

Strategies for Tuning the Catalytic Activity of Zinc Complexes in the Solvent-Free Coupling Reaction of CO₂ and Cyclohexene Oxide

This paper is dedicated to the memory of Renato Ugo, an exceptional scientist and beloved professor with an unforgettable humanity.

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Abstract

The catalytic activity of various zinc(II) complexes bearing a chelating nitrogen-donor ligand and different ancillary ligands (Cl, acetate, triflate) is investigated for the solvent-free coupling reaction of cyclohexene oxide and CO₂. The effect of a co-catalyst is also studied. Whereas the investigated zinc(II) complexes with chloride or acetate as ancillary ligand are inactive, those with triflate are active, allowing the selective formation of polyether or cyclic carbonate controlled by the presence of a suitable amount of [PPN]Cl.

1. Introduction

The anthropogenic emission of carbon dioxide in the atmosphere, due to combustion of fossil fuels and to various industrial plants, has been harmful for our environment in the last century. In fact, CO₂ contributes to the worrisome global warming, by trapping heat in the atmosphere, and to oceans and lakes acidification. On the other hand, CO₂, used by green plants for chemical production on a huge scale, is also a cheap, non-flammable, renewable and abundant green source of C1 building block which could become, if used in the suitable conditions, a sustainable alternative to produce chemicals

or polymers strategically interesting for the chemical industry. Therefore, the capture and conversion of CO₂ into value-added chemicals is a hot research topic which plays a key role towards a cleaner environment [1-7].

It was shown that, like carbon monoxide [8-11], CO₂ can be inserted in strained heterocycles [11-16]. In particular, the ring-expansive carboxylation of epoxides with CO₂, which affords cyclic carbonates, has gained significant recent attention not only due to the great current interest in carbon dioxide utilization but also because cyclic carbonates have various applications such as polar aprotic solvents, electrolytes for lithium batteries, synthetic intermediates of polymeric materials (e.g. polycarbonates and polyurethanes), fuel additives, alkylating factors for aromatic amines, phenols and thiols, precursors for pharmaceutical and fine chemicals [12-20]. The production of cyclic carbonates by coupling epoxide and CO₂ is of particular relevance since it represents a greener and safer alternative to the traditional preparation from diols and toxic phosgene with HCl as a side product.

Besides, the formation of polycarbonates by epoxide copolymerization with carbon dioxide, initially observed by Inoue et al [21], is of increasing interest because the introduction of stereoregularity into the polymer chain is a way to achieve materials with good thermal and mechanical properties [22]. Both cyclic carbonates [23] and polycarbonates [22] are valuable chemicals but they should be selectively produced, in order to minimize the separation and purification steps, by choosing a suitable catalyst and appropriate reaction conditions. Although it is a challenging task due to the high thermodynamic and kinetic stability of CO₂, a variety of catalysts allows the cycloaddition and/or copolymerization of epoxides and carbon dioxide [11, 20-29]. Among them, zinc complexes are of particular interest since their metal center is cheap and non-toxic. Thus, by working under suitable conditions, well-designed zinc compounds found application in the coupling of epoxides with CO₂ to give cyclic carbonates [30-34] or polycarbonates [35]. Besides, well-designed highly electrophilic cationic zinc complexes are useful as single-site catalyst for the ring opening polymerization of epoxides to polyethers [36-39], which are widely used as comonomers in the production of polyurethanes [40].

Interestingly, almost twenty years ago, it was reported that the coupling reaction of CO₂ and ethylene or propylene oxide to give the related cyclic carbonate can be performed in the presence of [(pyridine)₂ZnX₂] (X = Cl, Br, I), working at 100 °C and 34 bar [41]. The introduction of electron-donating substituents on the pyridine ligands increases the catalytic activity showing the importance of their nucleophilicity. The related complex with a strongly chelating 2,2'-bipyridine ligand was found to be totally inactive, indicating that pyridine dissociation is an important factor in determining the catalytic activity. From these observations, it was suggested that in the catalysis process, there is first substitution of one pyridine of [(pyridine)₂ZnX₂] by epoxide followed by ring opening of the

coordinated epoxide with pyridine which acts as nucleophile. In agreement with this reasoning, it was observed that the catalytic activity of [(pyridine)₂ZnX₂] increases with decreasing the electronegativity of the halide ligands due to an easier dissociation of the pyridine ligand [41]. These observations [41] prompted us to investigate the catalytic activity of various zinc(II) complexes, bearing a chelating nitrogen-donor ligand and different ancillary ligands (Cl, acetate, triflate), on the solvent-free coupling reaction of cyclohexene oxide and CO₂.

2. Experimental

2.1 Materials.

ZnCl₂, Zn(CF₃SO₃)₂·2H₂O, Zn(CH₃CO₂)₂·2H₂O, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 2,9-dichloro-1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 4,7-dichloro-1,10-phenanthroline, and 5-amino-1,10-phenanthroline were purchased from Sigma-Aldrich and were used without further purification. Cyclohexene oxide was bought from Sigma-Aldrich and freshly distilled over CaH₂. Carbon dioxide gas (99.999% purity) was purchased from Air Liquide. CD₂Cl₂, the deuterated solvent for NMR measurements was purchased from Sigma-Aldrich and was used as received.

4-(*tert*-butylphenyl)-2,2':6',2''-terpyridine [42], (1*R*,5*S*)-3-methyl-7-((*S*)-1-phenylethyl)-3,7-diazabicyclo[3.3.1]nonan-9-one [43], and bis-triphenylphosphine-iminum azide ([PPN]N₃) [44] were prepared according to the literature, whereas 2,9-dimesityl-1,10-phenanthroline [45] was prepared as described below. [(2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-N,O)₂Zn] (**8**) was synthesized by reaction of 2-(*R*)-(+)-1-phenylethyliminomethylphenol, deprotonated with NaHCO₃, and Zn(CH₃CO₂)₂·2H₂O in refluxing ethanol, as reported [46]. All the other zinc(II) complexes were prepared by reaction of the chelating ligand with an equivalent of the Zn salt in dichloromethane at room temperature (1,10-phenanthroline ligands [47]) or in methanol under reflux (terpyridine [48]), as described below.

