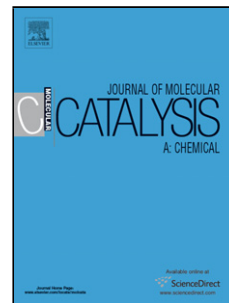


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Halogenated *meso*-phenyl Mn(III) porphyrins as highly efficient catalysts for the synthesis of polycarbonates and cyclic carbonates using carbon dioxide and epoxides

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Graphical Abstract

Highlights

- New halogenated Mn(III)-porphyrin catalysts for CO₂ fixation into polycarbonates and cyclic carbonates.
- This catalyst produces poly(cyclohexene carbonate) increasing by ten-fold the TOF respect to the non-halogenated analog. Cyclic carbonates are obtained from linear epoxides.
- This system uses very low catalyst loading, does not require a co-catalyst and, when soluble, it can be used in net substrate.

Abstract

Introduction of halogen electron withdrawing atoms (chloro and fluoro) in the *ortho* position of the aryl groups of *meso*-tetraphenylporphyrin manganese(III) complexes increased their activity as catalysts in the reaction of carbon dioxide with epoxides, when compared with the *meso*-tetraphenylporphyrin manganese(III) counterpart, even in the absence of co-catalysts. In the polymerization reaction of carbon dioxide and cyclohexene oxide, almost ten-fold increase of the TOF was observed when 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinatomanganese(III) acetate or 5,10,15,20-tetra(2,6-difluorophenyl)porphyrinatomanganese(III) acetate complexes were used as catalysts.

Under similar conditions, when terminal epoxides were used as substrates, the selective cycloaddition of CO₂ with styrene oxide, epichlorohydrin, propylene oxide, and 1,2-epoxytetradecane yielded exclusively the corresponding cyclic carbonates (conversion 54-98 %).

Keywords: polycarbonates, cyclic carbonates, metalloporphyrins, manganese(III), carbon dioxide.

1. Introduction

Carbon dioxide is a renewable C₁-building block for the synthesis of monomeric or polymeric organic carbonates [1]. Cyclic carbonates have wide applications such as polar aprotic solvents, antifoam additives, plasticizers [2,3,4] and also as raw materials for the synthesis of polyurethane and urea derivatives [5]. In addition, aliphatic polycarbonates are materials possessing extreme toughness, high impact strength, high transparency and biodegradability [2, 6, 7, 8], which explains its broad use as anti foam additives, as binders and plastic substitute derivatives [2,6,7,8]. However, the chemical transformation of carbon dioxide, an almost inert compound, requires the use of appropriate catalysts and highly reactive substrates, such as epoxides, to obtain cyclic carbonates or polycarbonates (Scheme 1) [9,10,11,12].

A variety of catalysts have been developed for carbon dioxide and epoxide coupling, which include halide, quaternary alkyl ammonium or phosphonium salts, ionic liquids and metal complexes [9]. Halides, quaternary salts and ionic liquids are known to produce preferentially cyclic carbonates, which are the most stable thermodynamic products [9], while metal complexes can catalyze the formation of polymers and/or cyclic carbonate products, depending from the co-catalyst, substrate and reaction conditions [9]. It should be mentioned that most of the metal based complexes, of which tetrapyrrolic macrocycles are privileged compounds for many applications [13,14,15,16,17,18,19,20,21], require the presence of a co-catalyst, acting as nucleophile, whether added to the reaction (binary catalytic systems) [22,23,24,25] or already included in the structure of the complex (bifunctional catalytic systems) [26].

On the other hand Inoue *et al.* [27] reported that 5,10,15,20-tetraphenylporphyrinato Mn(III) acetate (**Mn-TPP**, Figure 1), in the absence of any additional co-catalyst, was able to promote the copolymerization of CO₂ and cyclohexene oxide (CHO) with a moderate TOF of 16.3 h⁻¹ when compared with that reported for Cr(III)-salen based systems (1200 h⁻¹) [28]. Darensbourg and Frantz proposed the low ability of the five-coordinate Mn(III) complexes to bind the epoxide as a plausible explanation for their low activity [29]. So, the introduction of electron-withdrawing groups at the periphery of the porphyrin ligand would strengthen their Lewis acidity, favoring the coordination of the epoxide to the metal center as observed for other catalytic systems [30]. Therefore, herein we describe the synthesis of the 5,10,15,20-tetra(2,6-dichlorophenyl)- and 5,10,15,20-tetra(2,6-difluorophenyl)porphyrinato manganese(III) complexes having acetate or chloride as axial coordination ligands (**1**, **2** and **3**, Figure 1) and their evaluation as selective catalysts either for the copolymerization of cyclic epoxides with CO₂ or the cycloaddition of terminal epoxides with CO₂, without the addition of co-catalysts.

