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# Design of simple salophen chromium complexes for a two-steps oxidative carboxylation of styrene with CO<sub>2</sub> and O<sub>2</sub>

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## Abstract

In this work, chromium(III) Salophen complexes bearing tertiary dimethyl or diethyl amino substituents were synthesized and tested as homogeneous co-catalysts associated with <sup>n</sup>-Bu<sub>4</sub>NBr for the cycloaddition of CO<sub>2</sub> on styrene epoxide under 11 bar of CO<sub>2</sub>. Full conversion of styrene oxide into styrene carbonate was obtained after 23 h reaction at 50°C using Salophen-Me<sub>2</sub>N-Cr. These results emphasized that tertiary amine groups born by the aromatic cycles of Salophen clearly enhanced the co-catalytic activity of the corresponding Cr(III) complex. The direct conversion of styrene into styrene carbonate was then conducted at 80°C with O<sub>2</sub> and CO<sub>2</sub> either under a single set of conditions (reactants and catalysts together) or using a two-steps transformation. The latter was based on the prior epoxidation of styrene in the presence of isobutyraldehyde and O<sub>2</sub> (3.5 bar) with a delayed addition of the cycloaddition catalysts (<sup>n</sup>-Bu<sub>4</sub>NBr and Salophen-Me<sub>2</sub>N-Cr) and CO<sub>2</sub> (11 bar). Using these conditions, the maximum yield of styrene carbonate, obtained after 3 h of epoxidation and 20 h of cycloaddition (with Salophen-Me<sub>2</sub>N-Cr), was 31% at 80°C. This work demonstrates that the key-point to afford a high styrene carbonate global yield with that system was related to the implementation of a two-step protocol, since it allowed to minimize the amounts of undesired by-products.

## Introduction

The large amounts of carbon dioxide, released in atmosphere by human activities significantly contribute to the greenhouse effect. In this context, carbon dioxide utilization processes that convert CO<sub>2</sub> into commercially viable products are regarded with large interest[1] and research concerning CO<sub>2</sub> transformation has led to significant progress. [2] Nowadays, the utilization of CO<sub>2</sub> for the global production of chemicals ranges only 170 Mt/y worldwide and is dominated by the synthesis of urea (140 Mt/y).[3] Among the targeted molecules, cyclic carbonates offer many advantages as they are widely used in the manufacture of industrial products such as solvents, paint-strippers, lithium batteries, and biodegradable

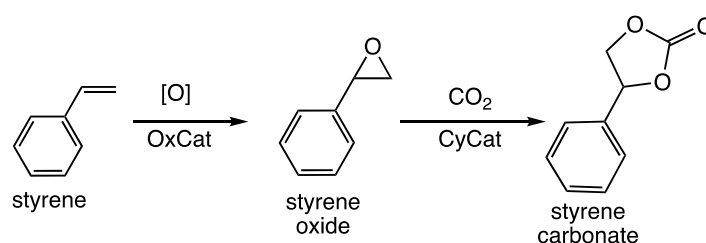
packaging. [4] Their typical industrial synthesis involves the reaction of glycols with phosgene, leading to the generation of environmentally harmful chlorinated wastes. However, a greener pathway involving the use of CO<sub>2</sub> also exists, requiring cycloaddition reaction of CO<sub>2</sub> onto epoxides. [5] Nowadays, ethylene cyclic carbonate is currently produced by BASF and Chimei-Asahi using CO<sub>2</sub> in the presence of quaternary ammonium salts as catalysts. [6] The process is carried out in drastic reaction conditions with high temperature (120-160°C) and CO<sub>2</sub> pressure (30-80 bar). As the result, the development of new processes to lower these reaction conditions is an important area of research. [7]

Furthermore, epoxides used as starting materials for the cycloaddition reaction can be obtained at laboratory or industrial scale either from chlorohydrin process (nearly 50% of the industrial production of propylene oxide) or by the transfer of an oxygen atom from an oxidant to the corresponding alkene. In this regard, the most common oxidants are peracids, but catalytic systems involving NaOCl,[8] iodobenzene PhIO[9] or organic hydroperoxide such as *tert*-butyl-hydroperoxide (TBHP) are also used.[10] The common drawback of all of these oxidants is related to the production of stoichiometric amounts of non-valuable by-products. In this context, there is a strong need for catalytic processes using “greener” oxidants such as dioxygen or hydrogen peroxide. Both offer the advantages of a high oxygen availability (50% for O<sub>2</sub> and 47% for H<sub>2</sub>O<sub>2</sub>) and releasing water as the only side-product.[11] Industrial production of epoxide using O<sub>2</sub> actually exists only in the case of propylene oxide in the presence of a silver-based catalyst.[12] In the case of alkenes with longer alkyl chains, the activation of the kinetically stable O<sub>2</sub> molecule implies the use of electron donors. One example of such approach is the so-called Mukaiyama epoxidation reaction which is considered as a promising pathway for the utilization of O<sub>2</sub> in mild conditions.[13]

Among all catalytic systems described in the literature, Schiff base metal complexes found a wide diversity of applications as catalysts or co-catalysts,[14] in particular for oxidation reactions (OxCat)[15] and CO<sub>2</sub> cycloaddition onto epoxides (CyCat) at once.[16] Indeed, the easy synthesis of the N<sub>2</sub>O<sub>2</sub> salen ligands and salophen derivatives in the corresponding complexes allows a great flexibility in their functionalization. Whatever the applications targeted, general strategies to tune the properties of such complexes are based on the introduction of substituents on the aromatic rings. Hence, bulky groups turned out to be useful to control the approach of substrates while groups with pronounced electron-withdrawing/donating properties have proved to be helpful to adjust the Lewis acidity of the metal center. The later strategy is worth to try when Schiff base metal complexes are used as co-catalysts in the formation of cyclic carbonates which are expected to be favored in the presence of strong Lewis acids.[17] However, some studies focused also on the use of electron

donating amino groups  $-R_2N$ . The very first investigation of salen complexes bearing  $-Et_2N$  groups as co-catalysts for cycloaddition with  $CO_2$  was described by Ulusoy and co-workers.[18] However, the most exciting results were obtained by North's group, who presented interesting yields (86%) at ambient temperature and 1 bar of  $CO_2$ , using such amino-functionalized salophen ligands.[19] Despite low TOF in this case, this remains one of the few examples of  $CO_2$  being used as a  $C_1$  precursor at such low pressure.

