



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.

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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 [3–6]. 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.

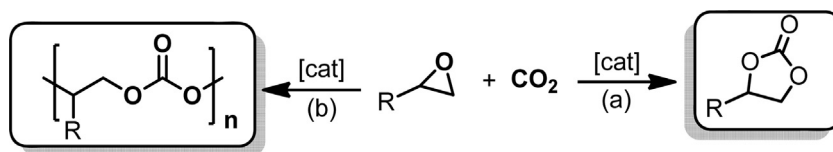
Catalysts for the coupling of carbon dioxide and epoxides include halide, quaternary alkyl ammonium or phosphonium salts, as well as ionic liquids and metal complexes [2,7]. Halide, quaternary salts and ionic liquids are known to produce the most stable thermodynamic product, which is the cyclic carbonate [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 Meléndez et al. [15] and the Al(III) aminotri(phenolate) complexes, developed by Whiteoak et al., 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 et al. 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

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

[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 [24–26] 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 centre [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 (Fig. 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** (Fig. 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(**1**- κ^3 N,N,O)(**1**- κ^2 N,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) d¹⁰ 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** (Fig. 1) in the coupling reaction of CO₂ and different epoxides. The catalytic activity of a Zn(II) complex with ligand **2H** (Fig. 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.

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 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

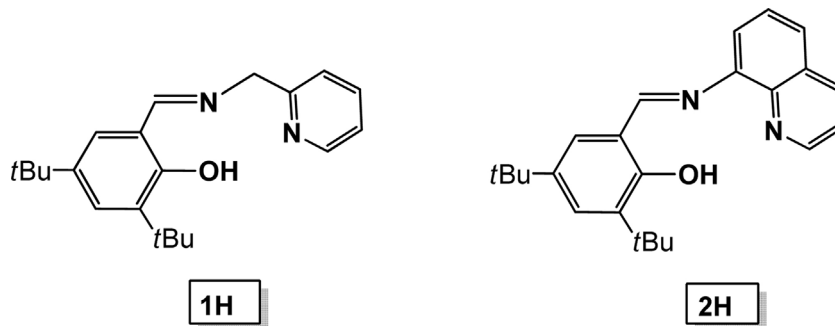


Fig. 1. NN'O-Schiff base ligands **1H** and **2H**.

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