2.1.1. Synthesis of 2,9-dimesityl-1,10-phenanthroline: 2,9-Dichloro-1,10-phenanthroline (801.5 mg, 3.22 mmol) has been dissolved in dry toluene (33 mL) under argon. Once it was completely solubilized, 2,4,6-trimethylbenzeneboronic acid (1.17 g, 7.73 mmol) and more dry toluene (33 mL) were added to the solution. The solution was cooled with a salt/ice bath and then a 2 M Na₂CO₃ solution (in 28 mL) and tetrakis(triphenylphosphine)palladium (372 mg, 0.322 mmol) were added. The obtained mixture was heated at 80°C for 16 hours. By letting the system cool down to room temperature, a solid precipitate was obtained. It was collected as white powder by filtration and recrystallized from dichloromethane and hexane. 70% yield.

¹H-NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 6.93 (s, 4H), 2.30 (s, 6H), 2.15 (s, 12H)

2.1.2. General procedure for the synthesis of complexes 1-7 and 9-13

Complexes 1–7 and 9–13 were prepared starting from the suitable 1,10-phenanthroline ligand (L) and Zn salt (ZnCl_2 , $\text{Zn}(\text{CF}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ e $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$). In a 50 mL flask, the opportune ligand (150 mg) was dissolved in dichloromethane (15 mL) and then the stoichiometric amount of the Zn salt was added. The mixture was stirred at room temperature overnight and evaporated to dryness, affording $[\text{ZnLY}_2]$ which was recrystallized from dichloromethane/pentane at room temperature.

[(2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)ZnCl₂] (1): Yield: 43 %

¹H-NMR (300 MHz, DMSO): δ 8.12 (s, 2H), 8.04 (s, 2H) 7.74-7.62 (m, 10H), 3.30 (s, 6H). Anal. calcd. for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Zn}$: C, 62.87; H, 4.06; N, 5.64. found: C, 62.93; H, 4.07; N, 5.67.

[(5-Nitro-1,10-phenanthroline)ZnCl₂] (2): Yield: 45 %

¹H-NMR (300 MHz, CD_2Cl_2): δ 9.50 (dd, $J_1=8.8$ Hz, $J_2=1.4$ Hz, 1H), 9.40 (dd, $J_1=4.8$ Hz, $J_2=1.4$ Hz, 1H), 9.35 (dd, $J_1=4.8$ Hz, $J_2=1.4$ Hz, 1H), 9.05 (s, 1H), 8.91 (dd, $J_1=8.8$ Hz, $J_2=1.4$ Hz, 1H), 8.34-8.21 (m, 2H). Anal. calcd. for $\text{C}_{12}\text{H}_7\text{Cl}_2\text{N}_3\text{O}_2\text{Zn}$: C, 39.87; H, 1.95; N, 11.62 found: C, 39.92; H, 1.94; N, 11.64.

[(2,9-Dichloro-1,10-phenanthroline)ZnCl₂] (3): Yield: 70 %

¹H-NMR (300 MHz, DMSO): δ 8.62 (d, $J=8.5$ Hz, 2H), 8.12 (s, 2H), 7.89 (d, $J=8.5$ MHz, 2H) Anal. calcd. for $\text{C}_{12}\text{H}_6\text{Cl}_4\text{N}_2\text{Zn}$: C, 37.40; H, 1.57; Cl, 36.80; N, 7.27; 16.97; found C, 37.38; H, 1.57; Cl, 36.80; N, 7.27.

[(5-Amino-1,10-phenanthroline)ZnCl₂] (4): Yield: 70 %

¹H-NMR (300 MHz, DMSO): δ 9.05 (dd, $J_1=4.4$ Hz, $J_2=1.5$ Hz, 1H), 8.72-8.64 (m, 2H), 8.04 (dd, $J_1=8.1$ Hz $J_2=1.6$ Hz, 1H), 7.77-7.70 (m, 1H), 7.55-7.47 (m, 1H), 6.86 (s, 1H). Anal. calcd. for $\text{C}_{12}\text{H}_9\text{Cl}_2\text{N}_3\text{Zn}$: C, 43.48; H, 2.74; N, 12.68; found: C, 43.50; H, 2.73; N, 12.69.

[((1R,5S)-3-Methyl-7-((S)-1-phenylethyl)-3,7-diazabicyclo[3.3.1]nonan-9-one)ZnCl₂] (5): Yield: 80 %

¹H-NMR (400 MHz, CD_2Cl_2) δ 7.42–7.15 (m, 5 H), 3.60 (q, $J=6.8$ Hz, 1 H), 3.12–2.89 (m, 6 H), 2.75-2.64 (m, 2 H), 2.60-2.52 (m, 2 H), 2.31 (s, 3H), 1.39 (d, $J=6.8$ Hz, 3H). Anal. calcd. for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{N}_2\text{OZn}$: C, 48.69; H, 5.62; N, 7.10; found: C, 48.72; H, 5.60; N, 7.12.

[(2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)Zn(OCOCH₃)₂] (6): Yield: 77 %

¹H-NMR (300 MHz, CDCl_3): δ 8.02 (s, 2H), 7.83 (s, 2H), 7.68-7.52 (m, 10H), 3.18 (s, 6H), 1.74 (s, 6H). Anal. calcd. for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_4\text{Zn}$: C, 66.25; H, 4.82; N, 5.15; O, 11.77; Zn, 12.02. found: C, 66.28; H, 4.84; N, 5.14

[(5-Nitro-1,10-phenanthroline) Zn(OCOCH₃)₂] (7): Yield: 44 %

¹H-NMR (300 MHz, CDCl₃): δ 9.53-9.38 (m, 3H), 8.97 (s, 1H), 8.80 (d, *J* = 9 Hz, 1H), 8.23-8.10 (m, 2H), 2.12 (s, 6H). Anal. calcd. for: C₁₆H₁₃N₃O₆Zn, 47.02; H, 3.21; N, 10.28; found: C, 47.07; H, 3.21; N, 10.30.

[(2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline)Zn(OSO₂CF₃)₂] (9): Yield: 49 %

¹H-NMR (300 MHz, CDCl₃): δ 7.94 (s, 2H), 7.75 (s, 2H), 7.65-7.48 (m, 10H), 3.27 (s, 6H).