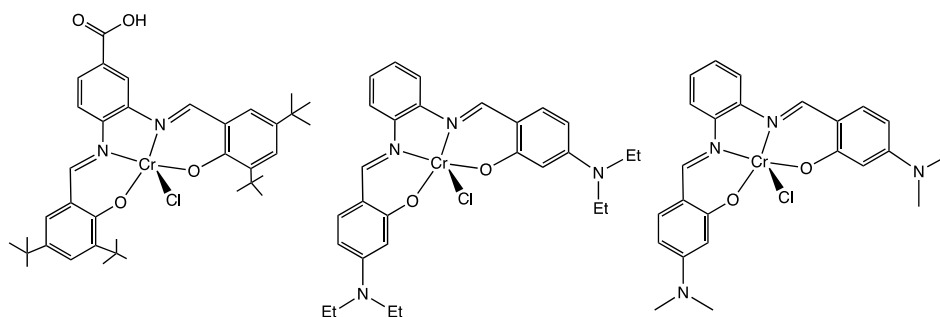
The present study was focused on the utilization of such salophen complexes as (co)-catalysts for alkenes epoxidation and  $CO_2$  cycloaddition onto epoxides at once (oxidative carboxylation of alkenes). The use of the same species for both reactions indeed opened the way to the direct synthesis of cyclic carbonates from alkenes, as described in scheme 1.



**Scheme 1:** Sequential synthesis of styrene carbonate through styrene epoxidation/ $CO_2$  cycloaddition on styrene oxide using an oxidant [O] and  $CO_2$ .

## Experimental

In this work, three Cr(III) complexes will be compared.

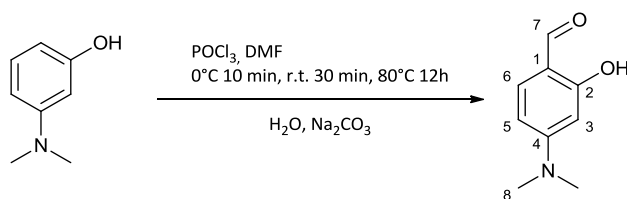


**Scheme 2:** Salophen-tBu-Cr, Salophen-Et<sub>2</sub>N-CrCl and Salophen-Me<sub>2</sub>N ligand (from left).

The Cr(III) complex obtained from the salophen-tBu ligand (Salophen-tBu-Cr) was prepared in agreement with the synthesis procedures previously described. [20-21]. The Salophen-Et<sub>2</sub>N ligand was synthesized according to the literature.[22] The details of the preparation, the characterization of Salophen-Et<sub>2</sub>N and of the corresponding Cr-Cl (Salophen-Et<sub>2</sub>N-CrCl), as well as Mn-Cl (Salophen-Et<sub>2</sub>N-MnCl) complexes are described in the supplementary information (Figures S1 to S3). See also Figure S8 for a global schematic overview of the synthetic protocols.

### - Catalysts synthesis and characterization in the Salophen-Me<sub>2</sub>N series

### Preparation of 4-(dimethylamino)-2-hydroxy-benzaldehyde [23]



**Scheme 3:** Synthesis reaction and labelling of 4-(dimethylamino)-2-hydroxy-benzaldehyde.

Phosphorus oxychloride ( $\text{POCl}_3$ ) (7 mL, 75 mmol) was added dropwise to a solution of 3-(dimethylamino)phenol (5.00 g, 36.5 mmol) in 15 mL dry DMF at  $0^\circ\text{C}$  over 10 min, then the reaction mixture was stirred for 30 min at room temperature, followed by 12 h at  $80^\circ\text{C}$ . After cooling to room temperature, 80 mL of distilled water was added and the resulting mixture was poured into crushed ice and neutralized by 60 mL of a saturated aqueous solution of  $\text{Na}_2\text{CO}_3$ . 4-(dimethylamino)-2-hydroxy-benzaldehyde (4.1 g) was recovered by filtration, washed with water and dried in a vacuum oven at  $25^\circ\text{C}$  for 4 h. Yield: 66%, m.p.  $79\text{--}80^\circ\text{C}$  (lit.  $80.5\text{--}81^\circ\text{C}$ ).<sup>[23]</sup> Later, 4-(dimethylamino)-2-hydroxy-benzaldehyde (or 4-(dimethylamino)salicylaldehyde) was used without further purification.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , Figure S4, ppm)  $\delta = 11.57$  (1H, s, C(2)OH), 9.50 (1H, s, C(7)H), 7.28 (1H, d, C(6)H), 6.27 (1H, d, C(5)H), 6.06 (1H, s, C(3)H), 3.05 (6H, s, C(8) $\text{H}_3$ ), see scheme 3 for  $^1\text{H}$  NMR labelling.

### Preparation of *N,N'*-bis(4-dimethylaminosalicylidene)-1,2-phenylenediamine (Salophen- $\text{Me}_2\text{N}$ ligand).

1,2-phenylenediamine (0.540 g, 5 mmol) was introduced in a two-neck round-bottom flask connected to a condenser under argon and dissolved in 50 mL of pure EtOH. In parallel, a solution of 4-(dimethylamino)salicylaldehyde (1.65 g, 10 mmol) in the same solvent (50 mL) was prepared under argon. This solution was then added dropwise using a syringe to the solution of 1,2-phenylenediamine over a period of 20 min. Thereafter, the mixture was stirred at room temperature for 72 h. The yellow solid formed (Salophen- $\text{Me}_2\text{N}$ ) was recovered by filtration on a glass frit ( $n^\circ 4$ ), rinsed twice with 20 mL of pure EtOH and 30 mL of petroleum ether and dried under vacuum, yielding 1.130 g (56%). IR (KBr,  $\text{cm}^{-1}$ ): 3425 (w), 2958 (s), 1686 (m), 1615 (s), 1574 (s), 1438 (m), 1361 (m), 1252 (m), 1172 (s), 1132 (w), 1026 (w), 771 (m)  $\text{cm}^{-1}$ . HRMS [Salophen- $\text{Me}_2\text{NH}^+$ ] (ESI):  $m/z = 403.21$  (Figure S5 (top)).  $^1\text{H}$  NMR ( $[\text{D}^6]$ dmsO, Figure S5 (bottom), ppm):  $\delta_{\text{H}}: 13.50$  (2H, s, C(2)OH), 8.65 (2H, s, C(7)H=N), 7.34 (4H, m, C(10)H + C(6)H), 7.26 (2H, s, C(9)H), 6.35 (2H, d, C(5)H), 6.09 (2H, d, C(3)H), 3.00 (12H, t,  $\text{NCH}_2\text{CH}_3$ ). See scheme S5 for  $^1\text{H}$  NMR labelling. Elem. anal. Calcd for  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2$ : C, 71.62; H, 6.51; N, 13.92. Found: C, 70.48; H, 6.54; N, 13.68.

### Preparation of *N,N'*-bis(4-dimethylaminosalicylidene)-1,2-phenylene-diaminechloro-chromium (III) (Salophen- $\text{Me}_2\text{N-CrCl}$ ).

