, single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from chloroform/diethyl ether after one week at room temperature. X-ray diffraction analysis revealed that **1b** has a polymeric structure (Figure 6a). Selected bond distances and angles are presented in Table 2. The geometry at the zinc atom (Figure 6b) is best described as a distorted square-pyramide, with O(26) occupying the axial position and N(8), O(25), N(1) and O(16) occupying the square-planar sites. The τ factor 0.19 is higher than in the case of **1a** (Figure 4). The metal-oxygen bond is typical of an alkoxide (1.990(2) Å), whilst that of the imino nitrogen atom is, as expected, appreciably longer (2.072(3) Å).

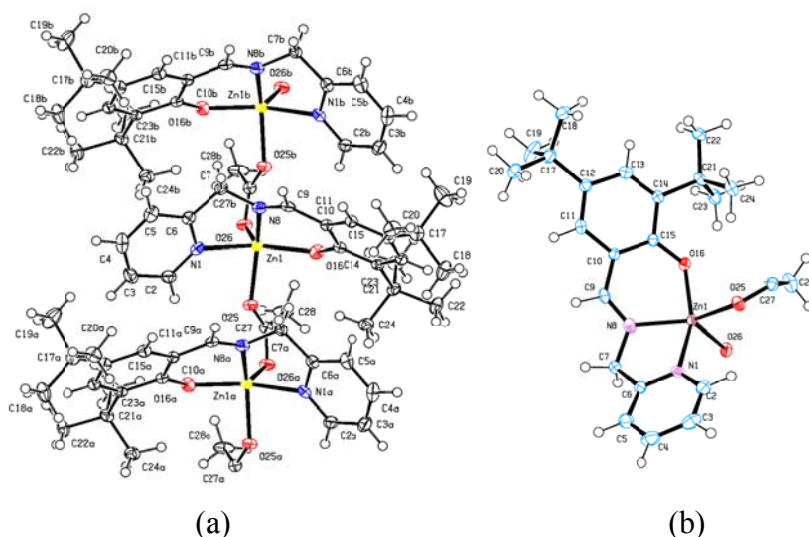


Figure 6. ORTEP drawing of complex **1b**. (a) Polymeric structure, (b) Repetitive unit.

Table 2. Selected bond lengths (Å) and angles (°) for **1a** and **1b**

1a		1b	
Zn1-O1	1.976(2)	Zn1-O25	2.032(2)
Zn1-O2	1.9785(19)	Zn1-O26	1.988(2)
Zn1-N2	2.086(2)	Zn1-O16	1.990(2)
Zn1-N4	2.033(2)	Zn1-N8	2.072(3)
Zn1-N1	2.152(3)	Zn1-N1	2.230(3)
N2-C7	1.284(4)	N8-C9	1.271(4)
N4-C28	1.279(4)	N8-C7	1.453 (4)
N2-C26	1.457(4)		
N4-C27	1.454(3)		
Zn1·····N3	4.418		
O1-Zn1-O2	95.66(8)	O25-Zn1-O26	98.46(10)
O1-Zn1-N4	103.39(9)	O16-Zn1-O25	91.17(10)
O2-Zn1-N4	92.08(8)	O26-Zn1-N8	121.83(10)
O1-Zn1-N2	86.76(9)	O25-Zn1-N8	137.60(9)
O2-Zn1-N2	153.42(9)	O26-Zn1-N1	101.06(10)
N4-Zn1-N2	113.17(9)	O16-Zn1-N1	149.27(10)
O1-Zn1-N1	155.09(9)	O25-Zn1-N1	85.57(10)
O2-Zn1-N1	90.61(9)	N8-Zn1-N1	74.97(11)
N4-Zn1-N1	100.44(9)		
N2-Zn1-N1	77.23(10)		

3.4. Cycloaddition of CO₂ and styrene oxide.

Complexes **1a-c** were tested as catalysts in the cycloaddition of epoxides to CO₂. The effect of co-catalyst, co-catalyst/catalyst ratio, pressure and temperature were optimized

in the reaction of CO₂ and styrene oxide. The scope of the catalyst activity was then extended to other substrates.