Anal. calcd. for C₂₈H₂₀F₆N₂O₆S₂Zn: C, 46.45; H, 2.78; N, 3.87; found: C, 46.50; H, 2.79; N, 3.85.

[(4,7-Dichloro-1,10-phenanthroline)Zn(OSO₂CF₃)₂] (10): Yield: 73 %

¹H-NMR (400 MHz, DMSO) δ 9.09 (d, *J* = 4.8 Hz, 2H), 8.41 (s, 2H), 8.08 (d, *J* = 4.8 Hz, 2H). Anal. calcd. for C₁₄H₆Cl₂F₆N₂O₆S₂Zn: C, 27.45; H, 0.99; N, 4.57 found: C, 27.49; H, 0.97; N, 4.60.

[(2,9-Dichloro-1,10-phenanthroline)Zn(OSO₂CF₃)₂] (11) Yield: 51%

¹H-NMR (300 MHz, DMSO): δ 8.66 (d, *J*=8.5 Hz, 2H), 8.15 (s, 2H), 7.92 (d, *J*= 8.5 MHz, 2H)

Anal. calcd. for C₁₄H₆Cl₂F₆N₂O₆S₂Zn: C, 27.45; H, 0.99; N, 4.57 found: C, 27.47; H, 1.00; N, 4.59.

[(5-Nitro-1,10-phenanthroline) Zn(OSO₂CF₃)₂] (12) Yield: 58%

¹H-NMR (300 MHz, CDCl₃): δ 9.58-9.36 (m, 3H), 8.99 (s, 1H), 8.82 (d, *J* = 9 Hz, 1H), 8.26-8.10

Anal. calcd. for C₁₄H₇F₆N₃O₈S₂Zn: C, 28.56; H, 1.20; N, 7.14 found: C, 28.59; H, 1.21; N, 7.17.

[(2,9-Dimesityl-1,10-phenanthroline)Zn(OSO₂CF₃)₂] (13): Yield: 85%

¹H-NMR (400 MHz, CD₃CN) δ 8.47 (d, *J* = 8.1 Hz, 2H), 8.00 (s, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.00 (s, 4H), 2.34 (s, 6H), 2.03 (s, 12H). Anal. calcd. for C₃₂H₂₈F₆N₂O₆S₂Zn: C, 49.27; H, 3.62; N, 3.59; found: , 49.25; H, 3.63; N, 3.61.

Synthesis of [(4-(*tert*-butylphenyl)-2,2':6',2''-terpyridine)Zn(OSO₂CF₃)₂] (14)

The terpyridine ligand (0.3 mmol) was added to a colorless solution of the stoichiometric amount of Zn(CF₃SO₃)₂·2H₂O (0.3 mmol) in CH₃OH (15 mL). The reaction mixture was stirred at room temperature for 30 min, then refluxed for 1h. The solvent was removed under vacuum affording the desired complex. which was recrystallized from dichloromethane/pentane at room temperature. Yield: 91%.

¹H- NMR (CDCl₃): 8.78-8.74 (m, 4H), 8.69 (d, *J*= 6Hz, 2H), 7.92-7.86 (m, 4H), 7.55 (d, *J*= 6Hz, 2H), 7.40-7.34 (m, 2H), 1.41 (s, 9H). Anal. calcd. for C₂₇H₂₃F₆N₃O₆S₂Zn: C, 44.48; H, 3.18; N, 5.76; found: C, 44.50; H, 3.19; N, 5.79.

2.2. Typical reaction of coupling of cyclohexene oxide and CO₂.

Catalyst (0.08 mol%, 39.5 μmol) and co-catalyst (1 eq) were dissolved in 5 mL of CH₂Cl₂, stirred at room temperature for 1 hour, then the solvent was removed under vacuum. 5 mL (1250 eq) of neat cyclohexene epoxide were added to the solid residue and the solution added in a 25 mL steel autoclave at ambient temperature. The autoclave was charged with 30 bar of CO₂ and heated to the reaction temperature. After a period of 17 h, the autoclave was cooled to room temperature and vented in a

fume hood. A portion of the crude product was collected for determination of conversion and selectivity by ^1H NMR analysis while the remaining portion was extracted as a dichloromethane solution and precipitated in a MeOH/HCl (9:1) solution. The purification process was repeated three times and the purified polymer dried in vacuo at 60°C overnight.

2.3 Polymer Characterization.

All the ^1H -NMR spectra were acquired on a Bruker DMX 600 MHz NMR spectrometer in CD_2Cl_2 at 300 K. Size exclusion chromatography (SEC) analyses were performed on a Waters GPCV2000 system, using THF as mobile phase, at 35°C with a 0.6 mL/min flow. Sample concentration was set at 3 mg/mL and injection volume at 150 μL . Calibration of the curves used polystyrene standards in a 162-380000 g/mol range. Calorimetric curves were acquired on a Perkin Elmer DSC 8000 under nitrogen atmosphere, samples being heated and chilled from -20 to 160°C twice at $20^\circ\text{C}/\text{min}$.

3. Results and discussion

It is known that the coupling of cyclohexene oxide (CHO) and CO_2 may lead to poly(cyclohexene carbonate) or to cyclic cyclohexene carbonate. The selectivity of the reaction is strongly related to the choice of the catalyst and to the reaction conditions (temperature and CO_2 pressure), the cyclic carbonate being the thermodynamically favoured product [49]. Moreover, it is well known that the electronic effect of the ligand strongly affects the copolymerization results according to the monomer used. As an example, for salen-type chromium catalysts, electron-rich diimine backbones are highly effective with cyclohexene oxide to give the related polycarbonate, whereas their use with propylene oxide mostly leads to the formation of cyclic carbonate [27, 50]. Besides, depending on the catalyst and reaction conditions, some homopolymerization can occur, from the consecutive insertion of epoxides [25]. Also, addition of a co-catalyst such as an alkylammonium salt can influence the ratio between cyclic and polycarbonate products depending on both its nature and its loading [51-52].