The Salophen-Me<sub>2</sub>N ligand (0.261 g, 1 eq, 0.65 mmol) was dissolved in 25 mL of dry THF under argon in a two-neck round-bottom flask connected to a condenser, then a solution of [CrCl<sub>3</sub>(THF)<sub>3</sub>] (0.243 g, 1 eq, 0.65 mmol) in 25 mL of dry THF was added dropwise under argon and the resulting mixture was stirred under reflux for 15 min. After cooling at room temperature, the solvent was evaporated under vacuum leading to a dark red solid (Salophen-Me<sub>2</sub>N-CrCl) (yield: 0.317 g, 94%). IR (KBr, cm<sup>-1</sup>): 3416 (m), 2958 (m), 1680 (s), 1610 (s), 1573 (s), 1466 (s), 1392 (s), 1361 (s), 1325 (s), 1249 (s), 1198 (s), 1178 (s), 1097 (s), 1026(s), 807 (s), 781 (s), 548 (m). HRMS [Salophen-Me<sub>2</sub>N-Cr<sup>+</sup>] (ESI): m/z = 452.13 (Figure S6). Elem. anal. Calcd for C<sub>24</sub>H<sub>24</sub>ClCrN<sub>4</sub>O<sub>2</sub>: C, 59.08; H, 4.96; N, 11.48. Found: C, 59.71; H, 5.05; N, 11.08.

***One-pot preparation of N,N'-bis(4-dimethylaminosalicylidene)-1,2-phenylene-diaminechloro-Manganese(III) (Salophen-Me<sub>2</sub>N-MnCl).***

A sample of 1,2-phenylenediamine (0.065 g, 0.60 mmol) was introduced, under argon, in a two-neck round-bottom flask connected to a condenser and dispersed in 10 mL of dry THF. In parallel, a solution of 4-(dimethylamino)salicylaldehyde (0.220 g, 1.2 mmol) in dry THF (10 mL) was prepared under argon and later added dropwise to the solution previously prepared. [MnCl<sub>2</sub>(THF)<sub>2</sub>] (0.160 g, 0.60 mmol) was then added to the mixture and the resulting medium was stirred at room temperature for 1 h, then refluxed for 20 min. After cooling at room temperature, triethylamine (0.12 g, 1.20 mmol, 0.17 mL) was then added and the mixture stirred for another 45 min. Thereafter, the volume of the solution was reduced up to 10 mL under vacuum and the reaction mixture allowed to stand at room temperature overnight. After this period, a white powder (triethylammonium chloride) was filtered and discarded. The solution was evaporated, leading to a brown solid (Salophen-Me<sub>2</sub>N-MnCl) that was recrystallized in toluene (yield: 0.279 g, 0.57 mmol, 95 %). The IR spectrum of the compound is identical to that of Salophen-Me<sub>2</sub>N-CrCl. HRMS [Salophen-Me<sub>2</sub>N-Mn]<sup>+</sup> (ESI) : m/z = 455.13 (Figure S7). Elem. anal. Calcd for C<sub>24</sub>H<sub>24</sub>ClMnN<sub>4</sub>O<sub>2</sub>: C, 58.73; H, 4.93; N, 11.41. Found: C, 59.23; H, 5.10; N, 11.01.

**- Catalytic tests**

***Study of the co-catalytic activity of the Salophen-type complexes in the styrene oxide conversion into styrene carbonate.***

Styrene oxide (StOx, 0.66 mL, 5.6 mmol), catalyst (<sup>n</sup>Bu<sub>4</sub>NBr, 31.1 mg, 96.2 μmol), co-catalyst (Salophen-R-M, 48.3 μmol), GC internal standard (*p*-xylene, 1 mL, 8.0 mmol) and benzonitrile (20 mL) were mixed into a Teflon bucket contained in a stainless-steel autoclave equipped with a magnetic stirrer and an electric heater. The autoclave was then purged with CO<sub>2</sub>, the system was pressurized with 11 bar of CO<sub>2</sub> and heated at the desired temperature. The reaction mixture was stirred for several hours (see Table 1). After each catalytic test, the

resulting reaction mixtures were analysed by gas chromatography GC after dilution of the liquid phase (samples of 25  $\mu\text{L}$  diluted in 10 mL of  $\text{CH}_2\text{Cl}_2$ ).

In all experiments, the possible presence of polycarbonates was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. In any cases, no trace of polymers was detected. This was confirmed by the mass balance determination by GC using *p*-xylene as an internal standard. Thereafter, styrene oxide conversion values will be considered to be equal to styrene carbonate (StCarb) yield values. Styrene carbonate can easily be separated from the reaction mixture by column (silica) separation. To do so, a first elution with a 3:1 cyclohexane:diethylether mixture was used to remove benzonitrile, followed by a second elution with a 1:1 cyclohexane:diethylether mixture. This procedure led to the isolation of approximately 85 to 90% of the amount of styrene carbonate determined by GC.

### ***Protocol for the one-pot oxidative carboxylation of styrene with a delayed addition of $\text{CO}_2$ and Cr(III) catalysts***

Styrene (0.70 mL, 5.6 mmol), isobutyraldehyde (1.33 mL, 15 mmol), GC internal standard (*p*-xylene, 0.66 mL, 5.3 mmol) and 13 mL of benzonitrile were mixed in a Teflon bucket that was further introduced in a stainless-steel autoclave equipped with a magnetic stirrer and an electric heater. The autoclave was then purged and pressurized with 3.5 bar of  $\text{O}_2$  and heated at  $80^\circ\text{C}$ . After 3h at  $80^\circ\text{C}$ , the autoclave was cooled down to room temperature, the oxygen evacuated, and the mixture stirred during 5 min. Later,  $^t\text{Bu}_4\text{NBr}$  (31.1 mg, 96.2  $\mu\text{mol}$ ) and Salophen-R-Cr (48.3  $\mu\text{mol}$ ) were added. The autoclave was then purged and pressurized with 11 bar of  $\text{CO}_2$  and heated at  $80^\circ\text{C}$ . At this end of the experiment, the autoclave was cooled down to room temperature. After each catalytic test, the resulting reaction mixtures were analysed by gas chromatography after dilution (samples of 25  $\mu\text{L}$  diluted in 10 mL of  $\text{CH}_2\text{Cl}_2$ ).

## **Results and discussion**

### **- Synthesis and characterization of the Salophen- $\text{Et}_2\text{N}$ and - $\text{Me}_2\text{N}$ ligands and of the corresponding Mn(III) and Cr(III) complexes.**

Salophen- $\text{Et}_2\text{N}$  was synthesized according to the protocol developed by Abu-Surrah *et al.*[22] by condensation of two equivalents of 4-(diethylamino)-2-hydroxy-benzaldehyde with one equivalent of 1,2-phenylenediamine in ethanol (Figure S8). To our knowledge, the preparation of Salophen- $\text{Me}_2\text{N}$  was not yet reported in the literature but it was easily adapted from the protocol for Salophen- $\text{Et}_2\text{N}$  using 1,2-phenylenediamine and 4-(dimethylamino)-2-hydroxy-benzaldehyde. The latter was prepared according to the protocol of Awwadi *et al.*[23] Salophen- $\text{Et}_2\text{N}$  and Salophen- $\text{Me}_2\text{N}$  were obtained as yellow solids in a single step in ethanol after 72 h reaction at room temperature, with 36 and 56% yields, respectively. Both ligands were characterized by  $^1\text{H}$  NMR (Figures S1 and S5) and FTIR. The Salophen- $\text{Et}_2\text{N}$ -CrCl and Salophen- $\text{Me}_2\text{N}$ -CrCl complexes were then obtained (both with

94% yield) by direct reaction of  $[\text{CrCl}_3(\text{THF})_3]$  with one equivalent of the corresponding Salophen ligands in THF. Both complexes were characterized by FTIR and HRMS (see Figures S3 and S6). Meanwhile, the corresponding  $\{\text{Mn}(\text{III})\text{-Cl}\}^{2+}$  Salophen complexes were prepared with 95% yield by one-pot synthesis starting from one equivalent of 1,2-phenylenediamine and two equivalents of the corresponding aldehydes in the presence of one equivalent of  $[\text{MnCl}_2(\text{THF})_2]$  as the manganese source. Both manganese complexes were characterized by FTIR and HRMS analysis (see Figures S2 and S7).