The cycloaddition of styrene oxide with CO₂ was initially studied using **1a** based catalytic systems. The initial conditions were 50 atm CO₂, 80 °C using 0.2 mol % catalyst in neat substrate as solvent during 24 h. The results are presented in Table 3. At these conditions the control experiments using as catalyst **1a** or **1H** gave very low conversion towards the formation of the corresponding cyclic carbonate (entries 1 and 2, Table 3). This fact suggests that the pyridino group of the coordinated ligand is not able to promote the opening of the cyclic epoxide as was reported for monodentate pyridine in [ZnBr₂Py₂] catalytic systems for the copolymerization of CO₂ and propylene oxide [19b].

The effect of the addition of ionic (NaI, bis(triphenylphosphine)iminium chloride: PPNCl and tetrabutylammonium bromide: TBAB) and neutral (dimethylaminopyridine: DMAP) co-catalysts was analysed. Addition of a simple salt such as NaI·2H₂O, that was reported to be very active in the cycloaddition of CO₂ to epoxides [50], produced an increase in the conversion up to 51 % (at 1 mol %, entries 3 and 4, Table 3). It is noteworthy that the combination of **1a** with NaI produced higher conversion than using only NaI as catalyst (entry 5, Table 3). Adding PPNCl and TBAB as co-catalysts very high conversion (97-98 %) was obtained at 0.14 mol % catalyst and 0.2 mol % co-catalyst (entries 6 and 9, Table 3). Increasing the co-catalyst/catalyst ratio **1a**/PPNCl did not improve the conversion (entry 7, Table 3). In the monometallic based catalytic system **1a**, with a highly saturated coordination sphere, the formation of the cyclic carbonate is favoured. No poly(carbonate) was detected by ¹H NMR in any of the experiments. At 6h reaction time, the conversion obtained with **1a**/TBAB was still good (48 %, entry 10, Table 3). PPNCl and TBAB gave lower conversions than combined with **1a** in both cases (entry 8 and 11, Table 3). When neutral DMAP was used as co-catalyst the conversion decreased slightly respect to when PPNCl or TBAB were used (83 %, entry 12, Table 3). As observed above the combination of **1a** with DMAP was better than using DMAP alone (entry 13, Table 3). Decreasing the catalyst loading to 0.05 mol % after 6h the conversion was 12 % (average TOF 80 h⁻¹; entry 10, Table 3). **1a** showed improved catalytic activity over our previously reported chromium related catalyst [Cr(**1**)₂Cl]/PPNCl for this substrate at the same conditions (TOF 52 h⁻¹) [14].

Table 3. Cycloaddition of styrene oxide and CO₂ using **1a-c** and **2a**.^{a)}

Entry	Cat	Co-cat	Cat/Co-cat (mol %) ^b	Conv (%) ^c	TOF (h ⁻¹) ^d	Y (%) ^e
1	1a	-	0.2/-	5	-	n.i.
2	1H	-	0.2/-	2	-	n.i.
3	1a	NaI·2H ₂ O	0.14/0.2	40	12	29
4	1a	NaI·2H ₂ O	0.14/1.0	51	15	49
5	-	NaI·2H ₂ O	-/0.2	25	7	n.i.
6	1a	PPNCl	0.14/0.2	97	28	65
7	1a	PPNCl	0.14/1.0	97	28	68
8	-	PPNCl	-/1.0	32	10	n.i.
9	1a	TBAB	0.14/0.2	98	28	63
10 ^{f)}	1a	TBAB	0.14/0.2	42	48	n.i.
11 ^{f)}	-	TBAB	-/0.4	18	8	n.i.
12	1a	DMAP	0.14/0.2	83	24	56
13	-	DMAP	-/0.2	30	10	n.i.
14 ^{g)}	1a	TBAB	0.05/0.07	12	80	n.i.
15	2a	TBAB	0.14/0.2	97	28	78
16	1b	TBAB	0.14/0.2	77	22	60
17	1c	TBAB	0.14/0.2	76	22	59

^{a)} Reaction conditions: T = 80 °C, time = 24 h, PCO₂ = 50 bar, styrene oxide: 0.0438 mol (5 mL). ^{b)} mol % respect to the substrate. ^{c)} measured by ¹H NMR, average two runs. ^{d)} averaged TOF (mol substrate converted·(mol catalyst)⁻¹·h⁻¹. ^{e)} Isolated yield, n.i.= not isolated. ^{f)} Time = 6h. ^{g)} Time = 3h.