In the present work, we investigated the catalytic activity of various zinc(II) complexes (Figure 1, complexes **1-14**) on the coupling reaction of CHO and CO_2 . Most of them have a 1,10-phenanthroline, substituted with a π -delocalized (phenyl, mesityl), electron-donor (NH_2) or acceptor (NO_2 , Cl) group, and chloride (**1-4**) or acetate (**6-7**) or triflate (**9-13**) as ancillary ligands. In addition, [((1*R*,5*S*)-3-methyl-7-((*S*)-1-phenylethyl)-3,7-diazabicyclo[3.3.1]nonan-9-one) ZnCl_2] (**5**), [2-[(*R*)-(+)-1-phenylethyliminomethyl]phenolato-*N*,*O*] $_2\text{Zn}$] (**8**), and [(4-(*tert*-butylphenyl)-2,2':6',2''-terpyridine) $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$] (**14**) were also studied as potential catalysts.

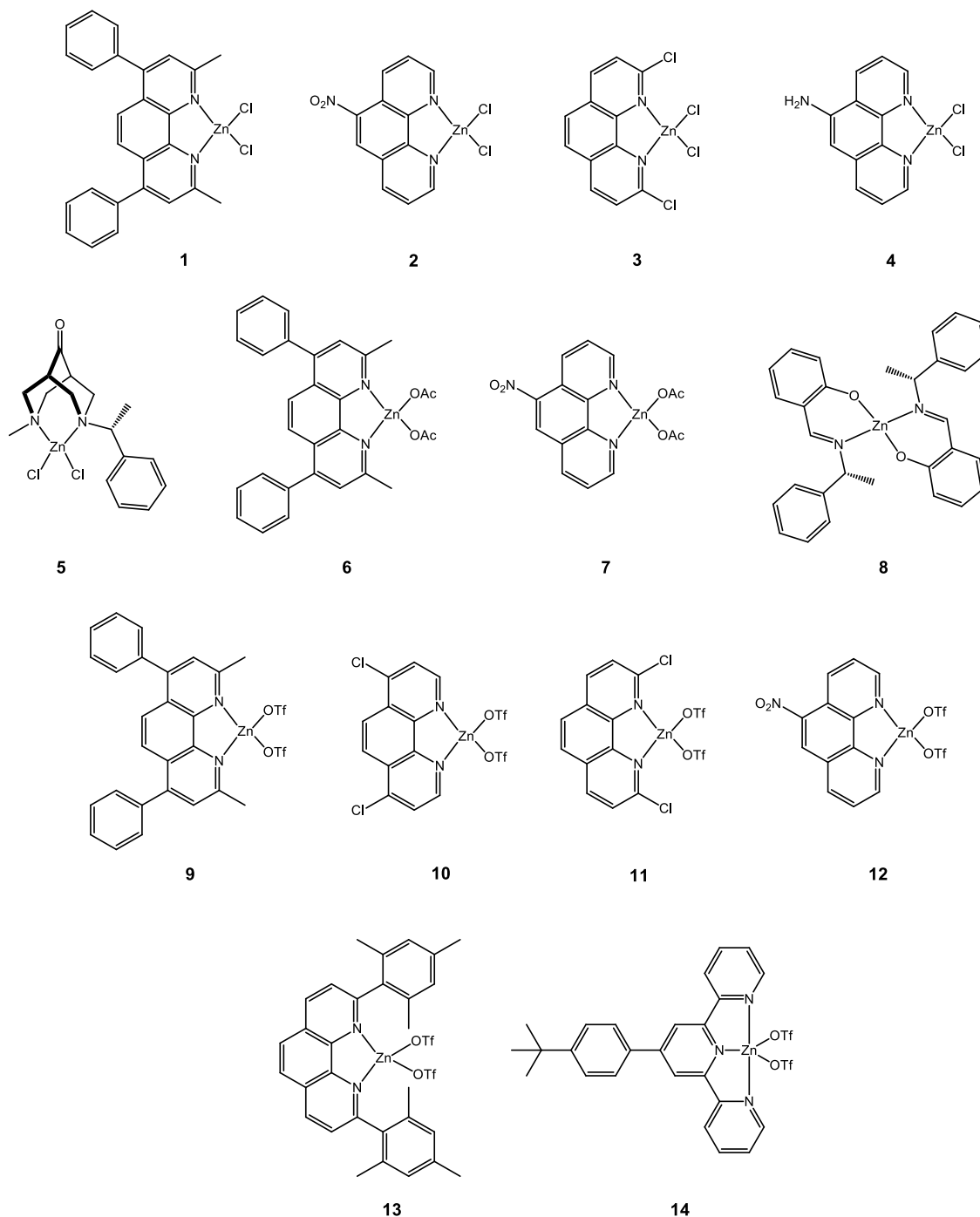


Figure 1. Structure of the investigated zinc(II) catalysts.

It turned out that complexes **1-8** are not catalytically active even in the presence of a co-catalyst such as [PPN]Cl. On the contrary, the triflate complexes are active, affording poly(cyclohexene ether) or cyclohexene carbonate depending on the presence of an adequate amount of a suitable co-catalyst. Results are summarized in Table 1, presenting conversion, selectivity, ether linkage, along with molecular weight, polydispersity index (PDI), and thermal properties of the polyether.

Table 1. Reaction of CHO with Zn triflate complexes and different co-catalysts^a

Entry	Catalyst	Cocatalyst	Conversion ^b (%)	Selectivity (%) ^b		M_n^c (g/mol)	PDI ^c	T_g^d (°C)
				Cyclic carbonate	Polyether			
1	9	-	83	0	100	3400	1.6	62
2		[PPN]Cl (1 eq)	81	0	100	3000	1.5	61
3	10	-	44	0	100	3800	1.5	61
4	11	-	80	0	100	3800	1.6	62
5		[PPN]Cl (1 eq)	35	0	100	3300	1.6	59
6		[PPN]Cl (3 eq)	12	100	0	-	-	-
7		[PPN]Cl (4 eq)	15	100	0	-	-	-
8		DMAP (2 eq)	3	0	100	Not determined	Not determined	Not determined
9		[PPN]N ₃ (2 eq)	1	8	92	-	-	-
10		P(Cy) ₃ (2 eq)	37	0	100	2600	1.5	56
11	P(Cy) ₃ (3 eq)	29	0	100	Not determined	Not determined	Not determined	
12	12	P(Cy) ₃ (2 eq) ^e	44	0	100	2400	1.5	54
13		P(Cy) ₃ (3 eq) ^e	32	0	100	2600	1.4	56
14		-	13	0	100	3500	1.6	60
15	13	-	35	0	100	3700	1.8	64
16	14	-	76	0	100	3900	1.5	64
17		PPNCl (1 eq)	20	0	100	Not determined	Not determined	Not determined

^a Reaction conditions: CHO= 1250 eq, cat = 0.08 mol%, cat: CHO=1:1250, T = 80 °C, P= 30 bar, t = 17 h; ^b from ¹H-NMR analysis on the crude product; ^c average molecular weight (M_n) and molecular weight distribution (M_w/M_n) by SEC using polystyrene standards; ^d Determined from DSC second heating cycle, ^e CHO= 625 eq.