**- Comparison of the activity of the Salophen complexes as co-catalysts in styrene oxide conversion into styrene carbonate.**

Tetrabutylammonium bromide ( $n\text{-Bu}_4\text{NBr}$ ) was utilized as  $\text{CO}_2$  cycloaddition catalyst (CyCat) in the presence of either Salophen- $t\text{Bu-CrCl}$ , Salophen- $\text{Et}_2\text{N-CrCl}$  or Salophen- $\text{Me}_2\text{N-CrCl}$ . The reactions were conducted under initial pressure of 11 bar of  $\text{CO}_2$  (measured at r.t.) at 80, 60 and  $50^\circ\text{C}$  in benzonitrile during 1, 3, 7 and 23 h. Results in Table 1 showed that, at 80 or  $60^\circ\text{C}$ , a complete conversion of styrene oxide into styrene carbonate was achieved for most of the co-catalysts after 23 h (see Table 1, entries 4-9).

**Table 1:** Styrene carbonate yield with soluble Salophen-chromium co-catalysts.

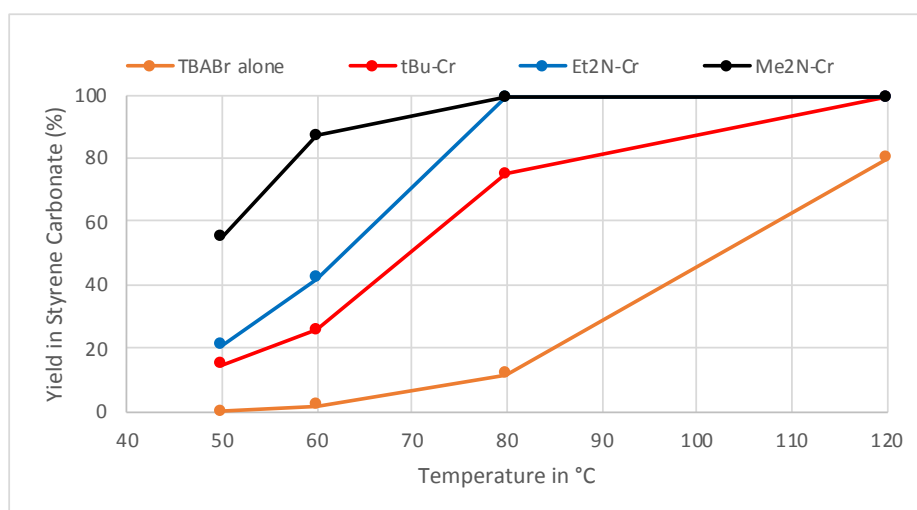
Entry	Co-catalyst	T ( $^\circ\text{C}$ )	Styrene carbonate yield (%)			
			1 h	3 h	7 h	23 h
<b>1</b>	Salophen- $\text{Me}_2\text{N-Cr}$	50	20	55	75	100
<b>2</b>	Salophen- $\text{Et}_2\text{N-Cr}$		8	21	40	89
<b>3</b>	Salophen- $t\text{Bu-Cr}$		5	15	29	67 [21]
<b>4</b>	Salophen- $\text{Me}_2\text{N-Cr}$	60	31	87	100	100
<b>5</b>	Salophen- $\text{Et}_2\text{N-Cr}$		16	42	79	100
<b>6</b>	Salophen- $t\text{Bu-Cr}$		12	26	47	96 [21]
<b>7</b>	Salophen- $\text{Me}_2\text{N-Cr}$	80	100	100	100	100
<b>8</b>	Salophen- $\text{Et}_2\text{N-Cr}$		78	100	100	100
<b>9</b>	Salophen- $t\text{Bu-Cr}$		41	75	92	100 [21]

Conditions: Styrene oxide (5.6 mmol),  $n\text{-Bu}_4\text{NBr}$  (0.1 mmol, 1.8 mol%), Salophen- $\text{Cr}(\text{III})$  (0.05 mmol, 0.9 mol%) in 13 mL of benzonitrile under 11 bar of  $\text{CO}_2$ .

Regarding the conversion of styrene oxide at the lowest temperatures ( $50$  and  $60^\circ\text{C}$ ), Salophen complexes with ligands bearing amino groups, especially dimethyl amino ones, clearly stood out compared to Salophen- $t\text{Bu-Cr}$  (Table 1, entries 1-3 and 4-6).[21] Hence, the styrene oxide conversion was almost complete after 23 h at  $50^\circ\text{C}$  in the case of Salophen- $\text{Et}_2\text{N-Cr}$  and 100% for Salophen- $\text{Me}_2\text{N-Cr}$ , while Salophen- $t\text{Bu-Cr}$  led to 67% only. As the result, Cr Salophen- $\text{Me}_2\text{N-Cr}$  was shown to be the most efficient co-catalyst among those tested, while affording a full conversion of styrene oxide within 7 h at  $60^\circ\text{C}$  (Table 1, entry 4). Additional tests performed within 1 h showed that a complete conversion of styrene oxide could be obtained in the case of Salophen- $\text{Me}_2\text{N-Cr}$  at  $80^\circ\text{C}$ . As expected, in the absence of  $n\text{-Bu}_4\text{NBr}$  no catalytic activity towards styrene carbonate was observed whatever the catalyst and/or the temperature used.



To better emphasize the influence of the metal complexes as co-catalysts, a series of reactions were conducted for 3 h at 50, 60, 80, and 120°C in their presence (either Cr(III) or Mn(III) complexes) or absence. As seen in Figure 1 (see also Table S1, entry 5 for details),  $n\text{-Bu}_4\text{NBr}$  alone (1.8 mol%) was found efficient in the cycloaddition process only at 120°C (styrene carbonate yield of 80% at 3 h). Hence, lower reaction temperatures allowed to better estimate the influence of the co-catalyst. While poor catalytic activity remained with  $n\text{-Bu}_4\text{NBr}$  alone at 80°C (12% for styrene carbonate yield, after 3h, Table S1, entry 5), it was possible to achieve much higher styrene carbonate yields with the addition of Salophen- $t\text{Bu-Cr}$  (75%, Table S1, entry 3) or *a fortiori* with Salophen-Cr(III) bearing tertiary amino groups (quantitative reaction for both complexes, Table S1, entries 1 and 2). As previously mentioned,[21]  $n\text{-Bu}_4\text{NBr}$  alone (1.8 mol%) was not active at 60 and 50°C, so that co-catalysts were mandatory to perform the cycloaddition reaction at lower temperatures. In comparison, the Mn(III) complex based on Salophen- $\text{Me}_2\text{N-Mn}$  was also efficient enough to achieve a 100% yield of styrene carbonate at 120 and 80°C, but failed for lower temperatures such as 60 and 50°C (see Table S1, entry 4). This comforted us in the choice of chromium(III) as a preferable metal centre for the cycloaddition reaction of  $\text{CO}_2$  onto styrene oxide.