Since we had observed that complex **1a** is pentacoordinated in the solid state and there are evidences of equilibrium with hexacoordinate species in solution, we examined the catalytic activity of the quinolino hexacoordinate complex **2a** [28e, 28f] (Figure 7). At the same reaction conditions than **1a**/TBAB, **2a**/TBAB produced similar conversion (98 % versus 97 % respectively; entry 15, Table 3). That demonstrates that six-coordinate species can also give rise to *in situ* formation of a reactive catalyst by creation of a required vacant coordination site in the Zn complex. The different basicity of the pyridino and quinolino fragments did not produce differences in the catalytic activities of the corresponding catalytic systems. At the optimised conditions, catalysts **1b**/TBAB and **1c**/TBAB were less active than **1a**/TBAB (77-76 % conversion, entries 16 and 17, Table 3).

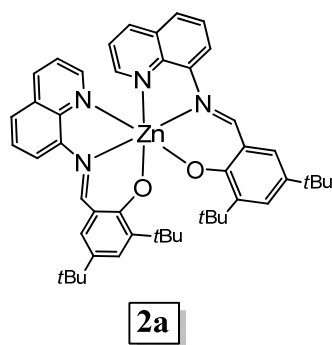


Figure 7. Complex **2a**

The effect of pressure and temperature using **1a**/TBAB at the optimized ratio (0.14 mol %/0.20 mol %) was then studied. The results are listed in Table 4.

Table 4. Cycloaddition of styrene oxide and CO₂ with **1a**/TBAB as catalysts at different P and T. ^{a)}

Entry	P (bar)	T (°C)	t (h)	Conv (%) ^b	TOF (h ⁻¹) ^c	Y (%) ^d
1	10	80	24	79	23	
2	1	80	24	42	12	-
3	1	80	48	48	7	42
4	1	100	24	77	22	71

^{a)} Reaction conditions: styrene oxide: 0.0438 mol (5 mL); catalyst 0.14 mol %; co-catalyst 0.2 mol %. ^{b)} measured by ¹H NMR, average two runs. ^{c)} average TOF (mol substrate converted·(mol catalyst)⁻¹·h⁻¹. ^{d)} isolated yield.

Catalytic system **1a**/TBAB was also active at 10 bar yielding a 79 % of conversion after 24 h (entry 1, Table 4). Even at atmospheric pressure, the conversion was still good (42 %, entry 2, Table 4). Prolonging the reaction time up to 48 h at these conditions the conversion did not increase very much indicating an inactivation of the catalyst (entry 3, Table 4). At 1 bar, increasing the temperature to 100 °C, the conversion reached a 77 % (entry 4, Table 4).

The effect of pressure was then analysed at 100 °C in 3 h reaction time (Figure 8). Raising the pressure up to 100 bar resulted in an increase of the catalytic activity (TOF up to 520 h⁻¹). Above this pressure a drop in activity was observed. Decreasing the catalyst loading (0.05 to 0.005 mol %) and the reaction time (3 to 0.5 h) afforded an optimised initial TOF of 3733 h⁻¹ (Figure 9). It was confirmed at these conditions that

the activity obtained with TBAB alone was lower than obtained with **1a**/TBAB (Figure 9).

The TOF value obtained with **1a**/TBAB is higher than the one reported for catalyst ZnBr₂/TBAI at 80 °C, 80 bar CO₂ and a ratio co-catalyst/catalyst of 4 (TOF 966 h⁻¹) [51]. Similar TOF was reported for Zn-salphen based catalysts although **1a**/TBAB required higher temperature [24c]. Catalysts based on a Zn-pyrrol-imino [13] or Zn-imino-phenolate [52] provided similar results although the formation of diol was reported in the first case.