In the absence of co-catalyst, the phenanthroline complexes **9** and **11** and the terpyridine complex **14** (entries 1, 4 and 16, respectively) show a comparable conversion of about 80% with a complete selectivity towards poly(cyclohexene ether). Complex **10**, similar to **11** but with the chlorine substituents in 4 and 7 positions, instead of 2 and 9, leads to a much lower conversion (44 vs 80, see entry 3 vs 4 in Table 1); the molecular weight of the polyether, of about 3800 g/mol, is comparable to those obtained with **11** and **14**. Complex **13**, with mesityl groups in 2 and 9 positions of the phenanthroline, gives a polyether conversion equal to 35% whereas **12**, the complex bearing a NO₂-group in 5 position, displays a complete selectivity towards polyether but the lowest conversion, 13%, among the different complexes. The results obtained for catalysts **10-12** indicate that the conversion follows the order **11**>**10**>**12**. This means that the conversion towards polyether is higher when the electron-withdrawing chloride substituents are in 2 and 9 positions of the phenanthroline, while, with the same substituents in 4 and 7 positions, the conversion is halved and further decreases with the strong electron-withdrawing nitro group in position 5.

Figure 2 shows $^1\text{H-NMR}$ spectra of the crude and purified polyether (entry 16, Table 1), with the well detectable signal at around 3.5 ppm assigned to polyether linkage. Moreover, in Figure 2a the methines of unreacted CHO at 3.05 ppm are well detectable too. The absence of the signal at 4.6 ppm, due to methine protons of poly(cyclohexene carbonate), confirms the lack of the formation of polycarbonate.

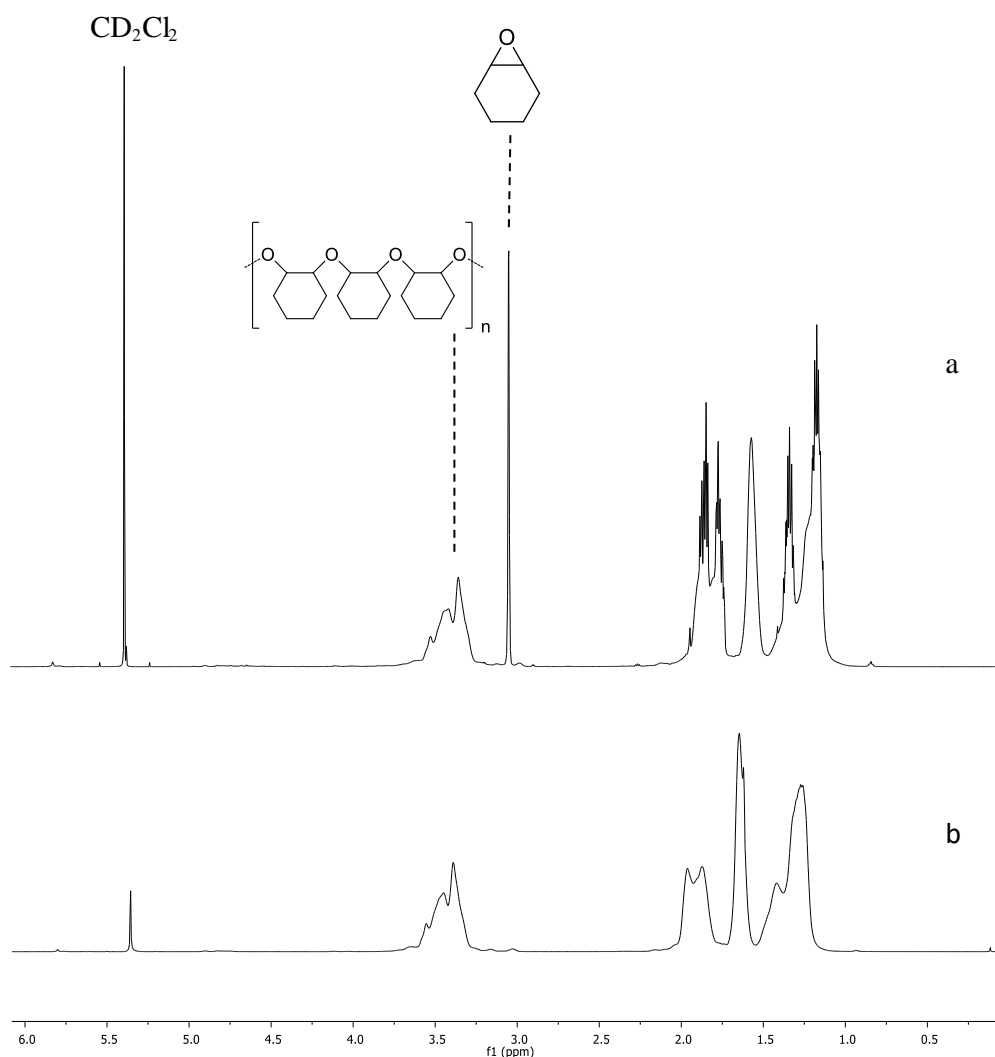


Figure 2. $^1\text{H-NMR}$ spectra of a poly(cyclohexene ether) (entry 16, Table 1) a) before and b) after precipitation in methanol.

Polyethers, obtained with all zinc triflate complexes without the addition of a co-catalyst, show a molecular weight ranging from 3400 to 3900 g/mol and a low polydispersity index (PDI) value, around 1.5-1.8.