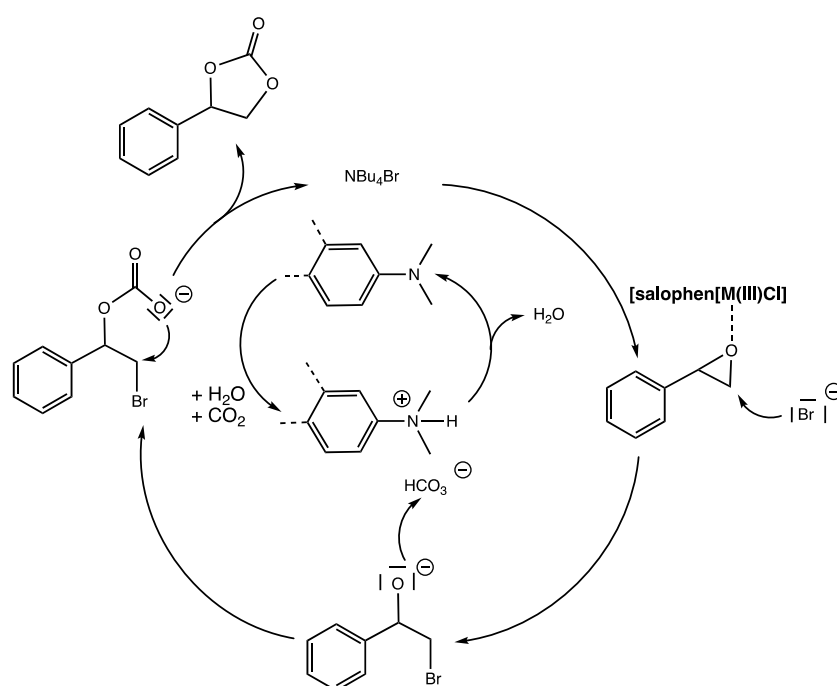


**Figure 1:** Comparison of the efficiency of  $n\text{-Bu}_4\text{Br}$  alone (in orange) or coupled with Salophen- $\text{Me}_2\text{N-Cr}$  (in black), Salophen- $\text{Et}_2\text{N-Cr}$  (in blue) and Salophen- $t\text{Bu-Cr}$  (in red) for the  $\text{CO}_2$  cycloaddition on styrene oxide within 3 h. Conditions: Styrene oxide (5.6 mmol),  $n\text{-Bu}_4\text{NBr}$  (0.1 mmol, 1.8 mol%), Salophen-M (0.05 mmol, 0.9 mol%) in 13 mL of benzonitrile under 11 bar of  $\text{CO}_2$  with  $50 < T < 120^\circ\text{C}$ .

These results led to the conclusion that the introduction of amino substituents onto Salophen ligands is beneficial to the  $\text{CO}_2$  cycloaddition reaction, as mentioned by others.[19] These results thus represent a significant improvement in the performance of Schiff base catalysts, which we have been studying systematically for some years with the idea to couple alkene epoxidation under mild conditions with  $\text{CO}_2$  cycloaddition.

Regarding the mechanism of cycloaddition of  $\text{CO}_2$ , previous DFT studies [24] suggested that salophen ligands can play an important steric role in their ability to provide an optimal environment to the metal ion at which the reaction takes place. The role of tertiary amines (such as the dimethyl or

diethyl aniline groups in our case) has been frequently mentioned or discussed in the literature of CO<sub>2</sub> cycloaddition. With N,N-dialkylbenzylamines, Gao and co-workers showed that the positive influence of the tertiary amines was obtained only after water addition.[25] Indeed, a significantly higher epichlorohydrin carbonate yield was emphasized in the presence of 0.4% of water which led these authors to propose a base-assisted mechanism. N,N-dialkylbenzylamine, added as a co-catalyst, would react with CO<sub>2</sub> and H<sub>2</sub>O leading to the formation of the corresponding ammonium hydrogen carbonate. The latter would then react with the opened form of the epoxide obtained after the attack by bromide, leading to the release of a water molecule and, in the end, to the cyclic carbonate. In our case, we suspected that amino groups borne by Salophen ligands close to the metal centre behaved similarly (see Figure 2). Compared to what was proposed by Gao and co-workers,[25] the metal centre present in our system played the role of a Lewis acid centre able to activate the epoxide in a better way than NBu<sub>4</sub><sup>+</sup> alone, as suggested by the literature.[17] In the absence of any drying treatments of benzonitrile and of CO<sub>2</sub> gas, we estimated that residual water in the reaction medium is *c.a.* 0.15 mol%. However, it was not possible to detect any trace of hydrogen carbonate by *in situ* infra-red monitoring, which is probably not sensitive enough.



**Figure 2:** Proposed <sup>n</sup>Bu<sub>4</sub>NBr /tertiary amine mechanism for the cycloaddition of CO<sub>2</sub> onto styrene oxide (adapted from reference [25]).

### - One-pot oxidative carboxylation of styrene using CO<sub>2</sub> and O<sub>2</sub>

Quaternary ammonium salts and Salophen complexes, such as those of Cr(III) and Mn(III), can be used in the one-pot conversion of styrene into styrene carbonate with O<sub>2</sub> and CO<sub>2</sub>. At best, this transformation involving both oxidation and cycloaddition steps should meet several criteria. First, a unique solvent should be used. Here, benzonitrile was selected since both individual steps were previously successfully performed by us in this solvent [20],[21],[26],[27] with similar

reagents/products concentrations. Here, the respective concentrations of the different reagents, *i.e.* Substrate :  $n\text{-Bu}_4\text{NBr}$  : Salophen complexe, were adjusted to *ca.* 112 : 2 : 1. Secondly, unique temperature conditions should be adopted during the duration of the whole transformation. In our case, it has been demonstrated that both oxidation [28] and cycloaddition (this paper) steps could be carried out efficiently at 80°C or below. Ideally, O<sub>2</sub> and CO<sub>2</sub> reactants, as well as the metal complex (used here as epoxidation catalyst and cycloaddition co-catalyst) and  $n\text{-Bu}_4\text{NBr}$  (used as cycloaddition catalyst) should be introduced at the beginning of the experiment.