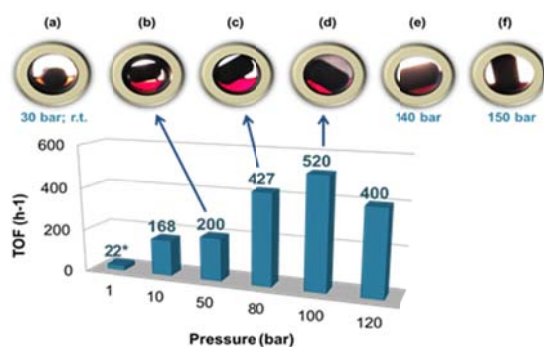


Figure 8. Effect of pressure on the TOF (h⁻¹) using catalytic system **1a**/TBAB. Reaction conditions: catalyst 0.05 mol %, co-catalyst 0.07 mol %, 100 °C, 3 h, data average of two runs. * catalyst 0.14 mol %, co-catalyst 0.2 mol %, 24 h. (a-f) Reactor photographs of the reaction systems at the indicated temperatures and pressures.

3.4.1. Reaction phase

The behaviour of the reaction phase respect to the pressure was analysed visually with a reactor equipped with sapphire windows. Figure 8 a-f shows the reaction mixture *in situ* at different CO₂ pressures. At low CO₂ pressure and at room temperature (a, Figure 9) it was observed that the yellow catalyst was dissolved in the styrene oxide. The solution changed to red by increasing the temperature to 100°C and the pressure to 50 bar (b, Figure 9). The change in colour observed may be indicative of formation of trace amounts of highly colored oxidized phenolate species that did not affect the conversion during the standard reaction time. The volume of the organic phase slightly increased when the pressure increased up to 100 bar due to the formation of the CO₂ expanded substrate phase (c and d, Figure 9). Furthermore, at this pressure the gas phase became cloudy indicating partial solubilisation of the substrate in the CO₂. Further increasing of the pressure lead to the dilution of the styrene oxide in the CO₂ phase inducing the precipitation of the catalyst (the volume of the liquid phase decreased and became

cloudy) with a concomitant decrease in conversion to carbonate (e and f, Figure 9). Similar phase behaviour was reported in the reaction of epoxidized methyl oleate with CO₂ using TBAB [53].

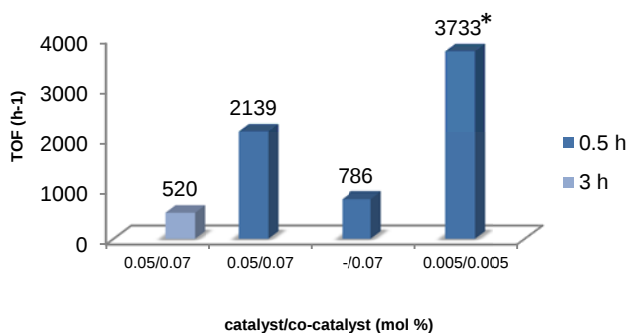


Figure 9. Optimisation of TOF (h⁻¹) using catalytic system **1a**/TBAB. Reaction conditions: co-catalyst 0.07 mol%, 100 °C, 100 bar, data average two runs. * co-catalyst 0.005 mol %, data average of three runs.

3.4.2. Reactivity of **1a**/TBAB with styrene oxide and CO₂

The reactivity of **1a**/TBAB with styrene oxide was analysed by ¹H NMR spectroscopy. The ¹H NMR spectrum of a mixture of **1a**/styrene oxide (1:10) at 60 °C (Figure 10a) showed new low intensity signals (1 %) at δ 3.22 (dd, *J* = 2.4, 4 Hz), 2.85 (dd, *J* = 4, 6 Hz), 2.55 (dd, *J* = 2.4, 6 Hz) and 2.41 ppm (dd, *J* = 4, 6 Hz) that may be attributed to species with coordinated epoxide [54]. These signals disappeared when TBAB (**1a**:TBAB = 1:1) was added to this mixture after being pressurized to 10 bar CO₂ and heated to 60 °C (Figure 10b). At these conditions the formation of the carbonate product was detected by ¹H NMR. This probes that the coordination of the epoxide takes place although in the high diluted NMR sample the concentration of the M-epoxide species is low.