2. Experimental

2.1. General Comments

Reagents for the synthesis of catalysts were acquired from Aldrich, and used as received. 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). 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 were performed on a Voyager-DE-STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. Dithranol was used as matrix, which was dissolved in MeOH at a concentration of 10 mg·mL⁻¹. The polymer (5 mg) was dissolved in 1 mL of CHCl₃. 1 μL of sample, 1 μL of matrix and 1 μL of potassium trifluoroacetate (KTFA) solution in the case of polymers (1 mg of KTFA in 1 mL of THF) were deposited consecutively on the stainless steel sample holder and allowed to dry before introduction into the mass spectrometer. Three independent measurements were made for each sample. For each spectrum 100 laser shots were accumulated. The molecular weights (M_n) of copolymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. Measurements were made in THF on a Millipore-Waters 510 HPLC Pump device using three-serial column system (MZ-Gel 100Å, MZ-Gel 1000 Å, MZ-Gel 10000 Å linear columns) with UV-Detector (ERC-7215) and IR-Detector (ERC-7515a). The software used to get the data was NTeqGPC 5.1. Samples were prepared as follow: 10 mg of the copolymer was dissolved with 2 mL of tetrahydrofuran (HPLC grade) stabilized with 2,6-di-*tert*-4-methylphenol.

2.2. Synthesis of Mn(III) porphyrin catalysts

5,10,15,20-tetra(phenyl)porphyrin (TPP), [36] 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin (TDCPP) [36] and 5,10,15,20-tetra(2,6-difluorophenyl)porphyrin (TDFPP) [36] were prepared according to our previously reported method [35] and their characterization data is in agreement with the literature.

2.3. General method of metallation of TDCPP and TDFPP

The corresponding porphyrin was dissolved in DMF and 10 equivalents of the corresponding metal salt were added. The reaction mixture was kept at reflux temperature ($\sim 150^{\circ}\text{C}$) for 24 hours. After cooling to room temperature, chloroform (50 mL) was added and the mixture was washed with distilled water (3 times x 100 mL). The organic phase was dried with anhydrous sodium sulfate and the solution was concentrated. Column chromatography was performed on silica gel with ethyl acetate:dichloromethane (3:1) as eluent to obtain the title porphyrins.

2.4. 5,10,15,20-tetrakis(phenyl)porphyrinatomanganese(III) acetate (Mn-TPP)

Following the general method, 500 mg (0.8 mmol) of TPP, 31.96 g (8.0 mmol) of manganese (II) acetate tetrahydrate were used, mixed in 50 mL of DMF. We obtained **Mn-TPP** in 80% yield (473 mg). Characterization data was in agreement with the literature [27].

2.5. 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinatomanganese(III) acetate (1)

Following the general method, 800 mg (0.9 mmol) of TDCPP, 2.20 g (9.0 mmol) of manganese (II) acetate tetrahydrate were used, mixed in 75 mL of DMF. We obtained metalloporphyrin **1** in 84 % yield (757 mg). Characterization data was in agreement with the literature [31].

2.6. 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrinatomanganese(III) acetate (2)

Following the general method, 300 mg (0.4 mmol) of TDFPP, 0.96 g (4.0 mmol) of manganese (II) acetate tetrahydrate were used, mixed in 25 mL of DMF. We obtained metalloporphyrin **2** in 40 % yield (138 mg). Characterization data was in agreement with the literature [32].

2.7. 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinatomanganese(III) chloride

(**3**) Following general method, 500 mg (0.6 mmol) of TDCPP, 1.19 g (6.0 mmol) of manganese (II) chloride tetrahydrate were used, mixed in 50mL of DMF. We obtained metalloporphyrin **3** in 88% yield (370 mg). Characterization data was in agreement with the literature [33].

2.8. General procedure for the catalytic reactions of epoxides with CO₂

The catalytic tests were carried out in a 100 mL Berghof reactor, which was previously kept for 4 hours, under vacuum, at 100 °C. After cooling down, a solution under inert atmosphere containing the catalyst dissolved in net distilled substrate or with solvent (when indicated) and the co-catalyst, when indicated, was injected into the reactor. The autoclave was pressurized with CO₂, and then heated to the specific temperature to reach the desired pressure. After the reaction time, the reactor was cooled with an ice bath and slowly depressurized through a dichloromethane trap. The % conversion was determined by ¹H NMR of the crude mixture by integral ratio between alkene oxide and cyclic carbonate. The work-up was as follow depending on the substrate.