In Figure 3, the size exclusion chromatography (SEC) curves corresponding to entries 1, 3, 4, 15 and 16 show a bimodal distribution of the molecular weights with the M_p value relative to the fraction at higher molecular weight corresponding to about 6000 g/mol almost always prevailing over that of the low-molecular-weight fraction. This behaviour is also commonly observed for poly(cyclohexene carbonate) from salen-type catalysts and is usually ascribed to the presence of traces of water in the reaction medium.

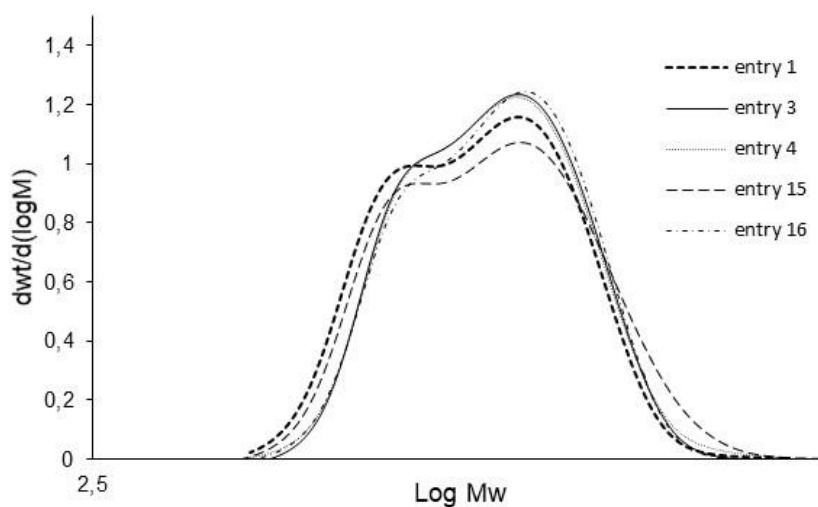


Figure 3. SEC bimodal curves of poly(cyclohexene ether) from different zinc triflate complexes (entries 1, 3, 4, 15 and 16, Table 1).

Once identified complexes **9**, **11** and **14** as the best catalysts in terms of conversion, the effect of 1 equivalent of the most used [PPN]Cl co-catalyst has been evaluated. With the three of them (entries 2, 5, and 17, respectively), the selectivity is confirmed at 100% but a slightly lower molecular weight is achieved (see Figure 4). Besides, the conversion decreases with both **11** and **14**.

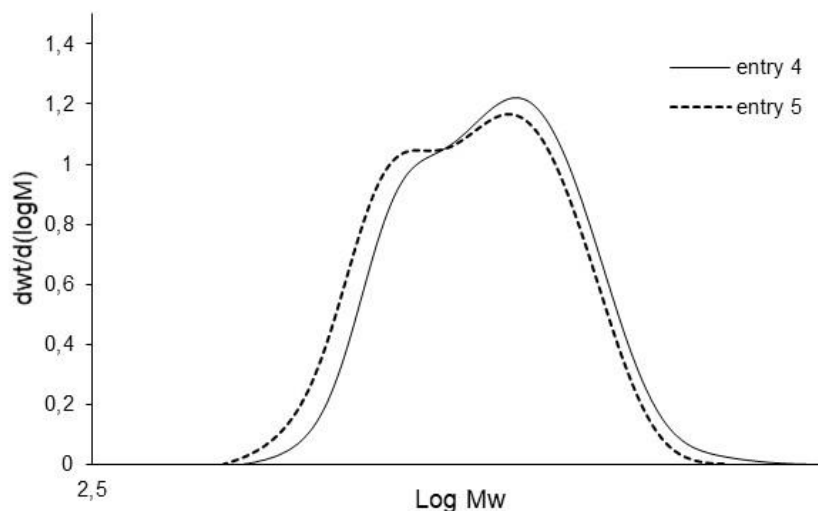


Figure 4. SEC bimodal curves of poly(cyclohexene ether) (entries 4 and 5, Table 1).

Therefore, to better understand the effect of the nature and amount of the co-catalyst, the reaction has been conducted with **11** by using the same co-catalyst, [PPN]Cl, and varying its loading (up to 4 equivalents) and then, for comparison, by using other co-catalysts, bis-triphenylphosphine-iminium azide ([PPN]N₃), 4-dimethylaminopyridine (DMAP), and tricyclohexylphosphine (P(Cy)₃). [PPN]N₃, analogous of [PPN]Cl with azide as anion, has been chosen because it has been shown, with traditional chromium salen complexes, to be the most effective in the copolymerization of epoxide and CO₂ [53, 54]. DMAP is an aromatic Lewis base, also widely used in CHO/CO₂ copolymerization, although it gives activities much lower than those reached with [PPN]Cl. P(Cy)₃ has been chosen since, in the copolymerization catalysed with [Zn(triflate)₂], it enhances the selectivity toward poly(cyclohexene carbonate) [51].

An increase of the [PPN]Cl co-catalyst loading from 1 to 3-4 equivalents leads to a lower conversion (12 and 15% for 3 and 4 equivalents, respectively; entries 6 and 7) and, surprisingly, to a change in the selectivity of the reaction affording cyclohexene carbonate only. It should be pointed out that, under our reaction conditions, no cyclic carbonate is formed by using [PPN]Cl alone, that is without a zinc triflate catalyst.

When [PPN]N₃ is used as co-catalyst (2 equivalents), a very low conversion is attained, affording mainly polyether along with some cyclic carbonate. A very low conversion is also achieved with 2 equivalents of DMAP, affording polyether only.

Since P(Cy)₃, as above mentioned, was reported able to give polycarbonate in the presence of zinc triflate, some reactions have been also investigated with 2 or 3 equivalents of this co-catalyst (entries 10 and 11 in Table 1) and at lower monomer loading (entries 12 and 13 in Table 1). The conversion is always below 50%, regardless of the reaction conditions, and the selectivity is completely shifted

towards the formation of polyethers. At increasing the co-catalyst loading, a decrease in conversion is always observed and at low monomer loading, lower molecular weights are achieved. A careful analysis of SEC curves for these samples pointed out the bimodal distribution of the molecular weights already observed but with the fraction at lower molecular weight being predominant, especially at higher equivalents of co-catalyst, thus confirming the tendency of this co-catalyst to behave as chain transfer agent. Moreover, the molecular weights observed are considerably smaller than the theoretical ones. This suggests that a chain-transfer process could occur due to the presence of a small amount of moisture or protic species.