Recently, we described the oxidative carboxylation of styrene with O<sub>2</sub> and CO<sub>2</sub> using Salophen-tBu-Cr complex and  $n\text{-Bu}_4\text{NBr}$  in the presence of isobutyraldehyde (IBA), [26] through a one-step approach with a single set of temperature and pressure parameters (see Table S2 for a reminder). The idea was to produce styrene oxide *in-situ* based on a Mukaiyama-type process requiring the use of a sacrificial aldehyde. However, in these conditions the results were disappointing: in the presence of  $n\text{-Bu}_4\text{NBr}$  with both O<sub>2</sub> and CO<sub>2</sub>, a small amount of styrene carbonate could be detected after 3 h (3%), the yield rising to a maximum of 14% after 24 h (see figure S9 for details). Such values were well below what could be expected by combining the yields of the individual reactions (epoxidation of styrene and cycloaddition of CO<sub>2</sub> onto styrene oxide) carried out under similar conditions.

### ***Oxidative carboxylation of styrene with a delayed introduction of CO<sub>2</sub>, (M)Salophen and $n\text{-Bu}_4\text{NBr}$***

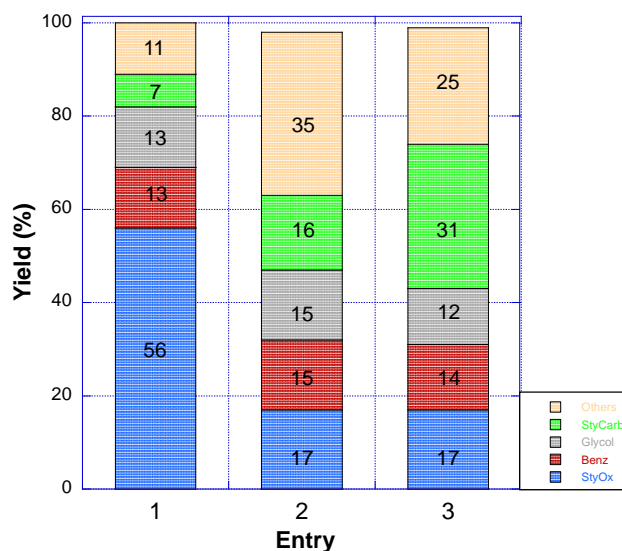
In the present work, a sequential implementation of the two steps in the same reactor was preferred. In this approach, the epoxidation of styrene was conducted first during 3 h at 80°C with the sole IBA under 3.5 bar of O<sub>2</sub>. After cooling, dioxygen was evacuated, then  $n\text{-Bu}_4\text{NBr}$  and the Cr(III) Salophen catalysts were introduced. The pressure was then set at 11 bar of CO<sub>2</sub> and the reaction carried out again at 80°C. The delayed introduction of CO<sub>2</sub>, (M)Salophen and  $n\text{-Bu}_4\text{NBr}$  was justified [26] by the fact that Salophen complexes are not mandatory during the oxidation step at 80°C (see also figure S9, Table S2, entry 1). Experimental settings for three different tests are presented in Table 2 and the corresponding results are displayed in Figure 3.

**Table 2:** Sets of experimental conditions used for the one-pot oxidative carboxylation of styrene with a delayed introduction of CO<sub>2</sub> and of the co-catalysts.

Entry	1	2	3
t (h)			
O <sub>2</sub> <sup>i)</sup>	3	3	3
CO <sub>2</sub> <sup>ii)</sup>	3	20	20
Catalysts	Salophen-tBu-Cr + $n\text{-Bu}_4\text{NBr}$	Salophen-tBu-Cr + $n\text{-Bu}_4\text{NBr}$	Salophen-Me <sub>2</sub> N-Cr + $n\text{-Bu}_4\text{NBr}$
$P_{\text{O}_2}$ (bar)	3.5	3.5	3.5
$P_{\text{CO}_2}$ (bar)	11	11	11

*i)* Styrene (5.6 mmol), isobutyraldehyde (15 mmol) in 13 mL of benzonitrile at 80°C under 3.5 bar of O<sub>2</sub>; *ii)* Addition of Salophen-R-Cr (0.05 mmol, 0.9 mol%),  $n\text{-Bu}_4\text{NBr}$  (0.1 mmol, 1.8 mol%) and 11 bar of CO<sub>2</sub>.

Oxidation conditions were kept constant (3 h, 3.5 bar of O<sub>2</sub>, 2.7 eq of IBA) while cycloaddition was carried out using 1.8 mol% of <sup>n</sup>Bu<sub>4</sub>NBr and either 0.9 mol% of Salophen-tBu-Cr (3 h vs. 20 h) or 0.9 mol% of Salophen-Me<sub>2</sub>N-Cr (20 h) at 80°C too. In the presence of Salophen-tBu-Cr and <sup>n</sup>Bu<sub>4</sub>NBr at 80°C, styrene conversion was complete after 6 h (oxidation time included) but the styrene carbonate yield was only 7% (Figure 3, entry 1). It became 16% after a total of 23 h (figure 3, entry 2), time during which a strong decrease of the styrene oxide quantity was observed. The epoxide was not 100% converted into styrene carbonate since the amount of other secondary products was shown to increase concurrently (from 11% at 6 h to 35 % after 23 h). It is worth noting here that in all the experiments, the yields of benzaldehyde and styrene glycol were similar, which indicates that the formation of these products represents a dead end for the reaction. Furthermore, avoiding the formation of benzaldehyde, which is the result of the oxidative cleavage of the styrene double bond and of styrene glycol was not possible whatever the conditions used.



**Figure 3:** Yields for styrene oxide (in blue), benzaldehyde (in red), styrene glycol (in grey), styrene carbonate (in green), other products (in yellow). *Initial conditions: See Table 2 for details.*

Finally, a more efficient cycloaddition co-catalyst, *i.e.* Salophen-Me<sub>2</sub>N-Cr, as shown earlier in this paper, was also tested. Using these optimized experimental conditions (epoxidation for a 3 h period, followed by 20 h for the CO<sub>2</sub> cycloaddition step), a complete styrene conversion could be emphasized. More encouragingly, a 31% yield of styrene carbonate was obtained which is the highest yield observed in the course of this study (see Figure 3, entry 3).

From a more general point of view, it is noteworthy that only 5 independent studies concerning the use of O<sub>2</sub> as the oxidant for the oxidative carboxylation reaction have so far been conducted and published in the literature.[28] We believe that the catalytic performances of our system are encouraging. In particular, a low-cost metal complex based on the first series

of transition metals, rather than noble metals[29] was used and it was shown that it worked in milder conditions than in the other systems reported in literature.[30] Finally, we would like to emphasize the fact that two separate teams have also recently shown the interest of implementing a sequential one-pot procedure for the overall reaction, especially when a Mukaiyama-type strategy is used for the alkene epoxidation step.[31],[32]

## Conclusion

In this work, chromium(III) Salophen complexes bearing tertiary dimethyl (Salophen-Me<sub>2</sub>N-Cr) or diethyl phenylamino (Salophen-Et<sub>2</sub>N-Cr) groups were successfully synthesized. Their performances as co-catalysts (0.9 mol%) of tetra-*n*-butylammonium bromide (1.8 mol%) were evaluated in the cycloaddition of CO<sub>2</sub> onto styrene epoxide under 11 bar of CO<sub>2</sub>. Excellent yields of styrene carbonate were obtained after 23 h at 50°C using Salophen-Me<sub>2</sub>N-Cr. It comes that the presence of tertiary amine groups on the aromatic cycles of Salophen truly enhanced the co-catalytic activity of the corresponding Cr(III) complexes, in comparison with the Salophen-*t*Bu-Cr previously described. We have hypothesized that the origin of this effect might be due to the reaction of the tertiary amino groups with residual water, leading to the *in-situ* formation of hydrogen carbonate species.