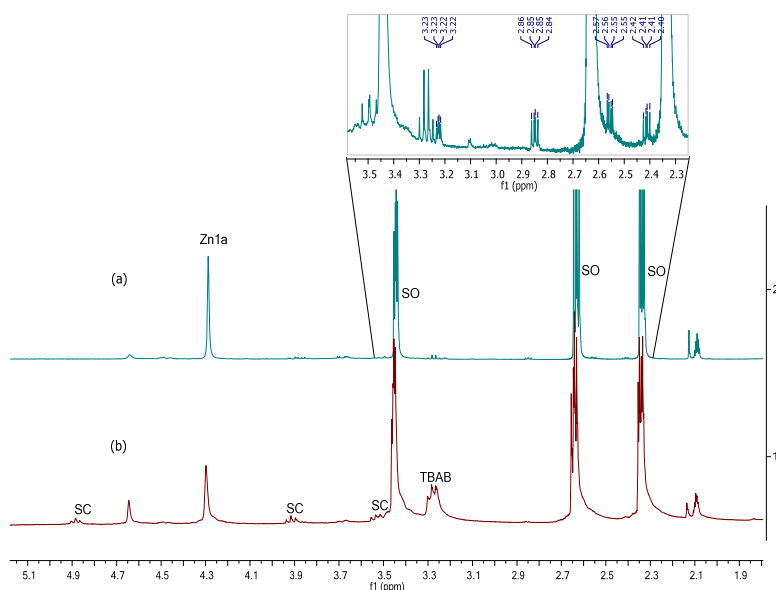


Figure 10. ^1H NMR spectrum of **1a**/styrene oxide (1:10) in toluene- d_8 at a) 60 $^\circ\text{C}$ and b) added TBAB (1:1 **1a**:TBAB) at 10 bar CO_2 after 1h.

According to these observations and based on previously reported mechanisms for binary catalytic systems [55], we propose that the initial step in the catalytic cycle is the activation of the epoxide by coordination to the metal centre. To do this, a substitution of a pyridine moiety must take place (step a, Figure 11). Once the epoxide is activated, the nucleophilic attack with the Br^- and subsequent insertion of CO_2 take place (steps b and c, Figure 11) leading to the carbonate $\text{Zn}(\text{II})$ species. The stability of the hexacoordinate $[\text{Zn}(\mathbf{1})_2]$ species may favour the ring closing step (d, Figure 11) against the formation of the poly(carbonate) (e, Figure 11).

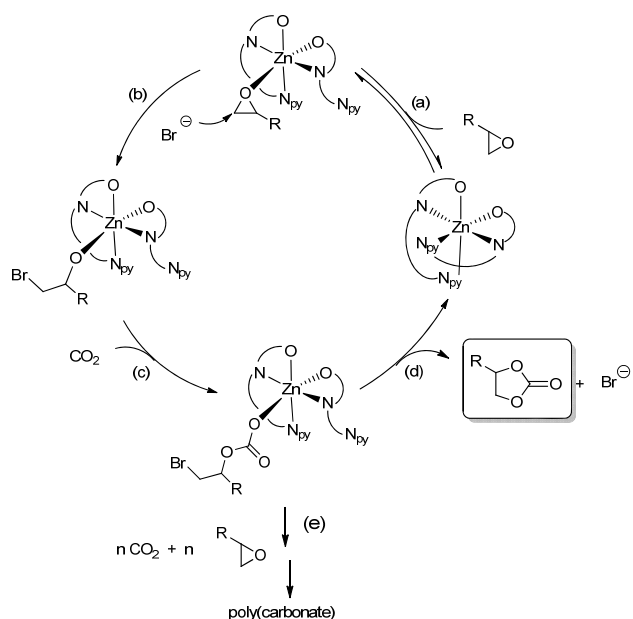


Figure 11. Proposed reaction mechanism for the conversion of epoxides into the corresponding carbonates with catalyst system **1a**/TBAB.