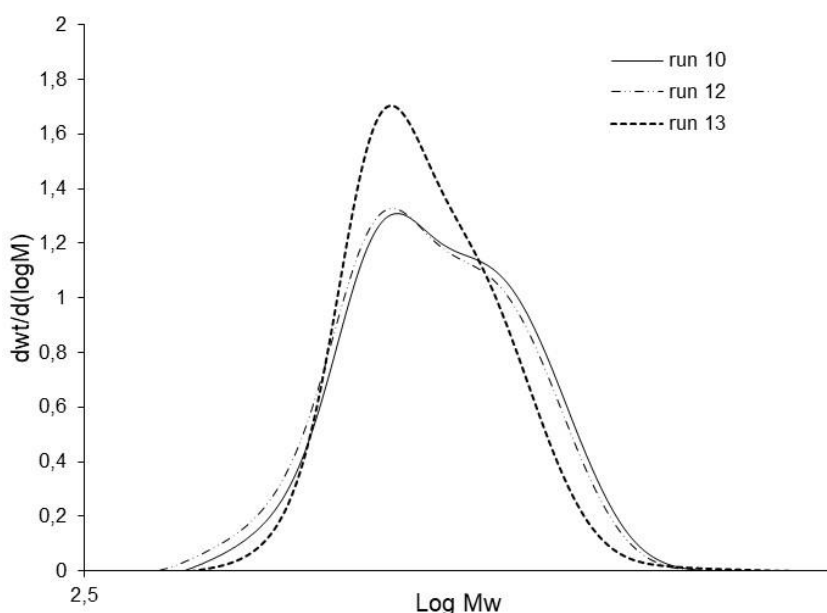


Figure 5. SEC bimodal curves of poly(cyclohexene ether) (entries 10, 12 and 13, Table 1).

The thermal characterization of the polyethers shows T_g values around 61 °C and 55 °C. The lower value, typical of polyether from **11** and P(Cy)₃, can be ascribed to lower molecular weights.

These preliminary results show the importance of the loading and nature of the co-catalyst on the selectivity of the reaction catalysed by complex **11**.

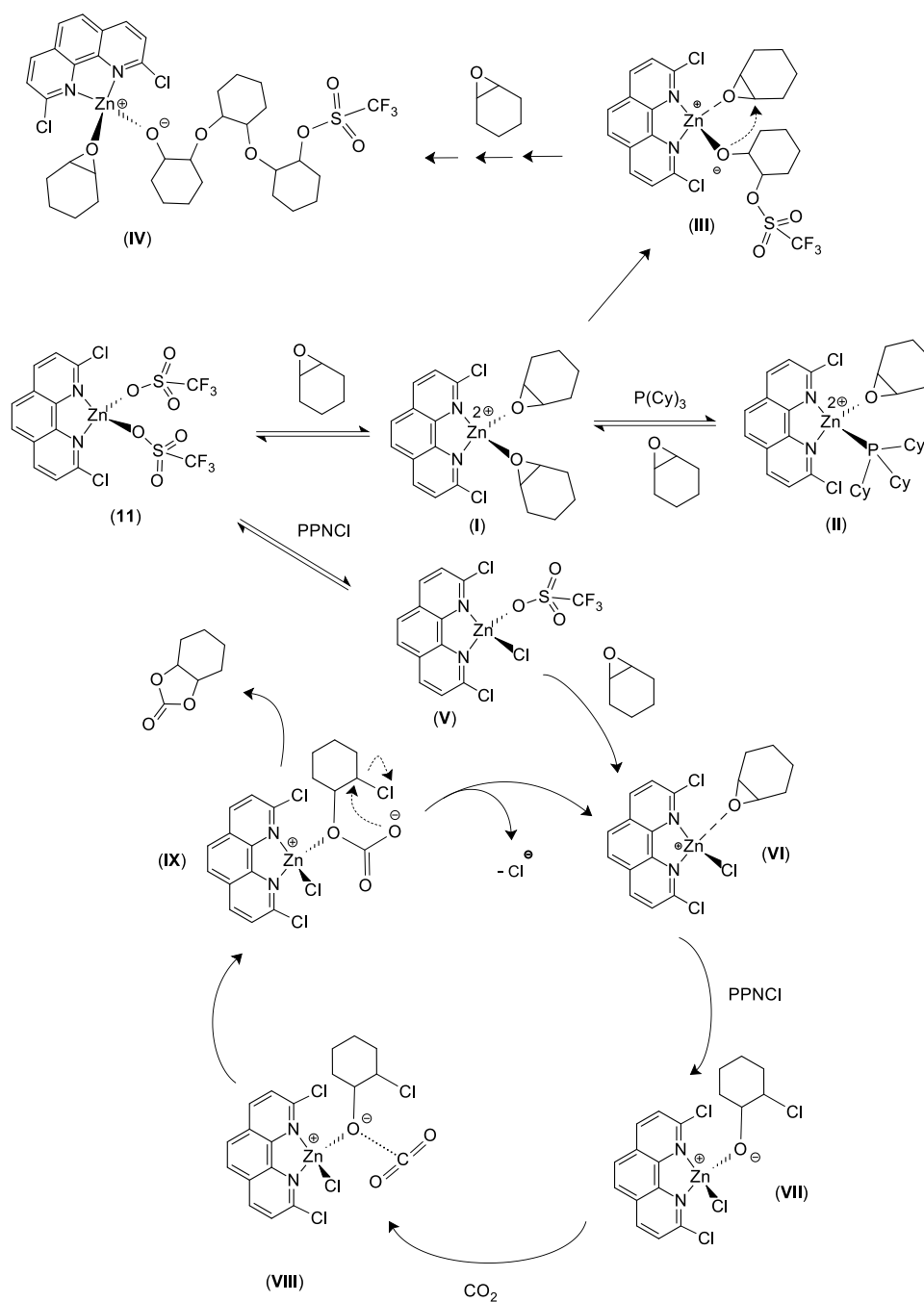
It is worth pointing out that the lack of catalytic activity of complexes **1-7**, bearing a chelating ligand and chloride or acetate as ancillary ligand, is in agreement with the previous observation that [(2,2'-bipyridine)ZnBr₂] is totally inactive contrarily to the related complex bearing two pyridines instead of the chelating bipyridine ligand [41]. As mentioned in the introduction, this different catalytic activity suggested that pyridine dissociation is important to allow coordination of the epoxide [41]. Interestingly, in the present work we found that the use of triflate as ancillary ligand turns on the