The conversion of styrene into styrene carbonate was conducted at 80°C in one-pot, but proceeding with two steps: first under O<sub>2</sub> (3.5 bar) in the presence of IBA and in the absence of any metal catalyst, then, in the presence of CO<sub>2</sub> (11 bar) after removing O<sub>2</sub> and adding the cycloaddition catalysts (*i.e.* <sup>*n*</sup>Bu<sub>4</sub>NBr (1.8 mol%) and Salophen-R-Cr complex (0.9 mol%)). In these conditions, the yields of styrene carbonate, obtained after 3 h of aerobic epoxidation and 20 h of CO<sub>2</sub> cycloaddition at 80°C, were 16% and 31%, with Salophen-*t*Bu-Cr and Salophen-Me<sub>2</sub>N-Cr, respectively. Such results emphasized the better catalytic efficiency of the amino-functionalized salophen complex, which also tends to minimize the amounts of unwanted co-products. As a final concluding remark, as already mentioned in the literature [30], it is noteworthy that the key-point for a high styrene carbonate global yield is related to the implementation of a multistep protocol at the lowest temperature (here 80°C) instead of a single step one,

## Author Contributions

FL and RV conceptualized and formulated the original ideas for this work. MB carried out the research and investigation process, specifically performing the experiments, and data/evidence collection. The experimental part was supervised and validated by FL and RV. MB collected and formatted the experimental data and bibliography necessary for the writing of the manuscript. The preparation of the first draft of the manuscript was done by RV. FL and MB participated in the writing and correction of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## References

- [1] M. Aresta, I. Tommasi, Carbon dioxide utilization in the chemical industry, *Energy Convers. Manag.* 38 (1997) 373-378. M. Aresta, A. Dibenedetto, A. Angelini, The changing paradigm in CO<sub>2</sub> utilization. *J. CO<sub>2</sub> Util.* 3-4 (2013) 65-73.
- [2] A. W. Kleij, M. North, A. Urakawa, CO<sub>2</sub> Catalysis, *ChemSusChem* 10 (2017) 1036-1038. M. North, Across the Board: Michael North on Carbon Dioxide Biorefinery, *ChemSusChem* 12 (2019) 1763-1765. M. Aresta, My journey in the CO<sub>2</sub>-chemistry wonderland, *Coord. Chem. Rev.* 334 (2017) 150-183. M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, Chemical technologies for exploiting and recycling carbon dioxide into the value chain, *ChemSusChem* 9 (2011) 1216-1240. Special Issue: Catalysis for CO<sub>2</sub> conversion, *ChemSusChem* 10 (2017) 1034-1297. C. Chauvier, T. Cantat, A Viewpoint on Chemical Reductions of Carbon–Oxygen Bonds in Renewable Feedstocks Including CO<sub>2</sub> and Biomass, *ACS Catal.* 7 (2017) 2107-2115. S. Sopena, G. Fiorani, C. Martín, A.W. Kleij, Highly Efficient Organocatalyzed Conversion of Oxiranes and CO<sub>2</sub> into Organic Carbonates, *ChemSusChem* 8 (2015) 3248-3254. M. Cokoja, M.E. Wilhelm, M.H. Anthofer, W.A. Herrmann, F.E. Kühn, Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts, *ChemSusChem* 8 (2015) 2436-2454. M. Alves, B. Grignard, S. Gennen, C. Detrembleur, C. Jerome, T. Tassaing, Organocatalytic synthesis of bio-based cyclic carbonates from CO<sub>2</sub> and vegetable oils, *RSC Adv.* 5 (2015) 53629-53636.
- [3] P. Friedlingstein, M. W. Jones, M. O'Sullivan, R. M. Andrew, D. C. E. Bakker, J. Hauck, C. Le Quéré, G. P. Peters, W. Peters, J. Pongratz, S. Sitch, J. G. Canadell, P. Ciais, R. B. Jackson, S. R. Alin, P. Anthoni, N. R. Bates, M. Becker, N. Bellouin, L. Bopp, T. Tuyen Trang Chau, F. Chevallier, L. P. Chini, M. Cronin, K. I. Currie, B. Decharme, L. M. Djeutchouang, X. Dou, W. Evans, R. A. Feely, L. Feng, T.s Gasser, D. Gilfillan, T. Gkritzalis, G. Grassi, L. Gregor, N. Gruber, Ö. Gürses, I. Harris, R. A. Houghton, G. C. Hurtt, Y. Iida, T. Ilyina, I. T. Luijkx, A. Jain, S. D. Jones, E. Kato, D. Kennedy, K. Klein Goldewijk, J. Knauer, J. Ivar Korsbakken, A. Körtzinger, P. Landschützer, S. K. Lauvset, N. Lefèvre, S. Lienert, J. Liu, G. Marland, P. C. McGuire, J. R. Melton, D. R. Munro, J. E. M. S. Nabel, S.-I. Nakaoka, Y. Niwa, T. Ono, D. Pierrot, B. Poulter, G. Rehder, L. Resplandy, E. Robertson, C. Rödenbeck, T. M. Rosan, J. Schwinger, C. Schwingshackl, Roland Séférian, Adrienne J. Sutton, Colm Sweeney, T. Tanhua, P. P. Tans, H. Tian, B. Tilbrook, F. Tubiello, G. R. van der Werf, N. Vuichard, C. Wada, R. Wanninkhof, A. J. Watson, D. Willis, A. J. Wiltshire, W. Yuan, C. Yue, X. Yue, S. Zaehle, J. Zeng, Global carbon budget 2021, *Earth System Science Data* 14 (2022) 1917-2005, DOI: 10.5194/essd-14-1917-2022.
- [4] T. Sakakura, K. Kohno, The synthesis of organic carbonates from carbon dioxide, *Chem. Commun.* (2009) 1312-1330. M. North, R. Pasquale, C. Young, Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>. *Green Chem.* 12 (2010) 1514-1539.