2.9. Work-up for cyclohexene oxide: the final mixture 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. The final residue was washed several times with hexane to purify the poly(cyclohexene carbonate) and was analyzed by ¹H NMR spectroscopy. The productivity in polymer was calculated from the mass of the isolated product-weight of the catalyst and co-catalyst [34]. The % of CO₂ content

was calculated from ^1H NMR data by the integral ratio between copolymer carbonate linkages ($\delta = 4.65$ ppm) respect to ether linkage signals ($\delta = 3.45$ ppm).

2.10. Work-up for styrene oxide, propylene oxide, 1,2-epoxyhexane, 1,2-epoxydodecane, epichlorohydrin and cyclooctene

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 CH_2Cl_2 and passed through a silica pad to remove the catalyst. 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.

3. Results and discussion

3.1. Catalysts synthesis

The *meso*-substituted porphyrins 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin (TDCPP) and 5,10,15,20-tetra(2,6-difluorophenyl)porphyrin (TDFPP) were prepared according to our previously reported methods by mixing equimolar amounts of pyrrol with the desired aldehydes in acetic acid/nitrobenzene using zeolite NaY as solid catalyst [35,36], while their Mn(III) complexes **1**, **2** and **3** were prepared by metal insertion with the appropriate metal salts ($\text{Mn}(\text{OAc})_2$ in the case of **1** and **2** and MnCl_2 for **3**), using DMF as solvent [37] (Scheme 1).

3.2. Catalytic polymerization studies

The effect of the halogen atoms at the 2,6-positions of the phenyl ring in *meso*-substituted porphyrin manganese(III) complexes was evaluated on the copolymerization

of CO₂ and cyclohexene oxide, in the absence of any co-catalyst, and the results are presented in Table 1. First, the catalytic activity of complex **1** on the copolymerization of CO₂ with cyclohexene oxide, at the same reaction conditions reported by Inoue et al. (0.2 molar % respect to epoxide, 50 bar of CO₂ and 80 °C) [27] was tested.

Complex **1**, bearing chlorine atoms in its structure, in absence of co-catalyst selectively afforded the poly(cyclohexene carbonate) (no cyclic carbonate was detected by ¹H NMR) with 84 % epoxide conversion and 72 % of polymer isolated yield (entry 1, Table 1). Additionally, very high alternate incorporation of CO₂ into the polymer linkages was obtained (98 %), with 4700 g/mol molecular weight.

Then, catalyst loading optimization was performed (from 0.07 mol% to 0.01 mol%; entries 2-4, Table 1) leading to a maximum TOF of 154 h⁻¹ at very low catalyst loading (0.01 mol %, entry 4, Table 1), which is nearly tenfold higher than the result previously described using the non-halogenated Mn(III)TPP-OAc catalyst [27]. Furthermore, the molecular weight of the copolymer obtained using catalyst **1** increased up to 5300-8800 g/mol, concomitantly with very narrow polydispersity (M_w/M_n = 1.09, 1.20; entries 2-3, Table 1). Next, decreasing the temperature to 60 °C, using catalyst **1** at 0.07 mol %, only 56 % of epoxide conversion and 47% isolated yield were obtained, but achieving the highest molecular weight polycarbonate (8800 g/mol ;entry 5, Table 1).

Catalyst **1** was still active using 1 bar of CO₂, although the reaction proceeded slower than under 50 bar of CO₂, since 43 % conversion and 39 % isolated yield of polycarbonate were obtained only after 90 h (entry 6, Table 1). Moreover, the use of catalyst **1** and dimethylaminopyridine (DMAP) as co-catalyst induced a decrease in the epoxide conversion towards the polycarbonate, and a mixture of polymer and cyclic monomeric carbonate was obtained (entry 7, Table 1). These results are in good agreement with the ones reported by Inoue and coworkers using [Mn(OAc)(TPP)]

catalyst [27]. An attempt to run the reaction at supercritical conditions (120 bar, 80 °C) produced only 10 % conversion toward polycarbonate, showing low incorporation of carbonate linkages (74 %) and low molecular weight (700 g/mol, entry 8, Table 1), which may be attributed to the low solubility of the catalyst in the supercritical media.

In addition, catalyst **2** (0.2 mol %; PCO₂=50 bar; T=80°C), possessing fluorine atoms in its structure, was also evaluated under the same reaction conditions, and 92 % epoxide conversion with 77 % polymer isolated yield was obtained (entry 9, Table 1) presenting higher conversion than **1** (entry 1, Table 1). In this case, the average molecular weight of the polycarbonate obtained was 6000 g/mol, displaying a narrow polydispersity ($M_w/M_n = 1.11$).