catalytic activity affording polyether (100% selectivity). This behaviour can be reasonably explained by the much weaker nucleophilicity of triflate with respect to chloride and acetate which leads to the formation of ion pairs such as [(1,10-phenanthroline)Zn(OSO₂CF₃)]⁺[OSO₂CF₃]⁻ [55] and therefore allows coordination and activation of cyclohexene oxide by the zinc(II) center. Addition of an excess of [PPN]Cl (3-4 equivalents, with respect to complex **11**) changes completely the selectivity of the reaction with formation of cyclic carbonate only.

Several papers already reported possible mechanisms for the reactions between CO₂ and epoxides promoted by Zn(II) complexes [41, 56-59] also including quantum chemical calculations [59], but the peculiarity of the results here obtained prompted us to find a possible rationalization of our experimental data through the reasonable mechanism described in Scheme 1.

In the presence of a large excess of CHO, the bis-triflate complex (**11**) could be converted in the dicationic bis-CHO complex (**I**) which, through the opening of one of the two epoxy rings by the triflate anion which can act as nucleophile [60], might transform into complex (**III**) whose evolution would lead to the formation of the corresponding polyether. The presence of two CHO ligands in the coordination sphere of the Zn(II) derivatives prevents interaction with CO₂, thus explaining the high selectivity in polyether. The addition of a relatively soft Lewis base probably decreases the amount of the bis-CHO complex (**I**) which is in equilibrium with derivative (**II**) so that, in the presence of P(Cy)₃ or DMAP, we observe a significant decrease in the conversion of CHO to polyether, but with the same selectivity. On the other hand, the addition of different amounts of [PPN]Cl could promote the formation of complexes (**V**) and (**VI**) in which one chloride anion is strongly coordinated to the metal atom; in these conditions the epoxy ring opening would occur in the absence of a second coordinated CHO molecule so that derivative (**VII**) could interact with a CO₂ molecule with a tetrel bond formation [61-63] (**VIII** and **IX**), giving rise to the formation of cyclohexene carbonate whereas the reaction paths leading to the formation of polycarbonate and/or polyether would be precluded. Scheme 1 gives a reasonable explanation for our results, but more work needs to be dedicated to better understand the involved mechanism. For example, in the absence of [PPN]Cl, the ion-pair [(2,9-dichloro-1,10-phenanthroline)Zn(OSO₂CF₃)]⁺[OSO₂CF₃]⁻ [55] could also catalyse the polymerization of cyclohexene oxide by a cationic mechanism, as previously proposed for other ion-pairs such as moisture sensitive [(Et₂O)₃ZnCH₂CH₃][B(C₆F₅)₄] and [(Et₂O)₃ZnN(SiMe₃)₂][B(C₆F₅)₄] [38]. In any case, the key role of the triflate ligand is surely to allow the formation of catalytically active cationic zinc species, a behaviour that does not occur with chloride and acetate ligands. The observation that complex **12** is the less active triflate zinc catalyst can reasonably be attributed to the presence of the strong electron-withdrawing NO₂ group that tends to hamper the formation of cationic zinc species. Similarly, complex **10** with chloro substituents in position 4 and 7 of the phenanthroline

is less active. Interestingly, the zinc triflate complex with the chloro substituents in position 2 and 9 (**11**) is much more efficient than **10** and behaves as the bathocuproine complex (**9**), whereas the related complex with bulky mesityl groups (**13**) is less active: such a trend suggests that a crucial catalytic role is also played by the substituents in alpha of the phenanthroline nitrogens, near the catalytic zinc center.



Scheme 1. Proposed mechanism for the reactions of CHO and CO₂ promoted by Zn(II) triflate with chelating aromatic diamine ligands.

Besides, it is worth pointing out that, in the presence of [PPN]Cl, [Zn(OSO₂CF₃)₂] is known to catalyse the polymerization of cyclohexene oxide and CO₂, affording "ether" and "carbonate" linkages with a 90% and 10 % selectivity, respectively, without cyclic carbonate formation [51]. As observed in the present work, the introduction of the chelating 2,9-dichloro-1,10-phenanthroline ligand in the coordination sphere of the zinc(II) center completely changes the selectivity of the coupling reaction, affording cyclic carbonate only. This versatile catalytic activity of the "Zn(OSO₂CF₃)₂" moiety is fascinating.

4. Conclusion

Our work shows how it is possible to tune the catalytic activity of zinc complexes in the solvent-free coupling reaction of CO₂ and cyclohexene oxide. The use of triflate as ancillary ligand turns on the catalytic activity of zinc(II) complexes bearing a chelating 1,10-phenanthroline or terpyridine ligand, due to the formation of cationic zinc species, allowing the formation of low molecular weight polyethers with a 100% selectivity. Our preliminary results suggest that the percentage conversion is controlled by (i) the nature of the substituents in alpha of the coordinated nitrogens, bulky substituents decreasing the conversion due to steric hindrance near the catalytic zinc center, and (ii) the nature of the substituents on the chelating ligands, electron-withdrawing groups decreasing the conversion due to destabilization of the catalytically active cationic zinc species. Addition of a suitable amount of bis(triphenylphosphine)iminium chloride favours the fixation of CO₂, leading to the exclusive formation of the cyclic carbonate. This selectivity shows the potential of simple zinc(II) complexes bearing triflate ancillary ligands as multitasking catalysts.

The present study opens the route to zinc triflate complexes bearing chelating nitrogen donor ligands for catalytic reactions of epoxides. It should be extended. For example, it would be worth to investigate the use of other substituted 1,10-phenanthrolines and to study other types of halide salts as co-catalysts in order to get a better understanding of these appealing zinc(II) catalysts. Due to their low cost, non-toxicity, and insensitivity to air and moisture, it would also be worth investigating other epoxides for possible industrial application.

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Graphical abstract