- [5] S. Fukuoka, M. Kawamura, K. Komiyama, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, A novel non-phosgene polycarbonate production process using by-product CO<sub>2</sub> as starting material, *Green Chem.* 5 (2003) 497-507.
- [6] E.A. Quadrelli, G. Centi, J.L. Duplan, S. Perathoner, Carbon dioxide recycling: Emerging large-scale technologies with industrial potential, *ChemSusChem* 4 (2011) 1194-1215.
- [7] D.J. Darensbourg, M.W. Holtcamp, Catalysts for the reactions of epoxides and carbon dioxide, *Coord. Chem. Rev.* 153 (1996) 155-174.
- [8] B. Meunier, E. Guilmet, M.E. De Carvalho, R. Poilblanc, Sodium hypochlorite: a convenient oxygen source for olefin epoxidation catalyzed by (porphyrinato)manganese complexes, *J. Am. Chem. Soc.* 106 (1984) 6668-6676.
- [9] Y. Yang, F. Diederich and J.S. Valentine, Lewis acidic catalysts for olefin epoxidation by iodobenzene, *J. Am. Chem. Soc.* 113 (1991) 7195-7205.
- [10] M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, M.M. Javadi, Molybdenum Schiff base-polyoxometalate hybrid compound: A heterogeneous catalyst for alkene epoxidation with tert-BuOOH, *Polyhedron* 29 (2010) 648-654.
- [11] R.A. Sheldon, E factors, green chemistry and catalysis: An odyssey, *Chem. Commun.* (2008) 3352-3365.
- [12] J. Tsuji, J. Yamamoto, M. Ishino, N. Oku, Development of New Propylene Oxide Process, *R&D Reports Sumitomo Kagaku* 1 (2006) 1-8.
- [13] T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, Direct Epoxidation of Olefins Catalyzed by Nickel(II) Complexes with Molecular Oxygen and Aldehydes, *Bull. Chem. Soc. Jpn.* 64 (1991) 2109-2117.
- [14] S. Shaw, J. D. White, Asymmetric Catalysis Using Chiral Salen–Metal Complexes: Recent Advances, *Chem. Rev.* 119 (2019) 9381-9426.
- [15] Shimazaki, Y., 2013, Oxidation Chemistry of Metal(II) Salen-Type Complexes, in M. A. A. Khalid (ed.), *Electrochemistry*, IntechOpen, London. 10.5772/48372.
- [16] A. Decortes, A. M. Castilla, A. W. Kleij, Salen-Complex-Mediated Formation of Cyclic Carbonates by Cycloaddition of CO<sub>2</sub> to Epoxides, *Angew. Chem. Int. Ed.* 49 (2010) 9822-9837.
- [17] C. Baleizão, H. Garcia, Chiral salen complexes: An overview to recoverable and reusable homogeneous and heterogeneous catalysts, *Chem. Rev.* 106 (2006) 3987-4043.
- [18] M. Ulusoy, Ö. Birel, O. Ahin, O. Büyükgüngör, B. Cetinkaya, Structural, spectral, electrochemical and catalytic reactivity studies of a series of N<sub>2</sub>O<sub>2</sub> chelated palladium(II) complexes, *Polyhedron* 38 (2012) 141-148.
- [19] J.A. Castro-Osma, M. North, X. Wu, Synthesis of Cyclic Carbonates Catalysed by Chromium and Aluminium Salphen Complexes, *Chem. Eur. J.* 22 (2016) 2100-2107.
- [20] M. Balas, S. Beaudoin, A. Proust, F. Launay, R. Villanneau, Advantages of Covalent Immobilization of Metal-Salphen on Amino-Functionalized Mesoporous Silica in Terms of Recycling and Catalytic Activity for CO<sub>2</sub> Cycloaddition onto Epoxides, *Eur. J. Inorg. Chem.* (2021) 1581-1591.
- [21] M. Balas, L. K/Bidi, F. Launay, R. Villanneau, Chromium-salphen as a soluble or silica-Supported co-catalyst for the fixation of CO<sub>2</sub> onto styrene oxide at low temperatures, *Front. Chem.* 9 (2021) 765108.
- [22] A.S. Abu-Surrah, H.M. Abdel-Halim, H.A.N. Abu-Shehab, E. Al-Ramahi, Iron and cobalt salicylaldehyde complexes as catalysts for epoxide and carbon dioxide coupling: effects of substituents on catalytic activity, *Transit. Met. Chem.* 42 (2017) 117-122.

- [23] F.F. Awwadi, H.A. Hodali, Anagostic interactions in chiral separation. Polymorphism in a [Co(II)(L)] complex: Crystallographic and theoretical studies, *J. Mol. Struct.* 1154 (2018) 373-381. R. Flasik, H. Stankovicova, A. Gaplovsky, J. Donovalova, Synthesis and study of novel coumarin derivatives potentially utilizable as memory media, *Molecules* 14 (2009) 4838-4848.
- [24] F. Castro-Gómez, G. Salassa, A.W. Kleij, C. Bo, A DFT study on the mechanism of the cycloaddition reaction of CO<sub>2</sub> to epoxides catalyzed by Zn(Salphen) complexes, *Chem. Eur. J.* 19 (2013) 6289-6298.
- [25] L. Ji, Z. Luo, Y. Zhang, R. Wang, Y. Ji, F. Xia, G. Gao, Imidazolium ionic liquids/organic bases: Efficient intermolecular synergistic catalysts for the cycloaddition of CO<sub>2</sub> and epoxides under atmospheric pressure, *Mol. Catal.* 446 (2018) 124-130.
- [26] M. Balas, A. Mayoufi, R. Villanneau, F. Launay, Revisiting the Mukaiyama-type epoxidation for the conversion of styrene into styrene carbonate in the presence of O<sub>2</sub> and CO<sub>2</sub>, *React. Chem. Eng.* 8 (2023) 345-354.
- [27] C. Carvalho Rocha, T. Onfroy, F. Launay, Towards a combined use of Mn(Salen) and quaternary ammonium salts as catalysts for the direct conversion of styrene to styrene carbonate in the presence of dioxygen and carbon dioxide, *C. R. Chim.* 18 (2015) 270-276.
- [28] M. Balas, R. Villanneau, F. Launay, Bibliographic survey of the strategies implemented for the one-pot synthesis of cyclic carbonates from styrene and other alkenes using CO<sub>2</sub> and green oxidants, *J. CO<sub>2</sub> Util.* 65 (2022) 102215.
- [29] D. Bai, H. Jing. Aerobic oxidative carboxylation of olefins with metalloporphyrin catalysts, *Green. Chem.* 12 (2018) 39-41.
- [30] S. Kumar, N. Singhal, R.K. Singh, P. Gupta, R. Singh, S.L. Jain, Dual catalysis with magnetic chitosan: direct synthesis of cyclic carbonates from olefins with carbon dioxide using isobutyraldehyde as the sacrificial reductant, *Dalt. Trans.* 44 (2015) 11860-11866.
- [31] Z. Shi, G. Niu, Q Han, X. Shi, M. Li, A molybdate-incorporated cooperative catalyst: High efficiency in the assisted tandem catalytic synthesis of cyclic carbonates from CO<sub>2</sub> and olefins, *Mol. Catal.* 461 (2018) 10-18.
- [32] L.D. Dias, R.M.B. Carrilho, C.A. Henriques, M.J.F. Calvete, A.M. Masdeu-Bulto, C. Claver, L.M. Rossi, M.M. Pereira, Hybrid metalloporphyrin magnetic nanoparticles as catalysts for sequential transformation of alkenes and CO<sub>2</sub> into cyclic carbonates, *ChemCatChem* 10 (2018) 2792-2803.