To corroborate the relevance of the presence of halogens on the catalyst structure a comparative experiment using **Mn-TPP** as catalyst (0.01 mol %) at 50 bar and 80°C was carried out and only 3% conversion was obtained (entry 10 vs 4, Table 1).

In sum, it can be clearly seen that the presence of halogens at the *meso*-phenyl groups of the Mn(III) porphyrins plays a key role on the efficiency of the catalysts on the reaction of cyclohexene oxide with CO₂ (entries 1, 9 and 10, Table 1), being the halogenated ones the best performing catalysts. Moreover, the addition of co-catalyst (DMAP) also caused a significant decrease of the conversion of cyclohexene oxide (entries 7, Table 1), which demonstrates the considerable effect of the fifth axial ligand. As proposed by Rao et al., the competitive effect of free DMAP decreased conversion and selectivity [38].

3.3. Catalytic monomeric carbonate synthesis

Using the best reaction conditions previously determined, the scope of catalyst **1** was analyzed in the reaction of CO₂ with different epoxides, at 0.07 mol % catalyst loading, 50 bar of CO₂ pressure and temperature of 80 °C (Scheme 2).

When terminal epoxides such as styrene oxide, propylene oxide and tetradecylene oxide were used as substrates, the corresponding cyclic carbonates were exclusively formed in 56, 54 and 6% isolated yields, respectively (entry 1-3, Table 2). In the case of hexylene oxide, the presence of the corresponding polycarbonate was detected by ¹H NMR spectroscopy by comparison with reported data [39]. The presence of acetate (AcO⁻) as Mn(III)porphyrin axial ligand enhances the efficiency of the catalyst, when compared with the corresponding Mn(III)porphyrin bearing chloride (Cl⁻) as axial ligand (entries 1 and 2, Table 2).

In the case of propylene oxide and 1,2-epoxyhexane, a co-solvent (CH₂Cl₂) was required due to the low solubility of the porphyrin complex in the epoxide. It is worth mentioning the excellent conversion (> 98%) and selectivity (> 98%) obtained in the cycloaddition reaction of epichlorohydrin with CO₂ (entry 6, Table 2). Conversely, reaction of cyclic cyclooctene oxide with CO₂ did not occur, neither in the presence of **1** nor using a combination of catalyst **1** and DMAP as co-catalyst (entries 7-8, Table 2).

In sum, when terminal epoxides were used, the selectivity for the production of cyclic carbonates was very high, while when cyclohexene oxide was used it was found that the reaction selectivity shifted toward the production of polycarbonates

3.4. MALDI-TOF determination of poly(cyclohexene carbonate) chain end groups

The polycarbonate chain end groups obtained in the experiments described in Table 1, at entry 5 (using catalyst **1** at 50 bar, 60°C), at entry 6 (using catalyst **1** at 1 bar, 80 °C) and entry 7 (using catalyst **1**/DMAP), were analyzed by matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) (Supplementary Information). They all presented repeating peaks at differences of 142 m/z corresponding to a cyclohexylcarbonate $-C_6H_{10}C(O)O-$ repeating unit. A common main peak distribution was observed in all three cases, attributed to fragments at m/z 1149.50, that may correspond to a chain with two $-OH$ terminal groups (**a** + K in Scheme 3, expected for $n = 7$ $HO(C_7H_{10}O_3)_7C_6H_{10}OH$; m/z 1149.52). Using catalyst **1**/DMAP a different mass spectrum peak distribution was observed, which fitted with the presence of $DMAP^+$ as end group (**b** + H) as well as $-OH$ (observed m/z 1215.66; expected for $n = 7$ $[(DMAP)(C_7H_{10}O_3)_7C_6H_{10}OH]^+$; m/z 1215.60).

The formation of poly(cyclohexene carbonate) using catalyst **1** alone (a, Scheme 4) suggests that the initiation step involves the epoxide opening by a nucleophilic attack, with $-OH$ arising from water traces present in the reactor (Scheme 5). On the other hand, when DMAP is present, the formation of polymer b (Scheme 6) may be explained by an initiation step involving nucleophilic attack of DMAP to the coordinated epoxide and a termination step produced by hydrolysis (Scheme 7). The role of DMAP as initiator in the CO_2 /propylene oxide polymerization using salen- and salan-Cr(III)/DMAP catalytic systems was studied by Rao et al. [38]. They proposed that coordination of DMAP took place before the opening of the epoxide, and simultaneously, the axial ligand anion produced the initiation. Contrary, Darensbourg and co-workers proposed that DMAP coordinates to Mn center and subsequently activate the CO_2 to afford a weak zwitterionic carbamic complex, followed by a reaction with CHO to provide a stabilized zwitterion [22] We did not find any chain end

containing a carbamate or acetate group; therefore, the role of DMAP should be the ring opening of the epoxide although we do not have evidences whether it coordinates prior to nucleophilic attack.

