



## New zinc/tetradentate N<sub>4</sub> ligand complexes: Efficient catalysts for solvent-free preparation of cyclic carbonates by CO<sub>2</sub>/epoxide coupling



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### ARTICLE INFO

#### Keywords:

Key-words  
CO<sub>2</sub> valorization  
Solvent-free  
Homogeneous catalysis  
Transition metal catalysis  
N<sub>4</sub> Schiff base  
Ligands  
Zn complexes  
Cyclic carbonates  
Green chemistry

### ABSTRACT

Tetra-nitrogenated Zn-Schiff-base complexes have been synthesized and studied by X-ray diffraction. The prepared Zn-N<sub>4</sub>-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*-tosylamino-benzylidene)-1,2-diaminocyclohexane, Zn(Cy-Ts) combined to tetra-butylammonium iodide (TBAI) in a ratio of 1:1, or to triethylamine, catalyzed efficiently the CO<sub>2</sub>/epoxides coupling. These catalytic reactions were carried out without solvent at 120 °C under CO<sub>2</sub> pressure. Cyclic carbonates were selectively obtained with high yield up to 99% (TON up to 4900). Two plausible pathways of CO<sub>2</sub>/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<sub>2</sub> 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<sub>2</sub> must be balanced by nature. Thus, decreasing the emissions of anthropogenic greenhouse gases is becoming more urgent. Therefore, utilizing CO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> by coupling with epoxides. This reaction, which can be called CO<sub>2</sub>/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<sub>2</sub> are based on the coordination of the CO<sub>2</sub> 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<sub>2</sub> 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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<https://doi.org/10.1016/j.mcat.2018.07.001>

Received 23 May 2018; Received in revised form 28 June 2018; Accepted 2 July 2018

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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<sub>2</sub>/epoxide coupling when complexed to ligand scaffolds such as N<sub>4</sub> porphyrins, [15] N<sub>4</sub> Schiff bases, [16] N<sub>2</sub>O<sub>2</sub> Salphen and Salen Schiff bases, [17] N<sub>4</sub>O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 CO<sub>2</sub>/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 N<sub>4</sub>-Schiff bases-based zinc complexes comprising sulfonamides functions and N<sub>4</sub>-tetraamines and their evaluation in carbon dioxide/epoxides coupling. The three ligands are derived from Salen-like N<sub>4</sub>-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 18-electron 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<sub>2</sub> gas used is of 99.995% purity from air liquide.

### Method and techniques

<sup>1</sup>H NMR spectra were recorded on Bruker spectrometers (250, 300 and 400 MHz). Samples were prepared in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>, chemical shifts (δ) are expressed in ppm and are measured by referring to the residual solvent as references: 7.26 ppm for CDCl<sub>3</sub> and 2.50 ppm for DMSO-d<sub>6</sub>.

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 μm). Program of temperature: 60 °C (hold time 1 min), then ramp at 10 °C.min<sup>-1</sup> to reach 220 °C (hold time 1 min), and finally 10 °C.min<sup>-1</sup> 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*)-H<sub>2</sub>CyTs (**L1**) and (*trans*)-H<sub>2</sub>CyTf (**L2**) were synthesized according to the procedure we already reported, [23] and (*trans*)-CyTA-NH<sub>2</sub> (**L3**) was prepared according to the procedure already reported in the literature. [24]

### [Zn(*trans*)-CyTs] (**C1**)

To a mixture of (*trans*)-H<sub>2</sub>CyTs (**L1**) (1 g, 1.59 mmol) in MeOH (40 mL), Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O (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 CH<sub>2</sub>Cl<sub>2</sub>/MeOH were suitable for X-ray diffraction study. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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, 3H), 1.95 (m, 4H, Cy) and 1.5 (m, 4H, Cy). MS-ESI: in positive mode: m/z = 691 for [M + H]<sup>+</sup>, 729 for [M + AcCN]<sup>+</sup> and 730 for [M + AcCN + H]<sup>+</sup>. CCDC number: 1841123.

### [Zn(*trans*)-CyTf] (**C2**)

To a mixture of (*trans*)-H<sub>2</sub>CyTf (**L2**) (500 mg, 0.855 mmol) in MeOH (30 mL), Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O (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 CH<sub>2</sub>Cl<sub>2</sub>/MeOH were suitable for X-ray diffraction study. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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, CH<sub>2</sub>), 2.15 (m, 2H, CH<sub>2</sub>), 1.5-1.4 (m, 4H, CH<sub>2</sub>). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C): δ(ppm) = -76.14 (s, 6F, CF<sub>3</sub>). MS-ESI: in positive mode, m/z = 685 for [M + AcCN]<sup>+</sup> and 686 for [M + AcCN + H]<sup>+</sup>. CCDC number: 1841180.

### Zn[(*trans*)-CyTA-NH<sub>2</sub>](AcO)Cl (**C3**)

To a solution of (*trans*-CyTA-NH<sub>2</sub>) (**L3**) (0.3 g, 0.93 mmol) in MeOH (40 mL), Zn(AcO)<sub>2</sub>·2H<sub>2</sub>O (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 CH<sub>2</sub>Cl<sub>2</sub>/pentane were suitable for X-ray diffraction study. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C): δ (ppm) = 7.1-6.8 (m, 8H, Ar-H), 5.3 (broad s, 4H, NH<sub>2</sub>), 4 (m, 2H, H<sub>2</sub>C-NH), 3.85 (m, 2H, H<sub>2</sub>C-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, OCOCH<sub>3</sub>), 1.7-0.8 (m, 8H, cyclohexyl). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 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 (CH<sub>2</sub>-N), 30.5 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>) and 23.24 (CH<sub>3</sub>). MS-ESI: in positive mode, m/z = 424 (75%) and 426 (25%) of [Zn(*trans*-CyTA-NH<sub>2</sub>)Cl + H]<sup>+</sup>, in negative mode m/z = 558 (75%) and 560 (25%) of [Zn(*trans*-CyTA-NH<sub>2</sub>)(AcO)Cl + AcCN + 2H<sub>2</sub>O - H]<sup>+</sup>. CCDC number: 1841124.

## X-ray crystallographic study

A suitable crystal was selected and mounted on a Xcalibur kappa-geometry diffractometer [25a] equipped with an Atlas CCD detector and using Mo radiation (λ = 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

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