3.5. Cycloaddition of CO₂ to other epoxides.

Catalyst **1a**/TBAB was also active and selective for the cycloaddition of CO₂ to other epoxides at 50 bar and 80 °C (Figure 12). Conversions to the cyclic product were high for terminal epoxides (71-92 %, Figure 12). The polycarbonate was not detected by ¹H NMR spectroscopy when neither terminal epoxides nor cyclohexene oxide were used as substrates. It is interesting to remark that although the related chromium catalytic system [Cr(**1**)₂Cl] with PPNCI or DMAP as co-catalysts were more active catalysts than **1a**/TBAB in the reaction of CO₂ and cyclohexene oxide, they produced mixtures of poly(carbonate) and cyclic cyclohexene carbonate [14]. Catalyst **1a**/TBAB was also active for internal hindered substrates, such as the methyl epoxyoleate derived from a natural product [53, 56]. Cyclohexene- and methyl epoxyoleate carbonates were obtained as a mixtures *cis/trans* 90/10 and 95/5 respectively. This indicates that the ring opening and ring closure steps proceeds both by the expected S_N2 mechanism, giving place to the *cis* isomer, and also by the S_N1 mechanism that forms the *trans* isomer [53].

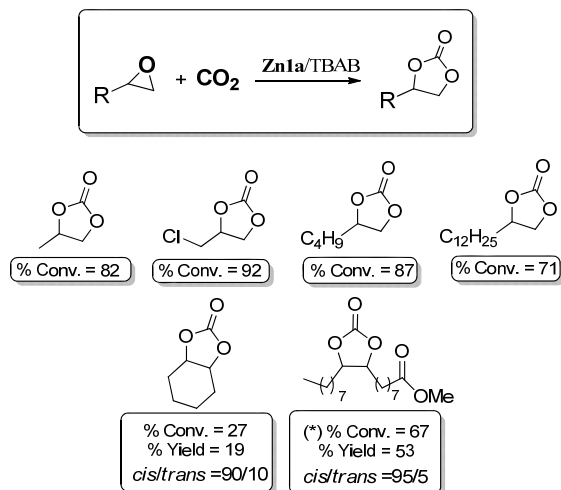


Figure 12. Cycloaddition of different epoxides to CO₂ with catalyst **1a**/TBAB. Reaction conditions: T = 80 °C, time = 24 h, P_{CO₂} = 50 bar, substrate: 0.0438 mol; catalyst: 0.0633 mmol (0.14 mol %); co-catalyst: 0.4378 mmol (0.2 mol %), data average of two runs. (*) cat/co-cat: 2 mol %/2 mol %; T = 100 °C, P_{CO₂} = 100 bar.

4. Conclusion

Mononuclear Zn(II) complexes with NN'O-donor base Schiff ligands combined with a co-catalyst are active for the cycloaddition of CO₂ and epoxides. They provide cyclic carbonates selectively with high activity and at low co-catalyst/catalyst ratio. The best conditions were achieved running the reaction in expanded CO₂ in neat substrate as solvent at 100 bar and 100 °C at very low catalyst loading. The activity obtained with **1a**/TBAB catalytic system reached an initial TOF of 3733 h⁻¹. The catalytic activity in the cycloaddition of CO₂ to styrene oxide of **1a**/TBAB is higher than the one obtained with analogous Cr(III) complex, [Cr(**1**)Cl] [14]. Compared to other Zn(II) reported catalytic systems **1a**/TBAB is highly active in the cycloaddition of CO₂ to styrene oxide at 100 °C and 100 bar although at mild reaction conditions the activity is lower than Zn(II)-salen derived catalysts [24c]. These Zn catalysts become activated at higher temperatures such that the epoxide coordination can more efficiently compete with intramolecular N-coordination. High conversions were obtained with catalyst **1a**/TBAB for other terminal aliphatic epoxides. More sterical hindered substrates such as cyclohexene oxide and methyl epoxyoleate were also transformed selectively in the cyclic carbonate product but at lower conversion than terminal epoxides.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at XXXXXX. CCDC 1050660 and CCDC 1050661 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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