5. Conclusions

We demonstrated the significantly beneficial presence of halogen atoms at the *meso*-phenyl groups of the Mn(III) porphyrins, which act as catalysts for the copolymerisation of cyclohexene oxide with CO₂, without the presence of any co-catalyst, yielding poly(cyclohexene carbonate), with TOF up to 154 h⁻¹. Moreover, we also observed a strong influence of the Mn(III)porphyrin fifth axial ligand, where acetate (AcO⁻) enhanced the efficiency of the catalyst, while chloride (Cl⁻) and DMAP axial ligands almost inhibited the reaction.

In addition, a direct correlation between the nature of the epoxide structure and the catalyst used was observed, using the same reaction conditions. Thus, while terminal epoxides form cyclic carbonates with high selectivity by cycloaddition with CO₂, cyclohexene oxide selectively react in the copolymerization with CO₂, forming exclusively poly(cyclohexene carbonate).

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Figure Caption

Scheme **Error! Main Document Only..** a) Cycloaddition and b) copolymerization of CO₂ with epoxides

Scheme 1. Synthesis of complexes **1-3**

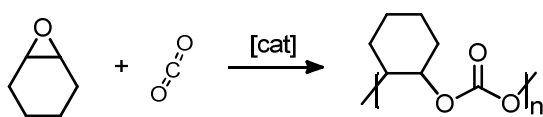
Scheme **Error! Main Document Only..** Cycloaddition of CO₂ with different epoxides.

Scheme 3. General mechanism proposed for the formation of polycarbonate chains **a** and **b**

Figure **Error! Main Document Only..** Manganese(III) meso-substituted porphyrin based complexes.

Tables









Table **Error! Main Document Only**. Copolymerization of cyclohexene oxide (CHO) and CO₂ using catalysts **1**, **2**, and **Mn-TPP**.^a



Entry	Cat	Cat (mol %)	P (bar)	T (° C)	Conv ^b (%) (TOF)	% CO ₂ content ^c	Yield ^d (%)	M _n ·10 ³	M _w /M _n ^e
1	1	0.2	50	80	84 (17)	98	72	4.7	1.50
2	1	0.07	50	80	75 (19)	96	52	8.8 ^f	1.20
3	1	0.036	50	80	76 (86)	96	71	5.3	1.09
4	1	0.01	50	80	37 (154)	96	29	3.3	1.09
5	1	0.07	50	60	56 (33)	98	47	8.8 ^f	1.22
6 ^g	1	0.07	1	80	43 (25)	91	39	1.7	1.12
7 ^{h,i}	1	0.07	50	80	33 (19)	89	23	1.4	1.14
8	1	0.07	120	80	10 (6)	74	10	0.7	1.11
9	2	0.2	50	80	92 (19)	98	77	6.0	1.11
10	MnTPP	0.01	50	80	3 (13)	51	n.d.	n.d.	n.d.

^a Reaction conditions: t = 24h, n.d. = not determined. ^b % Based on ¹H NMR. ^c Determined by ¹H NMR integral ratio of carbonate linkages/(carbonate linkages+ether linkages). ^d Isolated yield. ^e Determined by GPC using polystyrene as standard. ^f bimodal ^g90h ^h using DMAP/**1** = 1/1. ⁱ 78 % selectivity, 22 % cyclic carbonate

Table **Error! Main Document Only..** Cycloaddition of CO₂ to different epoxides using catalyst **1**.

Entry	Epoxide	Cat.	Solvent (mL)	Co-cat (mmol)	Conv. (%) ^b	Select. (%) ^b
1		1	-	-	56	> 98
2		3	-	-	6	>98
3		1	CH ₂ Cl ₂ (1.2)	-	54	> 98
4		1	CH ₂ Cl ₂ (1.8)	-	74	77 ^c
5		1	CH ₂ Cl ₂ (1.8)	-	6	> 98
6		1	-	-	> 98	> 98
7		1	CH ₂ Cl ₂ (3)	-	< 2	< 2
8		1	CH ₂ Cl ₂ (3)	DMAP (0.025)	< 2	< 2

^a Reaction conditions: 35 mmol of epoxide and 0.025 mmol of catalyst (epoxide/catalyst = 1400 /1), P = 50 bar, T = 80 °C, t = 24 h. ^b Estimated by ¹H NMR. ^c 23 % polycarbonate